Int. J. Environ. Sci. Technol. (2016) 13:631–638
DOI 10.1007/s13762-015-0883-1

ORIGINAL PAPER

Potential of some soil amendments in reducing leaching of fipronil to groundwater

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Received: 2 February 2015 / Revised: 24 August 2015 / Accepted: 2 September 2015 / Published online: 16 September 2015

Abstract The efficacy of different soil amendments in reducing the leaching of fipronil to groundwater was examined in soil columns under laboratory conditions. The polyvinyl chloride columns were sequentially filled with soils of different depths simulating natural conditions. Different soil amendments namely fresh cow dung (FCD) slurry @ 0.5 t ha^{-1}, farmyard manure @ 5.0 t ha^{-1}, press mud compost @ 5.0 t ha^{-1}, cereal straw @ 5.0 t ha^{-1} and gypsum @ 5.0 t ha^{-1} were applied on the top soil. The application of farmyard manure, cereal straw and gypsum decreased the soil pH, and except FCD, all the amendments increased the electrical conductivity of the soil. Among different soil amendments, press mud compost and cereal straw were the most effective in reducing leaching of the fipronil to groundwater. Fipronil residues in soil columns after leaching indicated that all soil amendments effectively increased the retention of fipronil in soil; however, press mud compost and cereal straw also dissipated higher amount of fipronil. The results also revealed a higher retention of applied fipronil with lower degradation and leaching under application of 0.5 t FCD ha^{-1} as organic amendment in soil in comparison with the unamended soil.

Keywords Cereal straw · Efficacy · Polyvinyl chloride (PVC) columns · Press mud compost

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Introduction

Fipronil [5-amino-1-(2,6-dichloro-α,α,α-trifluoro-*p*tolyl)-4-trifluoromethyl-sulfinyl pyrazole-3-carbonitrile] is a phenylpyrazole insecticide developed by Rhône-Poulenc Agro (now called Aventis, Paris, France). It is commonly used on rice and cotton crops, turf management and against residential insects. It has also been used for control against a wide range of soil and foliar insects, such as rice grasshoppers, rice skippers, vine weevil, termites and black ants in agricultural, forestry as well as in urban environments (Bobe et al. 1998a; Valerio et al. 1998).

The insecticide works by disrupting the central nervous system of the insects and blocking the passage of chloride ions through the gamma-aminobutyric acid (GABA) receptor and glutamate-gated chloride channels, resulting in the paralysis and later death of the insect (Zhao et al. 2003, 2004, 2005; Islam and Lynch 2012). Fipronil present in soil has been found to be harmful for earthworms which play a major role in the degradation of waste material (Yu et al. 2013). Besides this, it also acts as a slow poison and provides a serious threat to aquaculture as it is highly toxic to fish, aquatic invertebrates, etc. (Stehr et al. 2006; Li et al. 2010).

Fipronil can undergo degradation in water and soil through abiotic and biotic processes resulting in the formation of fipronil sulfide through reduction, desulfinyl through photolysis (Fenet et al. 2001), amide through hydrolysis (Bobe et al. 1998b; Ramesh and Balasubramania 2009) and fipronil sulfone through oxidation (Zhu et al. 2004). Fipronil sulfide, fipronil sulfone and desulfinyl are biologically active against insect pests, and their degradation is slow in soil as compared to parent fipronil. Therefore, the metabolites of fipronil are more hazardous than the parent compound (Hainzl et al. 1998).

Bobe et al. (1998a) reported that half-life of fipronil is dependent on the type of soil. In loam soil, the $t^{1/2}$ was found to be 34 days, while in a sandy loam it ranged from 30 to 194 days (Rhône-Poulenc Ag Company 1998; Tingle et al. 2003). The $t^{1/2}$ of fipronil and its breakdown products in soil revealed that they are persistent and their degradation ranges from 111 to 350 days. The sorption Koc of fipronil-sulfide and fipronil-desulfinyl soils was higher than the parent compound and ranged from 1479–7159 to 669–3976, respectively (Ying and Kookana 2001; Rhône-Poulenc Ag Company 1998). The degradation of fipronil was found to increase with increase in the moisture content of the soil (half-life 68 days) with greatest production of the sulfide (increased reducing conditions at the higher moisture content) (Ying and Kookana 2002).

