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Dissipation of Fipronil in Water Under Laboratory Conditions

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Abstract Fipronil belongs to phenyl-pyrazole class of chemical compounds. Its dissipation in water has been studied for 90 days under laboratory conditions at two dose 0.028 (T_1) and 0.056 (T_2) μg mL^{-1}. Residues were extracted with 15% dichloromethane in hexane by liquid-liquid partitioning and were estimated by GC-ECD system equipped with capillary column. Fipronil was found to persist up to 30 days after application and 100% dissipation was observed after 60 days of application. Dissipation followed a biphasic first order kinetics with half-life values of 19.13 and 20.63 days in water at (T_1) and (T_2) treatments, respectively.

Keywords Insecticide · Fipronil · Dissipation · Half-life · First order kinetics · GC-ECD

Pesticides are invaluable inputs for increased agricultural production. The safe use of the pesticide depends on its toxicological properties and its distribution and persistence in the environment with consideration of any unusual photoproducts and metabolites that might be performed. Improper usage of pesticides by farmer leads to environmental contamination (Barcelo et al. 1994; Lartiges and Garrigues 1995; Vink and Vanderzee 1996). As the movement of water through the soil is the main principal mechanism for the pesticides to reach the surface and groundwater, there has been increased research interest aimed at understanding the process that controls the penetration of pesticides into the soil and their subsequent contamination of groundwater and surface water. Accumulation of these toxic pesticides in groundwater is influenced by the physical, chemical, and biological mechanisms. Thermal decomposition, pH variations in water and hydrolysis have a major role in the breakdown and degradation of pesticides (Lee et al. 1986; Ou and Rao 1986; Singh et al. 1990; Cavalier et al. 1991). Water being a principal reactive agent of chemical degradation is responsible for considerable breakdown of pesticide molecules and varies extensively with pH extremes. Fipronil{5-amino-3-cyano-1-[2,6-dichloro-4-(trifluoromethyl) phenyl]-4 (trifluoromethyl) sulfinyl}pyrazole, is a phenylpyrazole insecticide that acts as a potent blocker of the GABA- regulated chloride channel (Moffat 1993; Cole et al.1993). It controls a broad spectrum of insects such as cockroaches, mosquito, locust, ticks and fleas at both larval and adult stages (Chaton et al. 2001; Aajoud et al. 2003). Fipronil is effective, at low field application rates, against insects that are resistant to pyrethroids, organophosphates and carbamate insecticides (Bobe et al. 1997). All of these characteristics recently allowed increased use of this insecticide, both in household uses and in agriculture. Although the effective amounts are clearly lower in fipronil as compared to other compounds, traces of this compound, its metabolites, or its transformation products are likely to be found in water. Dissipation processes and rate for this molecule have therefore to be carefully and precisely documented. Keeping this in mind, the studies were carried out to investigate dissipation behaviour of fipronil in water under laboratory conditions.

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Materials and Methods

The experiment was conducted from January to April 2007 in the laboratory at room temperature to study the persistence and degradation kinetics of fipronil. The physico-chemical characteristics of canal water were as follows: EC × 10^{-6} (μ Sm^{-1}), 240; HCO$_3^{-1}$ (meq L^{-1}), 1.2; Cl^{-1} (meq L^{-1}), 0.5; Ca^{+2}(meq L^{-1}), 1.0; Mg^{+2}(meq L^{-1}), 2.2 and pH 7.7. Water samples (200 mL) replicated thrice were treated with fipronil (Regent 0.3% G) at the rate of 0.028 µg mL^{-1} (T$_1$) and 0.056 µg mL^{-1} (T$_2$) and kept in 54 brown colour bottles excluding untreated control samples. The treated water samples were processed for fipronil residues on 0 (1 h after treatment), 3, 7, 15, 30, 60 and 90 days after treatment (DAT).

Extraction and clean-up was carried out as per method of Kumari et al. (2007). Treated water samples (200 mL) at different time intervals were taken in a separatory funnel and 10 g sodium chloride was added. The fipronil residues were extracted by liquid-liquid partitioning thrice with 15% dichloromethane in hexane (50, 30, 20 mL). Combined the organic layers and concentrated to near dryness on a rotary vacuum flash evaporator followed by gas manifold evaporator. The process was repeated thrice after adding 5 mL hexane in order to eliminate the traces of dichloromethane Final volume (2 mL) was made in n-hexane for analysis.

Gas liquid chromatograph (GLC), Model Shimadzu 2010, equipped with ^{63}Ni electron capture detector (ECD) and capillary column HP-1 (30 m × 0.32 mm i.d × 0.25 µm film thickness of 5% diphenyl/95% dimethyl polysiloxane) was employed for the estimation of fipronil residues. Other GC parameters were as follows: Temperature (°C): Oven: 150 (5 min) → 8°min^{-1} → 190 (2 min) → 15° min^{-1} → 280 (10 min). Injection port, 280; Detector, 300. Carrier gas (N$_2$) flow was 2 mL min^{-1}, with split ratio 1:10. Retention time (R$_t$) observed for fipronil was 14.069 min. The percent recovery of fipronil in canal water at 0.25 µg mL^{-1} and 0.50 µg mL^{-1} fortification levels were 91.10 and 96.57, respectively. Limit of detection was 0.00 1 µg mL^{-1}.

