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Studies on Dissipation Pattern of Diafenthiuron on Cauliflower

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ABSTRACT

The present study was conducted during *rabi* season of October, 2019 to February, 2020 at College Farm, College of Agriculture, Rajendranagar, Professor Jayashankar Telangana Agricultural University (PJTAU) to determine the dissipation pattern of Diafenthiuron in Cauliflower. Diafenthiuron 50 WP @ 300 g *a.i.* ha^{-1} was sprayed twice at 15 days interval during the curd initiation stage. The cauliflower curds were collected at 0 (2 hrs after spray), 1, 3, 5, 7, 10, 15, 20 and 25 days after second spray. The samples were brought to the Laboratory of AINP on Pesticide Residues, PJTAU where dissipation studies were carried out. Extraction and cleanup of the samples was done following the validated QuEChERS method and the residues were quantified on Liquid Chromatography Mass Spectrometry (LC-MS/MS). The limit of quantification (LOQ) of this method was 0.05 mg kg^{-1}. The analytical method adopted for analysis on LC-MS/MS was evaluated through linearity, LOD, LOQ, fortification and recovery studies. Linearity studies gave satisfactory R^2 value of 0.998, while the fortification studies recorded recovery in the acceptable range of 98.31–101.52%. The results indicated that the mean initial deposit of 5.356 mg kg^{-1} recorded at 0 days (2 hrs) in cauliflower curds after second spray dissipated to 0.227 mg kg^{-1} by 10th day and to below LOQ by 15th day after final spray with calculated half-life of 2.33 days.

KEYWORDS: Dissipation, diafenthiuron, cauliflower, LC-MS/MS, limit of quantification, half-life

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Data Availability Statement: Legal restrictions are imposed on the public sharing of raw data. However, authors have full right to transfer or share the data in raw form upon request subject to either meeting the conditions of the original consents and the original research study. Further, access of data needs to meet whether the user complies with the ethical and legal obligations as data controllers to allow for secondary use of the data outside of the original study.

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1. INTRODUCTION

Cauliflower is one of the important brassica vegetables. It is a rich source of nutrients (Fats, Protein, vitamin-A, C and minerals) and is consumed as vegetable in curries, soups, salads and pickles. It is widely grown in the tropical and subtropical regions of the world. The quantitative and qualitative yield of cauliflower is adversely affected by abiotic (environmental stress) and biotic (pests and diseases) factors. Among insect pests, *Plutella xylostella* Linnaeus and *Spodoptera litura* Fabricius are important and destructive pests throughout the world (Ramzan et al., 2019). Farmers mostly rely on pesticides to manage these pests. Indiscriminate use of pesticide particularly at curd initiation stage and non-adoption of safe waiting period results in accumulation of residues in final produce. The retention of pesticides depends on its physico-chemical properties and the crop on which it is sprayed. Thus, selection of insecticide, spraying right dosage at the right stage and following safe waiting periods are important.