Leaching refers to the transport of pesticide from soil under gravitational flow of water. It is a natural phenomenon by which water-soluble substances (such as Ca, fertilizers, pesticides) are washed out from soil or wastes. These leached-out chemicals pollute the surface and subsurface water and cause the dissolution of metals, solids and chemicals into drinking water (Chezom et al. 2013). Leaching is one of the major transportation processes responsible for groundwater contamination. In soil, it depends on the physicochemical properties of soil and water recharge rate and is predicted to be highest for shallow soils and for persistent compounds with low sorptivity (Singh and Tandon 2015). Fipronil has been found to be relatively mobile in soils. Leaching studies have confirmed the mobility of fipronil in soils since results showed that 31–37 % of surface soil-applied fipronil moved into the 6–12 cm layer of the soil (Rhône-Poulenc Ag Company 1998). The intermediate mobility of fipronil in the field collected soils was also reported by Spomer and Kamble (2010) under laboratory conditions.

The presence of pesticide residues in groundwater has been reported by many workers. Fipronil has been reported to contaminate the groundwater as some of its degradation products including MB 46136 (fipronil sulfone) and RPA 200766 were found at above the recommended limits in groundwater. It has been considered as a possible carcinogen and a potential groundwater contaminant (Gan et al. 2012; Ou et al. 2006). Leaching of fipronil in soils is less under intermittent wetting and drying conditions; however, during flooded field conditions, its transport increases significantly (Ying and Kookana 2006).

As groundwater is a prime source of drinking and irrigation, therefore leaching of the pesticide is a major concern worldwide. Pesticides persist for longer durations in groundwater as compared to surface water or air because of the absence of light and microbes which are potential degraders of pesticides. Since fipronil is being used continuously for a long time on paddy in the subtropical region of Uttarakhand (India), its residue build up may gradually lead to its leaching to the groundwater because of irrigation and heavy rainfall. Hence it is important to restrict the leaching of this insecticide to prevent groundwater contamination. Organic amendments are known to improve soil structure and fertility by adding essential nutrients and increasing the microbial community in the soil (Ahmad et al. 2015). Organic matter also plays an important role in the retention of pesticides in soil. The use of organic amendments can significantly change pesticide adsorption–desorption and leaching behavior in soils (Chun-xian et al. 2013). An increase in the adsorption of fipronil in soil with increasing organic matter has been observed by Spomer and Kamble (2010) which is helpful in retaining the insecticide in soil and reduces the risk of leaching to groundwater. Many organic soil amendments have been reported to decrease the leaching of different pesticides (Briceno et al. 2007; Larsbo et al. 2009; Major et al. 2009). The inorganic soil amendment gypsum has been found to reduce the mobility of contaminants in the metal-contaminated soils and permitted the valorisation of the waste materials (Gonzalez-Nunez et al. 2015).

Since organic amendments can play an important role in reducing the leaching of fipronil, the present investigation was undertaken in the month of September and October at Agricultural Chemicals Laboratory, Department of Chemistry, G.B.P.U.A&T Pantnagar, Uttarakhand (India), to determine the ability of some cost-effective organic soil amendments in addition to gypsum, an inorganic soil ameliorant and important sulfur source, in decreasing the leaching of fipronil to groundwater, and examine their potential to retain fipronil in soil.

