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Sorption Kinetics of Fipronil on Soils

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Abstract Sorption kinetics of fipronil was studied on five soils of varying physico-chemical properties by batch equilibration method. Fipronil sorption on soils conformed to pseudo-second order kinetics and both the initial uptake rate and rate constant had a significant and positive correlation with clay content. The sorption kinetics of fipronil onto soils could be explained by intraparticle diffusion model consisting of an initial faster step followed by later slower step. The intraparticle diffusion rate constants for the initial faster and later slower step showed a significant and positive correlation with clay content (r = 0.978, significant at $p \leq 0.01$) and soil electrical conductance (r = 0.901, significant at $p \leq 0.05$), respectively.

Keywords Film- and intraparticle-diffusion · Fipronil · QuEChERS method · Sorption kinetics

Soil acts as a sink for pesticides used in agriculture or public health programmes. Pesticides may reach into water bodies (surface and ground) by runoff and leaching from soil. It is important to understand the interaction of a pesticide with soil for accurate assessment of its contamination potential and fate in the environment (Kah and Brown 2006). A number of factors influence the sorption of an organic pesticide by soil solids that include: the physical and chemical characteristics of the pesticide; nature of the soil solution and composition of the soil. The characteristics of the chemical such as solubility, size, hydrophobicity, presence of charged or uncharged functional groups etc. and also that of soil like particle size distribution, nature and content of organic matter, pH, and CEC are key factors governing the degree of sorption. Fipronil [5-amino-1-(2,6-dichloro-α,α,α-trifluoro-*p*-tolyl)-4-trifluoromethyl-sulfinylpyrazole-3-carbonitrile] is a broad spectrum, phenylpyrazole insecticide commonly used in rice, cotton and sugarcane production, turf management etc. and residential insecticide mainly for the control of cockroaches, mosquito, locust, ticks, and fleas at both larval and adult stages (Tomlin 2009). The oral LD_{50} for rats is 97 mg kg^{-1}. It is slightly toxic to nontoxic via the dermal route, with a reported dermal LD_{50} of greater than 2,000 mg kg^{-1} in rats. Fipronil has moderate inhalation toxicity with an acute LC_{50} of 0.682 mg L^{-1} in rats. Fipronil is considered highly toxic to rainbow trout and very highly toxic to bluegill sunfish with an LC_{50} of 0.246 mg L^{-1} and 0.083 mg L^{-1}, respectively (USEPA 1996). Many reports have been published regarding adsorption of fipronil on soils (Doran et al. 2006; Mukherjee and Kalpana 2006; Masutti and Mermut 2007; Lin et al. 2008; Shuai et al. 2012) but so far no studies have been reported about its sorption kinetics on soils which is necessary for understanding the reaction paths, mechanism of adsorption and migration through soil matrix. A rapid sorption of a compound is likely to reduce its migration velocity through soil and potential to contaminate surface water bodies and aquifers. This paper presents the results of investigation on sorption kinetics of fipronil on five soils of varying properties for understanding its sorption behaviour in soils.

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Materials and Methods

Technical grade fipronil of 98 % purity was obtained from Gharda Chemicals Pvt. Ltd., Mumbai, India. All the chemicals used in the study were of AR or HPLC grade. Five surface (0–15 cm) soils were collected from different location of Uttarakhand and Uttar Pradesh states of India. Soil samples were dried in shade, crushed with a wooden roller and passed through a sieve having openings of 2 mm diameter. Soil samples were analysed for their physico-chemical properties following standard methods.

Sorption kinetics of fipronil on soils was carried out by batch equilibration method. One gram of each soil was taken in 20 centrifuge tubes. To each tube, 1 mL of fipronil solution (20 mg fipronil L^{-1}) and 1 mL of 0.1 M $CaCl_2$, were added and the final volume was maintained to 10 mL with distilled water. These tubes were shaken at room temperature (27 °C) for different time intervals i.e. 0, 1, 2, 4, 6, 12, 24, 48 and 72 h in duplicate. Two tubes were maintained as blank (control) i.e. without soil to monitor adsorption on centrifuge tube. After each time interval, samples were centrifuged at 7,000 rpm ($\sim$5,000*g*) for 10 min. Extraction of fipronil from the supernatant was done by modified QuEChERS method. Five mL of supernatant was taken into a 15 mL centrifuge tube. Two mL of acetonitrile was added to centrifuge tube and vortexed for 10 s. Three grams of anhydrous magnesium sulphate and 2 g of sodium chloride were added to the centrifuge tube. Again, the centrifuge tube was vortexed for 2 min. Then, the tubes were centrifuged for 5 min at 3,000 rpm ($\sim$900*g*). After phase separation, the upper organic layer was retained and analysed for fipronil by HPLC. A Dionex Ultimate 3000 HPLC system was used for the analysis of fipronil. The HPLC conditions were: column-C_{18}, 250 × 4.6 mm i.d., 5 µm, mode-isocratic, mobile phase-acetonitrile:water (8:2 v/v), flow rate: 1 mL min^{-1}, detector: UV (276.0 nm). Under these conditions fipronil showed a sharp peak at retention time of 4.05 min with no other interfering peaks. The linearity of the HPLC assay was evaluated at six concentration levels consisting of 0.2, 0.4, 1.0, 2.5, 5.0 and 10.0 µg mL^{-1} fipronil. The detector response for fipronil on HPLC showed a good linearity with its concentration ($r = 0.999$, significant at ≤ 0.01).

