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RESEARCH

DISSIPATION BEHAVIOUR OF ETHALFLURALIN HERBICIDE IN SOIL

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Abstract: A laboratory experiment was undertaken to investigate the persistence of ethalfluralin (35 EC) at recommended and double dose in Inceptisol soil. To carry out this study, surface soil samples (0-15 cm) were collected from experimental farm of Krishi Vigyan Kendra, Fatehabad (Haryana) in year 2021 and processed for initial soil physico-chemical properties analysis. Also separately, 2 kg of Inceptisol soil in pots along with a control in which no herbicide was added was taken for study. During experimental period pots were kept at room temperature of 25 ± 2ºC and field capacity moisture level. 20 g of soil samples were drawn in triplicate and analyzed periodically after 0 (1 hr), 1, 3, 7, 10, 15, 30, 45, 60, 90 and 120 day after treatment (DAT). The soil samples were further processed and 20 g representative soil was taken as test sample and processed for residue analysis. For improved extraction and cleanup various techniques were optimized and maximum recovery of ethalfluralin was obtained in MSPD without florisil at three fortification levels. Residues of ethalfluralin reached below detectable limit after 90 and 120 DAT at recommended and double dose, respectively. Half-life of ethalfluralin ranged from 38-42.1 days. Slightly more persistence was observed at double dose as compared to recommended dose. Faster dissipation was observed upto 10 days and that might be due to microbial degradation.

Keywords: Inceptisol, Florisil, Herbicide, Dissipation, Soil

INTRODUCTION

The population of the globe has surpassed seven billion people very quickly, and by 2050, it is predicted to reach nine billion (Young and Pierce, 2013). The amount of food produced currently is insufficient to support the world's expanding population, and it may be extremely difficult for humanity to meet this need in the future. Despite occupying only 1.33% of the country's total land area, Haryana, one of India's most agriculturally significant states, produces around 7% of the country's food grain output. Haryana's soils are among the most significant types of arable soil in North India, and increasing their production is thought to be a practical way to guarantee the country's food security. Webster *et al.* (1999) expressed that "considerable economic losses" would be endured without use of pesticides. Ethalfluralin, [N-ethyl-N-(2-methyl-2-propenyl)-2,6-dinitro-(trifluoromethyl)benzenamine], is a pre-emergent herbicide widely used in agricultural practices to control annual grasses and broadleaf weeds (Karasali *et al*., 2017) in various crops, including soybeans, sunflowers, and vegetables (Fig. 1). It belongs to the dinitroaniline chemical family, known for their role in disrupting weed growth by inhibiting cell division. Specifically, ethalfluralin targets the microtubules during cell mitosis, effectively preventing the formation of the spindle fibers necessary for chromosome separation, thereby halting cell division and leading to the death of the plant.

The use of ethalfluralin has been prevalent due to its effectiveness and relatively low toxicity to non-target organisms as compared to other herbicides. Understanding the dissipation behavior of ethalfluralin in soil is crucial for developing sustainable agricultural practices and mitigating potential negative effects on the environment. However, its environmental impact, particularly its behavior and persistence in soil, has raised concerns. The dissipation of ethalfluralin involves complex interactions between chemical degradation (Gaynor, 1985), microbial activity (Serrano *et al*, 2010), volatilization, and adsorption to soil particles. Factors such as soil type, pH, temperature, and moisture significantly influence these processes, affecting the herbicide's persistence and efficacy. Previous studies have explored the degradation kinetics of ethalfluralin, often observing first-order kinetics where the concentration decreases exponentially over time. However, the variability in dissipation rates across different soils and environmental conditions indicates a need for more localized and detailed investigations. Additionally, understanding the half-life of ethalfluralin in various

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soil types helps in designing appropriate application schedules to avoid residues that could harm subsequent crops or the surrounding ecosystem. Previous studies reported that dinitroaniline herbicides are highly persistent (half-life: 4-146 days) in soil (Hayden and Smith, 1980; Weber, 1990). However, no study was done in Inceptisol soil (loam) which is commonly found in Haryana and this will provide a comprehensive understanding that can inform best management practices in agriculture. By investigating the combined effects of biotic and abiotic factors on ethalfluralin dissipation, this research seeks to contribute to the development of more sustainable and environmentally friendly herbicide usage protocols.

