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Dissipation study and persistence of diafenthiuron in green chilli fruits

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Abstract
The dissipation patterns of diafenthiuron in green chilli fruits were studied after application of diafenthiuron at fruiting stage at recommended doses (RD) and double the recommended doses (DRD). Diafenthiuron was applied at the rate of 1 g/L (225 g *a.i*/ha) and 2 g/L (450 g *a.i*/ha) on chilli fruits and the fruit samples were collected at the 0, 1st, 3rd, 5th, 7th, 10th, 15th, 21st, 25th, and 30th day after spray. The initial deposits of diafenthiuron in chilli fruits from the two treatments were leads to 0.684 and 1.168 mg/kg with half-life of 1.35 and 2.40 days at recommended and double the recommended dose, respectively. Based on the persistence studied waiting period of 9.76 and 11.31 days is suggested for diafenthiuron on chilli from consumer safety point of view.

Keywords: Chilli, dissipation pattern, diafenthiuron

Introduction
Chilli [*Capsicum annuum* L.] is one of the major spice crop in India. It is a member of Solanaceae family which represents a diverse plant group. The name is derived from Latin word Capsa that means hallow pod. Indian chillies have gained global demand due to high color value and low pungency (Mathur *et al*., 2000) [1]. Chillies contain potent pungent substance capsaicin, with almost 80 percent of the capsaicin being in its seeds and membranes. Besides, chillies are a good source of vitamins, minerals and beta-carotene. The capsaicin, an antioxidant is having medicinal properties. In India, Chilli was grown in an area of 136 (in '000 ha) and production of 3634 (in '000 MT) and the productivity, 11.5 (in '000 MT/ha) in 2016-17 (Anon., 2016-17) [2].
India is the world leader in chilli production followed by China and Pakistan. This shows that the bulk share of chilli production is held by the Asian countries, though it is produced throughout the world. At present, Karnataka ranks second in area (132.20 thousand ha) and production of chilli (148.00 thousand tonnes) after Andhra Pradesh. The pest spectrum of chilli is complex with more than 293 insects and mite species debilitating the crop in the field as well as in storage (Anon., 1987) [3].
In Karnataka, thrips, mites and white flies have been identified as key sucking pests of chilli of which leaf curl caused by mite and thrips is serious (Puttarudraiah, 1959) [4]. The yield loss due to chilli mite may go up to 96.39 percent leading sometimes to complete failure of the crop itself (Kulkarni, 1922) [5]. Chilli thrips multiply appreciably at a faster rate during dry weather periods and causes yield loss of 30 to 50 percent in South India (Vasundarajan, 1994) [6] and sometime more than 90 percent yield reduction (Krishnakumar, 1995) [7]. Chilli leaf curl complex is one of the most destructive syndrome affecting chilli in India and is considered to be caused by thrips and mites. The crop is also vulnerable to fruit borer, *Helicoverpa armigera*. Shivaramu and Kulkarni (2001) [8] reported 20 to 30 percent damage due to fruit borer, *H. armigera.* An extensive study was done on dissipation of diafenthiuron in/on chilli revealed the persistence of diafenthiuron in chilli fruits. In order to recommend a safe waiting period, it is essential to determine the dissipation behavior of diafenthiuron.

Materials and Methods
Field Experimentation
Field experiment was carried out to evaluate the dissipation pattern of diafenthiuron 50% WP on chilli during *kharif* 2017 at Agricultural Entomology experimental block, Main Agricultural Research Station, UAS, Raichur in a Randomised Block Design (RBD). A hybrid HPH 5531 was used for experiment wherein, 3 treatments of the recommended dose, double the

recommended dose and untreated plots with 8 replications were maintained. The Application of diafenthiuron 50% WP at 1 g/L (225 g *a.i*/ha) as a recommended dose and 2 g/L (450 g *a.i*/ha) as double the recommended dose was sprayed during fruit formation stage including untreated control plot. The green chilli fruit samples were drawn on 0 (2hr after spraying), 1, 3, 5, 7, 10, 15, 21, 25 and 30 days after spray. The collected samples were extracted and analysed through LC-MS/MS and calculated the residue of diafenthiuron at different days.

Solvents and Reagents

Acetonitrile (≥ 99.9 LCMS grade) was used for extraction from JT Baker®, USA.

