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RESEARCH ARTICLE

Metribuzin + clodinafop-propargyl (ready-mix) efficacy in managing weeds in wheat and assessment of its residues in the soil and wheat at harvest

Pardeep Goyal*, Pervinder Kaur[1] and Makhan Singh Bhullar[2]

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ABSTRACT

Indiscriminate use of herbicides may raise human and animal health and environmental concerns due to residues on consumables and soil. Hence, field experiments were conducted during rabi season of 2021-22 and 2022-23 at PAU Ludhiana and KVK Sri Muktsar Sahib, Punjab, India. The objectives were to assess efficacy of metribuzin + clodinafop-propargyl (ready-mix) in managing weeds in wheat and quantify its residues retained in soil and in wheat produce. It involved spray of metribuzin and clodinafop-propargyl (ready-mix) at rates of 275, 220 and 165 g/ha along with unsprayed for weed management in surface seeded wheat. Metribuzin and clodinafop-propargyl at 275 and 220 g/ha significantly lowered weed density and biomass and improved wheat grain yield compared to its lowest dose of 165 g/ha and unsprayed control. Metribuzin and clodinafop-propargyl residues in soil and crop produce were assessed at harvest time and it was observed that their residue levels were below detectable limits (<0.01 µg/g) and below the maximum residue limit fixed by Food Safety and Standards Authority of India (FSSAI), indicating metribuzin + clodinafop-propargyl safety to use as an herbicide in wheat production and consumption of wheat produced after its usage.

Keywords: Herbicide residues, Metribuzin + clodinafop-propargyl, Wheat, Weed management

INTRODUCTION

Weeds are among the most important biological constraints that can adversely affect wheat productivity (Rao *et al.* 2014, Yadav and Brar 2025). Mechanical and chemical methods are most commonly used to manage weeds but of these methods, herbicides are most preferred method of weed control due to fast action, selectivity, lesser cost and drudgery (Singh *et al.* 2008, Singh and Chhina 2025). *Phalaris minor* is among the most problematic weeds and difficult to control as it mimics wheat. *Phalaris minor* has potential to cause yield reduction to the extent of 100% (Chhokar and Malik 2002). Metribuzin + clodinafop-propargyl (ready-mix) is an effective broad-spectrum herbicide especially against herbicide resistant *Phalaris minor* (Abbas *et al.* 2016, Singh *et al.* 2015). But using herbicide with similar modes of action year after year has resulted in development of multiple herbicide resistance in *Phalaris minor* (Bhullar *et al.* 2014, Kaur *et al.* 2015) in north-west part of India. Apart from this, there are environmental, and health concerns associated with herbicide use in wheat as it may leave its residues which may be harmful for human and animal health as they both are end users of crop produce i.e. grains and straw (Sondhia and Mishra 2005, Thakur *et al.* 2019). Keeping this in view, a study was conducted to evaluate metribuzin + clodinafop-propargyl (ready-mix) efficacy in managing weeds in wheat and to quantify its residues in the soil and in wheat produce, at wheat harvest.

Regional Research Station (Punjab Agricultural University), Faridkot, Punjab 151203, India

[1] Department of Agronomy, Punjab Agricultural University, Ludhiana, Punjab 141004, India

[2] Directorate of Extension Education, Punjab Agricultural University, Ludhiana, Punjab 141004, India

* Corresponding author email: pardeepinpau@gmail.com

MATERIALS AND METHODS

Experiments were conducted at Punjab Agricultural University (PAU) Ludhiana (Latitude: 30° 53’ N, Longitude: 75° 47’ E) and Krishi Vigyan Kendra (KVK) Sri Muktsar Sahib (SMS) (Latitude: 30° 26’ N, Longitude: 74° 30’ E). At PAU, soil was sandy loam in nature (sand: 68, silt:16 and clay: 16%) with 0.38% organic carbon, situated in sub-humid climate with total rainfall for 2021-22 and 2022-23 from 44th SMW (Standard Meteorological Week) to 16th SMW were 158 and 113 mm, respectively. In contrast, KVK soil was characterised as sandy clay loam (sand: 54, silt:12 and clay 34%) with organic carbon of 0.60%, located in semi-arid region with 92 and 83 mm of total rainfall, respectively for the corresponding period.

