



RESEARCH ARTICLE

Dissipation of metribuzin, pendimethalin and clodinafop-propargyl, applied in pea, as influenced by mulching and climatic variables

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ABSTRACT

Pea (*Pisum sativum* L.) is a major legume valued for its high protein content and nitrogen fixation, but persistence of herbicides like pendimethalin, metribuzin and clodinafop-propargyl raises concerns of food safety and their carryover effect on succeeding crops. A field study was conducted to evaluate dissipation kinetics of pre-emergence application (PE) of pendimethalin 750 g/ha and post-emergence application (PoE) of clodinafop-propargyl + metribuzin 169, 202, 236 and 270 g/ha in pea crop with the paddy straw mulch of 7.5 t/ha, under varying climatic conditions that prevailed in different years of evaluation. Clodinafop-propargyl remained below 0.01 µg/g due to rapid hydrolysis into clodinafop acid. The half-lives of pendimethalin and metribuzin varied markedly across years, with faster dissipation in the 2024–25, year with higher early-season rainfall, and slower degradation in the 2022–23 and 2023–24, years with limited rainfall. Mulching increased pendimethalin persistence by moderating soil temperature and moisture, and reducing volatilization and photodegradation whereas clodinafop-propargyl + metribuzin dissipated rapidly when applied over mulch due to greater exposure to sunlight and air. At harvest, residues of all herbicides were below the limit of detection (<0.01 µg/g) in soil and pea across all study years, indicating that at recommended application rates these herbicides dissipate efficiently without leaving harmful residues, thereby ensuring food safety.

Keywords: Pendimethalin, Metribuzin, Clodinafop-propargyl, Crop safety assessment, Herbicide residues

INTRODUCTION

Weeds represent one of the most persistent biotic constraints in modern agriculture, severely impacting crop growth, yield and quality by competing for light, water, nutrients and space (Rao *et al.* 2020). In response to these challenges, herbicides have become an essential component of integrated weed management strategies due to their efficacy, convenience and ability to control a wide spectrum of weed species with minimal labour input (Rao 2022). The widespread adoption of herbicides has contributed significantly to the intensification of agricultural systems, enabling high crop productivity and enhanced food security (Abraham *et al.* 2014, Rao 2022). However, the extensive and often indiscriminate use of herbicides has also raised critical environmental and health concerns, particularly with respect to their persistence in soil, potential leaching into groundwater and accumulation in edible crops (Sondhia *et al.* 2019).

Pisum sativum (pea), an agronomically and nutritionally important legume, plays a vital role in

sustainable agriculture by contributing to soil nitrogen enrichment through symbiotic nitrogen fixation, improving soil structure and providing rotational diversity in cropping systems (Akshit *et al.* 2024). Pendimethalin and metribuzin + clodinafop-propargyl have been widely recognized for their efficacy in controlling annual weeds in leguminous and other pea crops, providing a valuable tool for modern weed management (Chikoye *et al.* 2014). Pendimethalin, a dinitroaniline herbicide, is commonly used for pre-emergence weed control and exerts its action by inhibiting microtubule polymerization during cell division (Giglio and Vommaro 2022). Metribuzin is a selective triazinone herbicide primarily targeting broad-leaved and some grass weeds. It inhibits photosystem II by attaching to the D1 protein of chloroplast thylakoid membrane, thereby interrupting electron transport and halting photosynthesis (Teixeira *et al.* 2024). Clodinafop-propargyl, a post-emergence herbicide, selectively controls grassy weeds by inhibiting acetyl-CoA carboxylase (ACCase), an enzyme critical for fatty acid biosynthesis in susceptible species (Zand and Foroushani 2015, EFSA 2015). However, the continued persistence of these herbicides in agricultural soils is a critical concern, directly

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impacting crop rotation and the potential for carryover damage to subsequent crops. Accurate and timely monitoring of their dissipation is essential not only to ensure food safety and compliance with maximum residue limit (MRL) standards but also to protect soil fertility, maintain beneficial microbial populations and safeguard the long-term sustainability of agricultural ecosystems.

Despite their widespread use, there is notable scarcity of published research dealing with dissipation kinetics and terminal residues of pendimethalin, metribuzin and clodinafop-propargyl when applied to pea crop (Sondhia 2013) specifically in sub-tropical climatic conditions of Punjab. Considering the widespread reliance on herbicides for pea production, the present study was undertaken over three consecutive years (2022-23, 2023-24 and 2024-25) with the objective of evaluating the dissipation kinetics and terminal residues of pendimethalin, metribuzin and clodinafop-propargyl applied in pea for the assessment of residue risk and to provide a scientific basis for safe herbicide usage in pea-based production systems.