Instrumentation

The pesticide residues were analyzed by Liquid chromatography mass spectrometry (LC-MS/MS).

LC-MS/MS parameters

Model	Shimadzu LC-MS 8040®
Column	Shimpack XR, ODS C18, 2mm id x 150mm
Flow rate	0.4 mL/min.
Heat block	400 ºC
N B gas flow	3 L/min.
Source	ESI +ve probe
Dissolution temperature	250 ºC
Drying gas flow (N_2)	15 L/min.
Injection volume	2 µL

Extraction and Clean up procedure

The collected samples were extracted without solvent evaporation, solvent exchange or extract clean-up. Science and advice for Scottish Agriculture (SASA), Agricultural Food and Rural Communities Directorate (Reid *et. al*, 2012) [9]. About 5 g of grounded sample was weighed in analytical balance and transferred into 50 mL centrifuge tube and 20 mL of acetonitrile (the matrix concentration is equivalent to 0.25 g/mL) was added. The sample mixture was then homogenized at 10000-13000 rpm for 3 min. Crude extracts were filtered by using 0.22 µ PTFE nylon filter in LC vials.

Fortification and Recovery studies

The recoveries of diafenthiuron in the untreated chilli matrix were carried out by spiking at LOQ level (0.01 mg/kg), 5 times of LOQ (0.05 mg/kg) and 10 times of LOQ (0.1 mg/kg) six with replications each and injected three times each. Fortification levels and the samples were extracted and cleaned up as per acetonitrile method to validate the suitability of the method. Calculated the obtained concentration from the spiked sample and then calculated the percent recovery by using formula.

$$\text{Residues (mg/kg)} = \frac{\text{Sample peak area} \times \text{Conc. of std. injected} \times \text{Std injected (µL)} \times \text{final volume of the sample (mL)}}{\text{Std peak area} \times \text{weight of sample analyzed} \times \text{sample injected (µL)}}$$

$$\text{Wt of the sample analyzed (g)} = \frac{\text{Sample weight (g)} \times \text{Aliquot taken (mL)}}{\text{Volume of extract (mL)}}$$

$$\text{Per cent recovery} = \frac{\text{Residue quantified in fortified sample}}{\text{Fortified level}} \times 100$$

$$\text{Dissipation percentage} = \frac{\text{Initial deposit (mg/kg)} - \text{Residues at given time (mg/kg)}}{\text{Initial deposit (mg/kg)}} \times 100$$

Results and Discussion

Average recoveries from six different replications for diafenthiuron in chilli fortified at 0.01, 0.05 and 0.1 mg/kg were 85.92%, 80% and 81.70%, respectively. The overall recovery was calculated to be 82.54% (Table 1). The acceptance criteria for recovery were 70 to 120%. However, the diafenthiuron recovery obtained in the present study was accepted as because it falls within the acceptable range as per the method validation guidelines according to SANTAE-2017.

The average initial deposits of diafenthiuron at recommended dose were 0.684, 0.063, 0.040 and 0.002 mg/kg at 0 (2 hours after spray), 1, 3, 5, 7, 10, 15, 21, 25 and 30 days after spray, respectively (Table 2). The residue gradually dissipated to 0.002 mg/kg on fifth day accounting to loss of 99.70 percent however; residues were below the detectable limit (BDL) on the seventh day sample. The residue half-life value was 1.35 days with the degradation rate constant (k) was 0.2219 day^{-1}. The values of correlation coefficient were 0.9991 for recommended dosage with safe waiting period was 9.76 days.

The average initial deposits of diafenthiuron at double the recommended dose were 1.168, 0.090, 0.055 and 0.004 mg/kg at 0 (2 hours after spray), 1, 3, 5, 7, 10, 15, 21, 25 and 30 days after spray, respectively (Table 2). The residue gradually dissipated to 0.004 mg/kg at fifth day accounting to loss of 99.65 percent, however, residues were below the detectable limit (BDL) on the seventh day sample. The residue half-life value was 2.40 days double the recommended dosage. The degradation rate constant (k) was 0.1249 day^{-1} with value of correlation coefficient was 0.9993 double the recommended dosage with safe waiting period was 11.31 days.

