Plant Archives Vol. 19, Supplement 2, 2019 pp.1974-1979 **e-ISSN:2581-6063 (online), ISSN:0972-5210**

PERSISTENCE OF FOMESAFEN HERBICIDE RESIDUES IN SOYBEAN CROP

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Abstract

An experiment was conducted during Kharif season of 2017 at experimental farm of Department of plant protection, Institute of Agriculture (PSB), Visva–Bharti, Sriniketan, Birbhum, West-Bengal. The treatments included application of Fomesafen 22.5% SL herbicides applied to Soybean crop @ 250 g a.i. ha^{-1} (T1) & 500 g a.i. ha^{-1} (T2). The study was aimed to evaluate the pattern of dissipation, persistence and residue in Soybean crop. As regarded to the observation on persistence residue and dissipation study reveals that higher content of residue was found in sample taken at initially as well as during growth period with an interval of 2 days exhibited successive depletion of herbicidal residue with progressive growth of the crop till harvest. HPLC method for detection for persistence residue and dissipation indicated that the average half life values for Fomesafen (T1 treated @250 g a.i. ha^{-1} dose), Fomesafen (T2 treated @500 g a.i. ha^{-1} dose) were 2.08 and 2.66 days respectively.

Keywords : Fomesafen Herbicide, Soybean, residue.

Introduction

Soybean contributes significantly to the Indian edible oil pool. Presently soybean contributes 43% to the total oilseeds and 25% to the total oil production in the country. Currently, India ranks fourth in respect to production of soybean in the world. The crop helps earn valuable foreign exchange (Rs. 62000 millions in 2012-13). It usually fetches higher income to the farmers owing to the huge export market for soybean de-oiled cake. While on one hand production of Soybean in India has increased at a CAGR of 9.60 per cent from 6.87 million tonnes in 2004-05 to 15.68 million tonnes in 2012-13. On the other hand Soybean meal consumption has also increased at a CAGR of 10.82 per cent over the last eleven years from 1365 thousand million tonnes in 2004-05 to 4225 thousand million tonnes in 2014-15 (Sondhia *et al*., 2009; US EPA guideline).

As herbicides play an important role in agriculture, their use in agricultural crops is increasing throughout the globe. In India herbicide use is likely to increase 10 % annually. The contaminated ground water used for drinking water and irrigation may be hazardous to humans and livestock communities. Moreover, determination of herbicide residue in soil and edible plant part is very essential to evaluate the consequent possible harmful effects on human health or community. Use of persistent herbicide may increase risk of accumulation of residue in soil, ground water, crop produce food chain etc. (Sondhia, 2009 and Sondhia, 2007). Hence, monitoring of herbicidal behaviour in the soil and plant parts is necessary to evaluate therefore the present study is designed to evaluate the persistence of Fomesafen in Soybean crop at different dose levels (T1 Treated @250 g a.i. ha^{-1} and T2 Treated @500 g a.i. ha^{-1}).

Materials and Methods

The experiment was conducted at Department of plant protection, Institute of Agriculture (PSB), Visva –Bharti, Sriniketan, Birbhum, West-Bengal The experiment was consisted of 3 treatment with 3 replications laid out in randomized block design. Soybean Plant samples were analyzed after 2 hours application and continued the analysis at 1, 3, 5, 7 and 10 days after application. Samples were collected following standard sampling process, i.e. samples (Soybean Plant in which fomesafen residue level is to be studied) were collected from different parts of the plot; those were then mixed and then representative sample was taken by quartering. A specific amount of the sample (20 g) was taken for extraction of the fomesafen residue with suitable solvent.

Estimation of herbicide residue

Collection of plant samples

In order to study the dissipation of Fomesafen 22.5% SL in Soybean crop samples were collected from each of the treated plots including control as per standard sampling procedures on initial 0 (after 2 hrs), 1, 3, 5, 7 and 10 days after application of the pesticide and transferred in dry ice boxes to the laboratory for analysis (Paliwal *et al*., 2017).