MATERIALS AND METHODS

Chemicals and sample preparation

Analytical standards of metribuzin (purity 98%), pendimethalin (purity 98%) and clodinafop-propargyl (purity 97.8%) was procured from TCI Chemicals, Tokyo, Japan. Solvents of HPLC and analytical grade were supplied by Qualikems Pvt, Ltd., Mumbai, India. A stock solution of each herbicide (1000 µg/mL) was prepared in HPLC-grade acetonitrile and working standard solutions ranging from 0.01 to 10 µg/mL were prepared through serial dilution of the stock solution. Commercial formulations, Shagun 21 11 (ready-mix of clodinafop-propargyl 12% plus metribuzin 42% WG) [hereafter: clodinafop-propargyl + metribuzin (ready-mix)] and Stomp (pendimethalin 30 EC) (hereafter: pendimethalin), were procured from the local market of Ludhiana, Punjab, India.

Degradation studies

Field experiments were conducted at the Agronomy Research Farm, Punjab Agricultural University, Ludhiana, during the *Rabi* seasons of 2022-23, 2023-24, and 2024-25 to evaluate the degradation behavior of herbicides in pea under different weed management practices. The soil of the experimental site was loamy sand and the experiment was laid out in a randomized complete block design (RCBD) with three replications. Each plot measured 4

m × 2.5 m. Pea variety 'Punjab 89' was sown on November 2, 2022; October 31, 2023 and November 5, 2024, at a spacing of 30 cm × 10 cm using a seed rate of 75 kg/ha. The seed was inoculated with *Rhizobium legumin Sarum* culture at 625 g/ha prior to sowing. Basal fertilization consisted of 50 kg/ha nitrogen (through 112.5 kg/ha urea) and 62.5 kg/ha phosphorus (through 387.5 kg/ha single superphosphate). In mulching treatments, paddy straw mulch was applied at 7.5 t/ha uniformly over the soil surface three days after sowing. The pre-emergence application (PE) of pendimethalin 750 g/ha was done one day after sowing (before mulch placement) on 03 November 2022, 01 November 2023 and 06 November 2024 using a calibrated knapsack sprayer fitted with a flat-fan nozzle at 500 L/ha spray volume. The post-emergence application (PoE) of clodinafop-propargyl + metribuzin (ready-mix) was applied 30 to 35 days after sowing (DAS) (05 December 2022, 05 December 2023 and 08 December 2024) at 169, 202, 236 and 270 g/ha. The inclusion of herbicide treatments in mulched plots was intended to study the interactive effects of chemical and physical weed suppression and to evaluate the degradation behaviour of metribuzin under conditions of reduced soil exposure and sunlight interception. Although mulching alone suppresses 60-70% of the weed flora, certain species still emerge through small gaps or along mulch edges; therefore, integrating herbicides with mulch represents a practical approach for more effective and prolonged weed control. This also allowed an assessment of influences of mulching on dissipation of herbicide. At the applied mulch rate, there was no adverse effect of mulching on pea emergence and growth. Meteorological data during the crop growth period is given in **Figure 1**. For herbicide dissipation and residue monitoring, soil samples (0-15 cm) were collected at 0 (4 hours after application), 3, 5, 7, 10, 15, 21, 30, 45, 60 and 90 days after herbicide application (DAA) and at harvest. Each composite sample represented 6-7 cores from random locations in each plot. Pea samples were collected at three successive pickings to monitor residue dynamics during the harvest period. Samples were stored at -4°C and analyzed within one week. Residue data from mulched and non-mulched plots were analyzed separately and dissipation kinetics curves were generated to depict metribuzin degradation patterns under different surface conditions.