Diafenthiuron[1-tert-butyl-3-(2,6-di-isopropyl-4-phenoxyphenyl) thiourea] is one of the most active thiourea compound that acts as a pro-insecticide and converts to carbodiamide under light or inside the plant. It inhibits mitochondrial respiration in the target insect resulting in quick knockdown through immediate paralysis of the pest. It has translaminar action, which allows control of hidden pests in the plant canopy and on the underside of the leaves and provides excellent control of Organo phosphorous and pyrethroid resistant pests. Being selective to beneficial insects (Streibert et al., 1988), it fits well in IPM programs (Stanley et al., 2016). Sarkar and Maity (2016) reported that diafenthiuron 50% WP @ 600 ml ha^{-1} provided most effective reduction of DBM population (88.68%–90.82% reduction of pest over control) with substantial increase in yield (184.75 q ha^{-1}) and highest cost benefit ratio of 1:5.89 in cabbage. It was also found to be safe to natural enemies like coccinellids and hymenopteran parasitoids and did not produce any phytotoxic symptoms. Bio-efficacy studies of different doses of Diafenthiuron 47.8 SC as foliar application against sucking pests of cotton crop along with standard checks i.e. Diafenthiuron 50% WP @ 600 g, Imidacloprid 17.8% SL @ 125 ml, Acetamiprid 20% SP @ 100 g ha^{-1} were conducted by Kalyan and Kalyan (2023) who reported that the maximum per cent reduction of whiteflies and jassids at 10 days after second spray was recorded in Diafenthiuron 47.8 SC @ 300 g a.i. ha^{-1}. Zala et al. (2014) reported that diafenthiuron 50 WP @ 300 g a.i. ha^{-1} was found highly effective in reducing the population of sucking pest in cotton followed by imidacloprid 17.8 SL @ 20 g a.i. ha^{-1}. Also, Kumar et al. (2015) reported that diafenthiuron was the most effective insecticide with 77.84% reduction of leafhoppers population with highest yield (2227 kg ha^{-1}) followed by imidacloprid 70% WG, fipronil, buprofezin and acephate. Pathipati et al. (2018) also reported that the highest per cent reduction of thrips population in Capsicum was by spinosad (98.05%) followed by diafenthiuron (87.52%) and thiamethoxam (72.98%).

The rate of dissipation of insecticide varies with several factors like species cultivated, climatic conditions, application parameters like number of applications, penetration rate, volume of water, type of nozzle *etc*., (Rahman et al., 2015). Since diafenthiuron is being widely used for managing diamondback moth in crucifers, it is essential to study its dissipation behaviour so as to establish safe waiting periods. Keeping this in view, the dissipation of diafenthiuron in cauliflower was taken up.

2. MATERIALS AND METHODS

2.1. Field study

Field experiment was conducted during *rabi* season of October, 2019 to February, 2020 at College Farm, College of Agriculture, Rajendranagar, PJTSAU to study the dissipation pattern of diafenthiuron on cauliflower. The experimental site is situated at an altitude of 542.3 m above mean sea level with 17°191 N latitude and 78°251 E longitude and it falls under semi-arid tropical climate. The variety "Dhawal" was transplanted at 60×45 cm^2 spacing in 20 m^2 plots replicated thrice. Diafenthiuron 50 WP @ 300 g *a.i.* ha^{-1} was sprayed twice at 15 days interval during the curd initiation stage. The curds were collected at 0 (2 hrs after spray), 1, 3, 5, 7, 10, 15, 20 and 25 days after final spray and were analyzed for residues using the validated QuEChERS methods on LC–MS/MS.

2.2. Laboratory analysis

For carrying out residue analysis, the certified reference material of diafenthiuron 98.3% purity was procured from HPC standards. Analytical grade solvents and reagents viz., Acetonitrile (HPLC grade), n-Hexane (HPLC grade), sodium chloride (NaCl), anhydrous sodium sulphate (Na_2SO_4) and anhydrous magnesium sulphate ($MgSO_4$) (Merck India Pvt Ltd.) primary secondary amine (59.6 µm particle size) (PSA–Ethylene diamine N-propyl bonding with silica gel base) (Agilent Technologies) and LC-MS/MS grade Methanol, Acetonitrile and Water (JT Baker) were used for extraction, clean up and detection of pesticide residues. Primary stock solutions (500 ppm) of diafenthiuron were prepared from which intermediate (20 ppm) and working standards (1 ppm) were made and stored at -20°C. To study dissipation dynamics, Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) method (Anastassiades et al., 2003) for extraction and clean up was validated as per SANTE 2017 guidelines at the laboratory.