Analytical methodology for determination of Fomesafen residues in Soybean Plant

Weighed a 20 g of representative aliquot of finely ground soybeans into a 250 ml of round bottom flask. Added 50 ml combination of Acetonitrile and concentrated hydrochloric acid (98:2 v/v), then sonication for 15 minutes. This solution was filtered through whatman no.1 filter paper using under vacuum condition. The solution transferred in a 250 ml of graduated cylinder and again wash the flask with the 50 ml combination of Acetonitrile and concentrated hydrochloric acid (98:2 v/v) and filtered. Transfer an aliquot of the filtrate to a 500 ml of separating funnel. Diluted the extract with water (100 ml), washed with hexane (2 x 50 ml) and discarded hexane. Check the pH of the solution <1. Adjust the pH if necessary by the addition of concentrated hydrochloric acid. Partition with dichloromethane (2 x 50ml). Combine the dichloromethane extracts, evaporate to dryness on a rotary evaporator and take up the residue in dichloromethane (2 ml).

Cleanup

Ultrasonicate the extract from the above solution to ensure complete uptake of any material adhering to the flask. Place a disposable NH_2 column in the "Agilent SPE Vacuum manifold" assembly. Wet the column with CH_2Cl_2 (2 ml).

Transfer the extract onto the column. Wash the flask with 8 ml of dichloromethane and transfer to the column. Discard the dichloromethane elute. Added 5 ml of (50:50) Acetonitrile : H_2O into the column and discard elute. Elute the column with 10 ml of 1M KNO_3 adjusted to pH 9.00 with sodium hydroxide solution (1Molor) prior to using and collect the elute. Transfer the elute into a 125 ml separating funnel. Wash with the 5 ml of potassium nitrate and added to the funnel. Acidify the solution with concentrated Hydrochloric acid to pH <1. Partition with dichloromethane (2 x 10 ml). Combine the dichloromethane extracts, evaporate down to small volume (2-3 ml) on rotary evaporator and transfer quantitatively to a graduated centrifuge tube. Blow down to dryness using cleaned dry air and taken up the residue in Acetonitrile : water pH = 3.0 (water adjusted to the pH 3.0 using ortho phosphoric acid) 35:65 (2ml, 1ml – 5g of crop). Ultrasonicate to ensure complete dissolution of the extract and filter if necessary to remove any particulate matter. Transfer the solution to a vial for analysis by HPLC.

Reference analytical standard

A quantity of 10.25 mg Fomesafen reference standard (Purity 98.2%) was weighed into a volumetric flask of 10 ml capacity, dissolved in 5.0 ml mobile-phase and the volume was made up to the mark with mobile-phase[Standard Stock Solution (A) Concentration 1006.55 ppm]. A volume of 0.5 ml of the solution (A) was taken into separate volumetric flask of 50 ml capacity and the volume was made up to the mark with mobile-phase [Solution (B) Concentration 10.07 ppm]. A volume of 1.0 ml of the solution (B) was taken into separate volumetric flask of 10 ml capacity and the volume was made up to the mark with mobile-phase [Solution (C) Concentration 1.01 ppm].

HPLC Determination

Fomesafen residues were analyzed by high performance liquid chromatography method. HPLC analysis is performed on a Shimadzu HPLC, coupled to UV detector. Fomesafen standard solution was injected and measured the peak area.

System	: Shimadzu LC 2010 – Quaternary Pump, Degasser, Auto sampler, Thermostat/ DAD.
Column	: Supelcosil LC-18
Column Specifications	: 250 mm length x 4.6 mm I.D., x 5.0 µm particle size
Detector	: UV
Detector wave length	: 290 nm
Mobile phase	: As per section 9.4.1
Column oven temperature	: Ambient
Flow rate	: 1.5 ml/min
Retention time	: Fomesafen– 7.5 min(Approx.)

Calculation $\text{Residue of Fomesafen (ppm)} = \frac{A \times C}{D}$

Where, A is Peak area of each Fomesafen sample; D Mean Peak area of Fomesafen standard and C is Concentration (ppm) of the standard solution

Half-life period

The long Half-lives of the herbicides were calculated from the logarithmic plot concentration of herbicides versus time (days) with the help of following equation

T1: y = – 0.145x + 1.682, R2 = 0.980, t½ = 2.08 days

T2: y = – 0.113x + 2.018, R2 = 0.965, t½ = 2.66 days

Where, T1 is Treatment @ 250 g a.i. ha^{-1}; T2 Treatment @ 500 g a.i. ha^{-1} and t½ :- Half-life of the herbicide

Results and Discussion

Persistence of herbicide residue is great concern as persistence of herbicide residue in the plant may adversely affect human and animal health due to bioaccumulation of residue in crop produce. The applied herbicide may find its way in to stream by runoff and may result in unfortunate consequences to non-target organism. Thus, persistence and bioaccumulation of various herbicides on crop plant was evaluated (Pannacci *et al*., 2006).