At PAU, sowing of wheat variety, PBW 766 was done on 10th November, 2021 and 2nd November, 2022 during first and second year, respectively. Similarly, at KVK, sowing of same variety was done on 16th and 17th November during 2021 and 2022 respectively. Post-emergence application (PoE) of active in-gradient of metribuzin 42% + clodinafop-propargyl 12% (ready-mix) at 275 g/ha, 220 g/ha and 165 g/ha was done on 2-3 days after first post emergence irrigation in surface seeded wheat. An unsprayed control was maintained. Wheat was raised as per standard procedure and harvesting was done on 12th April, 2022 in the first year and 17th April, 2023 in second year at PAU. At KVK, it was harvested on 18th April 2022 and 22nd April 2023.The data on weed density was collected 60 days after seeding (DAS) and on biomass, 90 DAS of wheat following standard procedures.

Statistical analysis

Analysis of variance (ANOVA) was performed to see effect of metribuzin + clodinafop-propargyl at different doses on weeds and wheat yield. Weed data was subjected to square root transformation ($\sqrt{x+1}$) to homogenize the distribution. Pooled analysis of two years data for each location was performed as experimental error for two years was homogenous according to the Bartlett's test of homogeneity of variance. To determine significant differences between means, the Fisher's least significant difference (LSD) test was employed at a 5% probability level.

Assessment of residues of herbicides in soil and wheat at harvest

Sample collection

From all the experiments during both years, the soil samples (taken from a depth of 0-15 cm), along with the grain and straw samples, were collected at harvest and were immediately stored at -4ºC in a deep freezer to prevent any degradation of herbicide residues.

Extraction of herbicide residues

Metribuzin was extracted from soil / wheat grain / straw using ultrasonic assisted extraction technique. Soil/wheat grain/straw (10 g) sample was ultrasonicated with 60 mL of acetone (2 cycles of 30 ml each) in ultrasonic bath (40 kHz, 20 W) maintained at 40±2°C for 3 minutes. The supernatant was collected, filtered and for quantification of metribuzin residues from soil, filtrate was evaporated to dryness using rotary vacuum evaporator and redissolved in 2 mL HPLC grade acetonitrile. For quantification of metribuzin from wheat grain and straw, filtrate was concentrated to 5 mL using rotary vacuum evaporator and concentrated extract was loaded on column packed with silica gel. The column was eluted with 60 mL acetone:hexane (8:2). Eluent was evaporated to dryness and the residues were then reconstituted in 2 mL of acetonitrile and quantified using HPLC.

Clodinafop-propargyl was extracted from soil, wheat grain and straw using matrix solid-phase dispersion (MSPD) technique. The procedure was carried out in a glass column packed with silica gel, activated sodium sulphate and charcoal. A 10 g sample of soil/wheat grain was blended with 5 g of silica (60-200 mesh, pre-activated at 200°C for 8 hours) for 7 minutes. This mixture was then transferred to the glass column containing 2g sodium sulphate and 3 mg of charcoal. The column was eluted with 70 mL of ethyl acetate:hexane (8:2) and the collected eluent was evaporated using a rotary vacuum evaporator. The residue was reconstituted in 2 mL of acetonitrile and quantified using HPLC. Wheat straw (10 g) was shaken overnight with 80 mL ethyl acetate for extraction of clodinafop-propargyl. The contents were filtered and concentrated to 5 mL using rotary vacuum evaporator. For cleanup, concentrated extract was loaded on column packed with silica gel, activated sodium sulphate, charcoal and eluted with ethyl acetate:hexane (8:2). Eluents were evaporated, reconstituted in acetonitrile (2 mL) and quantified using HPLC.

Quantification of herbicide residues

The residues of herbicides at harvest were quantified using high-performance liquid chromatography (HPLC) with UV detector. C_{18} column (5 µm; 4.6 × 250 mm) was used for the separation of the herbicides. Acetonitrile: water (80:20) was used as a mobile phase at a flow rate of 0.8 ml/min. The detector wavelength was set at 297 and 240 nm for metribuzin and clodinafop-propargyl, respectively. The retention time of metribuzin and clodinafop-propargyl were 4.467 and 7.700 minutes, respectively (**Figures 1a** and **2a**).

