

Dissipation and Persistence of Penoxsulam Herbicide in Two Different Soils of Haryana

Sachin Kumari, Anil Duhan

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ABSTRACT

The triazolopyrimidine sulfonamide class's latest post-emergence herbicide, penoxsulam, is thought to be detrimental to aquatic life, crop plants, and soil microbial populations at low dosages. As a result, laboratory tests were conducted to determine the dissipation and persistence of penoxsulam at two distinct application rates (50 and 100 g/g) in two different soils. To ensure efficient sample preparation, two approaches were used: Matrix solid phase dispersion (MSPD) and partition. Over partition, MSPD provided greater recoveries. The extracted components were assessed using high-performance liquid chromatography (HPLC). The method's validity in soil samples was tested by fortifying control samples of each matrix at 0.01 g/g and 0.05 g/g fortification levels in triplicate to assess the method's validity. The recovery rates in both soils were between 82.5 and 90.2%. The limits of quantification (LOQ) and quan-

tification (LOQ) for penoxsulam in two soils were 0.01 and 0.05 g/g, respectively, using HPLC-PDA.

Keywords Penoxsulam, Dissipation, Persistence, Half-life, Soil.

INTRODUCTION

Weeds and other vegetation stifle plant growth, which is a major issue in agriculture. For effective control of such unwanted growth, synthetic chemistry researchers have developed a wide range of chemicals and chemical formulations. Herbicides considered to be phytotoxic chemicals used on weed to growth prevention or control (Au 2003, Zimdahl 2018). Herbicides represented closely 48 per-cent of pesticides consumption worldwide (Gupta 2014). Many different types of chemical herbicides have been disclosed in the literature, and a substantial number of them are in commercial usage. Among Penoxsulam (2-(2,2-difluoroethoxy)-N-(5,8-dimethoxy)-[1,2,4] triazole-[1,5-C] pyrimidine-2-yl)- 6-(trifluoromethyl) benzenesulfonamide) belongs to the chemical class of triazolopyrimidine sulfonamide (Fig. 1). In particular, broad-leaved weeds and sedges, which are prevalent in rice farming, are resistant to its potent herbicidal effects against a variety of annual and perennial weeds (Roberts *et al.* 2003). The enzyme ALS (acetolactate synthase) is inhibited by penoxsulam. Plants, fungi, and microbes all have the ALS enzyme. The ALS enzyme is associated with the production of branched-chain amino acids such valine, leucine, and isoleucine (Whitcomb 1999). Plant species ab-

Dr (Mrs) Sachin Kumari*

Assistant Professor, Department of Chemistry, College of Basic Sciences and Humanities, Chaudhary Charan Singh Haryana Agricultural University, Hisar 125004, India

Anil Duhan

Assistant Scientist, Department of Agronomy, College of Agriculture, Chaudhary Charan Singh Haryana Agricultural University, Hisar 125004, India

Email : sachindalal @hau.ac.in

*Corresponding author

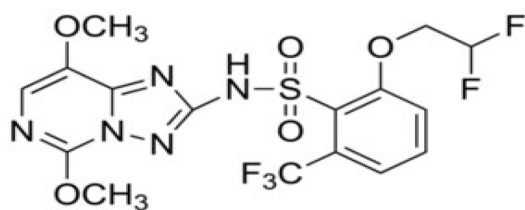


Fig. 1. Structure of penoxsulam.

sorb penoxsulam, which makes it harder for them to synthesis branched amino acids and, as a result, kills weeds. However, regular use of this herbicide in rice production could have a negative influence on soil quality and nearby natural water resources, which are home to a variety of ecosystems that include animals, birds, and aquatic species. Penoxsulam is extremely toxic to aquatic plants, and even in limited levels, its presence in surface water provides an unacceptable risk to aquatic plants and the microbial population of the soil (Sondhia *et al.* 2013). The permanence and mobility of agrochemicals are thought to be determined by agroclimatic conditions and application rates. As a result, it's critical to do research on its persistence in a lab setting. The degradation rate can be used to analyse and anticipate the agrochemical's environmental behaviour (Laskowski *et al.* 1983). There is currently no information available regarding the persistence and dissipation of the herbicide penoxsulam (21.7% SC) in the sandy loam and clay loam soils of Haryana. To ascertain the persistence and dissipation of penoxsulam in two soils with various soil characteristics, the current laboratory investigation was carried undertaken.

MATERIALS AND METHODS

Chemicals, reagents and standards

Mumbai, India's Dow Agro Science India Pvt. Ltd provided analytical grade penoxsulam (purity 99%). Merck provided HPLC grade chemicals acetonitrile. Hi media chemicals provided the rest of the chemicals. Only redistilled solvents were employed in the experiment. Penoxsulam stock solution (1,000 g mL⁻¹) was made by dissolving a suitable amount of penoxsulam in 10 mL acetonitrile. Dilution with

acetonitrile yielded working standards ranging from 0.01 to 20 g mL⁻¹ from this stock solution.