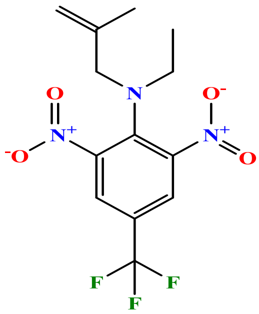

Fig. 1. Ethalfluralin

MATERIALS AND METHODS

Soil samples were collected from experimental farm of Krishi Vigyan Kendra, Fatehabad from a depth of 0-15 cm with no previous history of pesticide application in the year 2021. Samples were collected in polythene bags then air dried in shade, grounded and sieved through 2 mm sieve before further use for analysis. Different physico-chemical properties of the soil analysed by following the procedures given below:

a) Texture: Texture was determined by international pipette method (Day, 1965).

b) Soil pH and EC: It was measured according to method outlined by Jackson (2005).

c) Organic Carbon: The organic Carbon content of soils was estimated by Wet digestion method (Walkley and Black, 1934).

d) Soil Textural class: It was determined by following USDA system of soil classification for Textural class.

Physico-chemical characteristics of Inceptisol soil are listed in Table 1.

Parameter	Sand (%)	Silt (%)	Clay (%)	pH	EC (dS m^{-1})	OC (%)	OM (%)	Soil Textural class
Inceptisol	42	36	22	8.0	0.41	0.45	2.39	Loam

The analytical standards of ethalfluralin (purity 99.9%) were purchased from Sigma Aldrich, Germany, whereas formulation with trade name of "Sonalan" 35 EC, used for soil application, was purchased from Rallis India Limited, Banglore. Other chemical reagents such as acetone, silica gel and sodium sulfate were purchased from Merck, Darmstadt, Germany and prior to use filtered and de-gassed. Sodium sulfate after washing with acetone and then activated at 110ºC for 4 hr before use. The stock solutions (100 µg mL^{-1}) were prepared by dissolving 10 mg of ethalfluralin in 100 mL acetone. Further appropriate dilutions were carried out to prepare working standards of required concentration in acetonitrile for the fortification of soil samples and were freshly prepared. The stock standards were stored at - 4ºC till usage. Formulation was applied in triplicate at two doses, i.e. single dose of 720 µg g^{-1} equivalent to 102 g a.i. ha^{-1} and double dose of 1440 µg g^{-1} equivalent to 204 g a.i. ha^{-1} by taking 2 kg of Inceptisol soil in pot [25 × 25 (i.d.) cm] along with a control in which no herbicide was added. During experimental period pots were kept at room temperature of 25 ± 2ºC and field capacity moisture level of 1/3 bar tension. The moisture content of the soil was maintained by adding calculated amount of water at an interval of 2-3 days. 20 gram of soil samples were drawn in triplicate and analyzed periodically after 0 (1 hr), 1, 3, 7, 10, 15, 30, 45, 60, 90 and 120 day after treatment (DAT). The soil samples were air-dried under shade, grounded and passed through 2 mm sieve. After thorough mixing of soil, 20 g representative soil was taken as test sample and processed for residue analysis.

Recovery study: To obtain efficient recoveries, high sensitivity and accuracy in estimation of ethalfluralin residues in Inceptisol soil MSPD recovery experiments were performed at three fortification levels 0.005, 0.01 and 0.1 µg g^{-1}. Soil was fortified by using their analytical standards.