The residue data of diafenthiuron in chilli indicated that initially there was a rapid loss of insecticide residues followed by a slower rate of dissipation. The initial deposits of diafenthiuron on chilli fruits at single dose were found to be 1.7 times lower than that obtained from double dose. The results of the present findings showed a close similarity to those obtained by Stanley *et al.* (2014) [10] reported that the initial deposit of green cardamom capsules in diafenthiuron @ 400 g *a.i.*/ha was 3.82 and 4.10 µg/g in first and second field trials, respectively. The deposit was as high as 6.61 and 7.32 µg/g at the higher dose of diafenthiuron (800 g *a.i.*/ha). He reported an increase of about 1.73 and 1.8 fold deposits for a double dose over single dose in first and second trails on green cardamom capsules respectively. Keum *et al.* 2002 [11] reported that the initial concentrations of diafenthiuron in whole Chinese cabbage leaves after application were 4.61 and 27.03 mg/kg in plots A (1 g *a.i.*/1000m^2) and B (10 g *a.i.*/1000m^2), respectively and decreased rapidly at a similar rate.

The residue gradually dissipated at fifth day samples contained 0.002 and 0.004 mg/kg residues at a single and double dose respectively, accounting to loss of 99.70 to 99.65 percent, however residues were below detectable limit (BDL) on the seventh day sample as shown in fig. 1 and 2 and chromatogram is given in fig. 3, 4, 5, 6, 7, 8, 9 and 10. The results are in agreement with the findings of Stanley *et al.* (2014) [10], who reported that the residues of diafenthiuron and their metabolites in green capsules of cardamom were dissipated to below the detectable level (BDL) at 15 DAT in

both the concentrations evaluated in two seasons. The extent of reduction in diafenthiuron residues at one DAT was 14.39 to 20.68 percent in diafenthiuron 400 g *a.i.*/ha. The same workers also reported the residue in cured capsules of cardamom, The extent of dissipation of residues at one DAT was 22.33 to 24.19 and 19.07 to 21.07 percent in diafenthiuron at 400 g *a.i.*/ha and 800 g *a.i.*/ha, respectively. The percent dissipation was more than 95 percent in diafenthiuron at 400 g *a.i.*/ha at 10 DAT and the residues dissipated to BDL in 15 DAT.

Conclusion

As it is a new kind of study from this institution and published information is not available on dissipation of diafenthiuron in chilli fruit. This study clearly shows that, the dissipation pattern showed a fast decrease of residues from 1st day to 5th day for diafenthiuron because the diafenthiuron converts its metabolites and the diafenthiuron @ 225 g *a.i.*/ha can safely applied at an interval of 10 days and @ 450 g *a.i.*/ha at an interval of 12 days after last application. The chilli fruits is safely consume at harvest as the diafenthiuron residue were below detectable levels.

Acknowledgements

The authors wish to express their gratitude to Pesticide Residue and Food Quality Analysis Laboratory (PRFQAL), UAS, Raichur, Karnataka for providing facilities during research work.

Table 1: Recovery study and percent recovery of diafenthiuron at different spiked/fortification level

Insecticide	Spiking level (mg/kg)	Standard area	Sample area*	Residue concentration (mg/kg)*	Recovery%*	Overall Average
Diafenthiuron	0.01	355,926	76,457 (71,839-79,296)	0.0086 (0.0081-0.0089)	85.92 (80.73-89.12)	82.54
	0.05	1,660,552	332,104.50 (325,074-337,145)	0.0400 (0.0392-0.0406)	80.00 (78.31-81.21)	
	0.1	3,534,426	721,905.83 (704,221-740,683)	0.0817 (0.0797-0.0838)	81.70 (79.70-83.82)	

* Figures in parentheses indicate the range values for recovery of acephate and diafenthiuron

Table 2: Diafenthiuron residues (mg/kg) in chilli at different days after treatment of recommended and double the recommended dose

Insecticide	Treatments	Residue level (mg/kg)	Residue Level (mg/kg) Days after treatment			
			0	1	3	5
Diafenthiuron	Recommended dose	Mean ± SD	0.684±0.127	0.063±0.025	0.040±0.007	0.002±0.000
		% Dissipation	--	90.78	94.15	99.70
	Double the recommended dose	Mean ± SD	1.168±0.391	0.090±0.016	0.055±0.009	0.004±0.000
		% Dissipation	--	92.29	95.29	99.65

