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Research Article

Mitigation Strategies for Ethalfluralin Contamination in Entisol Soils: An Environmental Perspective

Monika* and Anil Duhan

Department of Chemistry, CCS Haryana Agricultural University, Hisar-125004

*Corresponding Author E-mail: monuloura97@gmail.com

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ABSTRACT

Weed control is an important part of crop production technologies, and within it, the chemical weed control method is more efficient & effective than conventional methods. Ethalfluralin is a widely used herbicide in agriculture. Its persistence in soil and potential for environmental contamination have made it a subject of concern among researchers and environmentalists. To undertake this objective, a laboratory experiment was planned to investigate the mitigation of ethalfluralin (35 EC) in Entisol soil. To carry out this study, surface soil samples (0-15 cm) were collected from the experimental farm of CCS HAU Hisar (Haryana) in 2021 and processed for initial soil physicochemical properties analysis. Ethalfluralin was applied to soil samples, and it was highly sorbed in the soil. A desorption study was carried out by using various extractants such as β-CD, SA, chitosan (LMW, MMW and HMW) and their combinations (β-CD-cLMW, β-CD-cMMWand β-CD-cHMW) to evaluate the efficiency of extractants. β-CD-cLMW biocomposite was most effective (approximately 2 times as compared to control) in removing the adsorbed ethalfluralin from the soil. Hydrophobic interactions and hydrogen bonding were found to be responsible for herbicides' greater affinity towards the sorption site of chitosan and β-CD complex. Ethalfluralin herbicide got highly sorbed in Entisol soil. So, it is necessary to mitigate sorbed herbicides by using compounds that do not cause pollution. β-CD-cLMW is the most effective biocomposite and can remove up to 80% of sorbed ethalfluralin.

Keywords: *Entisol, biocomposite, ethalfluralin, desorption*

INTRODUCTION

Chemical weed control is an integral part of modern crop production and is more effective than conventional methods. In global modern agriculture, herbicides are among the most frequently used agrochemicals to manage weeds. They have become an important tool for crop protection, and their use cannot be neglected due to their enormous benefits in agricultural outputs (Vig et al., 2008).

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On the other hand, it has been reported that herbicides are lost from agricultural fields to surface and groundwater by run-off and leaching, as well as via spray drift when they are applied at a near distance to water recipients (Sun et al., 2012; Konstantinou et al., 2006). It is expected that usage may increase by 15 % per year over the next five years. Sometimes, in a desperate effort to protect the crop, farmers may apply pesticides in larger doses or even give more sprays. The improper and injudicious application of pesticides not only endangers the health of farm workers but also leaves toxic pesticide residues on the crop and soil. Indiscriminate use of these pesticides has several detrimental effects on soil, plant, and environmental health, consequently impacting the sustainability of the environment. Ethalfluralin, a dinitroaniline herbicide, is widely used in agriculture to control a variety of annual grasses and broadleaf weeds. Its persistence in soil and potential for environmental contamination have made it a concern among researchers and environmentalists.

Ethalfluralin, chemically known as N-ethyl-N-(2-methyl-2-propenyl)-2,6-dinitro-4-(trifluoromethyl) benzenamine, belongs to the dinitroaniline class of herbicides. It is characterized by its low solubility in water (0.2 mg/L at 25°C) and a high affinity for soil organic matter, leading to significant sorption in soils (Tomlin, 2009). It is classified as a semi-volatile organic compound since it has a vapor pressure of 1.2 £ 10¡2 Pa, and thus increased potential for volatilization and re-deposition in soils and surface water recipients (Munoz et al., 2014). This herbicide is relatively stable, with a half-life ranging from 30 to 120 days, depending on soil conditions such as temperature, moisture, and organic content (Stork et al., 2014). Its persistence in soil can lead to prolonged environmental exposure and potential contamination of groundwater and surface water (Scribner et al., 1994). Ethalfluralin acts by inhibiting microtubule formation in plant cells, which disrupts cell division and leads to the failure of seedling emergence. Specifically, it binds to tubulin, a protein that is a key component of microtubules, thereby preventing the polymerization process necessary for microtubule formation (Horowitz et al., 2016). This mode of action makes ethalfluralin effective against a wide range of annual grasses and broadleaf weeds, providing farmers with a valuable tool for weed management in various crops such as soybeans, sunflowers, and canola (Fennimore et al., 2010).

