Full Paper

Interaction of a di-nitro aniline herbicide (Trifluralin) with soil vegetation system under sub-tropic condition: A dissipation kinetics study

Dwaipayan Sengupta[a*], Md. Wasim Aktar[b], Samsul Alam[c] and Ashim Chowdhury[a]

[a]Department of Agricultural Chemistry and Soil Science, Institute of Agricultural Science, University of Calcutta, Kolkata, West Bengal, India.
[b]Pesticide Residue Laboratory, Department of Agricultural Chemicals, Bidhan Chandra Krishi Viswavidyalaya, Mohanpur-741252, Nadia, West Bengal, India.
[c]Institute of Pesticide Formulation Technology Sector-20, Udyog Vihar, Opp. Ambience Mall (on NH-8), Gurgaon-122016, Haryana, India.

ABSTRACT: *A field study was carried out to investigate persistence and dissipation kinetics of Trifluralin (48 EC) applied pre emergently in Green gram (Variety T-44) @ 1 Kg ai ha^{-1} (T$_1$) and 2 Kg ai ha^{-1} (T$_2$) for the control of broad leaf weeds during kharif 2006. The dissipation on 90 days was around 71.56 - 64.55% in T$_1$ and T$_2$. Kinetics studies revealed that dissipation of Trifluralin residues followed first order kinetics. The half life values observed were 60.21 days in T$_1$ and 75.56 days in T$_2$. Irrespective of any dose no residues were detected in cropped soil as well as plant samples at harvest.*

Keywords: soil, green gram, residues, Trifluralin, dissipation, persistence

---

* Corresponding author. E-mail: sengupta_d@yahoo.co.in. Tel. +91 9432157130

Introduction

Green gram, *Vigna radiata* (L.) R. Wilczek is one of the important summer pulse crops grown in India. It is affected by a number of broad leaf weeds like *Trianthema portulacastrum, Dactylocterium aegyptium, Echinochloa colonum* and *Digera arvensis*. The weeds compete with crop for nutrients, moisture, space and light and cause an average loss of about 25-50% depending upon the species and density of weeds [1, 2]. Yield losses due to weeds in Green gram have been reported to be 42-68% [3, 4].

Trifluralin - 2,6-dinitro-*N,N*-dipropyl-4-(trifluoromethyl)benzenamine - is a representative of dinitroaniline herbicide group and widely used against weeds of various crops like soybean, legumes, beans etc. It has been found effective for the control of broad leaf weeds of green gram [5]. It also controls many annual grasses in cotton, fruit trees, nut trees, vines, ornamentals, soya beans, groundnuts, oilseed rape, sunflowers, lucerne, peas, sweet potatoes, mint, and non-crop areas [6]. Though this herbicide controls the weed but they may persist in the soil. It may exist in the harvested pod or green plant also and thus cause health hazard to human being [7]. Studies on analytical methods for Trifluralin determination, metabolism in animals, plants and fish, degradation in soil, photodegradation, adsorption to soil, volatilization, persistence in fields, residues in agricultural crops and river water are briefly reviewed [8].

This crop is highly remunerative and sprayed heavily with herbicides close to harvest, which may leave harmful residues in consumable parts of the plants. Since there are no data available on the persistence of Trifluralin on green gram, the present investigation was conducted to determine the dissipation pattern as well as the residue level of the herbicide (Trifluralin) in plants under West Bengal (East Indian) climatic condition when applied @ 1.0 Kg.a.i.ha^{-1} (T$_1$) and 2.0 Kg.a.i.ha^{-1} (T$_2$) along with untreated control (T$_3$).

Material and Methods

Design of field experiment

Green gram (Variety T-44) crop was raised in fields of Agricultural Research Farm, Baruipur under the operational area of Institute of Agricultural Science, University of Calcutta, Kolkata, West Bengal, India in the month of July 2006. A randomized block design (RBD) with 3 replications and two treatments, including an untreated control was used. The plot size was 6 x 3 m.