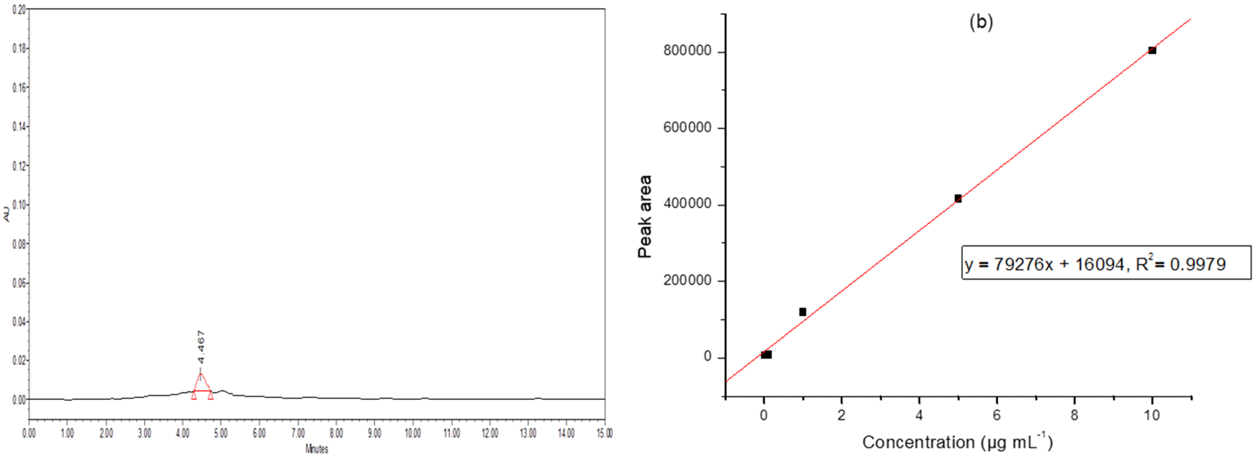

Figure 1(a). HPLC chromatogram of metribuzin (0.1 μg/mL) (b) Calibration curve of metribuzin

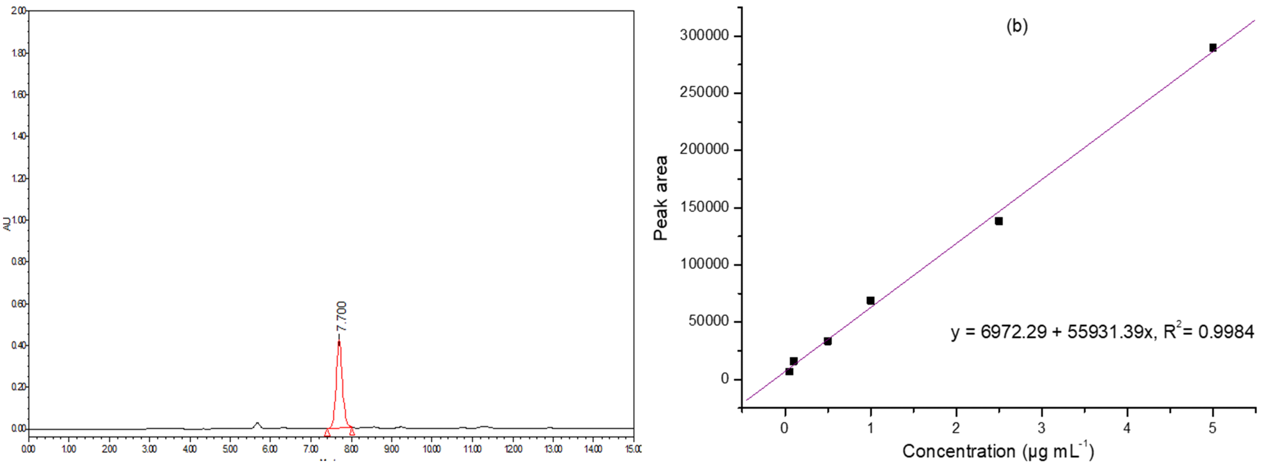

Figure 2(a). HPLC chromatogram of clodinafop-propargyl (0.1 μg/mL) (b) Calibration curve of clodinafop-propargyl

