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Adsorption-desorption, Mobility and Degradation behaviour of Kresoxim-methyl and acid Metabolite in Delhi Soil

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Abstract

Kresoxim-methyl, a new broad spectrum foliar-applied strobilurin group of fungicide, undergoes rapid transformation in soil to form acid metabolite. In this paper, adsorption-desorption, leaching and persistence behaviour of kresoxim-methyl and its acid metabolite in Delhi (Inceptisol) soil has been investigated. The adsorption studies were carried out at initial concentrations of 1.5, 1, 0.8, 0.5 and 0.2 μg ml^{-1} for kresoxim-methyl and 5, 2, 1, 0.5 and 0.2 μg ml^{-1} for acid metabolite. The K_d values for kresoxim-methyl and acid metabolite varied from 3.72-14.58 and 1.34-2.84 in test soils. On the basis of 1/n values, adsorption isotherms were classified as S- type. Around 11.6-26.8% and 38.1-80.4% of kresoxim-methyl and acid metabolite were desorbed in three desorption cycles. Lower values of K_d, K_F and higher values of hysteresis coefficients observed for acid metabolite indicate its leaching potential. Leaching studies revealed that in column soil >90% of the kresoxim-methyl undergo hydrolysis and changed into acid metabolite. Acid metabolite showed more leaching potential than the parent molecule. Increasing the organic matter content of the soil by sludge amendment (5%) reduced the leaching potential of both the compounds. Degradation of kresoxim-methyl in Inceptisol was studied under different moisture regimes. In the present study, quantification has been done on the basis of residues of kresoxim methyl alone and the total residues (sum of parent + acid metabolite), because for the purpose of monitoring of soil, residues of acid metabolite were also considered along with the residues of parent molecule. In dissipation studies, faster dissipation of kresoxim-methyl and total residues was observed in submerged soil conditions ($T_{1/2}$ 0.5 and 5.2 days) followed by field capacity ($T_{1/2}$ 0.9 and 33.8 days) and air dry ($T_{1/2}$ 2.3 and 51.0 days) conditions.

Keywords: Kresoxim-methyl, acid metabolite, sludge amendment, rapidly dissipation.

1. Introduction

Kresoxim-methyl (Fig. 1a) is a broad spectrum foliar fungicide of the strobilurin group. It has been introduced in India by Rallis India Ltd as Ergon 44.3 SC® and is presently registered for control of blast and sheath blight in paddy and downy and powdery mildew in grape at recommended doses of 250-350 g a.i./ha. Literature search revealed that kresoxim-methyl readily dissipates into its acid metabolite (Fig. 1b) and this metabolite is included in the residue definition of kresoxim methyl for the purpose of monitoring in soil (EFSA, 2010). Therefore, in the present study, quantification has been done on the basis of residues of kresoxim methyl alone and the total residues (sum of parent + acid metabolite).

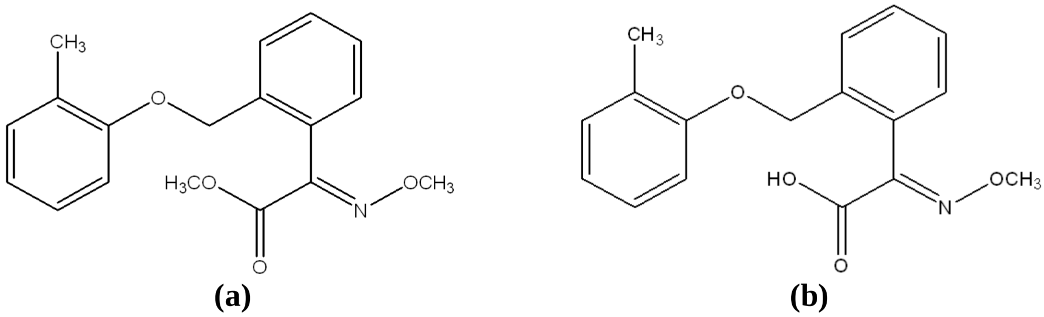

Figure 1: Chemical structure of (a) Kresoxim-methyl and (b) acid metabolite of kresoxim-methyl.

2. Materials and Methods

2.1 Chemicals

Analytical grade kresoxim-methyl (purity>98.4%) and its commercial formulation Ergon 44.3 SC® were supplied by the Rallis India Ltd. Kresoxim methyl acid metabolite (Fig. 1b) was prepared by hydrolysis of kresoxim methyl with ethanolic KOH solution. Structure of the hydrolytic product was elucidated using various spectroscopic techniques such as IR, NMR, LC-MS.

