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Behaviour of fipronil in soil under different moisture levels*

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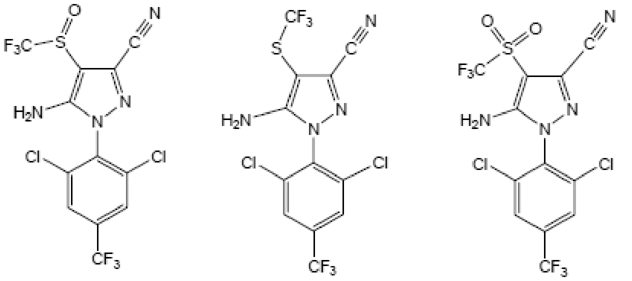
Fipronil {5-amino-1-[2, 6-dichloro-4-(trifluoromethyl) phenyl]-4-[(trifluoromethyl) sulfinyl]-1H-pyrazole-3-carbonitrile} is a phenylpyrazole insecticide having broad spectrum activity against household and agricultural pests. It is active against a wide range of soil and foliar insects such as rice grasshoppers, vine weevil, termites, black ants and dessert locust hoppers in agricultural, forestry and urban environment (Chaudhary *et al*. 2001). It is used for control of various insect-pests of vegetables crops, like chilli, brinjal, and okra (Jadav *et al*. 2004, Gupta *et al*. 2007, Sinha *et al*. 2007). Fipronil degrades faster when applied to crops, but remains undegraded in soil for long period of time. The half-life of fipronil was found to be in the range of 122–128 days in oxygenated sandy loam soil, 0.7 to 1.7 months on soil surfaces, and 3 to 7.3 months when incorporated in soil (NPTN 1997). The metabolites of fipronil are more toxic than the parent compound. The sulfone metabolite is 6.3 times more toxic to rainbow trout and 3.3 times more toxic than the parent compound to bluegill sunfish. Fipronil demonstrates a high toxicity towards freshwater aquatic invertebrates as well. The sulfone metabolite is 6.6 times more toxic and the desulfinyl photodegradate 1.9 times more toxic on an acute basis to freshwater invertebrates than the parent compound (US EPA 1996). In an earlier study conducted by Ying and Kookana (2002) on degradation of fipronil in laboratory and field soil its half-life in laboratory soil was 132 days and field soil it was 188 days. Usage of fipronil for agriculture as well as for ant and termite control is on the rise in India. Soil characteristics (organic matter, clay content etc.) and moisture level are important parameters that affect fipronil persistence. The study was therefore undertaken to know the behaviour of fipronil in 2 soils, i e sandy loam soil and organic matter rich soil at 20% field capacity moisture and submerged conditions.

Fipronil (purity 97.5%), fipronil sulfide (purity 98.8%) and fipronil sulfone (purity 99.7%) were obtained from Accu Standard, USA (Fig 1). All solvents used were of analytical and chromatographic grade. The soil properties of the soils used were sandy loam (Typic Haplustalf) (*p*H 6.6, EC 0.20 dS/m, CEC 6.9 meq/100g, organic carbon 0.4%, sand 70.6%, silt 7.4% and clay 10.3% and organic matter rich soil (cumic Hapludolls) (*p*H 5.8, EC 0.55, CEC meq/100g, organic carbon 3.4%, sand 31.9%, silt 22.8%, clay 35.3% which includes organic carbon content, *p*H, cation-exchange capacity etc. The soils classified as sandy loam and organic are varied in organic carbon, sand, clay and silt content. The sandy loam soil had organic carbon content of 0.4%, whereas for organic soil it was 3.4%. The sandy loam soil was collected from the experimental farm of the Institute. The organic matter rich soil was collected from Ooty, Tamil Nadu.

This study was conducted to assess the effect of moisture levels on fipronil degradation. The experiment was carried out under laboratory conditions in sandy loam and organic matter rich soil. The soils (20 g) were taken in test tubes (25 mm × 200 mm) and moisture level maintained at 20% field capacity moisture and submerged conditions. The tubes received 0.5 ml of fipronil solution (analytical grade) in acetone so as to obtain a concentration of 0.5 µg/ g of soil. Soil tubes without fipronil were treated as control. The tubes were kept at laboratory conditions where the room temperature was 22±2°C. The moisture loss was supplemented with deionized water every week.

On every sampling day 3 tubes were removed from each treatment. The contents of the tubes were transferred into