Climatic conditions

The climatic parameters for the season (July, 2006 - November, 2006) were: temp. min. 22.13 °C, max. 31.42 °C; relative humidity 93.65%; rain fall 258 mm.

Application of herbicides

Trifluralin (Treflan 48 EC) was applied @ 1 Kg ai ha^{-1} (T_1 recommended dose) and 2 Kg ai ha^{-1} (T_2, double the recommended dose) as a pre emergent herbicide. Identical portions of plants were maintained as controls and were sprayed with water.

Collection of samples

Representative samples (1 Kg) of soil from 0-15 cm depth were collected from 10 places using a steel auger tube. The samples were collected at 0 (2 h), 3, 7, 15, 30, 60 and 90 days after treatment. Plant samples (seeds or pods) along with cropped soil samples were collected only at harvest (120 days after application).

Extraction and clean up of residues

The soil samples were dried under shade, ground, sieved through 2 mm mesh sieve and 20 g representative sample was taken in a 250 mL conical flask. Two drops (0.5 mL) of ammonia solution was added to the flask and was thoroughly mixed and then left till there was no smell of ammonia.

The samples were extracted and cleaned-up as per following method. Soil samples were extracted with 100 mL acidic methanol (98% methanol, 2% concentrated HCl) by shaking for 1.5 h on a mechanical shaker. The extracts were centrifuged at 2000 rpm for 10 min and he supernatant transferred to 1 L separator funnels. Extracts were subjected to liquid-liquid partitioning with hexane thrice (50, 30, 20 mL) after diluting with 250 mL solution of 10% sodium chloride. The hexane extract was concentrated to 10 mL on rotary vacuum evaporator after addition of one drop of mineral oil.

Glass column (60 cm x 22 mm id) was compactly packed with 4.5 g adsorbent mixture (Florisil: Celite:activated charcoal 2:2:0.5) in between the layers of anhydrous sodium sulphate. The column was prewetted with hexane and concentrated extract loaded at the top. The column was eluted with 125 mL mixture of benzene: hexane (3:2). The eluent was concentrated first on rotary vacuum evaporator followed by gas manifold evaporator. The final volume was made to 2 mL with freshly distilled *n*-hexane.

Estimation of residues

The samples were analyzed on Hewlett Packard 6890N Network Series coupled with autosampler gas chromatograph equipped with ^{63}Ni electron capture detector (ECD) and SPB-5 capillary column (30 m x 0.32 mm Id, 0.25 m film thickness). The GC parameters were as follows: Temperatures - column 180°C, injector port 250°C and detector 250°C; flow of carrier gas (N_2) 2 mL/min, split ratio 1:10. Retention time

observed for Trifluralin was 3.31 min. The limit of detection (LOD) and limit of quantification (LOQ) were 0.01 µg g^{-1} and 0.03 µg g^{-1}, respectively.

Recovery experiment

In order to estimate the efficiency of the method, recovery experiment was conducted by fortifying untreated samples of green gram seeds or pods and cropped soil with Trifluralin (analytical standard, purity 98.97%, Sigma Aldrich) @ 0.25, 0.50 and 1.00 µg g^{-1} level. The fortified samples were analyzed and estimated following the method as described earlier.

Results and Discussion

Average recoveries of Trifluralin from different substrates fortified @ 0.25, 0.50 and 1.00 µg g^{-1} ranged from 90-96% and 88-98% for cropped soil and green gram seeds or pods, respectively (Table 1).

Table 1. Results of method validation by recovery analysis of Trifluralin (analytical grade) from test samples.