2.2 Soils

Soil used in this study was collected from vegetable field of Indian Agricultural Research Institute, Delhi. The Delhi soil was amended with sludge at 5% level to increase its organic carbon content. Sludge which was used in the study was collected from the water treatment plant, Keshopur, Delhi. The physico-chemical properties of soils and sludge (Table 1) were determined by the standard procedures (Singh et al. 2005).

Table 1: Physico-chemical properties of test soils.

Soil	Location	Texture	pH	EC	Organic Carbon (%)	Sand	Silt	Clay
Inceptisol	Delhi	Sandy loam	8.15	0.23	0.37	54.4	23.3	22.3
Sludge amended Inceptisol	Delhi	-	7.9	0.34	2.46	-	-	-
Sludge	Delhi	-	6.25	16.0	47.2	-	-	-

Adsorption-dsorption and mobility of kresoxim-methyl and acid metabolie was studied in Delhi and sludge amended Delhi soil. Dissipation kinetics of kresoxim-methyl alone was also studied in Delhi and sludge amended Delhi soil.

2.3 Sorption study

Adsorption studies for kresoxim-methyl and its acid metabolite were carried out in 1:5 soil:water (w/v) ratio separately using batch equilibration technique. The adsorption studies were carried out in triplicate at initial concentrations of 1.5, 1, 0.8, 0.5 and 0.2 $\mu g\ ml^{-1}$ for kresoxim-methyl and 5, 2, 1, 0.5 and 0.2 $\mu g\ ml^{-1}$for kresoxim-methyl acid metabolite. The tubes were stoppered and shaken for pre-determined equilibration time (4 hours for both kresoxim-methyl and acid metabolite) at room temperature and then centrifuged at 2000 rpm for 10 minutes. After centrifugation, clear supernatant solution (10 ml) was transferred to a separatory funnel. Sorption data for kresoxim-methyl and acid metabolite were fitted to the Freundlich adsorption equation Log Cs = log K_F + 1/n log Ce. The values of adsorption coefficient 'K_F' (adsorption capacity) and Freundlich equation exponent 'n' (adsorption intensity) were calculated from this equation.

2.3 Leaching study

Leaching studies were carried out in laboratory packed columns [25 cm (l) × 2.86 cm (i.d.)] separately with analytical grade kresoxim-methyl and its acid metabolite (BF 490-1). Dry weight of the soil packed in column was ~ 150 g. All the leaching experiments were conducted in duplicate. Different columns fortified with analytical grade material and acid metabolite was leached with 250, 500 and 1000 ml of water simulating 300, 600 and 1200 mm rainfall under continuous flow conditions. The effect of sludge on leaching of kresoxim-methyl and acid metabolite were also studied by packing top 15 cm of the column with 5% sludge amended soil. The column was leached with water under continuous flow condition simulating ~600 mm rainfall. Leachate fractions (~250 ml) from each column were collected, filtered and analysed for kresoxim-methyl/acid metabolite residues. At the end of the leaching experiment, soil columns were cut horizontally into five cores of 5 cm each. Soil from each core was processed for the kresoxim-methyl/metabolite residue using HPLC-PDA.

2.4 Persistence study

The effect of moisture regimes on dissipation of kresoxim-methyl was studied under air-dry, field capacity and submerged conditions in Delhi soil (Inceptisol) at 1 $\mu g\ g^{-1}$ fortification level. The treated soil (20 g) along with untreated control samples were transferred to beakers. All the beakers of above treatments were weighed and placed in BOD incubator at 25±1°C temperature and about 70% relative humidity. Samples in triplicate, i.e. three beakers per treatment were withdrawn along with control at different time intervals (0, 1, 3, 5, 10, 20, 30, 60, and 90 days after application) and processed. The residue data obtained from persistence experiment was subjected to first order kinetics ($\partial C/C = K\partial t$), where ‘C’ is the concentration and ‘t’ is the time. The value of half-life was calculated from the value of K by the formula ($T_{1/2} = 0.693/K$).

