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Sorption of Fipronil in Tropical Soils

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Fipronil (5-amino-1- [2,6-dichloro-4-(trifuromethyl) phenyl]-4-(1R,S)) trifluromethyl) sulfinyl)-1-4-pyrazole-carbonitrile, Figure 1), possessing a phenylpyrazole or fiprole moiety is a new broad spectrum insecticide. It has been developed by Rhone-Poulenc, and is active against a wide range of foliar and soil insects such as cotton boll weevil, Colorado potato beetle, thrips and various pests of rice, corn, vegetables and ornamental crops. Fipronil is also effective for locust and termite control, It has been recommended for use where the insects have developed resistence to conventional insecticides like synthetic pyrethroids, organophosphates and carbamates. It has been formulated as roach and ant baits, flea and tick sprays for pets and as granules to control mole cricket (Connelly 2001). Fipronil is registered for non-agricultural as well as agricultural use in many countries. Its application rate 0.6-200 g a.i./ha lower than the conventional insecticides thus, making it popular from environmental point of view. Fipronil is a polar molecule, stable at normal temperature for one year, but is not stable in presence of metal ions. It is stable in aqueous solutions under acidic and neutral conditions. It degrades in sunlight to produce a variety of metabolites, including fipronil-desulfinyl, which is extremely stable and is more toxic than the parent compound. It is only sparingly soluble in water (0.0024 g/L) but most soluble in acetone (545.9 g/L) ethyl acetate (264.9 g/L) and methanol (137.5 g/L). It has low octanol-water partition coefficient (Colin et al. 2003).

Fipronil is applied directly to the soil or reaches there indirectly through various mechanisms (as drift, washing off, spillage etc.) by wind and water. In soil its persistence and availability is determined by its adsorption-desorption on soil particles as other dissipating factors such as transport, microbial uptake or metabolic affects of the non-sorbed molecule only. There is a dynamic equilibrium between sorbed molecules and soil solution, so when there is decrease in solution concentration of pesticide, the sorbed molecules gets desorbed. The distribution of pesticide molecules between soil particles and soil solution (distribution coefficient, K_d) depends on the characteristics of the pesticide studied on a number of soils varying in their properties so that sorption of pesticide in a given soil type can be predicted and dosage for application can be accordingly adjusted.

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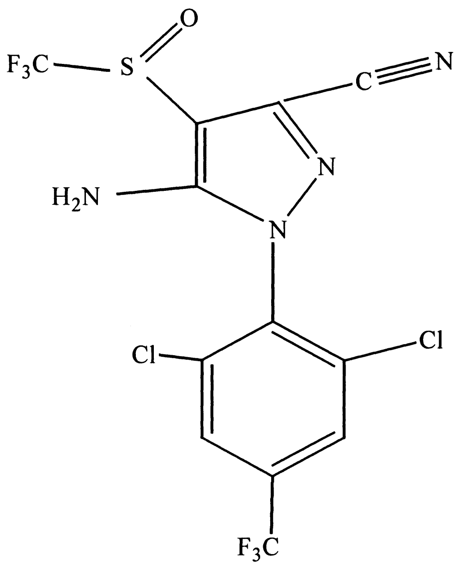

Figure 1. Fipronil

MATERIALS AND METHODS

Technical grade fipronil (99% purity) was obtained *gratis* from Bayer India Limited. All organic solvents were obtained from SD Fine Chemicals, India Ltd. All the solvents were distilled before use. Stock solution of 100-ppm fipronil was prepared in distilled acetone. Working solution of 10 and 1 μg/g were prepared from stock solution by serial dilution with acetone.

Soil samples were collected at a depth of 0-15 cm from different agro-climatic zones of India i.e. Delhi, Ranchi and Nagpur. Soil samples were air-dried, grounded and sieved through a 2 mm sieve. The physio-chemical properties of these soils were determined using standard methods described by Jackson (1973).