Substrates	Amount fortified (µg g^{-1})	Amount recovered (µg g^{-1})	Recovery of Propineb (%)	Avarage recovery of Propineb (%)
Cropped Soil	0.25	0.225	90	
	0.50	0.47	94	93.33
	1.00	0.96	96	
Green gram seeds or pods	0.25	0.22	88	
	0.50	0.48	96	94.00
	1.00	0.98	98	

The residue data is presented in Table 2. The initial residues were 1.778 and 3.179 µg g^{-1} in T$_1$ and T$_2$ which dissipated to 1.664 and 2.876 µg g^{-1} only in 3 days recording a mere loss of 6.38 and 9.54%, respectively. The residues persisted beyond 90 days. On 90th day, 71.56 and 64.55% dissipation was recorded. The residue data was subjected to analysis using Hoskin's method [9]. It is clear from the Figure 1 that Trifluralin exhibits first order dissipation. The dissipation was slow, probably because of its high affinity towards soil organic matter (Koc = 4400). No residue was detected in seeds as well as in cropped soil samples at harvest (120 days after application) irrespective of any dose (Table 3) indicating no translocation of the herbicide from soil to

different plant parts. The half-life values for single and double doses were 60.21d and 75.26d respectively indicating slightly slower dissipation at high rate of application (Table 4).
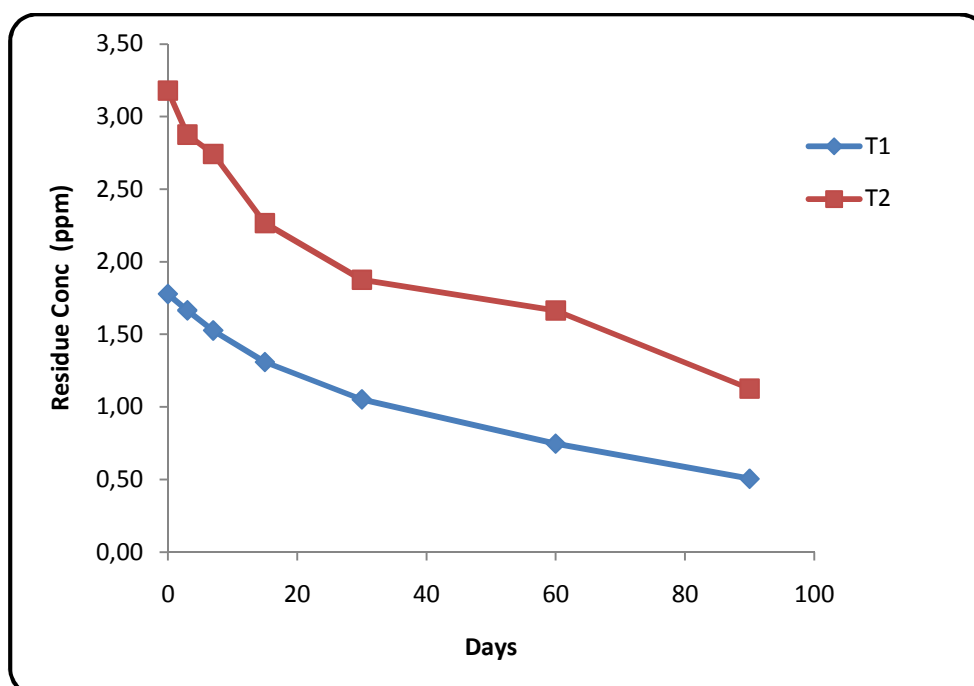

Figure 1. Dissipation of Trifluralin under green gram cropped soil.

Table 2. Persistence and dissipation of Trifluralin residues in cropped soil.

Sampling Interval (in days)	Residues (in μg g^{-1}) M*± SD (% of Dissipation)	
	T_1 (1.0 kg a.i. ha^{-1})	T_2 (2.0 kg a.i. ha^{-1})
0	1.778±0.173 (-)	3.179±0.743 (-)
3	1.664±0.097 (6.38)	2.876±0.106 (9.54)
7	1.526±0.069 (14.16)	2.742±0.476 (13.73)
15	1.309±0.030 (26.37)	2.267±0.017 (28.70)
30	1.052±0.066 (40.85)	1.876±0.021 (40.99)
60	0.748±0.036 (57.94)	1.664±0.540 (47.66)
90	0.506±0.004 (71.56)	1.127±0.005 (64.55)

M* = Mean of three replicate

As evident from the data, the dissipation of Trifluralin was slow (64.55-71.56% on 90d) under the field condition. Thus chemistry of Trifluralin after soil application was preferably governed by the adsorption phenomenon. The physicochemical as well as biological transformation processes such as volatilization and leaching loss, runoff, microbial degradation, hydrolysis etc. operates at a slow pace. In present study, results regarding uniphasic dissipation of Trifluralin are not in confirmatory to earlier reports

[10-12]. In another report, half- life period in fresh clay soil has been reported to be 94-99 day [13] which is similar to our observation. The differences could be due to depth of incorporation, soil temperature, availability of soil moisture, soil aeration and soil organic matter content. Quite similar to our results, half-life period of 27 and 30 days in vineyard soil has been reported from South Australia [14].