Materials and methods

For studying the effect of different soil amendments on leaching of fipronil under laboratory conditions, polyvinyl chloride (PVC) columns (60 cm long × 6 cm diameter) were taken. The soil (Typic Hapludoll) of four different depths viz. 0–15, 15–30, 30–45, 45–60 cm was collected in bulk from the E_1 field of Crop Research Centre (CRC) G. B. Pant University of Agriculture and Technology

Pantnagar, India. Soil samples were dried in shade, crushed by a wooden roller and sieved by a sieve having openings of 2 mm diameter. The physicochemical properties of the experimental soil-like mechanical analysis, pH, electrical conductivity and percentage of organic carbon of different soil depths were analyzed by standard analytical methods outlined by Jackson (1958). The analytical grade fipronil of 98 % purity was obtained from Gharda Chemicals Pvt. Ltd, Mumbai. Soil amendments namely farm yard manure (FYM), fresh cow dung (FCD) and cereal straw (CS) were collected from Pantnagar farms, press mud compost (PMC) was procured from sugar mill, and gypsum was obtained from S. D. Fine Chemical Limited. Triple distilled water used in the study was prepared in the laboratory, and all the other chemicals used in analysis were of analytical grade.

Preparation of amendment mixed soil

Soil amendments were mixed with soil of 0–15 cm depth according to their usual field application rates (FYM, PMC, CS and gypsum @ 5 t ha^{-1} and FCD @ 0.5 t ha^{-1}. Each of the amended soil was kept in separate poly bag and was moistened to near-field capacity moisture regime (15 % w/w) and incubated at room temperature (27 °C) for 1 week.

Preparation of columns

The PVC columns were longitudinally cut into three parts for proper filling of soil in the column and were rejoined using cellophane tape. The bottom of the last column was covered by perforated polythene, and a uniform layer of 1 cm glass wool was placed at the bottom to avoid seepage of soil in the leachate. Above the glass wool padding, a layer (5–6 cm) of acid-washed river bank sand was packed. Depth-wise moist (15 % on weight basis) soil samples were filled in the columns and gently tapped by a wooden plunger to maintain natural bulk density. The top column was filled with the treated soil or control (receiving no amendment) in duplicate. The column joints were covered by cellophane tape and clamped in stands for support.

A solution of the pesticide in methanol containing 2 mg fipronil was mixed with 10 g of amended or control soil and applied uniformly at the top of the column. The top soil column was saturated with distilled water. On the third day, the leachate was obtained. A continuous flow of water at the rate of about four drops per minute from the top of the column was maintained throughout the leaching process. The leachates were collected daily, filtered and extracted for fipronil residues, and the study was continued for 10 days.

The presented experimental setup under laboratory conditions was an open system. In the present study, the amount of fipronil was determined in leachate and the column soil at different depths. Dissipation/degradation of an agrochemical is a process of slow disappearance of the parent compound due to conversion to some other compound(s) which may occur both by the biotic and abiotic processes such as volatilization, photolysis, hydrolysis and microbial degradation. In this study, the possible degradation products of fipronil formed during the 10-day leaching event were not determined; however, the amount of fipronil degraded or dissipated during the event was quantified by subtracting the amount of fipronil in leachate and that retained in the column from the total fipronil applied to the soil column.

Extraction of fipronil from the leachate

Fipronil was extracted from the leachate following a modified QuEChERS method, a highly streamlined sample preparation method with excellent results for a wide range of pesticides analytes (Anastassiades et al. 2003). Four milliliters of the aliquot of the leachate was taken in a centrifuge tube, and 4 mL of acetonitrile (CH_3CN), 3 g of anhydrous $MgSO_4$ and 2 g of NaCl were added to it. The mixture was vortexed until fully dissolved. Thereafter, 150 mg primary secondary amine (PSA) reagent and 1 g $MgSO_4$ were added to the tube and the mixture was centrifuged for 5 min at 3000 rpm. After phase separation, the upper organic layer was retained for analysis. Prior to analysis, the samples were filtered through 0.2 µm PTFE disk filter.

