Bull Environ Contam Toxicol (2011) 86:242–245
DOI 10.1007/s00128-010-0180-0

Fate of Fipronil in Cotton and Soil Under Tropical Climatic Conditions

Indu Chopra · Reena Chauhan · Beena Kumari · K. K. Dahiya

Received: 2 July 2010 / Accepted: 28 October 2010 / Published online: 15 January 2011

Abstract Field study was carried out to investigate fate of fipronil (Regent 0.3G) in cotton and soil applied at the time of sowing of cotton crop (Variety: H-1117) @ 56 (T_1) and 112 g a.i.ha^{-1} (T_2) during kharif season (summer season, from April to November) 2006–07. The residues of fipronil in both the doses dissipated almost completely with in 90 days. Kinetic studies revealed that dissipation of fipronil followed first order kinetics with half-life period of 23.35 days in single dose and 24.31 days in double dose. At the time of harvest, residues in soil, cotton lint and seed were below the quantifiable limit of 0.01 mg kg^{-1}.

Keywords Fipronil · Cotton · Half-life · Degradation

Cotton (*Gossypium* spp.), white gold, is one of the most important commercial crop which is cultivated in about 80 countries of the world and 10 countries including India account for nearly 85% of the total production. It contributes to over 30% of foreign exchange earnings of the country (Sen 2003). With nearly 8.97 million hectare under cotton crop, India ranks first in the world in area (about 21%) and third in total production with the level of 14.2 million of cotton lint and the average productivity of about 293 kg lint cotton/ha (Gupta et al. 2008). This low rate of production in the country is due to many factors, out of which heavy attack of a wide variety of insect pests and lack of their effective control during crop season is most important. Among the insect pest of economic importance, American bollworm, spotted bollworms, pink bollworm, tobacco caterpillar, whitefly and leafhopper are the most important and have been reported to cause serious quantitative and qualitative losses (Dhaliwal et al. 2006).

Insecticides have been used widely to control the pests on cotton because of their easy adaptability, effectiveness and immediate control. The availability of wide range of synthetic insecticides though has been responsible for increased crop production and drastic reduction in the incidence of insect pests and vector borne diseases but at the same time heavy reliance of farmers on synthetic insecticides has led to shortening of the life span of many valuable insects, increased cost of production, pest resistance, resurgence and residues in food, fodder and feed, destruction of beneficial organisms and wild life and direct hazards to the users. The use of the eco-friendly insecticides to suppress the pest population is an important component of integrated pest management programme. Fipronil {5-amino-3-cyano-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-(trifluoromethyl)-sulfinyl}pyrazole is a low dose, relatively new broad spectrum phenylpyrazole insecticide with potential value for control of a wide range of crop, public hygiene, amenity and veterinary pests. It is one of the most persistent, lipophilic and toxic insecticides licensed for use since banned/restricted use of dieldrin, lindane and DDT. It is active against various insect pests of crops, notably rice insects, thrips (citrus, cotton, mango), termites (sugarcane, corn) and click beetles (cereals, corn, sunflower) (Mulrooney and Goli 1999). Fipronil is sold commercially under various trade names like regent, termidor etc. in India. Due to negligible literature of fipronil persistence on cotton crop, this experiment has been undertaken to generate data for the fate of

I. Chopra · R. Chauhan
Department of Chemistry and Physics,
Department of Entomology, CCS Haryana Agricultural University, Hisar 125 004, India

B. Kumari (✉) · K. K. Dahiya
Department of Entomology, CCS Haryana Agricultural University, Hisar 125 004, India
e-mail: beena@hau.ernet.in

fipronil on this crop and soil under tropical climatic conditions of Haryana, India.

Materials and Methods

Reference standards of fipronil (purity, 97.5%) were obtained from Bayer Crop Science Ltd, India. All reagents and solvents used were of analytical grade. A field experiment was conducted on sandy loam soil (EC 2 dSm^{-1}; K_c 10.08, P_2O_5 15 kg ha^{-1}) having pH 7.6 and organic carbon 0.67% at Research Farm of the Department of Plant Breeding, CCS HAU, Hisar using randomized block design (RBD) with a plot size of 25 m^2 on which cotton (*Gossypium hirsutum*) variety H-1117 was raised during *Kharif* season (summer season, from April to November) of 2006–07. Fipronil (Regent 0.3% G) was applied in the field manually along with the sowing at two different doses. The treatment one (T_1) consisted of 56 g a.i.ha^{-1} and treatment two (T_2) consisted of 112 g a.i.ha^{-1} and a control where no pesticide was applied. Residues of fipronil were estimated in soil under the cover of cotton crop drawn from top 15 cm of soil profile on 0 (1 h after treatment), 1, 3, 7, 15, 30, 60, 90 days of treatment and in lint and cotton seeds at the time of harvest.