For MSPD, a representative 20 g of clay loam and sandy loam soil samples were fortified. Then samples were divided into two sets- to one set of samples 20 gm silica gel and 0.5 gm charcoal was added then mixed thoroughly and to another set of samples 0.5 gm florisil was also added along with silica gel and charcoal and mixed well. Transferred the mixture in glass column and sandwitched between 2-3 cm layer of anhydrous sodium sulfate by gentle tapping. Samples were eluted with 150 mL acetonitrile and extract was evaporated upto 4-5 mL using rotary evaporator and residues were estimated by GC-MS/MS.

GC-MS/MS: Agilent 7890 A autosampler consisting triple quadrupole (QQQ) mass detector (mass 7000 GC-MS/MS) equipped with an ESI source and HP-5 column (30 × 0.32 mm i.d. × 0.25 µm film thickness) of 5% diphenyl/95% dimethyl polysiloxane was used for the determination of level of ethalfluralin residues. Injector and detector temperatures were 230ºC and 280ºC, respectively. Programming of oven temperature was initialized with a 2 min hold at 70ºC, then the temperature was increased at 25ºC min^{-1} to 150ºC then at 15ºC min^{-1} to 200ºC after that temperature was increased at 8ºC min^{-1} to 280ºC where it was finally held for 2 min. Helium was used as carrier gas with a flow rate of 1 mL min^{-1} through column and 2.25 mL min^{-1} in collision or quench flow. 2µL sample was injected in splitless mode. For analysing, the programming was developed in SCAN mode, PI mode and then in MRM mode. On the basis of m/z ration in SCAN and PI monitoring, the ethalfluralin was analyzed in MRM mode (multiple reaction monitoring). Under these experimental conditions, the retention time in MRM mode for ethalfluralin was observed to be 17 min.

Method validation: The analytical method was validated by optimizing the various parameters such as recovery, accuracy, efficiency, limit of detection (LOD), limit of quantification (LOQ) and concentration against the peak areas. The half-scale deflection was obtained for 0.001 ng as 0.001 ng which could be easily identified from the baseline of the compound produced 10% deflection, which is measured. No interference was observed at this level of quantification as evidenced by the control sample. Thus, LOD and LOQ for ethalfluralin was established as 0.001 µg g^{-1} and 0.005 µg g^{-1}, respectively.

Dissipation behaviour of ethalfluralin was studied in clay loam and sandy loam soil. Experiment was conducted under laboratory conditions in pots [25 × 25 (i.d.) cm] in completely randomized design using three replicates along with control for each treatment. Formulation (Sonalan 35 EC) was applied at 102 and 204 g a.i. ha^{-1} and in control pot water was sprayed. Soil samples were drawn at 0 (1 hr), 1, 3, 7, 10, 15, 30, 45, 60, 90 and 120 days interval with three replications. After homogeneous mixing of soil, 20 g of test sample was taken for residue analysis and processed further as explained above.

Analysis: Residue data were subjected to regression analysis Half-life was calculated from the first-order dissipation kinetics: $C_t = C_0 e^{-kt}$, where C_t = concentration after time t, C_0 = apparent initial concentration and k is the first order rate constant of the reaction.

RESULTS AND DISCUSSION

Before the analysis of experimental samples recovery experiments were performed for the validation of the method and for method validation criteria of acceptable recoveries 60-140% of SANCO 2009 (Document No.SANCO/10684/2009) was adopted. Results of the recovery study of ethalfluralin at the level of 0.005. 0.01 and 0.1 µg g^{-1} are depicted in Fig. 2. In MSPD without florisil, recoveries were in acceptable range. MSPD offers several advantages such as simple, cheap, use of smaller amount of organic solvent, less solvent cost and simultaneous extraction. Therefore, based on the recovery study sample preparation using MSPD was considered satisfactory for ethalfluralin.

