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# Bio-Efficacy of New Herbicide Molecules for Weed Management in Grain Legumes

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***Authors' contributions***

*This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.*

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## ABSTRACT

Grain legumes including pigeon pea, chickpea, peanut, soybean, lentil, cowpea, common bean, faba bean, pea, and horse gram are extensively cultivated globally. Higher protein content, coupled with symbiotic nitrogen-fixing bacteria in root nodules enabling nitrogen fixation, highlights their importance in minimizing fertilizer use for agricultural production systems. Legume cultivation is limited by prolonged weed interference which is managed either through mechanical, cultural, chemical, or biological methods separately or in combinations. Nevertheless, herbicides remain and will persist as a crucial and economical element in global crop cultivation. While first-generation herbicides benefit agriculture, their long-term persistence and off-target toxicity have significant negative consequences, causing harm to both the environment and humans. Moreover, weed resistance and similar chemistry enforce the demand for new modes of action. Therefore, continuous research into new herbicides is important for combating herbicide resistance and

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ensuring crop output. In recent years, a few herbicides with novel mechanisms of action have occurred. Plants treated with new-generation herbicides resulted in increased WCE (weed control efficiency), decreased weed dry matter, and seed yield. There were no or minimal phytotoxicity symptoms observed on the existing and succeeding crops. This review emphasizes the importance of newly formulated herbicides signifying high selectivity, low toxicity, target specificity, and minimal application rates, contributing to an enhanced understanding of human and environmental health. Furthermore, it emphasizes the significance of economic viability and environmental friendliness in these formulations.

*Keywords: Modes of action; New-generation herbicides; phytotoxicity; selectivity; environmentally friendly.*

## 1. INTRODUCTION

Generally, cultivating legumes provides resource and environmental benefits on a variety of dimensions, from small fields to the worldwide setting. Their impacts on pre-crop, supply of nitrogen, and the ability to promote nutrient as well as soil conservation contributes considerably to sustainable productivity in agriculture, resource conservation and emission-reduction for a more ecologically friendly farming practice [1]. However, their yield is limited by prolonged weed interference (Table 1.) which in turn elevates the production costs and diminishes the quality of produce [2]. These weeds continued to be managed either through mechanical, cultural, chemical, biological methods or their combinations. However, herbicides will continue to serve as an effective and cost-efficient input in global crop production.

**Table 1. Yield losses caused by weeds in various legumes**

| Legume | Average yield loss [%] | References |
|---|---|---|
| Pigeonpea | 41.9 | [3] |
| Chickpea | 77.8 | [4] |
| Urdbean | 43.3 | [5] |
| Mungbean | 38.6 | [6] |
| Lentil | 37.7 | [7] |
| Field pea | 50.0 | [8] |
| Rajmash | 49.5 | [9] |
| Lathyrus | 46.1 | [10] |
| Mothbean | 35 | [11] |

The evolving landscape and ongoing advancements in intensive agriculture are expected to continue relying on herbicides as a key tool for managing weeds. Generally, herbicide usage has proven to be effective in controlling weeds and significantly boosting crop yields. While first-generation herbicides had positive impacts on agriculture, they also introducing notable adverse impacts on the human health as well as environment due to their persistent nature and off-target toxicity. Recognizing these technical gaps in managing weeds presents comprehensive chances for innovative and creative solutions. The creation of new herbicide molecules emerges as one such solution. Growing awareness of human health and environmental protection underscores the importance of ensuring that recently developed novel herbicides must exhibit high selectivity, low toxicity, target specificity, minimal rates of application, and remain both cost-effective and environmentally sustainable.