Sorption-desorption experiments were carried out by batch equilibrium method in triplicate. For determining sorption coefficient five different concentrations of fipronil were used ranging between 0.01-0.2 μg/g. In all cases aqueous solutions of 0.01 N $CaCl_2$ was used as solvent. Appropriate quantity of acetone solution of fipronil was transferred in ground glass joint test tubes. Acetone was then allowed to evaporate completely. The residues were dissolved in 20 ml of 0.01 N $CaCl_2$ solution and used for adsorption studies. To this solution 10 g air-dried soil was added. The soil solutions were then shaken on horizontal mechanical shaker for 4 hours and then kept to equilibrate for 24 hours. After 24 hours soil samples were centrifuged for 10 min at 2000 rpm. 10 ml aliquot of the supernatant was pipetted out in a separating funnel. This supernatant was diluted with aqueous saturated sodium chloride solution (10 mL) and was extracted by partitioning thrice with dichloromethane (10 ml) each time. The combined extract was dried over anhydrous sodium sulfate and evaporated to dryness in rotary evaporator. The residues were re-dissolved in suitable volume of hexane and analyzed on GC using EC detector.

The determination of desorption coefficient and hysteresis of fipronil was carried out as given. After drawing 10 ml aliquot of the supernatant solution for adsorption study, the centrifuged soil solution was further dispersed again and 10 ml of 0.01 N $CaCl_2$ was added. This soil solution was again shaken for 4 hrs and equilibrated for 24 hrs. To determine the amount desorbed, soil solution was centrifuged for 10 min at 2000 rpm and 10 ml aliquot of the supernatant was pipetted out in a separating funnel. This supernatant was diluted with aqueous saturated sodium chloride solution (10 mL) and was extracted and quantified as in adsorption step. The process was repeated two more times to complete three desorption cycles. The desorption study was carried out in triplicate, where only 0.2 μg/g of fipronil was used. In addition blank sets i.e. fipronil solution (in $CaCl_2$) without soil were simultaneously processed to determine the pesticide loss during equilibration and processing. No significant loss of fipronil was observed during the experiment.

Quantification of fipronil residues was done by GLC-ECD. Gas chromatograph (Hewlett Packard 58900 series II) was equipped with ^{63}Ni electron capture detector (ECD) and megabore column 12 m × 0.53 mm i.d. × 2.65 μm film thickness. The operating temperatures were, column; 180° C, injector port; 220° C, detector; 250° C. The carrier gas was nitrogen with flow rate of 20 ml/min. Under these conditions fipronil eluted at retention time of 3.8 min. The maximum level of quantification (LOQ) from water and soil matrix was 0.005 μg/g.

The amount sorbed on soil (C_s) was calculated from the difference between the initial (C_i) and equilibrium concentrate (C_e). The data was fit to logarithmic form of the Freundlich equation, $\text{Log } C_S = \text{Log } K_f + 1/n_{ads} \text{ Log } C_e$, $\text{Log } K_f$ and $1/n_{ads}$ are the constants representing the intercept and the slopes of the isotherms respectively. The distribution coefficient K_d was calculated as ratio of amount adsorbed on soil to the amount present in soil solution (C_s/C_e).

The amount desorbed from soil was calculated from the difference between concentrations of fipronil before and after equilibration in desorption experiment. The data was fit to the logarithmic form of Freundlich equation. K_f and I/n_{ads} were obtained as intercept and slopes of the isotherm. A desorption hysteresis coefficient (h) was calculated as the ratio between the sorption and desportion isotherm slopes.

RESULTS AND DISCUSSION

Soils used in the study represent a range of physiochemical properties (Table 1). Nagpur soil has highest clay content, EC and CEC. Delhi and Ranchi soils are

Table 1. Physico-chemical properties of the test soils.

Property	Delhi	Ranchi	Nagpur
Type	Inceptisol	Ultisol	Vertisol
Texture	Sandy loam	Sandy loam	Clayey
Organic matter	0.951	0.072	0.734
CEC (meq 100 g^{-1})	7.43	4.21	14.27
PH	8.01	5.57	8.28
EC	0.19	0.35	0.52

sandy loam. Delhi soil has highest organic matter content, but in Ranchi soil organic matter is very low only 0.072%. While Delhi and Nagpur soils are slightly alkaline in nature, Ranchi soil is acidic (pH 5.57).