Recommended dose: Correlation Coefficient r = 0.999
Regression equation y = 0.8648+0.2219x
$t_{1/2}$ = 1.35 d
K = 0.2219
SWP = 9.76 d
Double the recommended dose: Correlation Coefficient r = 0.999
Regression equation y = 0.1117-0.1249x
$t_{1/2}$ = 2.40 d
K = -0.1249
SWP = 11.31 d

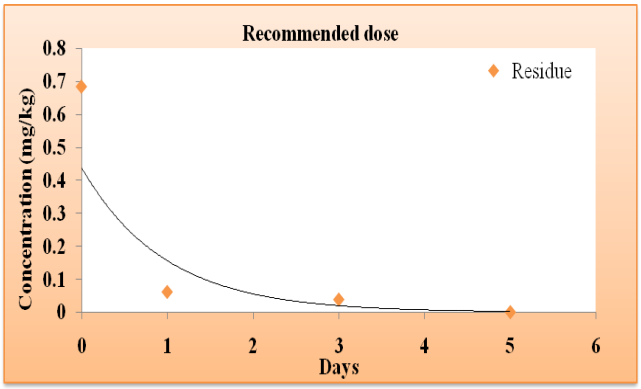

Fig 1: Dissipation curve for diafenthiuron 50% WP sprayed at recommended dose in chilli

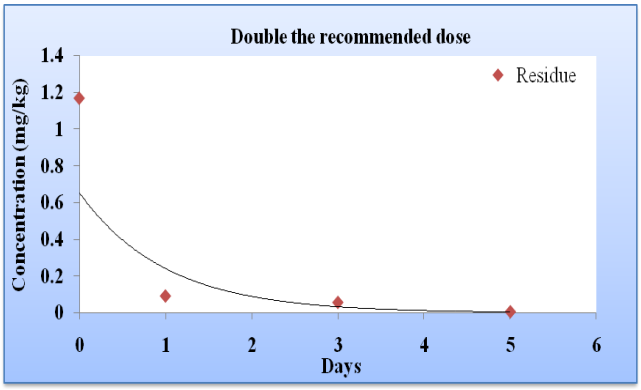

Fig 2: Dissipation curve for diafenthiuron 50% WP sprayed at double the recommended dose in chilli