Extraction methods

Matrix solid phase dispersion (MSPD) method was used for the extraction of herbicides from soil

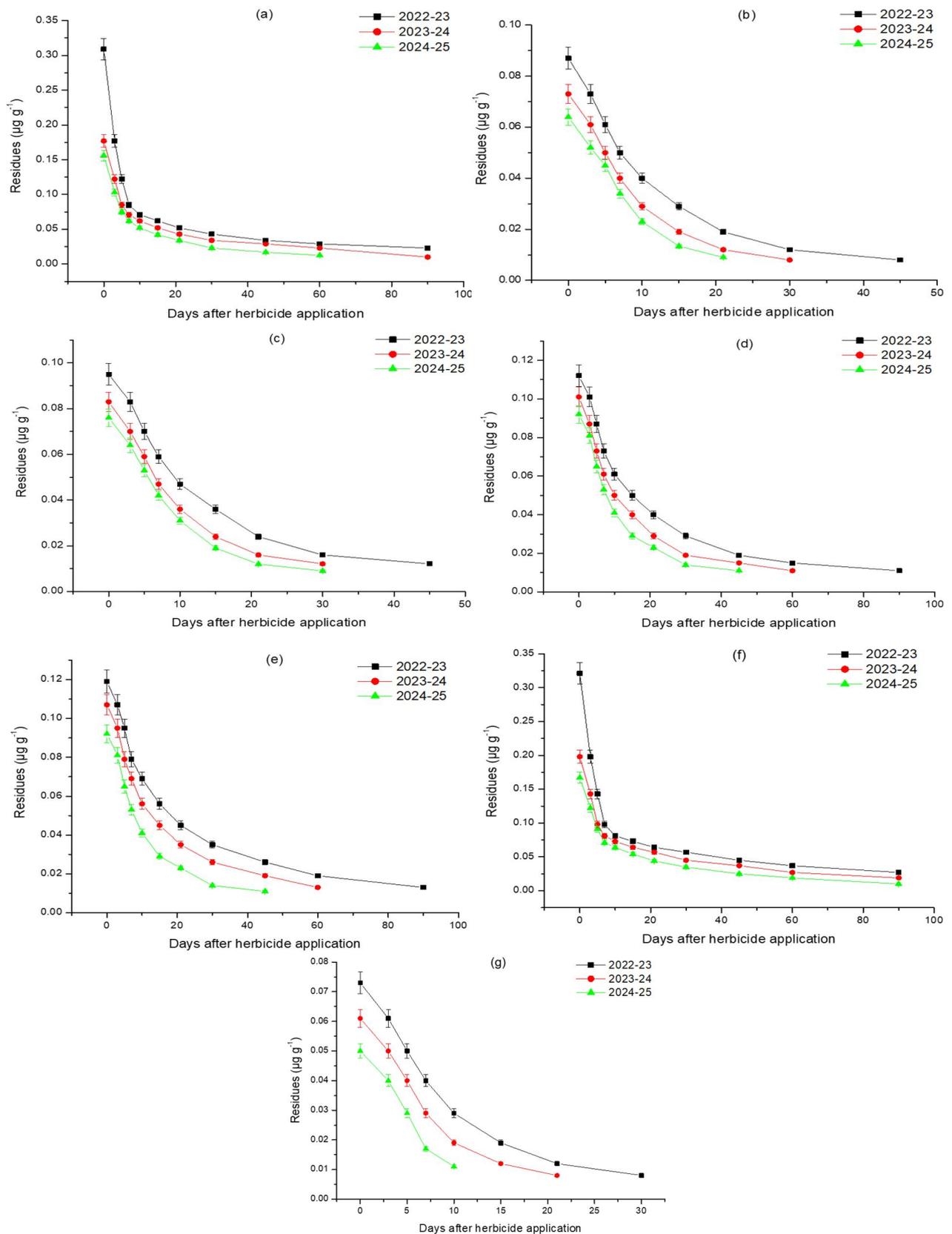


Figure 2. Dissipation curves of pendimethalin in (a) Pendimethalin 750 g/ha and metribuzin in (b) Clodinafop + metribuzin 169 g/ha (c) Clodinafop + metribuzin 202 g/ha (d) Clodinafop + metribuzin 236 g/ha (e) Clodinafop + metribuzin 270 g/ha; pendimethalin in (f) Pendimethalin 750 g/ha followed by paddy straw mulch 7.5 t/ha and metribuzin in (g) Paddy straw mulch 7.5 t/ha followed by clodinafop + metribuzin 169 g/ha in different years

and pea. Briefly, 10 g of soil/pea sample was blended thoroughly with 5 g of pre-activated florisil using pestle and mortar to ensure uniform dispersion. The activation of florisil was performed at 200°C for 8 hours prior to use. The homogenized mixture was then packed into clean glass column pre-layered with 3 g of activated charcoal and 2 g of anhydrous sodium sulfate. The column was eluted with 50 mL of acetone for pendimethalin and 60 mL for metribuzin and 50 mL of ethyl acetate for clodinafop-propargyl. The collected eluate was concentrated to dryness using a rotary vacuum evaporator and residues were redissolved in 2 mL of acetonitrile prior to chromatographic analysis.