Extraction of fipronil from the soil

At the end of leaching period, soil columns were separated and soil mass of each depth was removed from the column and spread over a clean plastic sheet under shade and mixed thoroughly. An aliquot of soil was drawn and extracted for fipronil residues following the simplified QuEChERS method. Three grams of soil was taken into a 15-mL centrifuge tube and after addition of 4 mL of CH_3CN and 5 mL of distilled water was vortexed for 2 min. The contents of the tube were allowed to stand for 10 min after which 3 g of anhydrous $MgSO_4$ and 2 g of NaCl were added. The mixture was vortexed for 2 min more. The contents were then centrifuged for 5 min at 3000 rpm, and in the aliquot obtained, 150 mg PSA reagent and 1 g $MgSO_4$ were added. The mixture in the tube was centrifuged for 5 min more which led to the separation of the two layers. The upper organic layer was decanted off and filtered through 0.2 µm PTFE disk filter for the analysis of fipronil by HPLC.

Analysis of the samples using HPLC

Residue analysis of fipronil was done using Dionex Ultimate 3000 HPLC containing C_{18} Column, (250 × 4.6 mm i.d., 5 µm) under isocratic mode, with CH_3CN: H_2O (7:3 v/v) as mobile phase and UV Detector (280.0 nm) at a flow rate of 1 mL min^{-1}. The retention time of fipronil was 5.99 min under the above conditions.

Results and discussion

The experimental soil was a coarse-textured sandy loam soil of slightly alkaline reaction (Table 1). The proportion of soil clay, soil organic C and electrical conductivity decreased with depth. The dynamic soil properties of surface (0–15 cm) sample which was treated with different soil amendments are presented in Table 2. In general, in comparison with the control, the application of FYM, CS and gypsum decreased the soil pH; the changes in soil pH due to the application of FCD or PMC were minor which could be related to the lesser quantity of the matter in the former case and presence of alkaline and alkaline earth metal ion in the latter amendment. Thus, all soil amendments decreased the soil pH except in the case of PMC which slightly increased the pH of the soil. Application of all amendments except FCD increased the electrical conductivity of soil due to mineralization of organic amendments and solubilization of gypsum in the soil. The content of soil organic C was increased by the application of all organic amendments; the magnitude of increase was the lowest for FCD possibly due to the ten times lower quantity of this organic amendment in comparison with other organic amendments.

The data on fipronil residues in soil columns of different depths are presented in Table 3. The fipronil residue in soil was significantly influenced by the main effects of both soil depth and type of the amendment used. A significant

Table 1 General properties of depth-wise drawn soil samples used for packing the columns

Soil properties						
Soil depth (cm)	Sand (%)	Silt (%)	Clay (%)	pH (1:2, soil water suspension)	EC (mSm-1, 1:2, soil water suspension)	Organic C (g kg^{-1})
0–15	64.84	20.0	15.16	7.80	0.086	6.11
15–30	70.84	18.0	11.16	8.12	0.042	5.73
30–45	76.84	14.0	9.16	7.55	0.048	4.20
45–60	80.84	10.0	9.16	8.21	0.035	3.25

Table 2 Effect of different soil amendments on some dynamic properties of surface (0–15 cm) soil

Soil properties			
Soil (0–15 cm)	pH (1:2, soil water suspension)	EC (mSm-1, 1:2, soil water suspension)	Organic C (g kg^{-1} soil)
Control	7.34	0.087	5.13
FCD @ 0.5 t ha^{-1}	7.21	0.077	5.31
FYM @ 5 t ha^{-1}	6.77	0.131	9.63
PMC @ 5 t ha^{-1}	7.54	0.351	8.65
CS @ 5 t ha^{-1}	6.74	0.158	6.29
Gypsum @ 5 t ha^{-1}	6.71	0.479	5.11

Table 3 Effect of different soil amendments on fipronil residues left in soil at different depths after 10 days of continuous leaching

Soil amendment	Soil depth (cm)				Mean
	0–15	15–30	30–45	45–60	
Control	0.022	0.017	0.044	0.012	0.023
FCD @ 0.02 t ha^{-1}	0.508	0.615	0.336	0.222	0.420
FYM @ 5.0 t ha^{-1}	0.328	0.219	0.099	0.014	0.165
PMC @ 5.0 t ha^{-1}	0.034	0.158	0.101	0.000	0.073
CS @ 5.0 t ha^{-1}	0.213	0.049	0.130	0.006	0.100
Gypsum @ 5.0 t ha^{-1}	0.049	0.264	0.045	0.006	0.091
Mean	0.192	0.220	0.126	0.043	0.145