Results and Discussion

Residue data and percent dissipation of fipronil in canal water at two treatments are given in Table 1. As evident from the analytical data (Table 1), the average initial residues in T$_1$ on 0 (1 h) day were 0.010 µg mL^{-1} which dissipated to 0.009 µg mL^{-1} in 1 day, 0.007 µg mL^{-1} in 3 day and 0.006 µg mL^{-1} in 7 days. The percent dissipation recorded in this period was 10.0, 30.0 and 40.0, respectively. In 15 and 30 DAT, the respective residues reached to the levels of 0.005, 0.003 µg mL^{-1}, with 50.0% and 70.0% dissipation, respectively in this period. The residues could not be detected beyond 60 days after treatment. The half-life period of fipronil was recorded to be 19.13 days in T$_1$ treatment.

In T$_2$, the analytical data (Table 1) revealed that the average initial residues were 0.021 µg mL^{-1} which dissipated to 0.018, 0.015, 0.013 µg mL^{-1} in 1, 3 and 7 days, respectively. The percent dissipation to the corresponding days was 14.28%, 28.57% and 38.09% respectively. After 15 and 30 DAT the residues reached to the levels of 0.011

Table 1 Dissipation of fipronil residues (µg mL^{-1}) in canal water at two doses

Days after treatment	Residue (µg mL^{-1})			
	T$_1$ (0.028 µg mL^{-1})		T$_2$ (0.056 µg mL^{-1})	
	Average[a] ± SD	% Dissipation	Average ± SD	% Dissipation
0	0.010 ± 0.0016	–	0.021 ± 0.0008	–
1	0.009 ± 0.0008	10.00	0.018 ± 0.0008	14.28
3	0.007 ± 0.0008	30.00	0.015 ± 0.0008	28.57
7	0.006 ± 0.0008	40.00	0.013 ± 0.0008	38.09
15	0.005 ± 0.0008	50.00	0.011 ± .00014	47.61
30	0.003 ± 0.0008	70.00	0.007 ± 0.0021	66.67
60	BDL	100	BDL	100
90	BDL	100	BDL	100
Rate constant K (dat^{-1})	0.0362		0.0335	
Correlation coefficient	$r = -0.9933$		$r = -0.9942$	
Regression equation	$y = 0.9398 - 0.01573x$		$y = 1.2605 - 0.01459x$	
	$t_{1/2} = 19.13$ days		$t_{1/2} = 20.63$ days	

[a] Average of three replicates; *BDL* Below detectable level (0.001 ppm)

CD ($p = 0.05$) for treatments = 0.0014; for days = 0.0025; for days × treatment = 0.003

and 0.007 µg mL^{-1}, respectively with percent dissipation of 47.61 and 66.67. The residues could not be detected in canal water beyond 60 days after application of fipronil. The half-life period of fipronil was found to be 20.63 days at T_2. Statistical interaction between days and treatment was found to be significant with CD ($p = 0.005$) value of 0.003. For treatments, the value was found to be 0.0014 and that for days, 0.0025. Irrespective of days after treatment, residue levels were significantly low in single dose as compared to double dose. Critical difference calculated through ANOVA revealed that the rate of dissipation was at par between zero and first day, between third day and seventh day and between 15th and 30th day of treatment.

It is clear from the data (Table 1, Fig. 1) that the residues at both the treatments dissipated quickly to about 40% up to 7 days in canal water followed by slow dissipation up to 30 days with per cent dissipation of 70 and 66.67 at T_1 and T_2, respectively. After 60 DAT, the residues could not be detected in any of the treatments showing thereby 100% dissipation of fipronil in water. Dissipation of fipronil followed a biphasic first order kinetics irrespective of doses (Fig. 1).

Dissipation was faster at the lower dose. Since the rate of any reaction decreases with the decrease in concentration, the slow rate of dissipation of fipronil residues with the passage of time was probably due to decrease in its concentration. Slightly higher dissipation of permethrin, cypermetharin, fenvalerate and deltamethrin in water at lower doses and of naled propetemphos and orthen in water has been reported (Agnihotri et al. 1986; Agnihotri et al. 1989). The linear relationship obtained by plotting of log [residues (µg $mL^{-1} \times 10^3$)] versus time shows that the dissipation of fipronil followed a first order kinetics in both the treatments as an acceptable first order kinetics is defined as $r^2 > 0.7$ (Organisation for Economic Co-operation and Development 1999). The correlation coefficient (r) values of -0.9933 (T_1) and -0.9942 (T_2) also confirm the above observations. Negative value of 'r' indicates that residue concentration decreases with the passage of time. Bobe et al. (1997) showed that fipronil residues rapidly moved from water to the sediments within 1 week of application. Under aerobic conditions, half-life for fipronil was 15 days while it was 116–130 days under anaerobic conditions. Our results are in accordance with these findings. Contrary to present results, Ramesh and Balasubramanian (1999) reported the half-life values of fipronil to be 91.68, 81.12 and 48.48 h in aqueous buffer solutions at pH 4.1, 7.1 and 9.1, respectively. The degradation of fipronil was rapid and it followed pseudo first order kinetics.

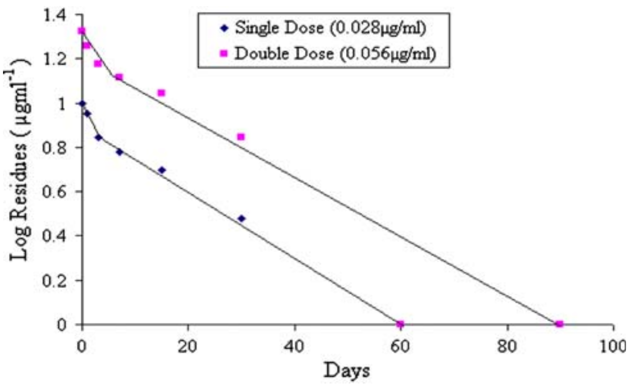

Fig. 1 Dissipation of fipronil in water

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