### 1.1 Trends in weed control systems through herbicides

The 2,4-D discovery in the 1940s marked the onset of a new era in weed management for modern agriculture [12]. Subsequent decades saw a surge in chemical technologies for weed control, leading to the emergence of numerous herbicides targeting specific proteins. In the 1950s and 1960s, auxins, PS-I, and PS-II inhibitors were predominant, succeeded by cell division inhibitors as a main category in 1960s and 1970s. The 1970s and 1980s witnessed the introduction of various modes of action, such as EPSP inhibitors (glyphosate), carotenoid biosynthesis, PPOs, and fatty acid biosynthesis inhibitors. ALS inhibitors characterized the 1980s and 1990s, each mode enabling weed control in new crops. In the late 1990s, advanced breeding skills facilitated the initiation of herbicide tolerance systems [17]. Despite many outstanding herbicides now being off-patent, no novel mechanism of action has been identified in the past two decades. Trends in pesticide consumption and herbicide consumption pattern are presented in Table 2. Herbicides recommended for use in different legumes are presented in Table 3. Further, herbicides banned, restricted in use and withdrawn in India and Kerala were presented in Table 4.

**Table 2. Trend in pesticide and herbicide consumption pattern in India (Million ton) [13]**

| S. No. | | 2016-17 | 2017-18 | 2018-19 | 2019-20 | 2020-21 | 2021-22 | 2022-23 |
|---|---|---|---|---|---|---|---|---|
| **Pesticides** | | | | | | | | |
| 1 | India | 58634 | 63406 | 59670 | 61702 | 62193 | 63284 | 52466 |
| **Herbicides** | | | | | | | | |
| 2 | India | 4075 | 2970 | 3998 | 4275 | 3297 | 2920 | 4155 |

**Table 3. Herbicides recommended for use in different legumes in India [14]**

| Crop | Herbicides |
|---|---|
| Chickpea/Lentil /Field peas | Fluchloralin 50% EC, Linuron 50% WP, Metribuzin 70% WP. |
| Pigeon pea | Alachlor 50% EC, Fluchloralin 50% EC, Pendimethalin 30% EC. |
| Black gram | Fenoxaprop-p-ethyl 9.3% w/w EC, Alachlor 50% EC, Imazethapyr 10% SL + Surfactant, Propaquizafop 10% EC, Quizalofop-ethyl 5% EC, Propaquizafop 2.5% + Imazethapyer 3.75% w/w ME, Fluchloralin 50% EC, Pendimethalin 30% EC. |
| Green gram | Alachlor 50% EC, Imazethapyr 10% SL + Surfactant, Pendimethalin 30% EC. |
| Groundnut | Fenoxaprop-p-ethyl 9.3% w/w EC, Quizalofop-ethyl 5% EC, Alachlor 50% EC, Alachlor 10% GR, Fluazifop-p-butyl 11.1% w/w + Fomesafen 11.1% w/w SL, Diclosulam 84% WDG, Imazethapyr 10% SL, Imazethapyr 10% SL + Surfactant, Pendimethalin 38.7% CS, Imazethapyr 35% + Imazamox 35% WG, Oxyflourfen 23.5% EC, Propaquizafop 2.5% + Imazethapyer 3.75% w/w ME. |
| Soybean | Alachlor 50% EC, Alachlor 10% GR, Bentazone 480 g/l SL, Chlorimuron Ethyl 25% WP + Surfactant, Clethodim 25% EC, Clomazone 50%EC, Diclosulam 84% WDG, Fenoxaprop-p-ethyl 9.3% w/w EC, Fluchloralin 45% EC, Fluazifop-p-butyl 13.4% EC, Pendimethalin 38.7% CS, Flumioxazin 50% SC, Propaquizafop 10% EC, Imazethapyr 10% SL, Haloxyfop R Methyl 10.5% w/w EC, Fluthiacet Methyl 10.3% EC, Imazethapyr 10% SL + Surfactant, Imazethapyr 70% WG + Surfactant, Metribuzin 70% WP, Pendimethalin 30% EC, Quizalofop-ethyl 5% EC, Pyroxasulfone 85% w/w WG, Quizalofop –p- tefuryl 4.41% EC, Sulfentrazone 39.6% w/w SC, Fomesafen 12 % + Quizalofop ethyl 3% w/w SC, Imazethapyr 35% + Imazamox 35% WG, Fluazifop-p-butyl 11.1% w/w + Fomesafen 11.1% w/w SL, Pendimethalin 30%+ Imazethapyr 2% EC, Propaquizafop 2.5% + Imazethapyer 3.75% w/w ME, Sulfentrazone 28% + Clomazone 30% WP, Sodium Aceflourofen 16.5% + Clodinafop Propargyl 8% EC. |

