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Effect of Biocompost-Amendment on Degradation of Triazoles Fungicides in Soil

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Abstract Soil amendments play an important role in management of pesticide residues. Present study reports the effect of biocompost-amendment on degradation of penconazole and propiconazole (triazole fungicides) in a sandy loam soil under flooded and nonflooded (60% water holding capacity) conditions. Penconazole degraded at faster rate than propiconazole. Both the fungicides were found to be more persistent in flooded soil than nonflooded soil, but application of biocompost at 2.5% and 5.0% levels enhanced their degradation under both moisture regimes.

Keywords Biocompost · Penconazole · Propiconazole · Degradation · Moisture regime

Triazole fungicides, penconazole [1-(2,4-dichloro-β-propylphenethyl)-1*H*-1,2,4-triazole] and propiconazole [1-(2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxalan-2-ylmethyl)-1*H*-1,2,4-triazole], are systemic, broad spectrum, eradicant, and protectant fungicides against powdery mildew, loose smut, and rust of cereals and other crops (Tomlin 1997). Information about pathways of degradation and factors influencing their degradation is important in predicting the levels of pesticides likely to remain in soils and allows assessment of the potential risk associated with the exposure.

Soil amendments play an important role in the management of pesticides residues in agricultural fields. Application of organic carbon (OC) in the form of compost, sludge, effluent, and crop residues has been a common agronomic practice followed in agriculture to increase the soil fertility and crop productivity. Generally, with increase in the organic matter content of soil the retention of pesticide on the soil particles increases, thus, lesser amount of the pesticides will be available in the soil solution for microbial degradation (Barriuso et al. 1997). However, the increased soil organic carbon may increase the soil microbial activity, which in turn may increase the microbially mediated degradation of the contaminants (Felsot and Shelton 1993).

Biocompost manufactured from the sugar mill/distillery plant waste, spent wash, and press mud, is an excellent humus (bio mass) and helps in maintaining organic carbon in soil, increases water holding capacity (WHC), improves and provides the essential nutrients in the form of NPK to the soil. Soils of Northern-India are low in soil OC content; therefore, amendment of organic carbon in the form of manure, compost, and effluent is a common recommended agricultural practice. Except registration data, no information is available on the persistence of penconazole in soils. Propiconazole has been reported to be a persistent in soils with half life varying between 200 days (Bromilow et al. 1999) and 1 year (Kim et al. 2003). However, half lives between 40 and 70 days are cited by Tomlin 1997. As no information is available on their persistence under Indian tropical conditions and the effect of biocompost amendment, the focus of present study was to understand the multitude of different interactions and processes that may occur in the biocompost-amended sandy loam soil of Northern India.

Materials and Methods

Soil used in the present study was a sandy loam soil from the experimental farm of Indian Agricultural Research

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Institute, New Delhi, India. Soil was collected from the surface 0–15 cm depth, dried in shade, ground to pass through 2 mm sieve, and was stored in polythene bags at room temperature. The physico-chemical characteristics of the soil were determined using standard analytical procedure: pH 7.8 measured at 1:1.25 soil-to-water ratio (Jackson 1967); organic carbon content – 0.51% by Walkley and Black method (Jackson 1967); soil mechanical fractions, sand – 78%, silt – 10%, clay – 12.4% employing the Bouyoucos hygrometer method (Black et al. 1965) and the cation exchange capacity – 11.2 cmol kg^{-1} by normal ammonium acetate (pH 7.0) method (Jackson 1967).

Analytical samples of penconazole and propiconazole (95% purity) were supplied by Ciba-Geigy Ltd. The solvents used were of analytical grade and were purchased locally.

Biocompost was obtained from the Simbhaoli Sugar Mills Ltd., Simbhaoli, Uttar Pradesh, India. The physico-chemical characteristics of the biocompost included: pH 7.6 and OC content 31.0%. The total carbon, nitrogen, and hydrogen content of biocompost were determined by elemental analysis and were 34.2%, 17.1%, and 8.7%, respectively.

Portions (10 g) of soils in sterilized glass test tubes (200 mm × 25 mm) were mixed with biocompost at 2.5% and 5.0% levels and these treatments were called as T-1 and T-2, respectively. Biocompost-unamended soil served as control and was labeled as T-0. Soils were supplemented with sterile distilled water to obtain nonflooded (60% WHC) and flooded (soil:water ratio of 1:1.25, w/v) moisture conditions. Prior to addition of fungicide, the flooded soils were incubated for 10 days at 28 ± 1°C to allow development of reducing conditions. Penconazole/propiconazole (50 µg) was added to the soils in 0.1 mL of acetone. The tubes were closed with cotton plugs and then incubated at 28 ± 1°C in dark. Moisture was maintained by adding required amount of water at weekly intervals and at periodic intervals duplicate samples were removed for analysis.