Soil samples were extracted as per method of Kumari et al. (2008). A representative soil sample of 20 g mixed with 0.5 g each of activated charcoal and florisil was filled in a 60 cm long glass column having 22 mm i.d. between two layers of anhydrous sodium sulphate. The residues were eluted with 125 mL of hexane: acetone (9:1 v/v). The organic layer was concentrated on rotary vacuum evaporator and final volume was made to 2 mL in n- hexane.

The analysis of cotton lint and seed for fipronil was done by adopting the method of Reddy et al. (2007). A representative sample of 10 g lint and 5 g of seeds was extracted with the solvent hexane: acetone (1:1 v/v) on mechanical shaker. The contents were filtered through 2–3 cm pad of anhydrous sodium sulphate and concentrated the extracts to 50 mL using a rotary vacuum evaporator and transferred to separatory funnel. The extract was diluted with 10% brine solution and partitioned thrice with hexane (50, 30, 20 mL) by vigorous shaking. The organic layer was collected each time and passed through the pad of anhydrous sodium sulphate and pooled together. The pooled organic layer was concentrated to 10 mL. For clean up the extracts were passed through column containing adsorbent mixture (neutral alumina: Florisil: activated charcoal, 1:2:0.5 w/w) in between two layers of anhydrous sodium sulphate. The column was eluted with 100 mL solution of hexane: acetone (9:1 v/v). The cleaned extract was evaporated to dryness and finally dissolved in 5 mL n-hexane for analysis. Fortification with fipronil in cotton lint seed and soil at the rate of 0.25, 0.50 and 1.0 mg kg^{-1} to validate the analytical method and get the percent recovery before the field samples were analysed.

A Shimadzu Gas Chromatograph GC-2010 equipped with electron capture detector (ECD) ^{63}Ni was used for residue analysis of fipronil in cotton lint, seed and soil. A capillary column HP-1 (30 m × 0.32 mm i.d. × 0.25 µm film thickness) was used and injector was kept at split mode with split ratio of 10. The column temperature was initially maintained at 150°C and programmed at 8°C min^{-1} to 190°C with hold time of 2 min then programmed at 15°C min^{-1} to 280°C with hold time of 10 min. Injector and detector temperature were maintained at 280 and 300°C, respectively. Under the above conditions, the retention time of fipronil was 14.069 min.

Result and Discussion

The percent recovery of fipronil conducted in control samples of cotton lint, seeds and soil are given in Table 1. In cotton lint, recovery of fipronil were in the range of 82.11–85.63%, in seeds it was 80.01–83.65% and soil 93.14–96.13%. The limit of quantification of the method was 0.01 mg kg^{-1}.

As evident from Table 2, the fipronil when applied @ 56 g a.i. ha^{-1}(T_1) had average initial deposits of 0.098 mg kg^{-1} on 0 day (1 h after treatment) which dissipated to 100% leaving residues below detectable level of 0.01 mg kg^{-1} after 90 days of the treatment. While at T_2 (112 g a.i. ha^{-1}), the initial residues of 0.189 mg kg^{-1} on 0 (1 h after treatment) day dissipated to 0.011µgg^{-1} residues in the soil after 90 days of the treatment showing percent dissipation of 94.17. The residues dissipated almost completely showing below detectable (<0.01 mg kg g^{-1}) residues at both levels of treatment at the time of harvest. In other words, complete dissipation took place from both the

Table 1 Recovery study of fipronil residues on cotton lint, seed and soil

Substrate	Level of fortification (mg kg^{-1})	Mean recovery (%)* ± SD
Cotton Lint	0.25	82.11 ± 2.45
	0.50	84.07 ± 3.80
	1.0	85.63 ± 3.01
Cotton Seed	0.25	80.01 ± 2.74
	0.50	82.13 ± 3.91
	1.0	83.65 ± 3.49
Soil	0.25	93.14 ± 2.64
	0.50	94.60 ± 4.01
	1.0	96.13 ± 2.90