Table 3. Residue of Trifluralin in green gram seeds and cropped soil at harvest.

Days after application	Substrates	Treatment	Residues in ppm (μg/g) (M* ± S.D.) [Dissipation (%)]	
			Season-I	Season-II
Harvest	Seeds	T_1 (1.0 kg a.i. ha^{-1})	BDL [-]	BDL [-]
	Soil		BDL [-]	BDL [-]
Harvest	Seeds	T_2 (2.0 kg a.i. ha^{-1})	BDL [-]	BDL [-]
	Soil		BDL [-]	BDL [-]

BDL = Below detectable limit (<0.01 ppm)
M* = Mean of three replicate

Table 4. Regression equations for first order dissipation of Trifluralin.

Treatments	Regression equation	Correlation coefficient (r)	Half life (days)
1.0 Kg ai ha^{-1}	Y = 3.226-0.005 X	0.991	60.21
2.0 Kg ai ha^{-1}	Y = 3.462-0.004 X	0.964	75.26

Conclusion

The dissipation of Trifluralin in soil under green gram in field conditions was quite fast. Although the residues remained in detectable amount beyond 90 days but the residues at these levels may not affect the next crop in rotation. As the residues were found below the detectable limit in all harvest samples (120 days after application), therefore it might be stated that Trifluralin may not cause any residual toxicity problem in green gram which is also befitting with the harvest schedule of green gram cultivation of eastern region of our country.

Acknowledgements

References and Notes

[1]   Bhan, V. M.; Malik, R. K. *Pesticides* **1993**, *17*, 100.

[2]   Badiger, R. G.; Hiremath, S. M.; Paul, S. A.; Chetti, M.B. Abstract of Proc Third Agricultural Science Congress, Punjab Agriculture University, Ludhiana, p. 327, 1997.

[3]   Patro, M.; Prostry, C. *Ind. J. Weed. Sci*. **1994**, *26*, 79.

[4]   Singh, S.; Singh, A. N.; Bhan, V. M. *Weed. Sci*. **1995**, *28*, 110.

[5]   Malik, R. S.; Yadav. A.; Malik. R. K. *Weed. Sci*. **2000**, *32*, 181.

[6]   Rivera, C. M.; Burnside, K.; Strait, A. O. Proceedings of North Central Weed Control Conference, p. 65-66, 1982.

[7]   Speich, P. *Progres Agricole Et Viticole **2003**,* 120, 113.

[8]   Mattern, G. C.; Liu, C. H.; Louis, J. B.; Rosen, J. D. *J. Agri. Food. Chem*. **1991**, *39*, 700.

[9]   Hoskins, M. L. *Plant. Protec. Bull*. **1961**, *9*, 163.

[10] Duseja, D. R.; Holmes, E. E. Soil Sci. **1978**, *125*, 41.

[11] Grover, G.; Smith, A. E.; Shewckuk, S. R.; Cessna, A. J.; Hunter; J. H. *J. Environ. Qual.* **1988**, *17*, 543.

[12] Lafleur, K. S.; Mccaskill, W. R.; Gale, J. R. *Soil. Sci*. **1978**, *126*, 285.

[13] Smith, A. E.; Aubin, A. J.; Derksen, D. A. *Bull. Environ. Contam. Toxicol.* **1988**, *41*, 569.

[14] Guang, G. Y.; Williams, B.; Ying, G. G. *Agri. Ecosys. Environ*. **2000**, *78*, 283.