



Column studies to assess behavior of fipronil in sandy loam soil

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Received: 02 January 2019; Accepted: 19 March 2019

Key words: Fipronil, GC, Leaching, Sandy loam soil

From last few years, there has been rising concern in relation to pesticides used in agriculture and their impacts on natural resources. As we all know that because of pesticides, our production not only get maximize but also evaluate risks of negative impacts on natural resources (Júnior *et al.* 2014). Soil deposition and various transport processes may occur after application of pesticides on crops which need to be characterized and recognized by field studies. According to Moreira *et al.* (2012) pesticides sprayed in tropical regions can dissipate faster than in temperate regions because of increased volatility and enhanced degradation rates.

Fipronil {5-amino-3-cyano-1-[2,6-dichloro-4-(trifluoromethyl) phenyl]-4-(trifluoromethyl) sulfinyl} pyrazole is a low dose soil and foliar insecticide which was developed by Rhone- Polenc Ag Company. It has been found to be effective against variety of pests including rice insects, thrips of mango, citrus, cereals and termites in corn and sugarcane (Hadjmohammadi *et al.* 2006). It is a broad spectrum insecticide which disrupts the insect central nervous system (CNS) by blocking the channel of chloride ions through the gamma amino butyric acid (GABA) receptor and glutamate-gated chloride channels (GluCl), components of the central nervous system (Zhao *et al.* 2003, 2004, 2005, Islam and Lynch 2012, Murillo *et al.* 2011). It is highly toxic to aquatic animals, bees and upland game birds as it acts as a slow poison (Li *et al.* 2010). It is carcinogenic and has potential to contaminate ground water (Gan *et al.* 2012). No information is available on the leaching behavior of fipronil in agricultural soil under Indian tropical conditions. Therefore the present investigation was designed to obtain information on the leaching behavior of fipronil (Regent 0.3G) in soil columns of a sandy loam soil of northern India.

Soil: The soil used in the study was collected from the experimental Research farm of the CCS Haryana

Agricultural University, Hisar, India during 2015–16. The soil was collected from the 0–15 cm soil profile, air dried, ground to pass through a 2 mm sieve and stored in plastic bags at room temperature. The physicochemical characteristics of the soil, determined by standard methods, were: pH 7.6, organic carbon 0.67, EC 2dS/m, K 10.08, P₂O₅ 15 kg/ha.

Chemicals and Reagents: Fipronil standard with high purity (99.5%) was supplied by M/S Bayer Crop Science India Ltd. whereas commercial formulation (Regent 0.3G) was purchased from local market. Stock solution (100 mg/L) of fipronil was prepared in acetone and was further diluted to prepare the working solutions of 2.00, 1.50, 1.00, 0.50, 0.25, 0.10 and 0.001 mg/L for constructing a calibration curve. Other common solvents including acetone, dichloromethane and hexane were procured from Merck, Darmstadt, Germany and were redistilled in glass apparatus before use.

Leaching experiment: The experiment was conducted in laboratory at ambient temperature (32°C ± 2). For this study, plexi-glass columns (90 cm × 5 cm i.d) fitted with a perforated sieve and covered with Whatman filter paper were used. Columns were sequentially filled with soil (bulk density 1.5 g/cm³) up to the height of 60 cm. The surface of each column was then covered with sand to maintain uniformity of the column surface during water application. Filter paper disks were placed on top of each column for uniform dispersion of water across column surface. A perforated PVC cap connected to a funnel with polyethylene tubing was attached to the bottom of each column for collecting leachates in the flasks.

Fipronil (Regent 0.3G) was dissolved in deionized water and simultaneously applied to the top of the column at equivalent dose of field dose, i.e. 56 and 112 g a.i./ha, respectively in three replicates. The columns were then irrigated with 98 ml of water daily for six days (equivalent to 300 mm rainfall) at the time interval of 24 h. One set of soil columns in triplicate receiving only respective amount of distilled water served as control. Water eluting from the column was collected as leachate in flask in three fractions and stored at 4°C for further analysis. After six days, when addition of water was completed, the soil columns were allowed to drain for 36 h. Columns were then cut into two

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equal halves and the soil was sampled from different segment of 10 cm each and used for residues analysis.

Chemical analysis: Extraction of fipronil residues from soil and leachates was done as per method of Kumari *et al.* (2008). Ground, sieved and dry representative subsoil (15 g) of each segment was mixed with activated charcoal, florisil (0.3 g each) and 10 g anhydrous Na_2SO_4 . The mixture was packed compactly in a glass column (60 cm $\times$ 22 mm i.d.) between two layers of anhydrous Na_2SO_4 . Fipronil residues were eluted with 125 ml of hexane: acetone (9:1 v/v). The organic layer collected was concentrated using rotary vacuum evaporator and final volume was made to 2 ml in n-hexane. The leachates were subjected to liquid-liquid partitioning with dichloromethane: hexane (15:85 v/v) thrice after diluting with 5% NaCl solution. The organic layer collected was processed similarly as mentioned above.

GLC Estimation: Residues of fipronil were determined by gas liquid chromatography [Model: Shimadzu 2010] equipped with ^{63}Ni ECD and HP-1 capillary column (30 m $\times$ 0.32 mm i.d. $\times$ 0.25 μm film thickness) of 5 % diphenyl and 95 % dimethyl polysiloxane. Other GC parameters were as follows: Temperature ($^{\circ}\text{C}$):

Oven: 150 $^{\circ}$ (5 min) 8 $^{\circ}$ /min 190 $^{\circ}$ (2 min) 15 $^{\circ}$ /min 280 $^{\circ}$ (10 min). Injection port: 280 $^{\circ}\text{C}$; Detector: 300 $^{\circ}\text{C}$. Carrier gas (N_2) flow was maintained at 2 ml/min with split ratio of 1:10. Retention time (Rt) for fipronil was observed at 14.069 min.