Quantification of herbicides

The residue analysis was carried out using HPLC-Waters equipped with 2489 UV-visible detector. Herbicide separation was achieved using C18 spherisorb column (5.0 µm ODS2, 4.6 mm × 250 mm) at 297 nm for metribuzin and 240 nm for pendimethalin and clodinafop. The mobile phase consisted of acetonitrile: water (8:2, v/v) at a flow rate of 0.8 mL/min. The retention time of metribuzin, pendimethalin and clodinafop was 2.84, 4.29 and 7.70 minutes, respectively.

Method validation

The analytical method was validated by evaluating matrix effect, limit of detection (LOD), limit of quantification (LOQ), accuracy and precision (SANTE 2020). Matrix effect (ME) was calculated as: $ME(\%) = \left[\frac{\text{slope of calibration curve for analyte in organic solvent (SSC)}}{\text{slope of calibration curve for analyte in matrix (MMC)}} - 1 \right] \times 100$ where, SSC is solvent calibration curve prepared in acetonitrile and MMC corresponds to the calibration curve obtained by spiking blank matrix samples. LOD and LOQ were established at the signal to noise ratios of 3:1 and 10:1, respectively. Accuracy was evaluated

by analysing samples fortified at two concentration levels: 0.05 and 0.01 µg/mL. To assess intraday precision (%RSD_t), the experiment was performed three times within a single day, while interday precision (%RSD_R) was determined by conducting the analysis on three different days, each with three replicate measurements at 0.05 and 0.01 µg/mL.

Data analysis

Dissipation kinetics of herbicides were estimated using first order model expressed as: $\ln C_t = \ln C_0 - kt$, where C_0 is initial and C_t is the concentration at time t (days) in µg/g and k (day⁻¹) is the degradation rate constant. Half-life (DT₅₀) was calculated using the equation: $DT_{50} = \ln 2/k$. Statistical analyses were performed using SPSS Statistics version 26.0 (IBM Corp., Armonk, NY, USA). Analysis of variance (ANOVA) was applied to assess significant differences among treatments.

RESULTS AND DISCUSSION

Validation studies

The matrix effect was found to be below 5%, confirming method's selectivity and reliability for the estimation of metribuzin, pendimethalin and clodinafop-propargyl in soil and pea samples (Table 1). The LOD and LOQ was 0.003 and 0.01 µg/g demonstrating good sensitivity, enabling the precise detection and quantification of studied herbicides in studied matrices. The mean percent recoveries from soil and pea at fortification levels ranging from 0.01 to 0.05 µg/g varied from 89.9 ± 2.99 to 95.4 ± 2.19 and 82.1 ± 2.01 to 89.3 ± 3.56, respectively (Table 1) with %RSD_r and %RSD_R <10% confirming that the method was accurate and precise for extracting pendimethalin, metribuzin and clodinafop-propargyl from soil and pea.

Table 1. Mean percent recoveries, inter and intra-day precision and matrix effect of studied herbicides from soil and pea

Parameters	Herbicide	Soil		Pea	
		0.05	0.01	0.05	0.01
Recovery %	Metribuzin	95.4 ± 2.19	91.0 ± 3.23	88.3 ± 2.76	84.3 ± 2.67
	Pendimethalin	92.3 ± 1.67	90.2 ± 2.18	89.3 ± 3.56	83.2 ± 2.99
	Clodinafop-propargyl	91.2 ± 2.10	89.9 ± 2.99	85.4 ± 3.51	82.1 ± 2.01
RSD _t	Metribuzin	2.63	1.61	3.21	2.51
	Pendimethalin	3.22	2.92	3.12	3.11
	Clodinafop-propargyl	2.61	3.11	2.01	3.93
RSD _R	Metribuzin	3.23	2.33	3.23	2.32
	Pendimethalin	1.71	3.21	1.53	3.23
	Clodinafop-propargyl	2.00	2.72	2.61	1.93
Matrix effect	Metribuzin		2.3		3.6
	Pendimethalin		3.8		4.1
	Clodinafop-propargyl		4.5		2.9