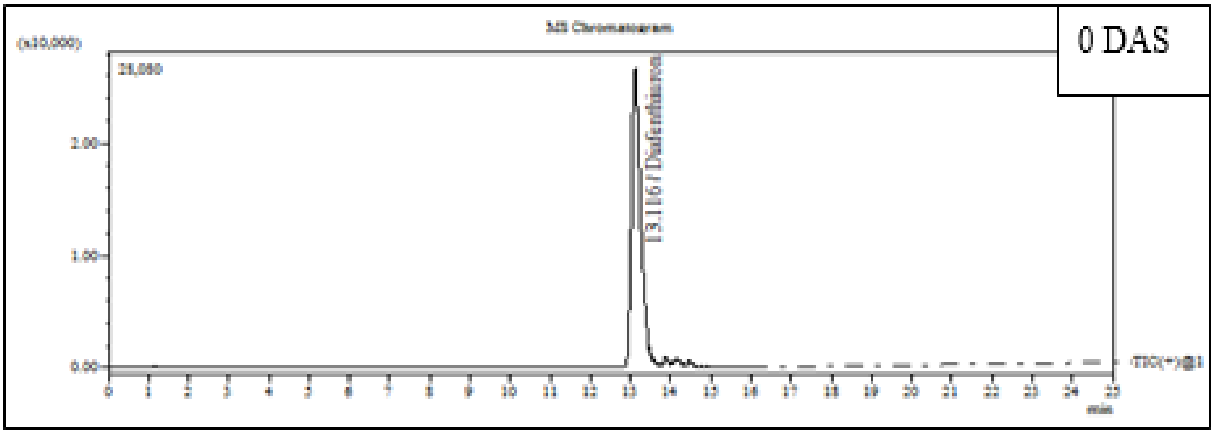

Fig 3: Chromatogram of diafenthiuron in zero day sample of the recommended dose

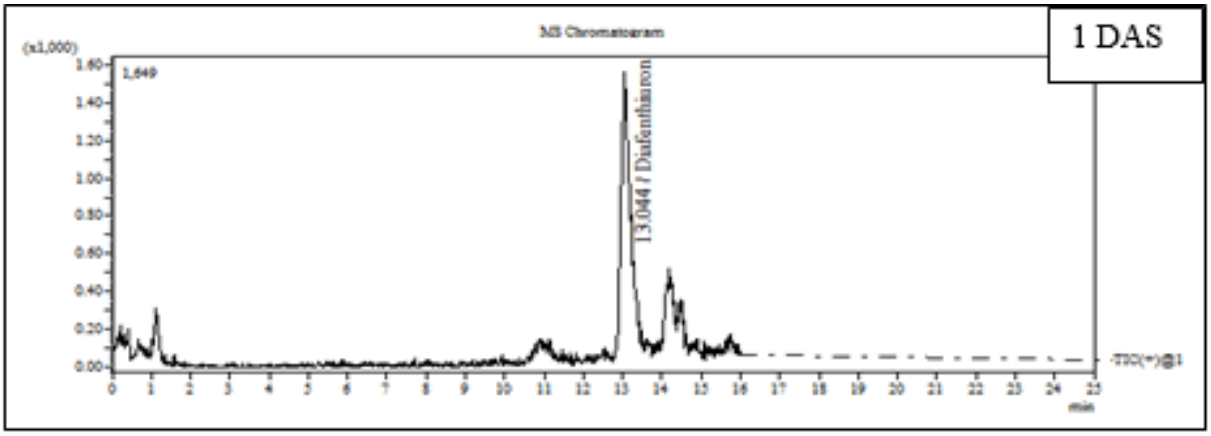

Fig 4: Chromatogram of diafenthiuron in one day sample of the recommended dose

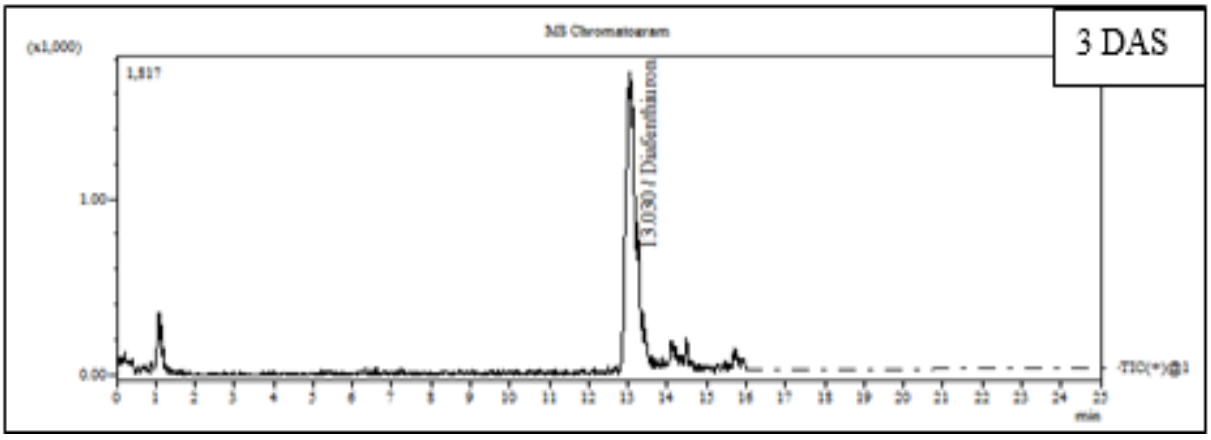

Fig 5: Chromatogram of diafenthiuron in three day sample of the recommended dose