The results of dissipation study of Fomesafen 22.5% SL in Soybean crop at different time intervals and their percent dissipation have been presented in Table-1. The control samples were devoid of any Fomesafen 22.5% SL residue (Singh *et al*., 2012a; Sondhia and Dixit, 2010; Sondhia *et al*., 2008).

Table 1 : Dissipation of Fomesafen in Soybean Crop

Treatment Dose (gm a.i./ha)	Days after application	Residue in ppm					(%) Dissipation
		R_1	**R_2**	**R_3**	**Mean**	**SD**	
T_0(Control)	0 (After 2 hrs.)	ND	ND	ND	-	-	-
T_1(250)	0 (After 2 hrs.)	0.45	0.46	0.44	0.45	0.01	-
	1	0.32	0.31	0.33	0.32	0.01	28.89
	3	0.21	0.20	0.22	0.21	0.01	53.33
	5	0.10	0.09	0.11	0.10	0.01	77.78
	7	0.04	0.05	0.03	0.04	0.01	91.11
	10	BDL	BDL	BDL	-	-	-
T_2(500)	0 (After 2 hrs.)	0.90	0.89	0.91	0.90	0.01	-
	1	0.82	0.83	0.81	0.82	0.01	8.89
	3	0.59	0.60	0.58	0.59	0.01	34.44
	5	0.29	0.28	0.30	0.29	0.01	67.78
	7	0.15	0.16	0.14	0.15	0.01	83.33
	10	BDL	BDL	BDL	-	-	-

Where, *ND is for Not detected and **BDL for Below Detectable Level

Regression Equations

T_1: y = – 0.145x + 1.682, R^2 = 0.980, $t_{½}$ = 2.08 days

T_2: y = – 0.113x + 2.018, R^2 = 0.965, $t_{½}$ = 2.66 days

The progressive decline of the amount of Fomesafen 22.5% SL was also evident from its dissipation curve (Fig.1) and (Fig. 2). The regression lines obtained for T1 Treated @250 g a.i. ha^{-1} and T2 Treated @500 g a.i. ha^{-1} doses corroborated that the continuous dissipation of the herbicide under study in Soybean crop followed first order reaction kinetics (Sondhia *et al*., 2008; Paliwal *et al*., 2017; Dixit and Gupta 2000; Sondhia, 2008). The half-life ($t_{1/2}$) values for Soybean crop of for T1 Treated @250 g a.i. ha^{-1} and T2 Treated @500 ga.i. ha^{-1} were calculated to be 2.08 and 2.66 days, respectively (Balasubramanian *et al*., 1999; Mehta *et al*., 2011; Singh and Singh 2011; Singh *et al*., 2012b; Ishii *et al*., 2004; Chen *et al*., 2012 and Paliwal *et al*., 2017).