Soil sampling

Soil samples (10–25 cm in depth) from various locations were taken, and they were chemically and texturally distinct. At latitude 29.1492°N and longitude 75.7217°E, sandy loam soil was gathered from the Chaudhary Charan Singh Haryana Agricultural University, campus in Hisar. The National Dairy Research Institute in Karnal, India, in latitude 29.5629°N and longitude 76.0547°E, provided the clay loam soil that was used for the study. Both soils were suitable for rice crop cultivation. The soil samples were air-dried, homogenized to fine powder, and passed through a 2-mm sieve and then used in the extraction procedure.

Dissipation study

During the months of September to November 2019, a dissipation experiment was carried out in the Department of Chemistry under laboratory settings. Agrochemicals Residues Testing Laboratory, Deptt. of Agronomy, CCSHAU, Hisar, analyzed the samples. Separate plastic pots [25 x 25 (i.d.) cm] were used in a complete Randomized Design (CRD) with three replications in the laboratory. Each pot was filled with 1000 g of sandy loam and clay loam soil that had already been dried and sieved. Before packing, each soil was watered to field capacity conditions. Soil samples from sandy loam and clay loam were fortified with 50 and 100 µg g⁻¹ of the herbicide, respectively. Throughout the experiment, the soil moisture was kept constant and equivalent to the field capacity moisture level of 1/3 bar tension by providing the needed amount of distilled water. During the experiment, the temperature was varied between 15 and 25°C. At [0 (2 h after treatment), 1, 5, 10, 15, 30, 45, 60 days] after treatment, from each treatment, a 5 g moist soil sample was collected in triplicate for further residue analysis.

Determination of the physico-chemical parameters

The pipette method was used to determine the texture of the soil. A combination glass electrode pH meter was used to access soil samples pH in a 1:2 soil water

suspension ratio. Soil samples in soil water suspension ratio of 1:2 was done with the help of conductivity meter. The wet digestion method was used to determine the amount of organic carbon in the soil.

Penoxsulam extraction from soil sample

Soil samples were collected in triplicates using two distinct methods. The procedures were followed to be matrix solid phase dispersion and partition.

Matrix solid phase dispersion (MSPD)

It's uses a process of simultaneous extraction and clean-up. MSPD could be an effective sample preparation approach, especially for reducing analyte losses. Both reinforced soil samples (5 g each) were taken and mixed with 10 g of silica gel. Pestle and mortar were used to adequately combine the soil and silica gel mixture. Add in a pinch of activated charcoal. With a spatula, transfer the mixture to the column filled with anhydrous sodium sulfate. 80 mL acetonitrile was used to elute the column. After passing through anhydrous sodium sulfate (3 g), the eluents were collected in reagent bottles and dried on a rotary vaccum evaporator (Buchi R-300). With acetonitrile, the final volume is made to be 2 mL. HPLC-PDA was used to analyze the samples.

Partition

In a 500ml flask, samples of both reinforced soils (5 g each) were taken. To soils, add 100 mL of an 80:20 v/v combination of acetonitrile and water. For 1 hour, shake the flasks with a mechanical shaker. Then, pour in the brine solution. Shake the contents thoroughly before transferring to a separating funnel and partitioning with dichloromethane three times (100,75, and 50 ml). Organic layer was collected. The collected samples were concentrated and dried using a rotary vaccum evaporator. For HPLC analysis, the samples were reconstituted to 2mL.

Residue analysis

The method's validity in soil samples was tested by fortifying control samples of each matrix at 0.01 µg/g and 0.05 µg/g fortification levels in triplicate

to assess the method's validity. The calculated and displayed residual data consisted of a mean and standard deviation (SD). The first order rate reaction was transformed to determine the degradation rates for both soils using simple linear regression. $DT_{50} = \ln 2/K$, where K is the degradation constant, was used to compute the half life.

RESULTS AND DISCUSSION

Table 1, shows the physico-chemical parameters of two soils. Penoxsulam's peak area was plotted against concentrations (0.01–0.05 µg/mL) and showed satisfactory linearity ($R^2 = 0.925$ and 0.948 , respectively). The recovery rates in both soils were between 82.5 and 90.2%. Using HPLC-PDA, the limits of detection (LOD) and limit of quantification (LOQ) for penoxsulam in two soils were 0.01 and 0.05 µg/g, respectively. Clay loam soil had slightly smaller recoveries due to stronger interactions between pesticide and organic carbon levels (0.36% in clay loam soil). Herbicide dispersion is always aided by the presence of organic carbon in the soil. Rouchad *et al.* 2000, reported that triketone herbicides dissipate faster in soil with higher organic carbon, which is consistent with the findings of the current study, which found that clay loam soil with 0.48% organic carbon offered slightly more dissipation for tembotrione and TCMBAs than sandy loam soil with 0.35% OC. Figures 2- 3 depict the penoxsulam herbicide's persistence and dissipation at two treatment rates in sandy loam and clay loam soils under a 25% moisture regime in a controlled laboratory environment. In both soils, the amount of penoxsulam residue decreased over time. When penoxsulam was applied to clay loam soil at a lower

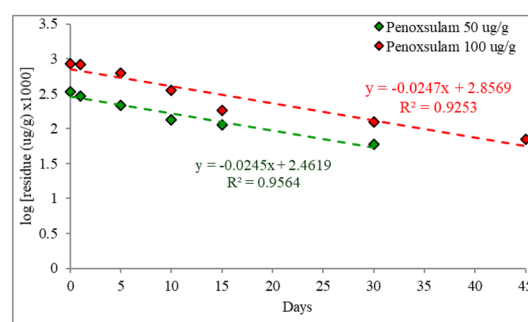


Fig. 2. Penoxsulam dissipation kinetics in clay loam soil.