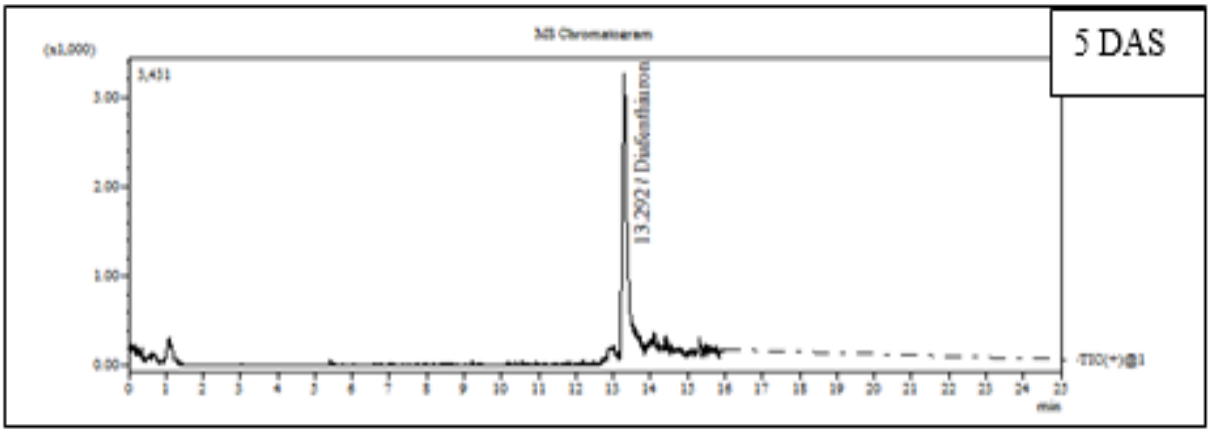

Fig 6: Chromatogram of diafenthiuron in five day sample of the recommended dose

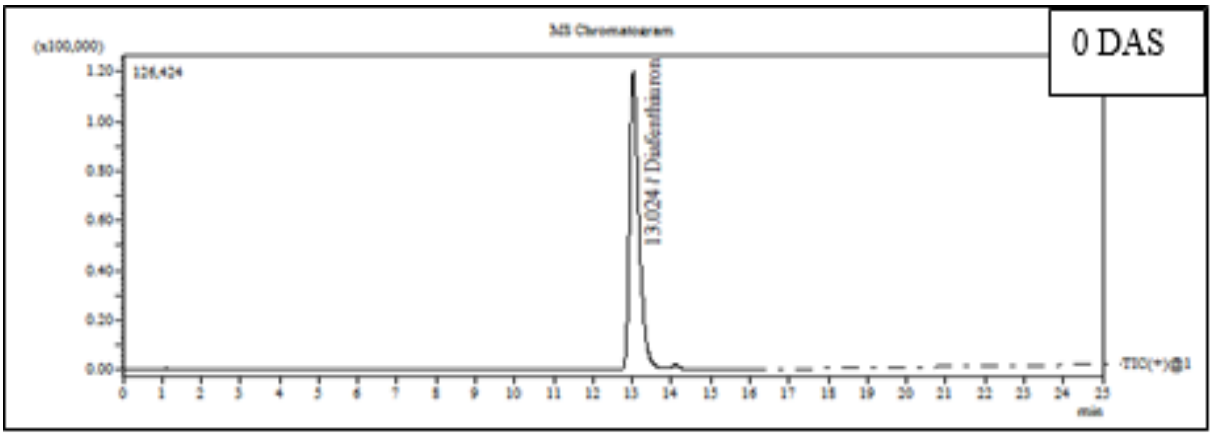

Fig 7: Chromatogram of diafenthiuron in zero day sample of double recommended dose

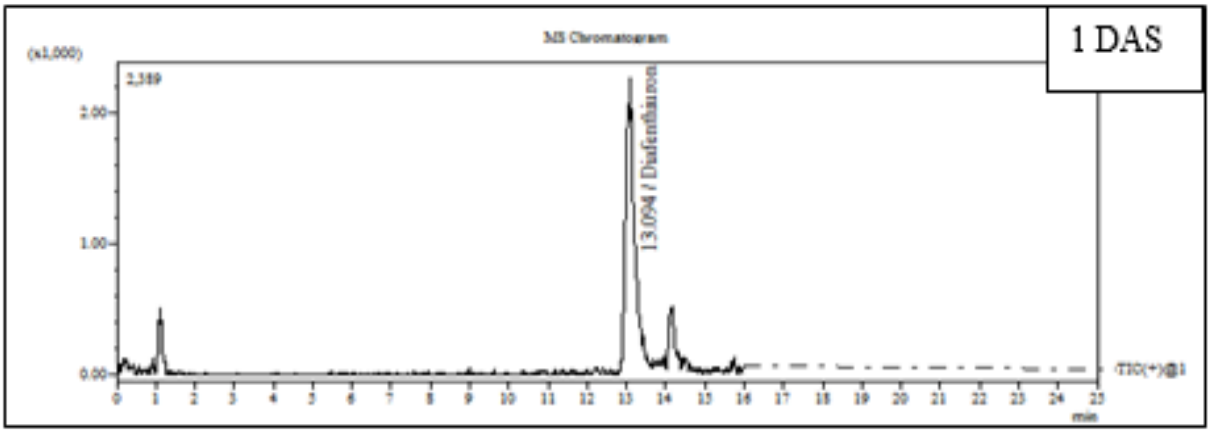

Fig 8: Chromatogram of diafenthiuron in one day sample of double recommended dose