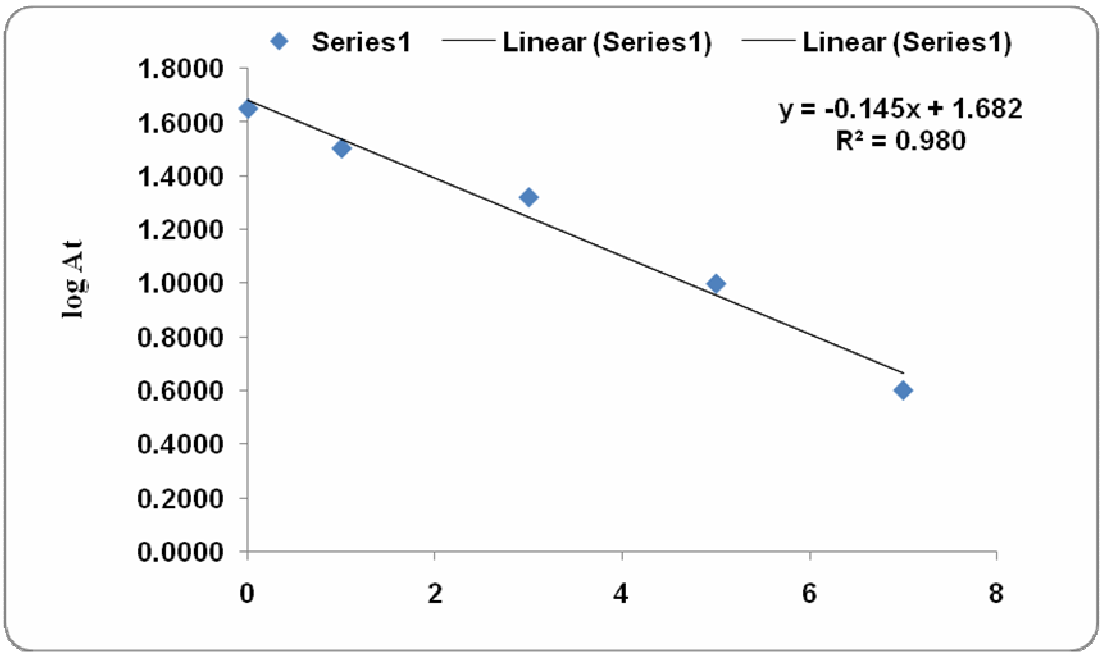

Fig. 1 : Dissipation of Fomesafen 22.5% SL residues in Soybean crop (Treated @250 g a.i. ha^{-1})

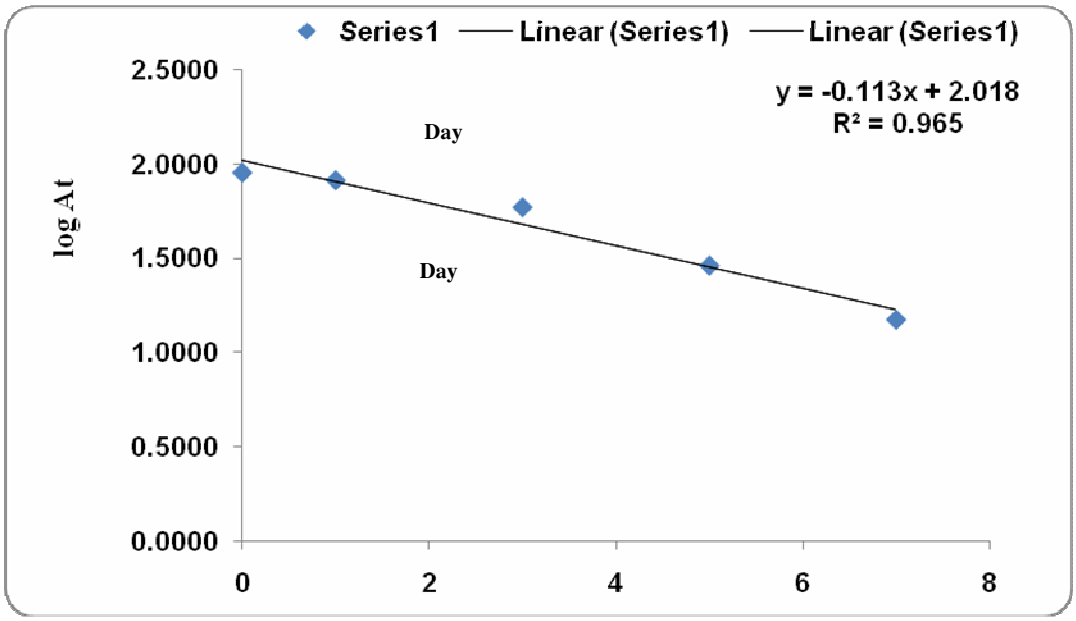

Fig. 2 : Dissipation of Fomesafen 22.5% SL residues in Soybean crop (Treated @500 g a.i. ha^{-1})

Table 2 : Results of Fomesafen in Soybean [0 Day (after 2 hrs.) Application]