The amount of fipronil sorbed by soil (Q_t) at a given time (t) was calculated as difference between the initial (C_0) and final concentration (C_t) of fipronil in solution. Since the adsorption of fipronil on the control centrifuge tube was negligible (<0.05 %) and it was, therefore, neglected in calculations.

The sorption data of fipronil were fitted to pseudo- first (Eq. 1) and -second order kinetics (Eq. 2) as well as to film diffusion- (Eq. 3) and intra-particle diffusion -models (Eq. 4). The observation obtained for 0 h shaking was assigned at time of 0.166 h considering the contact time of fipronil with soil during centrifugation (10 min).

Pseudo-first order kinetics

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \tag{1}$$

Pseudo-second order kinetics

$$t/Q_t = \left(1/k_2 Q_e^2\right) + t/Q_e \tag{2}$$

where, Q_t and Q_e are amount of fipronil adsorbed on soil at time t and equilibration (mg kg^{-1}), respectively while k_1 (h^{-1}) and k_2 (kg mg^{-1} h^{-1}) are rate constants. The quantity ($1/k_2Q_e^2$) is intercept (h).

Film diffusion model

$$\begin{aligned}\ln(C_t/C_0) = {} & [I_1 - (K_{f1} W S_w/V_f)t] \\ & + [I_2 - (K_{f2} W S_w/V_f)t]\end{aligned} \tag{3}$$

where, K_{f1} and K_{f2} are mass transfer coefficients for the initial rapid and later slower steps, respectively. I_1 and I_2 are the intercepts pertaining to the initial rapid and later slower steps, respectively. S_w = specific external surface of adsorbent on weight basis, W = adsorbent dose, V_f = volume of fluid

Weber's intra - particle diffusion model

$$Q_t = \left[k_{id1} t^{0.5} + I'_1\right] + \left[k_{id2} t^{0.5} + I'_2\right] \tag{4}$$

where, k_{id1} and k_{id2} are the intraparticle diffusion rate constants (mg h^{-1}) for the initial rapid and later slower steps, respectively. I'_1 and I'_2 are the intercepts for the initial rapid and later slower steps, respectively.

The goodness of data fit to a model was examined by linear co-efficient of determination (R^2) and Akaike weights (w_i) computed from second order Akaike Information Criteria (AIC_c) as described by Burnham and Anderson (2002).

The computed values of rate constants obtained for different models were also correlated to soil properties following the procedure outlined by Snedecor and Cochran (1967).

Results and Discussion

The data of physicochemical properties of soil are given in Table 1. Soil texture varied from coarse (sandy clay loam) to fine (silty clay loam). The pH of experimental soils ranged from acidic (4.75) to alkaline (8.16). Soil organic carbon status varied from low (3.45 g kg^{-1}) to high (17.47 g kg^{-1}). Electrical conductivities of these soils were 0.201–1.13 dSm^{-1}.

The modified QuEChERS method used for the extraction of fipronil under the experimental conditions described in the materials and methods section gave an instrument

Table 1 Physicochemical properties of soils

Soils	Location							Soil texture				pH	Electrical conductance (dS m^{-1})	OC (g kg^{-1})
	Latitude			Longitude			Altitude[a]	% Sand	% Silt	% Clay	Textural class			
	α°	β′	γ″	a°	b’	c″	(m)							
S1	28	47	27.205	79	44	47.378	136.91	15.8	51	33.2	Silt clay loam	4.57	0.201	9.05
S2	29	4	1.317	79	31	46.632	200.03	34.1	41	24.9	Loam	8.44	0.218	17.47
S3	28	56	16.476	79	46	58.853	147.01	23.1	50	26.9	Silt loam	7.77	0.279	7.65
S4	27	59	57.272	78	59	45.23	106.31	63.1	51	20.9	Sandy clay loam	7.34	0.18	3.45
S5	28	10	23.823	79	16	9.136	100.93	43.1	38	18.9	Loam	7.44	0.213	4.61