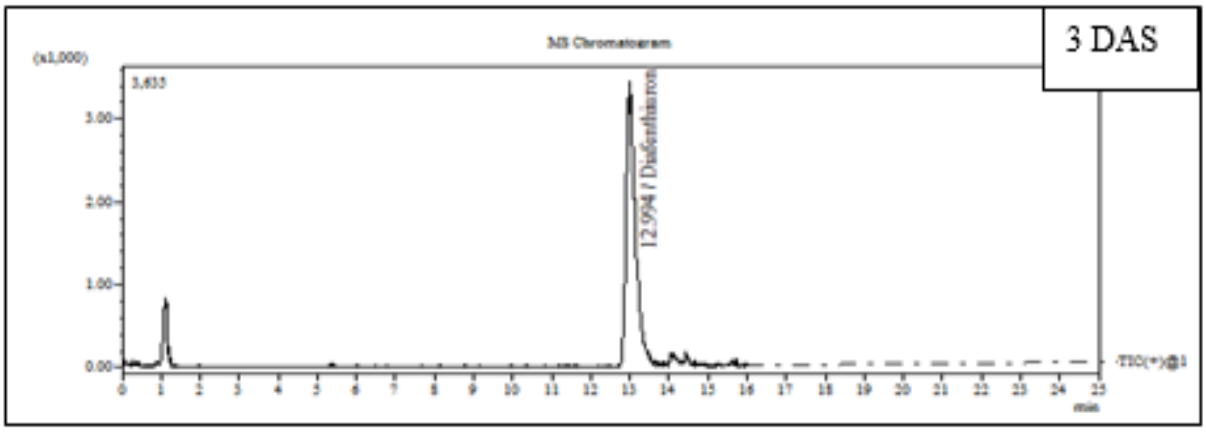

Fig 9: Chromatogram of diafenthiuron in three day sample of double recommended dose

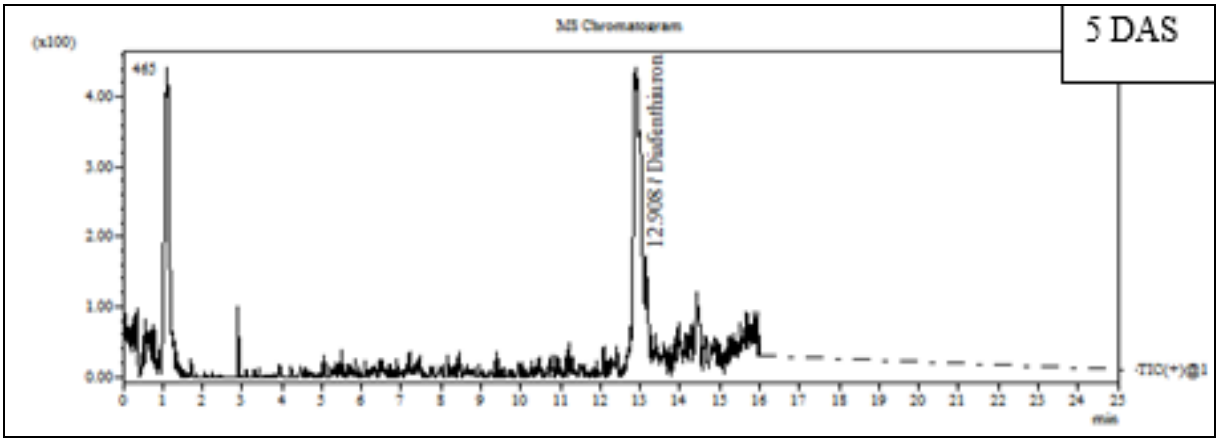

Fig 10: Chromatogram of diafenthiuron in five day sample of double recommended dose

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