Effect	Depth	Amendment	Depth × Amendment
S.Em. ±	0.010	0.008	0.019
LSD ($p \leq 0.05$)	0.028	0.023	0.056

influence of main effect of soil amendment indicated that the highest average fipronil residue was detected in the subsurface (15–30 cm) layer followed by the surface (0–15 cm), 30–45 cm and the least in 45–60 cm layer, thereby substantiating the earlier observations that under saturated flow condition the surface-applied fipronil could move to lower soil layers with a possibility of entering in groundwaters. The main effect of soil amendments also influenced the average concentration of fipronil in soil significantly. Application of FCD @ 0.5 t ha^{-1} and application of FYM, PMC, CS and gypsum each @ 5 t ha^{-1} increased the average concentration of fipronil in soil by 18.3-, 7.2-, 3.2-, 4.3- and 4.0-folds in comparison with control (no amendment application); however, the differences between PMC and gypsum or CS and gypsum were statistically not significant.

The interaction effect of soil depth and soil amendments also significantly influenced the fipronil residues in soil. Under 0.5 t FCD ha^{-1} treatment, the residue levels of fipronil at all soil depths were many folds higher than the control, indicating higher retention and mobility of the fipronil in soil due to the presence of both soluble and indecomposable organic matter. Similarly, under 5 t CS ha^{-1} significantly higher level of fipronil residues were detected at 0–15 and 30–45 cm levels than control. With application of 5 t PMC ha^{-1} which has soluble C content, higher fipronil residue at 15–30 and 30–45 cm was observed in comparison with control. With 5 t FYM ha^{-1} treatment, higher level of fipronil residues were observed in 0–15 and 15–30 cm layer in comparison with control as FYM has a relatively stabilized organic matter which had already undergone decomposition and maturation. Under 5 t gypsum ha^{-1}, significantly higher accumulation of fipronil residue was recorded at 15–30 cm depth only in comparison with control possibly due to relatively faster

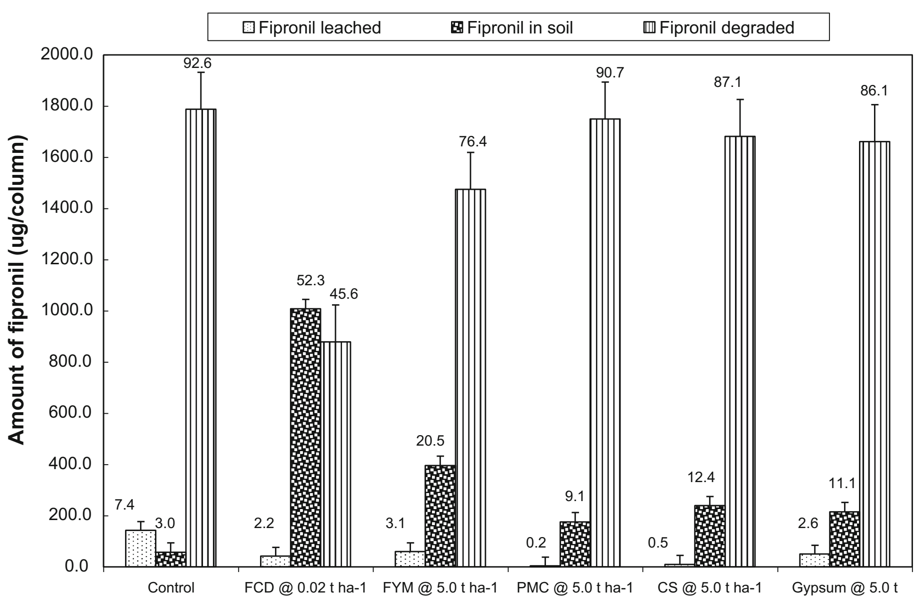

Fig. 1 Effect of different soil amendments on total amount of fipronil leached, retained in soil and degraded in soil columns under saturated flow conditions. The *vertical bars* indicate LSD ($p \leq 0.05$), and the numerical values appended above each *histogram* show the percent of initially applied fipronil