OC Organic carbon

[a] Above mean sea level

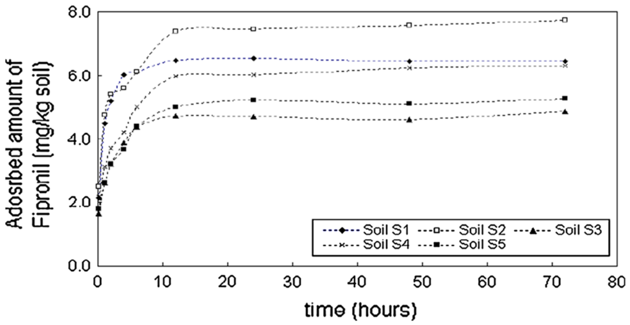


Fig. 1 Sorption of fipronil on soils at different time intervals

detection limit (IDL) of 0.06 µg fipronil mL^{-1}. The estimated method detection limit (EMDL) of modified QuEChERS method was 0.027 µg mL^{-1} with 94.5 % recovery. The EMDL in the present investigation was much lower than 0.1 µg mL^{-1} reported earlier by Hadjmohammadi et al. (2006) who developed a reversed phase-HPLC method for extraction of fipronil from water using dichloromethane (4:1 v/v) and from soil by refluxing it in dichloromethane–acetone (1:1, v/v) with low pressure evaporation and subsequent dissolution in acetonitrile prior to injection in HPLC with dichloromethane–acetone (1:1, v/v) as mobile phase.

The sorption of fipronil by soils used in the study regularly increased with time until it reached a quasi state equilibration (Fig. 1). In general, the sorption of fipronil by soils increased steadly up to 12 h shaking and beyond this time the magnitude of increase in sorption was less. The highest sorption of fipronil by soil was noted at 12 h in S1 and S3, 24 h in S5, 48 h in S4 and 72 h in S2.

The sorption data of fipronil was fitted to pseudo-first and -second order kinetics and the values of rate constants, experimental ($Q_{e\ exp}$) and predicted ($Q_{e\ cal}$) equilibrium sorption of fipronil are presented in Table 2. The highest value of $Q_{e\ exp}$ was observed in soil S2 (7.737 mg kg^{-1} soil) while the lowest value was recorded in S3 (4.719 mg kg^{-1} soil); these soils had 17.47 and 3.45 g organic C kg^{-1} soil, respectively. This indicated that soils of high organic C content have higher sorption capacity of fipronil (Bobe et al. 1997). Though the significant values of R^2 at $p \leq 0.01$ for both pseudo-first and -second order kinetics indicated that any of these two models could account for the sorption kinetics of fipronil in these soils, the many fold higher value of Akaike weight with the pseudo-second order kinetic model (0.977) as compared to that of pseudo-first order kinetic model (0.023) clearly provides support that sorption of fipronil by soil conformed to pseudo-second order kinetics model. The intercept (h) showed the initial uptake rate which was the highest in S2 which had the highest clay content (33.2 %); the correlation coefficient between h and clay content in these soil samples was significant and positive (r = 0.907, significant at $p \leq 0.05$). Thus, fine textured soils which were capable of initially sorbing higher content of fipronil could reduce the migration rate of fipronil through soil and the potential of fipronil to contaminate ground waters. Interestingly, the rate constant of pseudo-second order kinetics (k_2) also showed a significant correlation with clay% in these soils (r = 0.878, significant at $p \leq 0.05$). The dependence of fipronil uptake rate on particle size of adsorbent (clay particles <0.002 mm) also proved that retention of fipronil was a transport controlled mechanism rather than kinetically controlled mechanism (McKay et al. 1983).