The fungicide residues from soil samples were extracted using ethyl acetate (25 mL) by shaking on a shaker for 2 h. The ethyl acetate layer was separated and dried over anhydrous sodium sulphate (5 g). The samples were quantified GC on a Hewlett Packard (Palo Alto, CA, USA) gas chromatograph, Model 3840, equipped with a Ni^{63} electron capture detector (ECD) and fitted with HP-1 column [10 m (l) × 0.53 mm (i.d.) × 2.53 µm film thickness]. The GC operating conditions were: oven – 200°C, injector – 300°C, detector – 300°C, carrier gas (nitrogen) flow rate – 45 mL min^{-1}. The detection limit for fungicides was 0.05 µg and recovery from the soil at fortification levels of 0.1–10 µg g^{-1} soil was more than 90%.

Results and Discussion

Degradation data for fungicides under different incubation conditions fitted well to first-order kinetic equation: $\log(C/C_o) = -K_{obs}t$, where C_o is the initial concentration of fungicide (µg/g); C is its concentration (µg/g) after time t (days), and K_{obs} is the rate constant of the reaction.

Table 1 and Figure 1 represent the degradation behavior of penconazole and propiconazole in a sandy loam soil. In natural soil (without biocompost), both the fungicides were found to be more persistent in the flooded soils as compared to nonflooded soils held at 60% WHC. After 60 days of incubation 65% degradation was observed in the case of penconazole in the nonflooded soil and 55% degradation in flooded soil. Corresponding values for propiconazole degradation in nonflooded and flooded soils were 46% and 30%, respectively. This further indicates that propiconazole is more persistent in the soil. However, amendment of compost to soil enhanced the degradation of triazoles fungicides under both moisture regimes.

The half life ($T_{1/2}$) of penconazole in flooded and nonflooded soils was found to be 57.9 and 41.2 days, respectively. The application of compost drastically enhanced the degradation of penconazole in flooded soils.

Table 1 Degradation constants for penconazole and propiconazole in soils

Parameter	Nonflooded			Flooded		
	T-0	T-1	T-2	T-0	T-1	T-2
Penconazole						
$K_{obs} \times 10^{-3}$ (day^{-1})	−7.3	−9.0	−10.0	−5.2	−32.7	−91.0
$T_{1/2}$ (day)	41.2	33.4	30.1	57.9	9.2	3.3
R^2	0.910	0.933	0.894	0.923	0.986	0.883
Propiconazole						
$K_{obs} \times 10^{-3}$ (day^{-1})	−4.1	4.8	−5.3	−3.3	4.7	−5.5
$T_{1/2}$ (day)	73.4	62.7	51.9	91.2	64.2	54.7
R^2	0.984	0.877	0.888	0.972	0.878	0.984