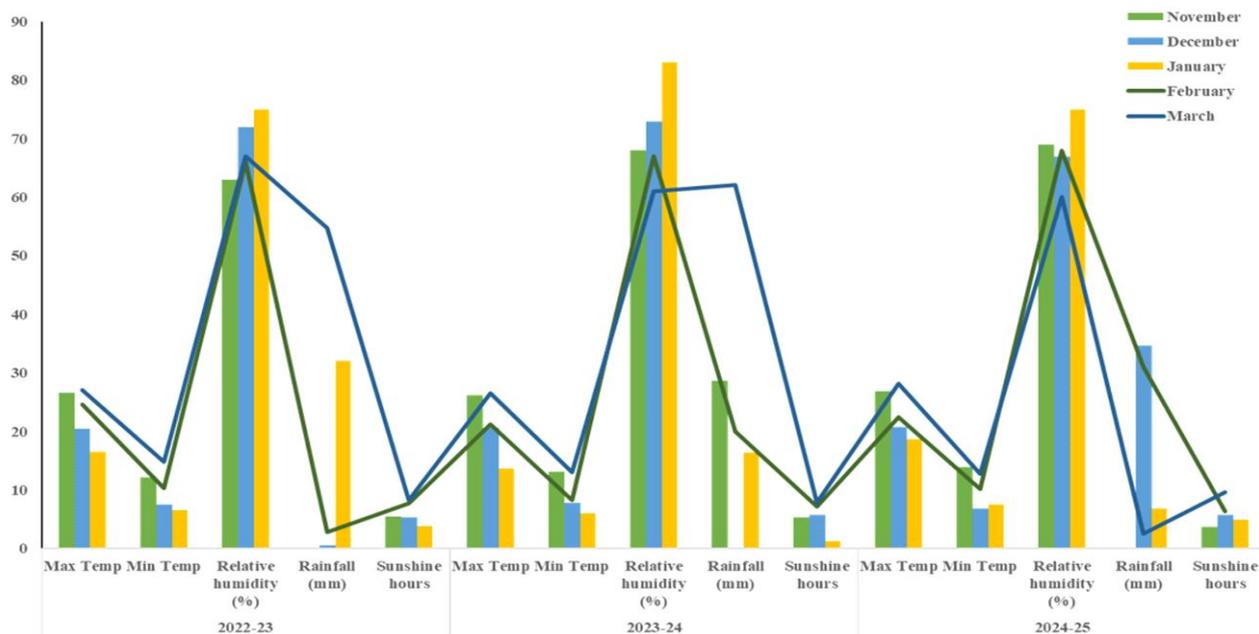


Figure 1. Weather data recorded during the experimental period (Source: Department of Climate Change and Agricultural Meteorology, PAU, Ludhiana)

Degradation studies

The initial residue of clodinafop-propargyl over three-year study was <0.01 µg/g probably due to its rapid hydrolysis into clodinafop acid. (Chhokar *et al.* 2009; Wang *et al.* 2018; Kaur *et al.* 2023). During the study period the initial residual concentrations of pendimethalin and metribuzin varied between 0.156 ± 0.012 to 0.321 ± 0.023 and 0.05 ± 0.015 to 0.119 ± 0.019 µg/g respectively (Figure 2). The residues of pendimethalin and metribuzin declined considerably over time. The dissipation behaviour of studied herbicides followed first order kinetics with determination coefficients (R²) > 0.99. ANOVA results indicated a significant interaction (p<0.05) between herbicide application rates and the prevailing environmental conditions. The half-lives (DT₅₀) for the different herbicide treatments are presented in Table 2. Across all three years, pendimethalin demonstrated a significantly higher persistence in the soil compared to all metribuzin-containing treatments.

The DT₅₀ of pendimethalin applied alone (750 g/ha) ranged from 24.46 to 38.86 days, while the DT₅₀ for the various clodinafop + metribuzin treatments were substantially lower, ranging from 4.32 to 25.56 days. This finding indicates that pendimethalin has a slower degradation rate and a higher potential for residual accumulation in the soil environment compared to metribuzin.