conduction of water through top layer as this amendment is known to promote soil aggregation in the surface soil. It appeared that in situ mobility of surface-applied fipronil depended both on water transmission characteristics of amended soil and the relative amount of soluble organic compound which are likely to form in soil if readily decomposable matter was incorporated in the soil. Srivastava et al. (2009) also reported that the water-soluble C content of bioactive materials was many fold higher than farmyard manure. The formation of low molecular weight organic acids like α-ketoglutaric acid and fumaric acids during initial stages of incubation in soil amended with fresh cow dung slurry, farmyard manure and sugar industry bio-sludge has also been reported by Bhatt et al. (2013).

The results of the mass balance studies to compute the net amounts of fipronil bound to the soil, leached from soil as leachate water and net degraded amount from soil during 10-day leaching event under saturated flow conditions with different soil amendments are shown in Fig. 1. Considering the initially applied amount of fipronil (2 mg), only 7.4, 2.2, 3.1, 0.2, 0.5 and 2.6 % of applied fipronil could enter in the leachate under control, FCD @ 0.5 t ha^{-1}, FYM; PMC; CS and gypsum each @ 5 t ha^{-1}, respectively. A significant amount of leachable fraction of fipronil in unamended soil could be attributed to coarse texture of the experimental soil. Barbash et al. (2001) also noted that leaching is the principal transport process responsible for groundwater pollution. As regards, the retention of added fipronil in soil column 3.0, 52.3, 20.5, 9.1, 12.4 and 11.1 % of initially applied fipronil was retained under control, FCD @ 0.5 t ha^{-1}, FYM; PMC; CS and gypsum each @ 5 t ha^{-1}, respectively. Singh et al. (2014) observed that the sorption of fipronil followed pseudo-second-order particle diffusion kinetics. Since the present study was carried out under saturated flow conditions in the laboratory simulating leaching of fipronil under anaerobic environment with only limited exposure to sunlight, some degradation of fipronil might also have occurred. Doran et al. (2006) studied the sorption and degradation of fipronil in two Australian rice soils and reported rapid degradation of fipronil over first few days followed by slower degradation indicating co-metabolism of fipronil by soil microbes. The computed amount of fipronil likely to be degraded in the present study under different treatments were 92.6, 45.6, 76.4, 90.7 and 86.1 % of initially applied fipronil that was dissipated under control, FCD @ 0.5 t ha^{-1}, FYM; PMC; CS and gypsum each @ 5 t ha^{-1}, respectively. Degradation of fipronil in the soil from exposure to sunlight at the surface has been reported to produce fipronil-desulfinyl, oxidation near the surface to yield fipronil-sulfone, hydrolysis throughout the upper layer to produce fipronil-amide and reductive processes below the surface to produce fipronil-sulfide (Gunasekara et al. 2007). Since the study was conducted under saturated flow condition, the principal degradation product under reducing conditions was likely to be fipronil sulfide as noted by Doran et al. (2006) for rice soils.

Thus, all soil amendments tried in the present study were effective in reducing the leaching of fipronil yet the highest reduction in the leaching of fipronil was recorded under PMC and CS treatments possibly due to faster degradation of applied fipronil under these treatments. Among all tried soil amendments, relatively higher retention of applied fipronil with lower degradation and leaching as compared to unamended soil was recorded under application of 0.5 t FCD ha^{-1}.

Conclusion

The leaching of fipronil under saturated flow condition especially in coarse-textured soil could be effectively controlled by application of 0.5 t FCD ha^{-1} as this treatment resulted in higher retention of applied fipronil with lower degradation and leaching as compared to unamended soil.

Acknowledgments The financial assistance provided by Ministry of Environment & Forests, New Delhi, and the DST Inspire fellowship (No. DST/INSPIRE Fellowship/2013/176) to one of the students during the research work is duly acknowledged.

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