Table 2 Persistence of fipronil residues in soil at two doses

Days after treatment	Residue (mg kg^{-1})*			
	T_1 (56 g a.i.ha^{-1})		T_2 (112 g a.i.ha^{-1})	
	Average	% Dissipation	Average	% Dissipation
0	0.098	–	0.189	–
1	0.079	19.38	0.155	17.98
3	0.066	32.65	0.130	31.21
7	0.041	58.16	0.083	56.08
15	0.034	65.30	0.070	62.96
30	0.020	79.59	0.043	77.24
60	0.013	86.73	0.027	85.71
90	BDL	100	0.011	94.17
180 (Harvest)	BDL	100	BDL	100
Rate constant k ($days^{-1}$) = 0.0296			Rate constant k ($days^{-1}$) = 0.0285	
Correlation coefficient r = −0.9679			Correlation coefficient r = −0.9709	
Regression equation y = 1.8278 − 0.01289x			Regression equation y = 2.1252 − 0.01238x	
$t_{1/2}$ = 23.35 days			$t_{1/2}$ = 24.31 days	

* Average of three replicates, Below detectable level (BDL): 0.01 mg kg^{-1}

CD ($p = 0.05$) for treatments = 0.0309; for days = 0.0618; for days × treatment = N.S

doses in 90 and 180 days i.e. time interval between fipronil application and harvest of the crop.

The dissipation of fipronil residues in soil followed first order kinetics (Fig. 1). Statistically analyzed data showed that the interaction between days and treatment was found to be non-significant and critical difference ($p = 0.005$) for treatments was found to be 0.0309 while for days it was 0.0618. The factors which have appeared to have played role in rapid dissipation/degradation of fipronil under the cover of cotton crop can be considered as relatively low dose (56–112 g a.i. ha^{-1}) and favourable climatic conditions like high temperature. Other factors such as volatilization,

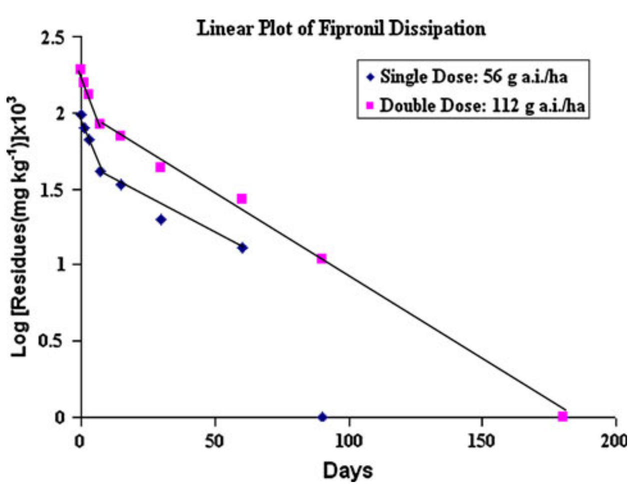

Fig. 1 Dissipation kinetics of fipronil in soil

leaching and uptake by the crop can also be considered to have played some role leading to complete dissipation of insecticide by the harvest of crop. The half life of fipronil in soil was found to be 23.35 and 24.31 days at T_1 and T_2 doses respectively.

Pei et al. (2004) reported that residues of fipronil in soil were below detectable levels after 47 days of the spray applied at levels of 24 and 48 g a.i hm^{-2} and the half life of fipronil in soil was found to be 7.3 days and value of 'r' was found to be −0.935. Mulrooney et al. (1998) reported that fipronil degraded slowly on loamy soil when exposed to light, with half life of 34 days. Residues of fipronil found in soil under the paddy crop applied @ 7.5 and 15.0 kg a.i. $acre^{-1}$ degraded in soil following biphasic first order kinetics with half life periods of 9.50 and 10.31 days in respective doses (Kumari, 2008).