A clear trend of decreasing herbicide persistence was observed over the three years of the study. The half-lives of pendimethalin and metribuzin ranged from 12.47 to 38.86, 8.89 to 32.77 and 6.94 to 24.46 days in 2022-23, 2023-24, 2024-25, respectively, indicating faster degradation of pendimethalin in 2024-25 compared to 2023-24 and 2022-23 (Table 2). This pattern reflects the influence of year-to-year climatic variation among the three growing seasons. Among the climatic factors, rainfall showed the most pronounced variation and was therefore the primary driver of differences in dissipation rates. The year

Table 2. Half-lives (days) of pendimethalin and metribuzin in different treatments in different years

Treatment	Half-lives (days)		
	2022-23	2023-24	2024-25
Pendimethalin 750 g/ha	38.86	32.77	24.46
Pendimethalin 750 g/ha followed by paddy straw mulch 7.5 t/ha	50.65	41.02	30.57
Paddy straw mulch 7.5 t/ha followed by clodinafop + metribuzin 169 g/ha	8.89	6.72	4.32
Clodinafop + metribuzin 169 g/ha	12.47	8.89	6.94
Clodinafop + metribuzin 202 g/ha	14.19	10.10	8.99
Clodinafop + metribuzin 236 g/ha	18.76	16.46	13.86
Clodinafop + metribuzin 270 g/ha	25.56	19.86	17.97

2024-25 received substantially higher early-season rainfall (34.6 mm), which likely increased soil moisture and stimulated microbial activity, conditions known to accelerate the degradation of soil-applied herbicides and resulted in shorter half-lives. In contrast, in the year 2022-23 was extremely dry with almost no rainfall (0.6 mm), leading to reduced soil moisture and less favourable conditions for microbial or hydrolytic breakdown, thereby prolonging herbicide persistence. The year 2023-24 season experienced intermediate rainfall, producing dissipation rates between the other two years. Although the experiments were conducted in the same field, accelerated dissipation due to microbial adaptation is unlikely because different herbicides were applied in the intervening maize crop each year. The absence of continuous exposure to the same herbicide prevented the sustained selection pressure required for microbial enrichment (Kaur *et al.* 2016, Kaur *et al.* 2017a, Kaur *et al.* 2017b).

The application of paddy straw mulch had a notable effect on the dissipation of pendimethalin. Treatments that included paddy straw mulch showed consistently higher DT_{50} values (30.57 to 50.65 days) compared to the treatments where pendimethalin was applied alone (24.46 to 38.86 days). This indicates that the presence of paddy straw mulch likely slowed the degradation of pendimethalin, thereby increasing its persistence in the soil. This effect could be attributed to the mulch layer moderating soil temperature and moisture levels or providing a physical barrier that reduces volatilization and photodegradation of pendimethalin. In contrast, the treatment involving paddy straw mulch followed by clodinafop + metribuzin resulted in the lowest DT_{50} values observed across all treatments, with a range of 4.32 to 8.89 days. This rapid dissipation is likely due to the herbicide being applied on top of the mulch layer. The straw provides a large surface area for the herbicide to come in contact with sunlight and air, potentially leading to faster photodegradation and volatilization before it can even reach the soil (Douibi *et al.* 2024, Chen *et al.* 2025). This suggests that the timing and placement of the herbicide relative to the mulch application are critical factors influencing dissipation.

The residues of pendimethalin, metribuzin and clodinafop-propargyl in soil at pea harvest were below the limit of detection ($<0.01 \mu\text{g/g}$) across all study years. This observation confirms that, under all the treatments these herbicides do not persist in the environment at levels that pose a risk to either the

subsequent crops or the broader agroecosystem. In pea, residues of pendimethalin, metribuzin, and clodinafop-propargyl were below detection limit of $<0.01 \mu\text{g/g}$ at each harvest stage (first, second, and third picking). Residue below the maximum residue limit (MRL) of 0.1 mg/g in pea samples at harvest demonstrates minimal risk of pendimethalin and pre-mix of clodinafop-propargyl + metribuzin (USEPA 1998; EFSA 2015; EFSA 2023), thereby confirming compliance with food safety regulations. Nevertheless, continuous monitoring and strict adherence to recommended guidelines remain essential to safeguard consumer safety and ensure the sustained quality of pea production.

Conclusion

The present study demonstrated that pendimethalin dissipates more slowly than metribuzin, highlighting its higher persistence in soil and greater potential for residual accumulation. Variability in degradation patterns was strongly influenced by mulching and environmental factors, with higher rainfall accelerating dissipation rates as in 2024-25 compared to lower rain fall years of 2023-24 and 2022-2023. Residues of metribuzin, pendimethalin and clodinafop-propargyl in soil and pea samples remained below detectable limits and below established maximum residue limits, confirming their safety when used at recommended application rates.

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