The persistence of ethalfluralin in soil poses significant environmental risks, making mitigation efforts essential. Prolonged soil residence times increase the likelihood of leaching into groundwater, contaminating drinking water sources and harming aquatic ecosystems (Caux et al., 1993). Additionally, the buildup of ethalfluralin in the soil can affect non-target organisms, including beneficial soil microbes and fauna, potentially disrupting soil health and ecosystem functions (Gilliom et al., 2006). Mitigation strategies are thus critical to minimize these adverse effects and ensure the sustainability of agricultural practice. One promising mitigation strategy is the enhancement of microbial degradation. Certain soil microbes possess the capability to degrade ethalfluralin, transforming it into less harmful compounds. Research has shown that the application of organic amendments such as compost or manure can stimulate microbial activity and accelerate the degradation process (Shaner et al., 2001; Zheng et al., 2015). Certain plant species can uptake and metabolize ethalfluralin, reducing its concentration in soil. For instance, studies have demonstrated that plant species such as maize and sunflower can absorb ethalfluralin from the soil, thereby mitigating its environmental impact (Kogan et al., 2002; Komárek et al., 2008). The application of soil amendments, including activated carbon and biochar, can enhance the sorption of ethalfluralin, reducing its bioavailability and mobility in soil (Beesley et al., 2011; Trigo et al., 2014). These amendments can bind ethalfluralin molecules, limiting their leaching potential and decreasing their uptake by plants and soil organisms. Chemical degradation methods, such as the application of oxidizing agents, can also be employed to break down ethalfluralin in soil. For example, Fenton's reagent (a mixture of hydrogen peroxide and iron) has been used to oxidize organic contaminants, including herbicides, in soil (Barber et al., 1995). This approach can be effective but requires careful management to avoid secondary pollution. In this context, the use of natural polymers, such as chitosan and cyclodextrins, appears to be an eco-friendly alternative for the adsorption of herbicides and remediation of contaminated sources. This will improve ecological health and output from agriculture. Utilizing biocomposites strategically to mitigate ethalfluralin from various soil types provides a long-term approach to managing herbicide exposure. Mitigating the persistentethalfluralin in soil is of paramount importance to protecting environmental health and ensuring sustainable agricultural practices. A combination of microbial degradation, phytoremediation, soil amendments, and chemical degradation can reduce the environmental impact of this persistent herbicide. Continued research and the development of innovative mitigation strategies will be essential to address the challenges posed by ethalfluralin and other persistent organic pollutants in the environment.

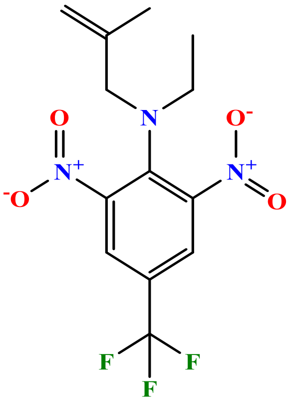

Fig. 1: Ethalfluralin

MATERIALS AND METHODS

Soil samples were collected from the experimental farm of CCSHAU, Hisar, 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 physicochemical properties of the soil analysed by following the procedures given below:

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

b) Soil pH and EC: This was measured using the method outlined by Jackson (2005).

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

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

Table 1: Physico-chemical characteristics of Entisol soil

Parameter	**Sand (%)**	**Silt (%)**	**Clay (%)**	**pH**	**EC (dS m^{-1})**	**OC (%)**	**OM (%)**	**Soil Textural class**
Inceptisol	50	39	11	7.9	0.17	0.25	1.23	Sandy 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 the required concentration in acetonitrile for the fortification of soil samples, which were freshly prepared. The stock standards were stored at - 4ºC till usage. Sorption studies of ethalfluralin in Entisols soils were carried out under laboratory conditions from March to April 2022. The batch sorption experiment was conducted in the Agrochemicals Residues Testing laboratory following the Organization for Economic Co-operation and Development, OECD 106 guidelines for batch sorption (OECD/ OCDE, 2000).

The experiment was performed in the following set: blank and spiked soil sample in $CaCl_2$ solution. All the samples were taken in triplicate. Sorption studies: Soil samples (air dried) were weighed (2 g) into a 25 mL polypropylene centrifuge tube and equilibrated with 10 mL of 0.01 M $CaCl_2$ (sorbent solution ratio-1:5 (w/v)) on rotospin. After 24 h, the samples were spiked with 0.5 mg/L of ethalfluralin in each tube. Again, samples were taken to the shaker i.e. rotospin for further 24h at the laboratory temperature (30 ± 2°C). The suspension was centrifuged at 3500 rpm for 15 min. For sorption study, supernatant was transferred directly to HPLC vials for further analysis. Desorption studies: Desorption studies were carried out in soils after the complete decanting of the supernatant obtained from the adsorption process by adding 10 mL of 0.01 M $CaCl_2$ solution. The samples were re-suspended using vortex and equilibrated for 24 hrs over rotospin. After equilibration, the samples were centrifuged and supernatant was collected to analyze the herbicide concentration in the solution. At each step, the tubes were weighed, which allowed for the correction of the small volume of the remnant solution entrained from the previous steps. The calculation for the amount desorbed was corrected using the known concentration in solution before starting the next desorption step. The desorption process was repeated thrice using 0.01 M $CaCl_2$ solution. The amount of herbicide remaining sorbed on the soil was calculated as the difference between initial sorbed and the desorbed amount.