2.3. Extraction and clean up

The cauliflower curd samples collected at regular intervals from various treatments were homogenized with robot coupe blixer. Each sample (15±0.1 g) was taken in 50 ml centrifuge tube and 30±0.1 ml acetonitrile was added and the samples were homogenized at 14000–15000 rpm for 2–3 min using Heidolph silent crusher. To the samples, 3±0.1 g sodium chloride was added and mixed by shaking gently followed by centrifugation for 3 min at 3000 rpm to separate the organic layer. After centrifugation, the supernatant organic layer of about 16 ml was taken into the 50 ml centrifuge tube and 9±0.1 g anhydrous sodium sulphate was added to remove the moisture content. 8 ml of extract was taken into 15 ml tube containing 0.4±0.01 g PSA sorbent (for dispersive solid phase cleanup) and 1.2±0.01 g anhydrous magnesium sulphate. The sample tube was vortexed for 30 sec followed by centrifugation for 5 min at 5000 rpm. The extract of 1 ml acetonitrile was transferred into 2 ml vial by filtering through 0.22 µm PTFE syringe filter for residue analysis of respective insecticides on LC-MS/MS under standard operational conditions.

2.4. Fortification and recovery studies

The untreated cauliflower samples were individually fortified with required quantity of diafenthiuron standard so as to obtain 0.5 mg kg^{-1}, 0.25 mg kg^{-1}, and 0.05 mg kg^{-1} fortification levels and their mean recoveries were calculated. The linearity was examined by injecting 10, 20, 50, 100, 200 and 500 ppb concentrations of diafenthiuron solution in three replications and correlation coefficient (R^2) was calculated. For repeatability and reproducibility studies, spiking was done at 5×LOQ (0.25 mg kg^{-1}) level on the same day for repeatability and next day for reproducibility and the accuracy of the analytical methods was determined based on relative standard deviation.

2.5. Chromatographic separation parameters

A Shimadzu 8040 LC-MS/MS with electrospray ionization (ESI) source was used for detection and quantification of residues from the samples. The chromatographic separation was performed on Kinetex C-18 Column (100×3 mm id, 2.6 µm). The mobile phase consisted of (A) 80:20 Acetonitrile: Water+0.5% Formic acid; (B) 95:5 Acetonitrile: Water+0.5% Formic acid. The solvent gradient started with 50% of B up to 4.10 mins. Flow rate was 0.4 ml min^{-1} with 1 µl injection volume with ESI operated in Positive mode. The Mass to Charge ratio (m z^{-1}) of diafenthiuron was 385.10 with a retention time of 2.267 min.

2.6. Calculation of residues

The standard peak areas obtained from the chromatograms of the samples collected at (2 hrs) 0, 1, 3, 5, 7, 10, 15, 20 and 25 days after final spray were analyzed for residues following the validated methods. Residues in mg kg^{-1} were calculated using the formula given

Residues in sample (mg kg^{-1})=(Sample peak area×Conc. of matrix match Std (µg ml^{-1})×µl of matrix match Std. injectedx final volume of the sample)/(Matrix match standard peak area×Weight of sample analysed×µl of sample injected)×Recovery factor

The data of degradation on the residues at different intervals was subjected to statistical analysis as per Hoskins (1961) to determine the half–life and pre harvest interval.

$$RL_{50} \text{ (or) } t_{1/2} = \frac{\text{Log }(2)}{b}$$

Where, b=Slope of regression line

3. RESULTS AND DISCUSSION

The results of the validation studies revealed that the mean per cent recoveries at fortification levels of 0.05, 0.25 and 0.50 mg kg^{-1} were 101.52, 98.31 and 101.4, respectively which is within the acceptable range of 70–120% as per SANTE, 2017 guidelines (Anonymous, 2017) (Table 1). Satisfactory correlation coefficients (R^2) of 0.998 for diafenthiuron was obtained from linearity studies (Figure 1). The method was suitable for analysis of diafenthiuron residues up to 0.05 mg kg^{-1} and was fixed as limit of quantification (LOQ).