Fipronil Fipronil sulphide Fipronil sulfone

Fig 1 Structure of fipronil and its metabolites

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* Short note

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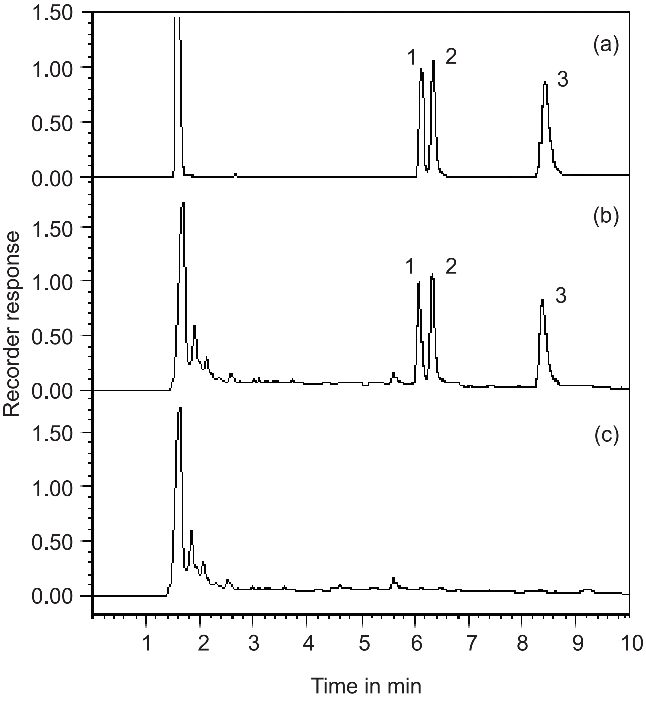

Fig 2 Chromatogram of fipronil and its metabolites in soil; (a) Standard of fipronilsulfide (1), fipronil (2), fipronil sulfone (3); (b) soil fortified with fipronil and its metabolites; (c) untreated control

250 ml conical flasks. Deionized water (20 ml) was added to soils maintained at 20% field capacity moisture. The soil samples were extracted with analytical grade acetone 3 times (30+30+30 ml). The extracts were filtered under vacuum after shaking on a mechanical shaker for 1 hr. The combined extracts were dried in a flash evaporator under vacuum. Fipronil residues in the aqueous extracts were partitioned into ethyl acetate (30+30+30 ml). The combined ethyl acetate fraction was dried over anhydrous sodium sulphate, concentrated to 5 ml for analysis by Gas Liquid Chromatograph (GLC).

The GLC (Varian 3800) was equipped with an electron capture detector (ECD) and fitted with a capillary column (fused silica 30 m × 0.25 mm i.d.). The column temperature was maintained at 200–240°C @ 5°C/ min. hold 7 min. Injector and detector temperatures were maintained at 280°C and 300°C, respectively. The carrier gas (UHP grade nitrogen) flow rate was 1.5 mL/min. Under these parameters, the retention time of fipronil sulfide, fipronil and fipronil sulfone was 6.05, 6.26 and 8.4 min., respectively (Fig 2). Recovery study was carried out in soil with fipronil and its metabolites and it was in the range of 95.2–101%. The limit of quantification of fipronil and all its metabolites was 0.01 mg/kg.

The results of degradation study of fipronil in sandy loam and organic matter rich soil is presented in Fig 3. At 20% field capacity moisture total toxic fipronil remained almost the same in both sandy loam and organic matter rich soil after 60 days, but formation of sulfone derivative was slightly higher. Under high moisture conditions conversion of fipronil to fipronil sulfide was much faster and it was more pronounced in organic matter rich soil. After 20 days of storage at room temperature about 60% of the total recovered fipronil (out of about 80% recovered total toxic fipronil) was the sulfide derivative. After 60 days almost complete conversion of parent fipronil had occurred in organic matter rich soil with some amount (4.85%) being oxidized to the sulfone derivative. In sandy loam soil 4.24% remained undegraded as fipronil and 1.95% was recovered as the sulfone derivative. However total toxic fipronil remained almost the same in both the soils. The half-life of degradation of fipronil was calculated as per Hoskins (1967). At 20% field capacity moisture level the half-life of degradation of fipronil was 78.4 days and that of total toxic components was 196 days, whereas under submerged conditions it was 13.6 and 162.43 days, respectively, in sandy loam soil. In organic matter rich soil it was 75.35 and 211.6 days under 20% field capacity moisture level and 8.3 and 135.0 days under submerged conditions.

In the present study on the degradation of fipronil in soil with different moisture showed that moisture affected fipronil degradation and it was independent of the soil type. As evident from studies conducted earlier that organic carbon may or may not have any effect on fipronil degradation. Bobe *et al.* (1997) reported that the increase in organic matter content increases adsorption of fipronil in soil. When applied at recommended doses fipronil is found to persist for more than 3 weeks and it persists longer in soil with high organic matter content (Belayneh 1998). Doran *et al.* (2006) reported greater sorption of fipronil in the soil containing less content of organic carbon, possibly as a result of the type of carbon present rather than the absolute amount. The results obtained from the present study showed that high organic carbon in the soil did not affect persistence of fipronil in soil. There was some difference in the half-life of degradation, but it was not significant.