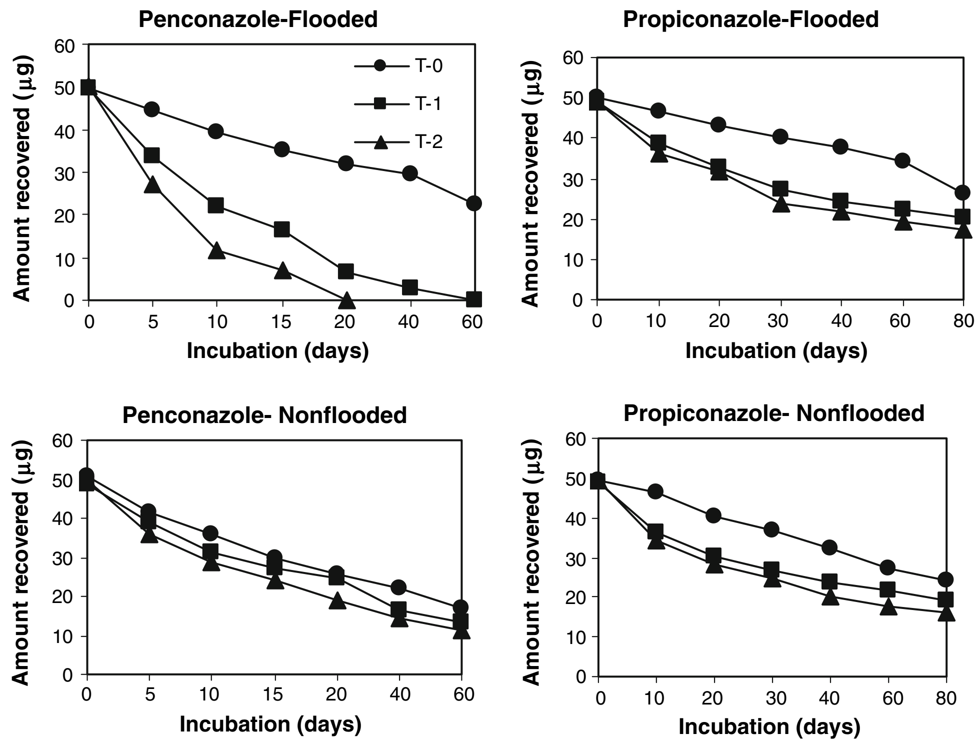

Fig. 1 Persistence of penconazole and propiconazole in soils

The half live of penconazole in the flooded soil for the treatment T-0, T-1, and T-2 were found to be 57.9, 9.2, and 3.3 days, respectively. The compost-amendment also enhanced the degradation of penconazole in nonflooded soils, but the effect was less prominent as observed in the flooded soils. The calculated half-life values for the treatments T-0, T-1, and T-2 were 41.2, 33.4, and 30.1 days, respectively. Biocompost amendment increases the soil organic carbon pool and will increase the soil microbial activity. Increased degradation of penconazole in compost-amended soil may be the result of greater microbial activity in compost-amended soils then the control soil. Further, it is known that application of compost to soils hastened the onset of soil reducing conditions and Eh of the compost-amended soil dropped faster than that of manure-unamended soil. It is probable that drastic increase in penconazole degradation rates in predominantly anaerobic soils (flooded) was mediated by anaerobic microorganisms, and because of faster attainment of reducing conditions following manure application, anaerobic microorganisms proliferated faster.

The half-life values for propiconazole in flooded and nonflooded soils were 91.2 and 73.4 days, respectively. Following biocompost-amendment, an increase in degradation of propiconazole in soils was found under both moisture regimes. The half life values in nonflooded soils for treatments T-1 and T-2 were found to be 62.7 and 51.9 days, while respective values in flooded soils were 64.2 and 54.7 days. Thus, unlike penconazole, the moisture regime did not make much change in propiconazole degradation in the compost-amended soils. The faster degradation of propiconazole in compost-amended soils may be due to higher microbial activity in amended soils. Earlier studies have shown that the rate of propiconazole mineralization was the same in anaerobic and aerobic soils (Kim and Suh 1998; Kim et al. 1999, 2003). However, Bromilow et al. (1999) and Kim et al. (2003) showed that mineralization of propiconazole was faster in sandy loam soil than the clay loam suggesting that due to lesser sorption of the fungicide in sandy loam soil than clay loam, the fungicide was more accessible to biological degradation. Thorestensen and Lode (2001) have reported that propiconazole degraded faster in soil with lower organic carbon content and its half life values in sandy loam (OC – 1.4%) and loam (OC – 2.5%) soils were 137 and 210 days, respectively.

GC chromatograms of ethyl acetate extracts from the nonflooded and flooded soils for penconazole and propiconazole did not show any additional peak. However, gas chromatography–mass spectroscopy (GC-MS) analysis of ethyl acetate extract from penconazole-applicated soil showed an additional peak at retention time (Rt) 11.88 min with molecular ion peak at *m/z* – 215 (M^+), a base peak at *m/z* – 200 [$M^+ - CH_3$], and fragment ion peaks at *m/z* – 172 ($M^+ - CH_2CH_2CH_3$), 138 ($M^+ - C_6H_5$), 95 ($M^+ - CH_2CH_2CH_3$; $-C_6H_5$) and 68 (1,2,4-triazole). It was tentatively characterized as di-dechlorinated penconazole [1-{-2-(phenyl)-pentyl}-1*H*-1,2,4-triazole].

Study suggests that biocompost amendment certainly enhanced the degradation of both the soil applied fungicides under both moisture regimes. These results have implication in managing fungicides residues, especially propiconazole as it is reported to persist in some soil types. However, to get more realistic picture, study under actual field conditions is advised.

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