The dissipation pattern of diafenthiuron in cauliflower is presented in Table 2. The residues dissipated continuously

Table 1: Recoveries of diafenthiuron in cauliflower curd

Fortification level (mg kg^{-1})	Recovered level*± SD	Per cent recovery
0.05	0.051±0.001	101.52±2.18
0.25	0.246±0.003	98.31±1.34
0.5	0.507±0.003	101.40±0.63

* Mean of three replicates

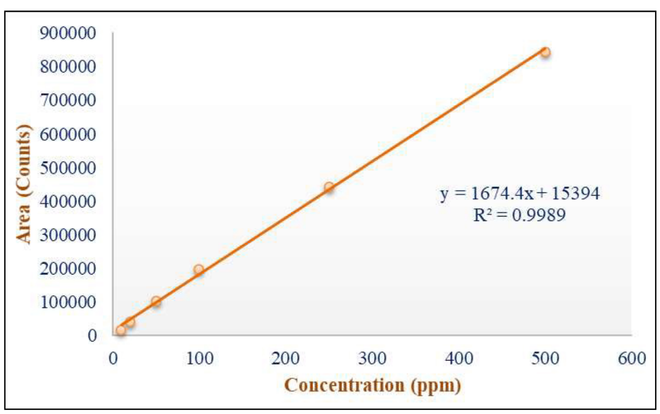

Figure 1: Linearity graph of diafenthiuron

Table 2: Dissipation pattern of diafenthiuron in cauliflower curd

Days after final spray	Residues of diafenthiuron* (mg kg^{-1})	Per cent dissipation
0	5.356±0.151	–
1	1.886±0.125	64.79
3	1.422±0.027	73.45
5	0.874±0.085	83.68
7	0.338±0.035	93.69
10	0.227±0.008	95.75
15	<LOQ	–
Regression equation	Y =–0.1293x+3.5575	
R^2	0.938	
Half-life (days)	2.33	

Mean of three replicates

with time. The mean initial deposit of 5.356 mg kg^{-1} recorded at 0 days (2 hrs) after final spray dissipated to 1.886, 1.422, 0.874, 0.338 and 0.227 mg kg^{-1} at 1, 3, 5, 7 and 10 days after second spray. The residues gradually dissipated and were found to be less than LOQ by 15th day after second spray (Table 2; Figure 2). The residues dissipated to 83.68% by 5th day and to >95% by 10th day. The correlation co-efficient was 0.938 and the residue half-life was 2.33

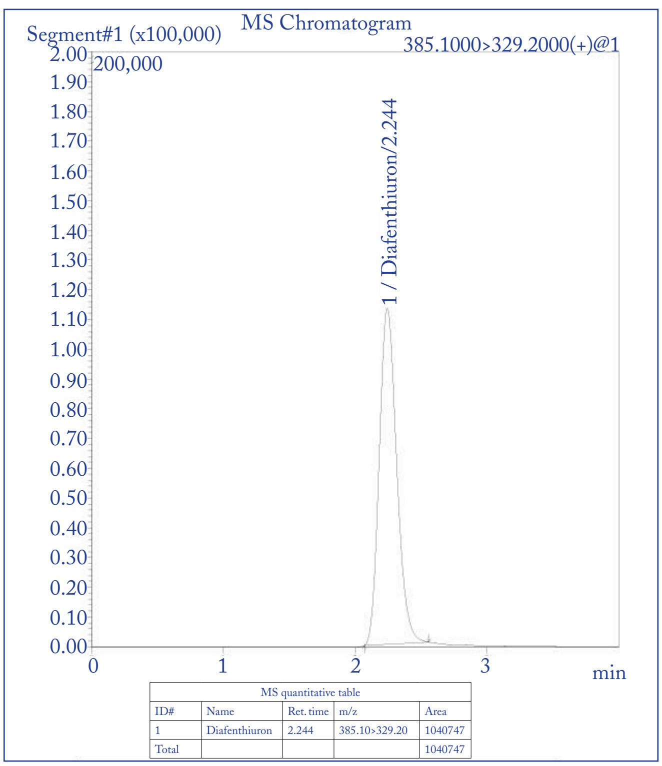

Figure 2: Standard chromatogram of diafenthiuron in cauliflower at 0.5 ppm

days (Figure 3). Diafenthiuron persisted up to ten days with rapid dissipation initially followed by slower rate of loss.