Sorption of a solute can be considered as partition of solute (pesticide) between solid (soil) and the liquid (soil solution) phase and is measured as distribution coefficient,K_d. K_d for a pesticide vary in each soil type. K_d for fipronil in Ranchi, Nagpur and Delhi soils was 0.60-0.85, 0.64-1.50 and 0.40-0.64, respectively (Table 2). As the initial concentration of fipronil in soil solution increased, its K_d value decreased. K_d value for fipronil in all cases was less than 1 except in the Nagpur soil at initial concentration up to 0.05 ppm indicating that fipronil has low affinity to soil particles than to soil solution. Bobe et al. (1997) also found that fipronil has low soil affinity at low initial concentrations, facing strong competition from aqueous phase.

Concentration of fipronil sorbed on soil particles when plotted against its concentration in soil solution at equilibrium form S- type curve (Gills et al. 1960) (Figure 2). This classification is based on the nature of slope of the initial portion of the curve and is indicative of the type of interaction between soil, solute and solution. Initial slope of isotherm depends on the rate of change of adsorption site availability with increase in solute adsorbed. In C type curve adsorption becomes easier as concentration rises. While the opposite is true for L and H type curves. Such type of curve is obtained when solute meet strong competition for substrate site from molecules of the solvent. Due to the non -polar nature and low water solubility of fipronil, it cannot displace water molecules from the adsorption sites on soil particles. Bobe et al. (1997) and Ying and Kookana (2001) also studied adsorption of fipronil and its metabolites on different soil types in the presence of organic solvent and found S and C type sorption isotherm. C type curve in their study was obtained probably because of increased water solubility of fipronil in the presence of water miscible organic solvent.

The log transformed data for fipronil sorption fitted well in Frendlich isotherm equation with a correlation coefficient (R^2) $\geq$ 0.97. The Freundlich constants K_f and 1/n were calculated from linear regression equation (Table 3). K_f values represents adsorption capacity of the soil was 2.05 (Ranchi), 2.68 (Nagpur) and 4.01 (New Delhi). The value of K_f corresponds to the organic matter content of

Table 2. Distribution coefficient K_d of fipronil.

Initial conc.	Ranchi	Nagpur	New Delhi
0.01	0.85 ±0.07	1.50 ± 0.05	0.64 ±0.06
0.05	0.61 ±0.03	1.00 ± 0.03	0.32 ±0.05
0.1	0.69 ±0.05	0.82 ±0.02	0.39 ±0.03
0.15	0.63 ±0.02	0.64 ±0.02	0.36± 0.03
0.2	0.60 ±0.02	0.64 ±0.03	0.40 ±0.02

Table 3. Sorption coefficient of fipronil on three soils.

Soil	K_f	1/n	r^2
Ranchi	2.05 ± 0.02	0.9	0.9959
Nagpur	2.68± 0.03	0.74	0.9983
New Delhi	4.01± 0.02	0.84	0.9731

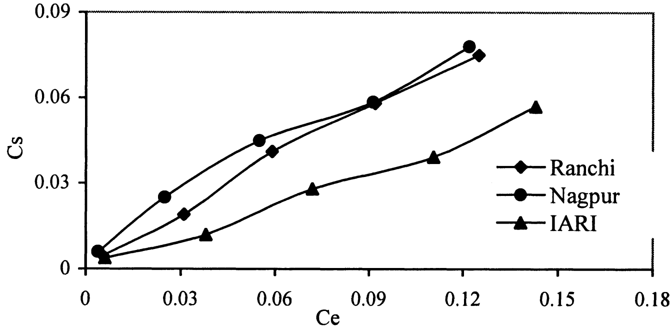

Figure 2. Adsorption isotherm of fipronil on tropical soils.

Table 4. Percent desorption of fipronil.

Treatment	Ranchi	Nagpur	New Delhi
I washing	11.7 ± 0.02	10.0 ±0.03	10.6± 0.03
II washing	9.3 ± 0.03	8.3 ±0.06	9.6 0.05±
III washing	10.2 ±0.03	8.5± 0.05	9.5 ±0.07

n=3

Table 5. Desorption coefficient of fipronil on three soils.

Soil	K_f	1/n	r^2	h
Ranchi	0.865 ±	1.01	0.9998	0.89
Nagpur	0.875 ±	1.01	0.9999	0.73
New Delhi	0.881 ±	1.01	0.9979	0.83

n=3

these soils. New Delhi soil has highest organic matter and highest K_f value. This trend shows that organic matter plays an important role in adsorption of fipronil. Fipronil being non- polar in nature had more affinity towards organic matter.