In order to analyse the transport mechanism of fipronil on soils, the sorption data of fipronil on soils at different time intervals were fitted to film diffusion and intraparticle diffusion models. The pattern of points for both the models (Figs. 2, 3) revealed that sorption occurred through a faster initial step followed by a slower later step (Boparai et al. 2011), therefore, the relevant constants and R^2 values of both the models were computed for both initial and later steps (Table 3). In general, a comparison of R^2 values for film diffusion and intraparticle diffusion showed that fipronil sorption kinetics onto soils could be better accounted by intraparticle diffusion. Akaike weights (w_i) calculated

Table 2 Rate constants and predicted sorbed amounts of fipronil on soils as per psuedo- first and -second order kinetics

Soils	$Q_{e,exp}$ (mg kg^{-1})	k_1	$Q^{-1}_{e,cal\ (mg\ kg)}$	R^2	k_2	$Q_{e,cal}$ (mg kg^{-1})	Intercept 'h' (mg kg^{-1} h^{-1})	R^2
S1	6.528	0.341	3.036	0.965	0.328	6.66	14.563	0.999
S2	7.737	0.067	2.487	0.765	0.128	7.802	7.788	0.999
S3	4.719	0.356	3.156	0.993	0.239	4.998	5.948	0.995
S4	6.313	0.081	2.585	0.883	0.12	6.412	4.952	0.999
S5	5.219	0.231	3.44	0.995	0.154	5.45	4.579	0.997

Intercept (h) = ($1/k_2Q_e^2$)

All R^2 values were statistically significant at $p \leq 0.01$

Akaike weights (w_i) for pseudo first- and pseudo second-order kinetic models were 0.023 and 0.977, respectively

Fig. 2 Film diffusion model fitting to the sorption data of fipronil on soils C_0 = initial concentration of fipronil in solution (mg L^{-1}), C_t = final concentration of fipronil in solution (mg L^{-1}) and t = time (in hours)

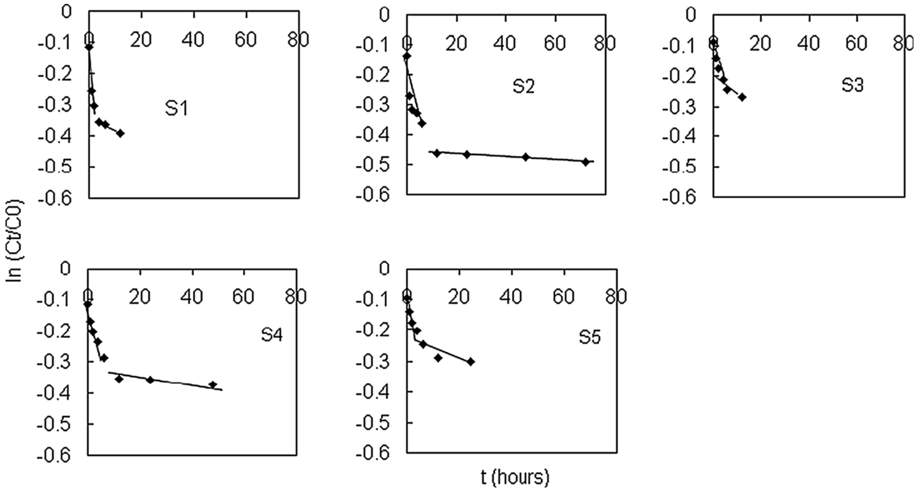
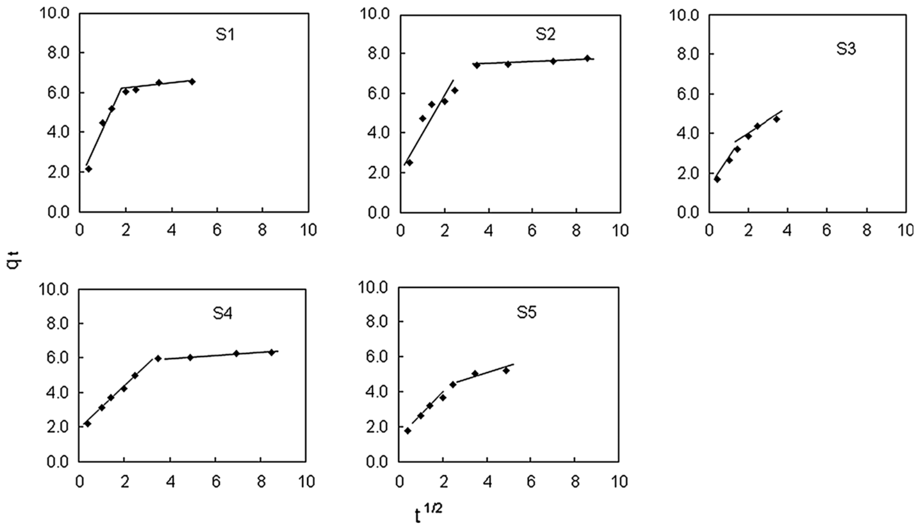