Estimation of metribuzin and clodinafop-propargyl herbicide residues

Method validation

The calibration curves of metribuzin and clodinafop-propargyl were linear with correlation coefficient R^2>0.99 (**Figure 1b** and **2b**). The limit of detection (LOD) and limit of quantitation (LOQ) for both metribuzin and clodinafop-propargyl were 0.003 and 0.01 μg/g, respectively. The mean percent recoveries of metribuzin from soil, wheat grain and wheat straw samples at fortification levels of 0.5, 0.1 and 0.01 μg/g ranged from 82.5 ± 2.21 to 94.3 ± 2.78, 78.4±1.72 to 87.4±3.88 and 74.5±2.50 to 84.5±1.56, respectively. The mean percent recoveries of clodinafop-propargyl from soil, wheat grain and wheat straw samples at fortification levels of 0.5, 0.1 and 0.01 μg/g ranged from 83.1 ± 3.45 to 93.7 ± 2.09, 79.1 ± 2.87 to 89.1 ± 1.65 and 76.8 ± 1.66 to 84.3 ± 2.83%, respectively (**Table 2**). Inter day precision (percent RSD_R) and intraday precision (percent RSD_r) of herbicides were assessed by repeating experiment three times a day and on three different days, respectively and were <10 percent in all matrices.

RESULTS AND DISCUSSION

Effect on weed density, biomass and wheat yield

Phalaris minor, *Rumex dentatus*, *Medicago denticulata* and *Coronopus didymus* were major weeds in experimental field, at both locations and sum total of all four weeds consisted of total weed density and biomass. Weed density and biomass showed differential response to metribuzin + clodinafop-propargyl at different doses. Metribuzin + clodinafop-propargyl at 275, 220 and 165 g/ha recorded 81, 76, 52% lower total weed density at PAU and 79,76 and 40% lower at KVK, respectively **(Table 1).** Similarly, total weed biomass was significantly lower with metribuzin + clodinafop-propargyl irrespective of dose than unsprayed control. Reductions compared to the weedy check were 70%, 68%, and 32% at the PAU location, and 72%, 68%, and 23% at the KVK location. Singh *et al.* (2015) also reported lower weed biomass with clodinafop-propargyl + metribuzin compared to weedy check. Metribuzin + clodinafop-propargyl at 275 g/ha recorded the highest wheat grain yield which was at par with next higher dose of 220 g/ha at both the locations, but both were significantly better than that of the lowest dose of 165 g/ha and untreated control. Nanher *et al.* (2015) also reported similar grain yield at both lower and higher doses of metribuzin + clodinafop-propargyl, and better than weedy check. Qazizada *et al.* (2022) also reported higher grain yield with herbicide use as compared to unsprayed check. Higher weed biomass and density were inversely related with the lower grain yield and vice versa. Our results are in conformity with that of Kaur *et al.* (2025) who observed inverse relationship between yield and weed biomass. Vigorous weed growth, resulting in severe competition with the wheat crop for nutrients, light, water, and space caused a 22% yield reduction at PAU and a 16% reduction at KVK compared to the with metribuzin + clodinafop-propargyl at 275 g ai/ha (**Table 1**). Similar trend was observed with straw yield. Minimum straw yield was observed in untreated spray, which was significantly lower than metribuzin + clodinafop-propargyl at all doses at both the locations.

Harvest time residues of metribuzin and clodinafop-propargyl in soil and wheat grain and straw

Residues of metribuzin and clodinafop-propargyl were below the detectable limits (<0.01 µg/g) at harvest in soil, wheat grain, and wheat straw (**Figures 3-4**) across all tested application rates (275, 220, and 165 g/ha) at both locations during both years. Consequently, the residues were significantly below the maximum residue limits (MRLs) set by the Food Safety and Standards Authority of India (FSSAI 2011).