The sorption of fipronil was slow and irreversible. Fipronil desorbed only 8-12 percent of the sorbed amount in the successive washings (Table 4). Less desorption show that adsorption is through strong interactive forces between pesticide and soil particles. Hydrophobic interaction between non-polar fipronil molecules and organic matter of the soil is stronger than Van-der Waals or hydrogen bonding forces. This suggest that sorption of fipronil is largely on the organic matter of soil.

Desorption data for fipronil followed the Freundlich equation and fitted well to the linearized Freundlich equation, the correlation coefficient being > 0.99. $K_{f\text{-}des}$ and $1/n_{des}$, Freundlich constants for desorption are listed in Table 5. The ratio of Freundlich components $(1/n_{des})/(1/n_{ads})$, gives an indication of adsorption desorption hysteresis (Van Genuchten *et al*, 1974; O'Connor et al., 1980). The parameter n_{des}/n_{ads} is referred as hysteresis coefficient (h) or hysteresis index. Theoretically, if there is no hysteresis h=1 and $K_{ads}=K_{des.}$ Positive hysteresis or irreversibility of adsorption is denoted by h < 1and $K_{ads} < K_{des}$. In case of negative hysteresis, i.e. greater desorption, h is greater than one and $K_{ads} > K_{des}$. In practice, however, no hysteresis can be defined when 0.7 > h > 1.0 (Barriuso et al. 1994).

Hysteresis coefficient for fipronil is less than one on all three-soil types indicating that it is difficult to desorb fipronil from soil due to hydrophobic interaction between soil organic matter and nonpolar fipronil molecules.

Sorption of fipronil at low concentrations is low because it faces strong competition from water molecules for adsorption sites. Fipronil adsorbed increasingly to soil with increasing organic content as is evident from the adsorption coefficient on different soil types and low desorption percentage. At the termiticidal application rate the adsorption will be more as sorption of fipronil increases with increase in solution concentration. Fipronil may thus be classified as moderately mobile and because of high affinity to soil particles most fipronil residues are contained in the top 10-12 cm soil and leaching into ground water would be non-existent.

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REFERENCES

Barriuso E, Laid DA, Koskinen WC, Dowdy RH (1994) Atrazine desorption from smectite. Soil Sci Soc American J 58:1632-1638

Bobe A, Coste CM, Cooper JF (1997) Factors influencing the adsorption of fipronil on soils. J Agric Food Chem 45:4861-4865.

Calliot F, Kukorowski KA, Hawkins DW, Roberts DA (1992) Fipronil: a new soil and foliar broad-spectrum insecticide. In: Proceedings, British Crop

Protection Conference, Pest and Diseases, 192 Brighton, Nov 23-26, pp 29-34.
Colin CDT, Joachim AR, Charles FD, Sasha L, William JK (2003) Fipronil: Environmental fate, ecotoxicology and human health concerns. Rev Environ Contam Toxicol 176:1-66.
Connelly P (2001) Environmental fate of Fipronil. Environmental Monitoring Branch, Department of Pesticide regulation, California Environmental Protection Agency, (www.pw.ucr.edu/textfiles/fipronil.pdf.).
Giles CH, MacEvan TH, Nakhwa SN, Smith D (1960) Studies in adsorption. Part XI A system of classification of solution adsorption isotherms and its use in diagnosis of adsoption mechanisms and in measurement of specific surface areas of solids. J Chem Soc 111: 3973-3993.
Jackson ML (1973) Soil chemical analysis. Prentice Hall Inc, Eaglewood, Cliff, New Jersey.
O'Connor GA, Wiereng PJ, Cheng HH, Doxtader KG (1980) Movement of 2,4,5-T through large soil columns. Soil Sci 130:157-162.
Van Genuchten MT, Davidson JM, Wierenga PJ (1974) An evaluation of kinetics and equilibrium equation for the prediction of pesticide movement through porous media. Soil Sci Soc American Proc 38:29-35.
Ying G, Kookana RS (2001) Sorption of fipronil and its metabolites on soils from South. Australia J Environ Sci Health 36:545-558.