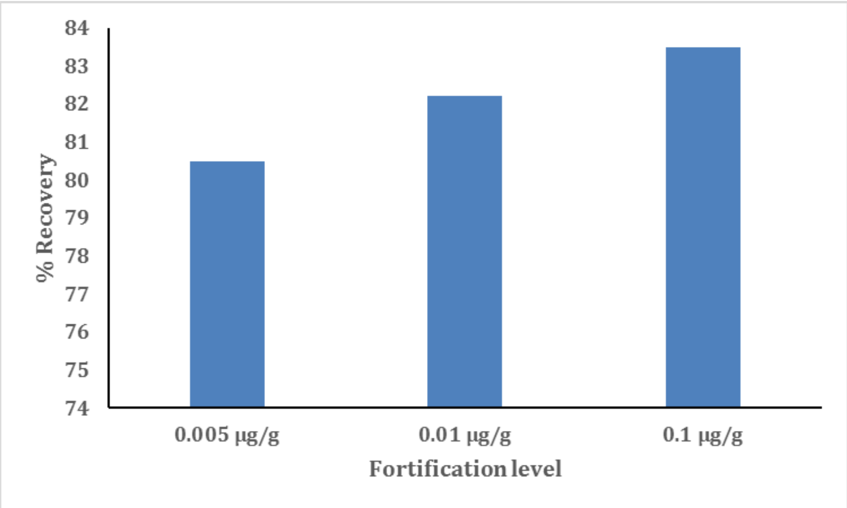

Figure 2. Percent recoveries of ethalfluralin from using MSPD.

Dissipation

Dissipation curve of ethalfluralin is presented in (Fig. 3; a and b). Mean initial residues of ethalfluralin in Inceptisol soil at single dose were 0.084 µg g^{-1} on 0 day (1 h after treatment). The residues were further declined to 0.056 µg g^{-1} on 7th DAT with 33% dissipation. At double dose, initial deposit of 0.178 µg g^{-1} which dissipated to 0.112 µg g^{-1} on 10th DAT with 37% dissipation and reached BDL on 60th and 90th day at single and double dose, respectively. The calculated half-lives of ethalfluralin were 38 and 42.1 days at single and double doses, respectively.

Dissipation followed first order kinetics. The results of ethalfluralin degradation corroborate with the findings of Jensen *et al.*(1983) and found that dissipation followed first-order kinetics with half-lives (DT_{50}) in Chalottetown fine sandy loam soils were 74 and 98 days.

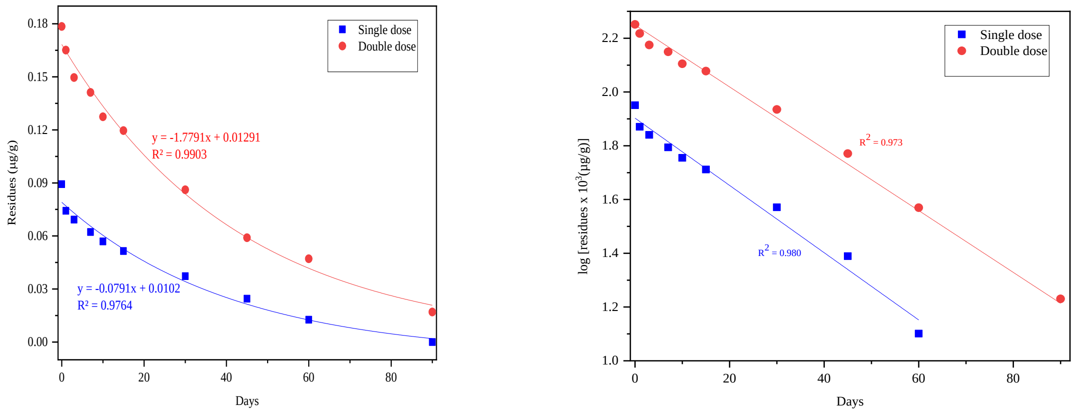

Fig. 3 (a and b): Dissipation curve of ethalfluralin in inceptisol soil

CONCLUSIONS

Thus, it can be concluded that, dissipation of ethalfluralin herbicide in Inceptisol soil conformed to follow first order kinetics. Fifty percent of residues were dissipated in 38 and 42.1 days at single and double dose, respectively under prevailing laboratory conditions. However, field studies need to be undertaken for further confirmation of dissipation pattern.

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