It was observed that the major metabolite formed was the sulfide derivative under both 20% field capacity as well as submerged conditions, while its concentration was much more under submerged conditions. Similar report exists on studies with Australian rice growing soils under flooded conditions, possibly as a result of greater exclusion of oxygen from the soil by floodwater (Doran *et al.* 2006). Aerobic conditions along with high clay content favoured formation of sulfone metabolites (Masuti and Mermut 2007). Bobe *et al.* (1998) reported that fipronil and its metabolites were persistent with half-life ranging from 111 to 350 days. Ying and Kookana (2002) reported that high soil moisture (>50%) favoured the formation of sulfide derivative by reduction, whereas low soil moisture favoured formation of fipronil sulfone by oxidation. The half-life of degradation of fipronil increased from 68 to 198 days when moisture level decreased

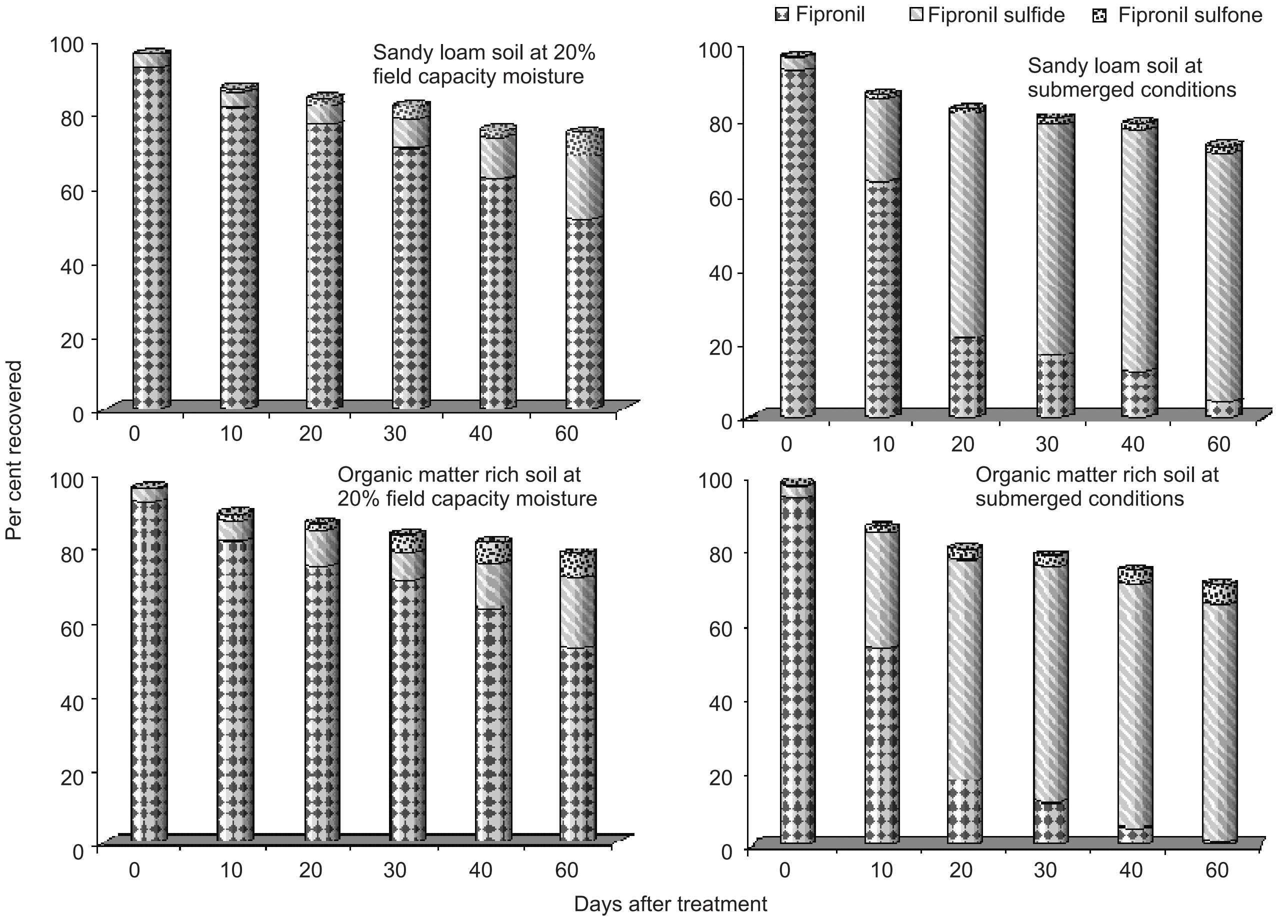

Fig 3 Persistence of fipronil in soil at different moisture levels

from 60 to 15% water-holding capacity level. In the present study it was evident that soil moisture accelerated conversion of fipronil to its sulfide. Even though fipronil is known to persist in soil for a very long time and high soil moisture can help reduce its concentration in soil.

SUMMARY

Behaviour of fipronil was studied in sandy loam and organic matter rich soil at 2 moisture levels, i e 20% field capacity moisture and submerged conditions. The results showed that degradation of fipronil was faster under submerged conditions compared to at 20% field capacity moisture in both the soils. The major degradation product of fipronil under submerged conditions was the sulfide derivative, but at 20% field capacity moisture some amount of sulfone derivative was formed. Half-life of degradation of fipronil varied widely with change in soil moisture. The half-life of degradation of fipronil was 78.4 and 75.3 days under 20% field capacity moisture and 13.6 and 8.3 days under submerged conditions, respectively, in sandy loam and organic matter rich soil. Submergence increased loss of total toxic fipronil (fipronil together with its metabolites) from soils and this was more evident in case of organic matter rich soil.

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