2.5 Quantification

Kresoxim-methyl and its acid metabolites both were simultaneously quantified by using High Performance Liquid Chromatography (HPLC). The instrument was equipped with Phenomenax® RP-18 column (250 X 4.60 mm, 5µm) and PDA detector set at 210 nm was used for quantifying the residues. Mixture of acetonitrile and water (80:20 v/v) was used as a mobile phase with a flow rate of 1 ml min^{-1}. The injection volume was 10 µl. Under the standardised conditions, kresoxim-methyl and its metabolite were eluted at 4.52 min and 1.83 min respectively. The calibration curve was linear over a range of 0.001 to 10 $\mu g\ ml^{-1}$ with R^2 value of 0.99 for both the compounds. Instrument limit of detection (LOD) of kresoxim-methyl was found to be 0.1 ng (0.01 $\mu g\ ml^{-1}$ with 10 µl injection volume) and for its metabolite was 0.05 ng (0.005 $\mu g\ ml^{-1}$ with 10 µl injection volume).

3. Results and Discussions

The recoveries of kresoxim-methyl and acid metabolite from water and soil were determined by analyzing the fortified samples in triplicate. The recoveries of kresoxim-methyl from water samples fortified at 0.5 and 0.01 $\mu g\ ml^{-1}$ levels varied from 84.8-92.3% and those from soil fortified at 1.0 and 0.01 µg g-1 levels varied from 86.4-93.0%. The recoveries of kresoxim-methyl acid metabolite from water samples fortified at 0.5 and 0.01 $\mu g\ ml^{-1}$ level varied from 79.9-89.3% and those from soil fortified at 1.0 and 0.01 $\mu g\ g^{-1}$ level varied from 82.7-84.4%.

3.1 Sorption study

The K_d values for kresoxim-methyl and acid metabolite varied from 3.72-14.58 and 1.34-2.84 in test soils. On the basis of 1/n values, adsorption isotherms were classified as S- type (Figure 2). According to Giles classification (Giles *et al.*, 1960), in the initial part of the S curves, more solute gets adsorbed and with the increase in initial concentration it becomes easier for the additional amounts to become fixed on the already adsorbed molecules. Around 11.6-26.8% and 38.1-80.4% of kresoxim-methyl and acid metabolite were desorbed in three desorption cycles. Hysteresis coefficient values observed for kresoxim-methyl and its acid metabolite were varied from 0.05-0.08 and 0.14-0.19. Lower values of K_d, K_F and higher values of hysteresis coefficients observed for acid metabolite indicate its leaching potential.

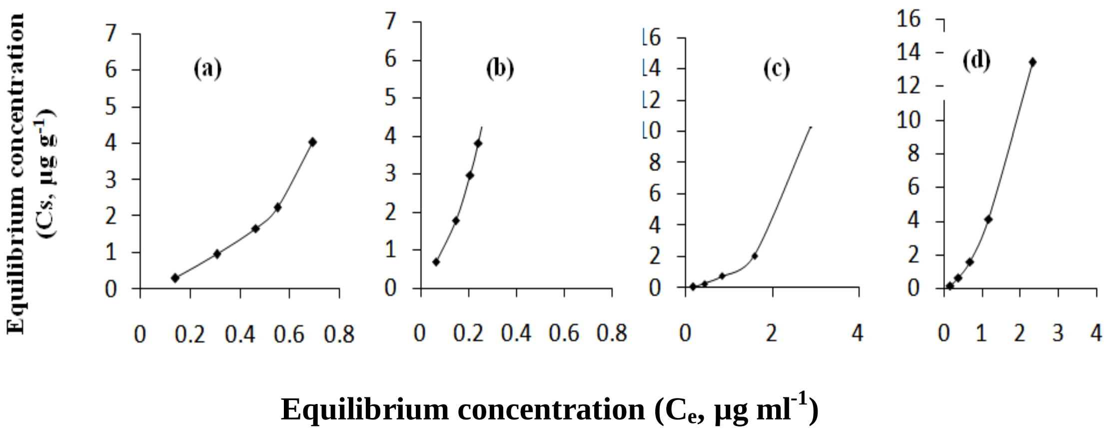

Figure 2: Adsorption isotherm of kresoxim-methyl in a) Inceptisol, b) sludge amended Inceptisol and acid metabolite in c) Inceptisol and d) sludge amended Inceptisol.