Sample Code	Sample Peak Area A	Standard Concentration C (ppm)	Standard Peak Area D	Results	
				Residue content (ppm)	Average Residue (ppm)
T0R1	0	1.01	103785	ND	ND
T0R2	0			ND	
T0R3	0			ND	
T1R1	46241			0.45	0.45
T1R2	47268			0.46	
T1R3	45213			0.44	
T2R1	92481			0.90	0.90
T2R2	91454			0.89	
T2R3	93509			0.91	

Typical Calculation (ppm)

	=	A x C			
		D			
	=	46241 x 1.01			
		103785			
	=	0.45			

Where, A is Sample Peak Area; C for Concentration of Standard (ppm) and D is Standard Peak Area (*ND = Not detected)

Table 3: Results of Fomesafen in Soybean [1 Day After Application]

Sample Code	Sample Peak Area A	Standard Concentration C (ppm)	Standard Peak Area D	Results	
				Residue content ppm)	Average Residue (ppm)
T0R1	0	1.01	103785	ND	ND
T0R2	0			ND	
T0R3	0			ND	
T1R1	32882			0.32	0.32
T1R2	31855			0.31	
T1R3	33910			0.33	
T2R1	84261			0.82	0.82
T2R2	85288			0.83	
T2R3	83233			0.81	

Table 4 : Results of Fomesafen in Soybean [3 Day After Application]

Sample Code	Sample Peak Area A	Standard Concentration C (ppm)	Standard Peak Area D	Results	
				Residue content (ppm)	Average Residue (ppm)
T0R1	0	1.01	103785	ND	ND
T0R2	0			ND	
T0R3	0			ND	
T1R1	21579			0.21	0.21
T1R2	20551			0.20	
T1R3	22607			0.22	
T2R1	60627			0.59	0.59
T2R2	61654			0.60	
T2R3	59599			0.58	

(*ND = Not detected)

Table 5: Results of Fomesafen in Soybean [5 Day after Application]

Sample Code	Sample Peak Area A	Standard Concentration C (ppm)	Standard Peak Area D	Results	
				Residue content (ppm)	Average Residue (ppm)
T0R1	0	1.01	103785	ND	ND
T0R2	0			ND	
T0R3	0			ND	
T1R1	10276			0.10	0.10
T1R2	9248			0.09	
T1R3	11303			0.11	
T2R1	29800			0.29	0.29
T2R2	28772			0.28	
T2R3	30827			0.30	

Table 6 : Results of Fomesafen in Soybean [7 Day after Application]

Sample Code	Sample Peak Area A	Standard Concentration C (ppm)	Standard Peak Area D	Results	
				Residue content (ppm)	Average Residue (ppm)
T0R1	0	1.01	103785	ND	ND
T0R2	0			ND	
T0R3	0			ND	
T1R1	4110			0.04	0.04
T1R2	5138			0.05	
T1R3	3083			0.03	
T2R1	15414			0.15	0.15
T2R2	16441			0.16	
T2R3	14386			0.14	

(*ND = Not detected)

Table 7 : Results of Fomesafen in Soybean [10 Day after Application]

Sample Code	Sample Peak Area A	Standard Concentration C (ppm)	Standard Peak Area D	Results	
				Residue content (ppm)	Average Residue (ppm)
T0R1	0	1.01	103785	ND	ND
T0R2	0			ND	
T0R3	0			ND	
T1R1	822			BDL	BDL
T1R2	719			BDL	
T1R3	925			BDL	
T2R1	1028			BDL	BDL
T2R2	2055			BDL	
T2R3	1028			BDL	

(*ND = Not detected, **BDL= Below Detectable Level)

Conclusion

It was concluded that higher content of residue was found in sample taken at initially as well as during growth period with an interval of 2 days exhibited successive depletion of herbicidal residue with progressive growth of the crop till harvest. HPLC method for detection for persistence residue and dissipation indicated that the average half life values ranged for Fomesafen 22.5 % SL @250 g a.i. ha^{-1} is 2.08 days & Fomesafen 22.5 % SL @500 g a.i. ha^{-1} is 2.66 days respectively and At 10 days after application, for Soybean crop, the residue of Fomesafen 22.5% SL was below detectable level @250 g a.i. ha^{-1} and @500 g a.i. ha^{-1} doses.

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