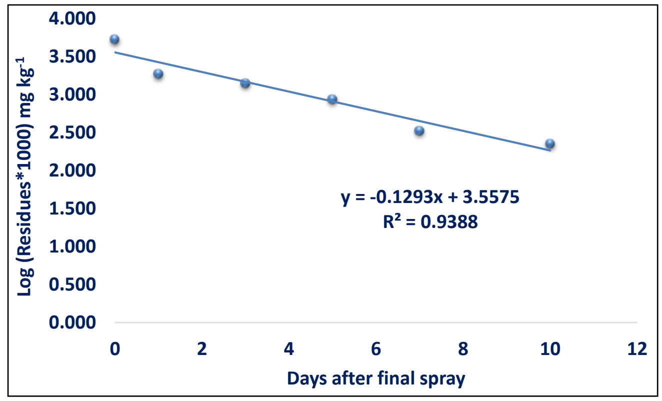

Figure 3: Semi logarithmic graph depicting dissipation kinetics of diafenthiuron in cauliflower

Similar studies were made in other vegetable crops. Two foliar applications of combined formulation (Cyantraniliprole 7.3% w/w+Diafenthiuron 36.4% w/w SC) were applied at 360 (X dose) and 720 g *a.i.* ha^{-1} (2X dose) in tomato. The total initial residues of diafenthiuron in tomato fruits were 0.33 and 0.75 mg kg^{-1}, which reached below LOQ on seventh and tenth day at X and 2X doses, respectively. Dissipation of cyantraniliprole followed first-order kinetics with half-life values of 1.31 and 1.84 days, while total diafenthiuron residues followed first-order kinetics with half-life values of 1.25 and 2.27 days, at X and 2X doses, respectively (Brar et al., 2025).

Sharma et al. (2022) carried out residue and dissipation studies of diafenthiuron, its metabolites and cyantraniliprole on okra under field conditions after two applications of Cyantraniliprole 7.3% w/w+Diafenthiuron 36.4% w/w SC @ 60+300 g *a.i.* ha^{-1}. The total initial residues of diafenthiuron in okra fruit were 0.28 and 0.55 mg kg^{-1} at single and double dose, respectively. The total residues of diafenthiuron dissipated below limit of quantification (LOQ) of 0.01 mg kg^{-1} at 10 days of application at both the doses. The initial residues of cyantraniliprole in okra were 0.23 and 0.42 mg kg^{-1} at single and double dose, respectively. The residues dissipated below <LOQ of 0.01 mg kg^{-1} at 7 and 10 days in both the dosages. For safe consumption of okra, they suggested a waiting period of 10 days.

Stanley et al. (2014) reported that the initial deposits of diafenthiuron in green cardamom capsules @ 400 g *a.i.* ha^{-1} was 3.82 and 4.10 µg g^{-1} while that of the higher dose of diafenthiuron (800 g *a.i.* ha^{-1}) was as high as 6.61 and 7.32 µg g^{-1}. The residues of diafenthiuron and their metabolites in green capsules of cardamom dissipated to below the detectable level (BDL) at 15 DAT in both the doses. Keum et al. (2002) reported that the initial concentrations of diafenthiuron in whole Chinese cabbage leaves after application were 4.61 and 27.03 mg kg^{-1} in plots A (1 g *a.i.* per 1000 m^2) and B (10 g *a.i.* per 1000 m^2), respectively and they decreased rapidly at a similar rate. The half-lives of diafenthiuron in packhoi and soil were 1.27 and 5.94 day, respectively. The final residue levels of diafenthiuron could not be detected in soil, while only trace amount of diafenthiuron residues were detected in pakchoi. The limit of quantification (LOQ) of method was 0.02 mg kg^{-1} for packhoi and soil (Wang et al., 2011).

4. CONCLUSION

The diafenthiuron persisted for 10 days in cauliflower head. The MRL values were unavailable in case of diafenthiuron hence waiting periods could not be calculated.

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