Residues below detectable limits can be attributed to the substantial time interval of over three-and-a-half months between herbicide application and crop harvest at PAU and KVK during both the years. The half-life of clodinafop-propargyl varies from 1.9 to 3.1 days (EFSA 2020) and of metribuzin from 15.2 to 46.6 days (EFSA 2006) in soil. In our study, the time between was sufficient to degrade these herbicides, by the time of crop harvest during both years and at both locations. The residues

Table 1. Effect of metribuzin + clodinafop-propargyl on total weed density, total weed biomass and grain and straw yield at two locations (pooled data of 2 years)

Treatment	Total weed density (no./m^2) 60 DAS		Total weed biomass (g/m^2) 90 DAS		Grain yield (t/ha)		Straw yield (t/ha)	
	PAU	KVK	PAU	KVK	PAU	KVK	PAU	KVK
Unspayed control	9.18(83.4)	7.36(53.3)	10.81(116.1)	8.24(66.9)	4.13	4.37	6.12	6.48
Metribuzin + clodinafop- propargyl (ready-mix) 165 g/ha	6.38(40.4)	5.72(32.0)	7.58(56.9)	6.48(41.3)	4.73	4.78	6.79	6.94
Metribuzin + clodinafop- propargyl (ready-mix) 220 g/ha	4.45(19.6)	3.69(13.0)	5.22(26.9)	4.17(16.8)	5.20	5.09	7.38	7.38
Metribuzin + clodinafop- propargyl (ready-mix) 275 g/ha	4.04(16.1)	3.43(11.1)	5.02(25.0)	3.93(15.0)	5.32	5.19	7.54	7.53
LSD(p=0.05)	0.31	0.17	0.31	0.18	0.14	0.15	0.17	0.18

Weed data subjected to square root transformation ($\sqrt{x+1}$); Figures in parentheses are original values; PAU: Punjab Agricultural University, Ludhiana; KVK: Krishi Vigyan Kendra, Sri Muktsar Sahib; DAS: days after seeding

Table 2. Mean percent recoveries of metribuzin and clodinafop-propargyl from soil, wheat grain and straw

Herbicide	Matrix	Recovery (%)		
		0.5 µg/g	0.1 µg/g	0.01 µg/g
Metribuzin	Soil	94.3 ± 2.78	90.9 ± 1.77	82.5 ± 2.21
	Wheat grain	87.4 ± 3.88	83.9 ± 1.98	78.4 ± 1.72
	Wheat straw	84.5 ± 1.56	80.2 ± 1.22	74.5 ± 2.50
Clodinafop-propargyl	Soil	93.7 ± 2.09	89.7 ± 2.02	83.1 ± 3.45
	Wheat grain	89.1 ± 1.65	84.0 ± 2.33	79.1 ± 2.87
	Wheat straw	84.3 ± 2.83	80.9 ± 1.21	76.8 ± 1.66