Recoveries of fipronil carried out for soil and water at two levels of 0.25 and 0.50 mg/kg were found to be 92 to 96% and 95 to 99%, respectively. Limit of detection (LOD) and limit of quantitation (LOQ) were 0.001 and 0.003 mg/L for water and soil.

Fipronil residues found at different depths of soil under study are presented in Table 1. The results showed that the insecticide leached up to the depth of 40 cm at 300 mm rainfall condition. The insecticide was found to be maximum at top soil with the depth of 0-10 cm at both the application rates though the concentration was higher at T_2 (112 g a.i./ha) dose as compared to T_1 (56 g a.i./ha).

Statistical analysis showed that there were significant differences in the recovered amount of fipronil residues at 0 to 30 cm depth at both application rates. It was also found that irrespective of soil depth, residue levels were significantly low in single dose as compared to the double dose. From 30 cm depth onwards, the residues of the insecticide could not be detected at single dose whereas fipronil concentration was found to be 0.003 mg/kg at double dose for the same.

Fipronil content at 0-60 cm depth in sandy loam soil is presented in Fig 1. At T_1 , the results indicate that more than 80% of the insecticide was found in top 0-10 cm layer of soil with the concentration of 0.010 mg/kg. The next two soil sections, 10-20 cm and 20-30 cm, contained 0.003 mg/kg (8.33%) of the fipronil each. Beyond this depth the amount of fipronil remained below detectable limit (BDL) of 0.003 mg/kg which shows that the insecticide did not move beyond 30 cm depth of the soil at T_1 . On the other hand, results for T_2 revealed that about 90% of the total fipronil

Table 1 Fipronil residues at 0-60 cm soil depth at two application rates

Depth (cm)	Residues (mg/kg)	
	$T_1(56 \text{ g a.i./ha})$ Average* $\pm$ SD	$T_2(112 \text{ g a.i./ha})$ Average* $\pm$ SD
0-10	0.010 $\pm$ 0.011	0.019 $\pm$ 0.256
10-20	0.003 $\pm$ 0.038	0.010 $\pm$ 0.121
20-30	0.003 $\pm$ 0.003	0.006 $\pm$ 0.013
30-40	BDL	0.003 $\pm$ 0.110
40-50	BDL	BDL
50-60	BDL	BDL

*Average of three replicates

Below determination/detectable level (BDL): 0.003 mg/kg

applied (0.038 mg/kg) was concentrated in 0-30 cm of the soil layer with individual concentrations for three sections i.e. 0-10 cm, 10-20 cm and 20-30 cm being 0.019 (50%), 0.010 (26.31%) and 0.006 (15.7%) mg/kg, respectively. With increase in depth, the concentration of fipronil got reduced to 0.003 mg/kg in 30-40 cm soil-section with 7.8% of total fipronil recovered. The insecticide did not move beyond 40 cm depth of the soil at T_2 dose.

Studies on leaching and adsorption/desorption of fipronil showed that fipronil has low mobility in soil. Belayneh (1998) also reported that fipronil residues tend to stay in the upper 15 cm of soil and exhibit low potential to leach to the groundwater. As reported by Mukherjee (2006), fipronil has been found to be moderately mobile in Indian tropical soils. However, work carried out by Sharma *et al.* (2008) on persistence and vertical distribution of fipronil showed that the insecticide persisted beyond 56 months and the residues were found up to 60 cm depth. On the other hand, studies carried out by Chatterjee and Gupta (2010) with different formulations of fipronil revealed that 80% of the compound remained in top 0-5 cm layer while substantial amount of fipronil moved to 5-10 cm depth. Thus, the present results are in corroboration with earlier findings.

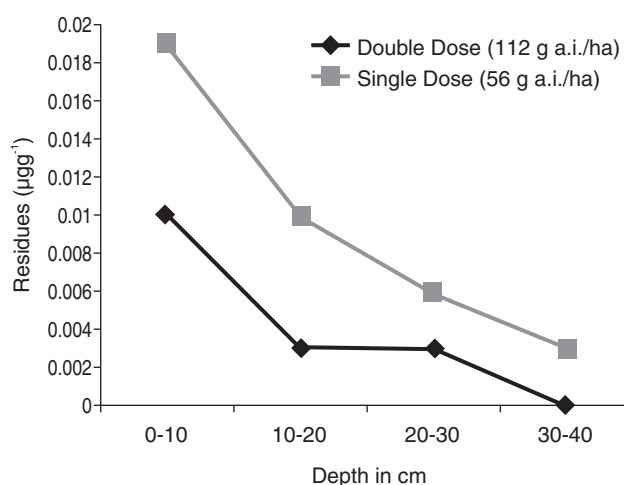


Fig 1 Distribution of fipronil at different soil depths at two application rates

On the basis of results, it can be concluded that residues of fipronil in leachates were below detectable level (BDL) of 0.003 mg/L concentration at both doses. The data generated here clearly indicated less mobility of fipronil in sandy-loam soil but continuous rainfall may result in the leaching of fipronil up to 40 cm depth at higher dose.

The mobility of fipronil was studied in sandy loam soil under laboratory conditions at two application rates of 56 and 112 g a.i./ha with simulated rainfall of 300 mm during 2015–16. Fipronil concentration was found to be maximum in the top 10 cm layer of the soil though it was found to be distributed up to depth of 30 cm at single dose and up to 40 cm depth at double dose. The experiment was carried out in plexi-glass columns and the residues of fipronil in leachates were found to be below detectable level (BDL) of 0.003 mg/kg at both application rates

ACKNOWLEDGEMENTS

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

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