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 that 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. Samples were quantified by using HPLC equipped with PDA (photo-diode array) detector.

Analysis: Mathematical equation is generally fitted to isotherm data to summarize the relationship between equilibrium concentration and amount adsorbed. The amount of ethalfluralin adsorbed on soil after equilibrium was calculated as the difference between the initial and final equilibrium solution concentrations by the following equation)

$$Cs = (Ci - Ce) \times \frac{V}{m}$$

Cs (µg/g) is the amount of herbicide adsorbed by soil

Ci (µg/mL) is the initial aqueous concentration in case of adsorption and the concentration of herbicide remaining adsorbed on soil in case of desorption

Ce (µg/mL) is the equilibrium aqueous concentration

V (mL) is the solution volume

m (g) is the mass of the soil

The linear distribution sorption coefficient Kd (L/kg) was also determined to evaluate the extent of herbicide sorption using following formula: $K_d = \frac{\text{Amount adsorbed } (C_s)}{\text{Initial concentration } (C_o)}$

The amount of ethalfluralin adsorbed on soil after equilibrium was calculated in terms of adsorption per cent (ads %) using the given equation: $Ads\ \% = \frac{(Ci-Ce)}{Ci} \times 100$

The desorption per cent (des %) was calculated according to the given equation:

$$Des\ \% = \frac{Amount\ desorbed}{Amount\ adsorbed} \times 100$$

RESULTS AND DISCUSSION

Considering the irreversible binding of ethalfluralin and its less bioavailability, desorption was carried out with β CD, SA, chitosan, and biocomposites, with the envision of facilitating the transfer of herbicide from the soil to the solution phase, where it could become bioavailable and be degraded by soil microorganisms. The application of these environmentally benign extractants could be a superior decontamination strategy to remove herbicides from contaminated soil. The mobility of a compound in soils can be effectively assessed through desorption studies.

In Entisol soil 6.5 µg of applied ethalfluralin was sorbed and desorption experiment was conducted for the removal of adsorbed ethalfluralin by using various extractants including SA, β-CD, chitosan (LMW, MMW, and HMW), and biocomposites (β-CD-cLMW, β-CD-cMMW, and β-CD-cHMW) in Entisol soil, yielding the following results: control (2.4 ± 0.05), SA (2.6 ± 0.07), cLMW (3.2 ± 0.06), cMMW (2.9 ± 0.05), cHMW (2.6 ± 0.08), β-CD (3.3 ± 0.04), β-CD-cLMW (5.0 ± 0.06), β-CD-cMMW (4.5 ± 0.07), and β-CD-cHMW (3.9 ± 0.04). Only 37% of adsorbed ethalfluralin was desorbed in control samples. The amount of ethalfluralin desorbed was highest in β-CD-cLMW (Table 2). Total cumulative desorption followed the order: β-CD-cLMW>β-CD-cMMW>β-CD-cHMW>β-CD>cLMW>cMMW>cHMW=SA>Control.

Table 2: Desorption behavior of ethalfluralin from Entisol

Ethalfluralin	**Mass desorbed (µg/g)**
Control	2.4 ± 0.05
SA	2.6 ± 0.07
cLMW	3.2 ± 0.06
cMMW	2.9 ± 0.05
cHMW	2.6 ± 0.08
β-CD	3.3 ± 0.04
β-CD-cLMW	5.0 ± 0.06
β-CD-cMMW	4.5 ± 0.07
β-CD-cHMW	3.9 ± 0.04

Lower desorption of ethalfluralin from soil could be due to its strong affinity with soil matrix, *i.e.* OC and clay fraction of soil. Hydrophobic interactions and hydrogen bonding were found to be responsible for herbicides' greater affinity towards the sorption site of chitosan and β-CD complex. The removal efficiency of β-CD to remove ethalfluralin from studied soils was probably due to the formation of a water-soluble inclusion complex between herbicide and β-CD as the latter has a non-polar hydrophobic cavity and polar hydrophilic functional groups on the exterior, which allows complexation with the herbicide. This process potentially makes the bioavailable fraction of herbicide pass more rapidly to the soil solution. Similar enhanced removal of herbicides from soils using β-CD as extracting agent has been reported by Perez-Martinez et al. (1999), Mill (2001), Villaverde et al. (2004), (2005), (2012).

CONCLUSION

Thus, it can be concluded that ethalfluralin herbicide got highly sorbed in Entisol soil. So, it becomes necessary to mitigate the sorbed herbicide by using compounds that do not cause any pollution, as pesticide residue is becoming a major concern nowadays and affects soil biology. β-CD-cLMW is the most effective biocomposite and can remove up to 80% of sorbed ethalfluralin. However, field studies must be undertaken to further confirm mitigation behaviour.

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There is no such evidence of conflict of interest.

Author Contribution
Both authors have participated in critically revising of the entire manuscript and approval of the final manuscript.

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