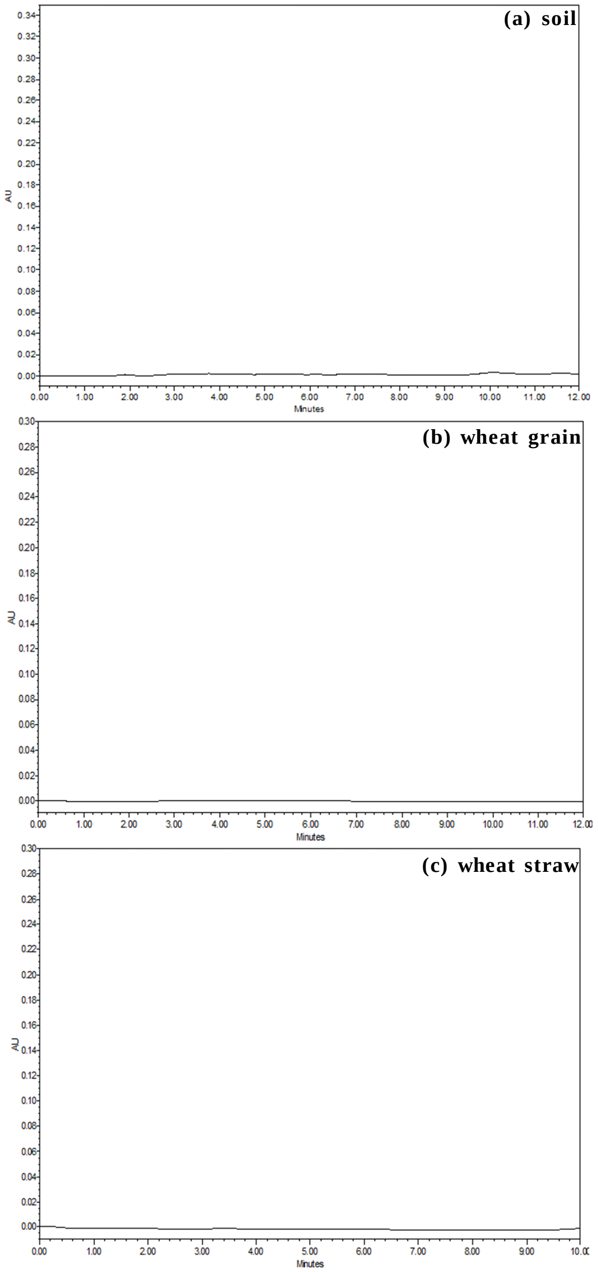

Figure 3. Chromatograms of metribuzin in (a) soil (b) wheat grain (c) wheat straw at wheat harvest

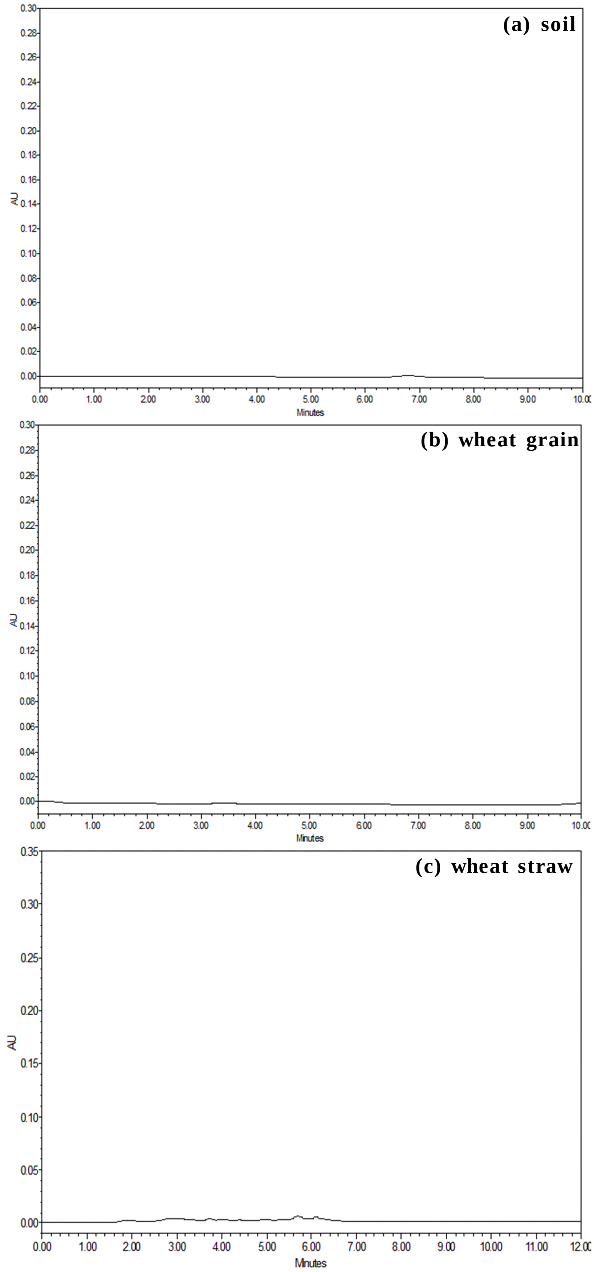

Figure 4. Chromatograms of clodinafop-propargyl in (a) soil (b) wheat grain (c) wheat straw at wheat harvest

of pendimethalin, imazethapyr, and carfentrazone-ethyl in soil (Walia *et al.* 2021), metsulfuron-methyl in wheat grain and straw (Thakur *et al.* 2019) and clodinafop-propargyl in wheat (Singh *et al.* 2004, Sondhia and Mishra 2005) were reported earlier to be below detectable limits when applied at recommended and lower doses.

It can be concluded that the use of metribuzin + clodinafop-propargyl (ready-mix) is safe for effective weed management in wheat, as its residues were below detectable limits (<0.01 µ/g) and below the maximum residue limit fixed by FSSAI, both in the soil or in wheat produce.

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