Kharbade and Dethe (2000) reported non detectable residues of fipronil (0.3% G and 5 SC) in sugarcane juice applied at the levels of 100–200 g a.i.ha^{-1}. Both formulations, even at the double dose of 400 g a.i.ha^{-1} did not leave the detectable levels of residues. Fipronil residues were also found to be below detectable levels in vegetable applied @ 24 and 48 ga.i.hm^{-2} by Pei et al. (2004). Gupta et al. (2008) reported that in gram, fipronil residues applied @ 50 and 100 g a.i. persisted beyond 7 and 13 days at low dose and high dose with half-life of 1.08 and 2.88 days. In case of okra 98%–100% dissipation was recorded in 7 days with half life varying from 0.65 to 1.12 days on brinjal, the residues persisted beyond 10 days at both the doses and half life varied from 1.84 to 2.31 days. Fipronil residues

Table 3 Residues (mg kg^{-1}) of fipronil in lint and cotton seed at harvest

Commodity	T_1 (56 g a.i.ha^{-1})	T_2 (112 g a.i.ha^{-1})
Lint	BDL	BDL
Cotton seed	BDL	BDL

were found to be below detectable levels in paddy grains and straw at the time of harvest when applied @ 7.5 and 15.0 kg a.i. $acre^{-1}$ by Kumari (2008).

Absence of detectable amount of fipronil residues in cotton lint as well as seed from T_1 and T_2 during 2006–2007 (Table 3) indicates either complete degradation of the insecticide in the plant or absence of translocation of the pesticide even in the trace amounts. Interval between application of fipronil and harvest of crop was 180 days, during which the total biomass increased tremendously resulting in dilution of the translocated pesticide and enhanced enzymatic degradation due to enzymatic activity in the cotton lint.

Similarly in cotton seed also, enzymatic activity appears to have contributed towards more or less complete degradation of the residue which might have accumulated there. Additionally, fipronil applied at pre emergent stage, got exposed to drastic climatic conditions (high temperature) resulting in rapid dissipation of residues. However, role of photo degradation, chemical degradation and to some extent volatilization can not be ruled out. Keeping all these factors in consideration absence of detectable residues in cotton lint and seed, at the tested doses appeared to be justified and logical.

As per the present study, though fipronil is highly persistent in soil it can degrade faster in plants, the temperature and rainfall of tropical climate of India may further reduce the residue deposit. There is no carry over of this insecticide to the next crop as no residues were found in soil at harvest. Therefore insecticide can be used safely on cotton crop under tropical climatic conditions of India.

Acknowledgments The authors wish to express their gratitude to the Head, Department of Entomology for providing research facilities.

References

Dhaliwal GS, Singh R, Chhillar BS (2006) Essentials of Agricultural Entomology. Kalyani Publishers, Ludhiana, p 451

Gupta S, Gajbhiye VT, Gupta RK (2008) Persistence of fipronil in/on okra,brinjal and gram. In: First International Conference on Agrochemicals Protecting Crop, Health and Natural Environment held at New Delhi from 8–11 January 2008. p 193

Kharbade SB, Dethe MD (2000) Residues of fipronil in sugarcane. Pestology XXIV(10):38–39

Kumari Beena (2008) Degradation of fipronil in soil under paddy crop. In: First international conference on agrochemicals protecting crop, health and natural environment held at New Delhi from 8–11 January 2008. p 124

Kumari B, Madan VK, Kathpal TS (2008) Status of insecticide contamination of soil and water in Haryana, India. Environ Monit Assess 136:239–244

Mulrooney JE, Goli D (1999) Efficacy and Degradation of Fipronil applied to cotton for control of *Anthonomus grandis grandis* (Coleoptera: Curculionidae). J Econ Entomol 92(6):1364–1368

Mulrooney JE, Wollenbarger DA, Howard KD, Goli D (1998) Efficacy of ultra low volume and high volume applications of fipronil against the boll weevil. J Cotton Sci 23:110–116

Pei Z, Yitong L, Gan JJ (2004) Dynamics of fipronil residue in vegetable- field ecosystem. Chemosphere 57(11):1691–1696

Reddy KD, Reddy KN, Mahalingappa PB (2007) Dissipation of fipronil and profenphos residues in chillies (Capsicum annum L.). Pestic Res J 19(1):106–107

Sen A (2003) www.India.OneStop.com.GlobalBusinessNetwork