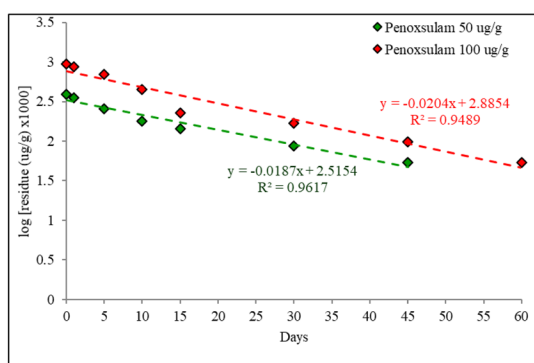


Fig. 3. Penoxsulam dissipation kinetics in sandy loam soil.

application rate ($50 \mu\text{g per g}^{-1}$), it was anticipated that residual levels would decrease to below detectable limits (BDL) on day 30. However, when penoxsulam was applied at a higher application dose ($100 \mu\text{g g}^{-1}$), BDL was attained on day 45. Penoxsulam residues in clay loam soil dropped to below detectable limit (BDL) on the 45th day of herbicide treatment at a lower application rate ($50 \mu\text{g g}^{-1}$), but were reached below detectable limit (BDL) on the 60th day of herbicide application at a higher application dose ($100 \mu\text{g g}^{-1}$). The quantity of penoxsulam recovered from soil samples at both application rates was fitted using a first order kinetic equation:

$$C = C_0 e^{-\lambda t} \cdot \text{eq}^{-1}.$$

where C is the amount of penoxsulam that was extracted from the samples at time t. C_0 is the amount of recovered penoxsulam at time zero, λ is the degradation constant, and t is the amount of time in days. At 50 and $100 \mu\text{g/g}$ application dosages, penoxsulam dissipation in clay loam and sandy loam soil follows first order kinetics, with half-life periods of 7.5 and 7.8 days in clay loam soil and 8.9 and 9.3 days in sandy loam soil, respectively. In clay loam soil, residues of penoxsulam reached below quantification limit (0.05

g/g) within 45 to 60 days after application (DAA); in sandy loam soil, residues required 60 days to get below quantification threshold. Penoxsulam dissipation in both soils is expected to take place in a single separate phase that follows first-order kinetics. In two soils, estimated coefficients of determination (R^2) ranged from 0.925 to 0.948. In both soils, the half-life values ranged between 7.5 and 9.3 days at 50 and $100 \mu\text{g/g}$ soil treatment rates. Numerous factors, including as soil organic carbon, pH, soil moisture, and temperature, affect pesticide dissipation in soil and, consequently, microbial activity and herbicide breakdown (Chen *et al.* 2012, Sondhia *et al.* 2016). Due to differences in soil properties, there is a difference in penoxsulam half life in both soils. Table 1 show that clay loam soil has a higher pH value than sandy loam soil. Penoxsulam is weakly adsorbed to sandy loam soil because it has a higher pH value than sandy loam soil (moderately adsorbed). Vischetti *et al.* (2000), showed a difference in herbicide half life due to dose variation. Because the investigation was conducted under laboratory circumstances, the dissipation of penoxsulam was equivalent to that reported in the literature. Florasulam, which belongs to the triazolopyrimidine sulfonamide class of herbicides, has shown similar results (Mukherjee *et al.* 2016, Kaur and Kaur 2018), found that penoxsulam dissipation increased with increasing soil moisture content and temperature, regardless of soil type. The dissipation of penoxsulam appeared to be aided by both microbiological and photodegradation as assessed by Monika *et al.* 2017.

CONCLUSION

As a result, it can be stated that penoxsulam herbicide persistence in clay loam and sandy loam soils followed first-order kinetics. Interactions between soil and herbicides, as well as the amount of organic matter in the soil, have a significant impact on the rate

Table 1. Physico-chemical parameters of two soils.

	Sand (%)	Silt (%)	Clay (%)	pH	Electric conductivity (dS cm^{-1})	OC (%)
Clay loam	52.0	18.0	30.0	8.4	0.4	0.36
Sandy loam	65.5	22.5	12.0	7.6	2.0	0.30

of deterioration. In laboratories, penoxsulam residues in clay loam and sandy loam soils dissipated in 7.5 and 8.9 days at a lower rate of application ($50 \mu\text{g g}^{-1}$) and in 7.8 and 9.3 days at a higher rate of application ($100 \mu\text{g g}^{-1}$). Leaching potential, toxicological effects on soil microorganisms, and an adsorption-desorption experiment in the same soils all needed more research.

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