3.2 Mobility study

Different columns were leached with 250, 500 and 1000 ml of water simulating 300, 600 and 1200 mm rainfall respectively. In different columns, out of total applied amount (150 µg) only 2-5.9% of kresoxim-methyl was recovered whereas 81.8-86% residues were recovered as acid metabolite. ~9-42% of the acid metabolite was recovered from the leachate. Results revealed that with increasing amount of water available for leaching, downward mobility of both parent and the metabolite go on increasing. Similar results have been reported by Gunasekera *et al*., (2007). The effect of sludge was also studied with 5% sludge amended soil in 600 mm rainfall condition. Results revealed that out of total applied amount of kresoxim-methyl, 8.6% and 64.5% was recovered as kresoxim-methyl and acid metabolite respectively. In another column experiment, leaching behaviour of acid metabolite was studied and it was observed that with 300, 600 and 1200 mm rainfall, ~ 7.2%, 31.8% and 60% of the residues were recovered in leachate respectively. In sludge amended column at 600 mm rainfall, only 5.5% of acid metabolite was recovered in the leachate fraction which indicates sludge reduces the leaching of acid metabolie.

3.3 Persistence study

The dissipation of parent compound and formation of acid metabolite were presented in fig. 3a and fig. 3b respectively. Under air-dry condition, residues of the parent molecule, kresoxim-methyl, were detected up to 20 days. Percent dissipation of ~43.6, 77.7 and 94.7% was recorded for the parent molecule on 3, 5 and 10 days. The total residues (kresoxim-methyl + acid metabolite) persisted beyond 90 days with the mean initial deposits of 1.06 µg g-1. Residues declined with time and were 0.78, 0.57 and 0.28 µg g-1 on 10, 30 and 90 days. The mean half-life values for parent and total residue calculated from first order dissipation kinetics were 2.2 and 51 days. Under field capacity moisture regime, parent molecule kresoxim-methyl dissipated beyond detectable level within 5 days. Initial deposits of 1.09 µg g-1 declined to 0.47 and 0.10 µg g-1 on 1 and 3 days amounting to the loss of ~57.3 and 90.9%. Total residues of kresoxim methyl (kresoxim-methyl + acid metabolite) persisted beyond 90 days. Residues declined with time and were 0.69, 0.52 and 0.14 µg g-1 on 10, 30 and 90 days respectively. The half-life values of parent and total residues calculated from first order dissipation kinetics were 0.9 and 33.8 days. Under submerged conditions, more than 98% dissipation of parent molecule was recorded on 3rd day. The total residues (kresoxim-methyl + acid metabolite) declined with time and were 0.62, 0.38 and 0.01 µg g-1 on 5, 10 and 30 days respectively. The half-life values of parent and total residues calculated from first order dissipation kinetics were 0.5 and 5.2 days. Slow dissipation of another strobilurin fungicide pyraclostrobin under air dry condition in comparison to wet conditions has been reported by Reddy *et al.*, (2013).

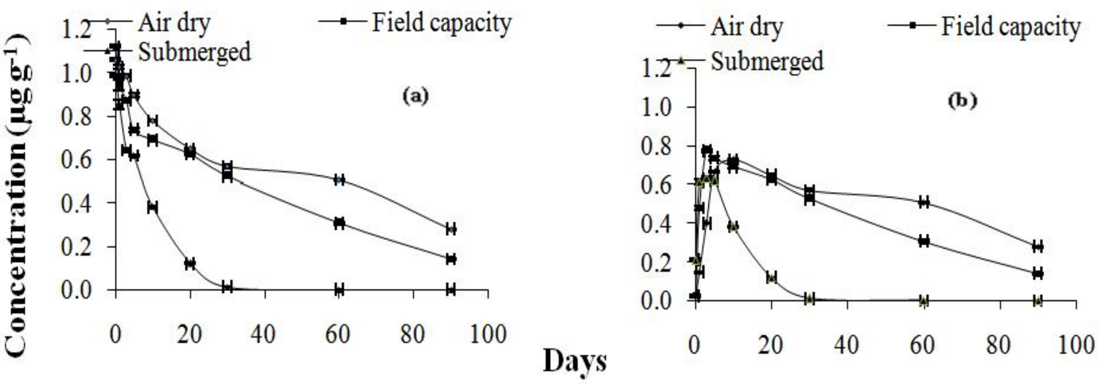

Figure 3: Dissipation of a). kresoxim-methyl and b). formation of acid metabolite under different moisture regime.

4. Conclusion

The adsorption studies reveal that different soils have moderate to high adsorption capacities for kresoxim-methyl and acid metabolite. Kresoxim methyl undergoes very fast dissipation in soil and form acid metabolite. Acid metabolite has much more leaching potential as compared to parent molecule. Amending the soil with sludge reduces the leaching potential of acid metabolite. Because of the easy transformation of parent molecule into acid metabolite and high leaching potential of acid metabolite, it must be used cautiously in the high rainfall areas.

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