Fig. 3 Intraparticle diffusion model fitting to the sorption data of fipronil on soils. Q_t = amount of fipronil adsorbed on soil at time t (mg kg^{-1} soil), Q_e = amount of fipronil adsorbed on soil at equilibration (mg kg^{-1}) and t = time (in hours)



for both the film diffusion- and intraparticle diffusion-models also clearly indicated that the intraparticle diffusion model best approximated the kinetics of fipronil sorption onto soils. Jodeh et al. (2014) also reported that the rate of imidacloprid adsorption onto soil was limited by mass transfer across the boundary layer and kinetics of imidacloprid adsorption could be accounted well by intraparticle diffusion model. According to Weber and Morris (1962), if the rate limiting step is intraparticle diffusion then the curve should pass through the origin or the intercept in the

Table 3 Fitting of soil sorption kinetic data of fipronil to film- and intraparticle-diffusion models

Soil	Film diffusion model					
	Initial faster phase			Later slower phase		
	K_{f1}	I_1	R_1^2	K_{f2}	I_2	R_2^2
S1	0.010	0.117	0.891	0.005	0.341	0.998*
S2	0.032	0.199	0.687	0.001	0.455	0.988*
S3	0.048	0.083	0.971	0.006	0.199	0.949
S4	0.019	0.150	0.919*	0.001	0.348	0.957*
S5	0.027	0.105	0.900	0.003	0.241	0.803

Soil	Intraparticle diffusion model					
	Initial faster phase			Later slower phase		
	k_{id1}	I'_1	R_1^2	k_{id2}	I'_2	R_2^2
S1	2.385	1.587	0.928*	0.183	5.695	0.862
S2	1.605	2.539	0.829*	0.068	7.134	0.960*
S3	1.554	1.036	0.999*	0.719	2.366	0.916*
S4	1.229	1.828	0.990**	0.076	5.68	0.963*
S5	1.06	1.55	0.976**	0.325	3.701	0.867

Akaike weights (w_i) for film diffusion- and intraparticle diffusion-models were 0.254×10^{-4} and 0.999, respectively

* Significant at $p \leq 0.05$

** Significant at $p \leq 0.01$

linear equation must be zero. In the present study, however, the intercept values for both initial rapid and later slower phases were not zero which indicated that along with intraparticle diffusion mechanism some other mechanism often associated with highly energetic heterogenous surfaces might also be operative which could result in rapid uptake of fipronil prior to the equilibrium stage. Since the fipronil molecule possesses many polar moieties, there is a likelihood that an additional mechanism like hydrogen bonding might also be operational besides diffusion. A higher intercept value for the later slower step as compared to the initial faster step indicated slower mass transfer rate in the later step of sorption (Mohanty et al. 2005; Kavitha and Namasivayam 2007). The intercept values for both the steps failed to show any significant correlation with any of the examined soil property. The intraparticle diffusion rate constants of the initial step (k_{id1}) in all soils were many folds higher than those of the later step (k_{id2}). Considering the polydispersive nature of the soils where clays and natural organic colloids exist together along with varied pore size range (meso- and micro-pores), the fipronil molecules are likely to diffuse in pores filled with soil solution having dissolved ions and therefore, the differences in k_{id1} and k_{id2} are likely. In the present investigation, k_{id1} showed a significant correlation with clay content ($r = 0.978$, significant at $p \leq 0.01$) while k_{id2} showed a significant positive correlation with soil electrical conductance ($r = 0.901$, significant at $p \leq 0.05$). Therefore, it appeared that fipronil molecules in soils are quickly retained around the clay micelles through hydrogen bonding and their further diffusion in clay pores (possibly in interlayer space) is slower and the closer approach to effect their entry in clay pores is related to the thickness of double diffuse layer which in turn depends the concentration of electrolytes in soil solution. More investigations are required to confirm the validity of this speculated mechanism of fipronil sorption in soils.

Thus, it can be concluded that fine textured soils quickly sorb fipronil. The sorption of fipronil onto soils follows a pseudo-second order rate kinetics. The sorption kinetics of fipronil could be well accounted by intraparticle diffusion model consisting of an initial faster step followed by a latter slower step. The intraparticle diffusion rate of fipronil for the initial faster step increases with soil clay content while the later slower diffusion rate increases with soil electrical conductance. Owing to faster sorption of fipronil onto fine textured soils, the migration of fipronil through soil profile would be low with little danger to contaminate ground waters. Ying and Kookana (2006) assessed the mobility of fipronil in soil columns and also noted that fipronil was not mobile under simulated weather conditions of wetting (five cycles of 20 mm rain) and drying.

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