**Table 4. Herbicides banned, withdrawn, refused, and restricted for usage in India [15]**

| Type of prohibition | Herbicides |
|---|---|
| Banned | Nitrofen, Metoxuron, Paraquat dimethyl sulphate, |
| Withdrawn | Dalapon, Simazine |
| Refused registration | 2,4,5-T, Calcium arsenate, TCA, Ammonium sulphamate |
| Restricted in use | 2,4-D, Glyphosate (in some states), Dazomet (tea) |

## 2. FACTORS DRIVING THE NEED FOR NOVEL MODES OF ACTION

Following the initial detection of triazine resistance in weeds in the late 1960s, subsequent reports of categories resistant to almost all herbicides have been documented globally in over 154 distinct weed species [16]. The overutilization of a single mode of action during crop period encourages weed shifts, leading to herbicide resistance emergence.

The need for innovative modes of action is driven by the prevalence of comparable chemistry, often distinguished by specific performance weaknesses. The identification of a promising herbicide often initiates the synthesis of analogs, sometimes resulting in a multitude of closely related products that target the same biochemical pathway. Within a mode of action group, certain compounds might exhibit comparable properties (Table 5).

Traditional, high-dose formulations often lose registration because of elevated dosage requirements and persistent effects, primarily over concerns about groundwater contamination. Examples include urea herbicides (diuron) or triazines (atrazine or simazine) [17]. However, novel molecules may not always offer a comparable lasting impact or be cost-effective.

Herbicide resistance *i.e.,* an altered response to herbicide by a species which was earlier susceptible within a population is a major concern in worldwide agricultural production [18]. Herbicide resistance reported in the world in various grain legumes are presented in Table 6. Therefore, the demand for new herbicides develops as weeds gain resistance to existing formulations. Despite this demand, the development of herbicides with novel modes of action (MOAs) has been somewhat slow during the last two decades. As a result, the continual development of novel herbicides, including novel chemical classes or MOAs, remains an important strategy for combating herbicide resistance and ensuring sustainable agricultural production [12].

**Table 5. Characteristics of ALS-, ACCase- and PPO-inhibitors [17]**

| **Characteristics** | **ALS inhibitors** | **ACCase- inhibitors** | **PPO-inhibitors** |
|---|---|---|---|
| | **Sulfonyl ureas** | **FOPs** | **PPO** |
| Dose (g a.i./ha) | Very low (<100g) | Low (<500g) | Variable (50-2000) |
| Spectrum | Dicots+ monocots | Grasses only | Primarily dicots |
| Speed of action | Slow | Slow | Fast |
| Environmental risks | Carryover and soil mobility | Soil mobility | Phytotoxicity after drift |

**Table 6. Herbicide resistance weeds for different herbicides in various grain legumes in the world [19]**

| **Legumes** | **Herbicide resistant weeds** | **Herbicides** | **Mode of action** |
|---|---|---|---|
| Groundnut | *Amaranthus palmeri* | imazapic, and imazethpyr | Inhibition of Acetolactate Synthase (ALS) |
| | *Ambrosia artemisiifolia* | diclosulam | |
| | *Sorghum halepense* | clethodim, fluazifop-butyl, and haloxyfop-methyl | Inhibition of Acetyl CoA Carboxylase (ACC ase) |
| Groundnut, soybean | *Amaranthus palmeri* | imazapic, imazaquin, and imazethapyr | Inhibition of Acetolactate Synthase |
| Chickpea, Faba beans, Lentils, Peas, | *Lolium rigidum* | chlorsulfuron, diclofop-methyl, fluazifop-butyl, haloxyfop-methyl, metsulfuron-methyl, quizalofop-ethyl, sethoxydim, tralkoxydim, triasulfuron, and trifluralin | Multiple Resistance: 3 Sites of Action Inhibition of ACC ase, Inhibition of ALS, inhibition of microtubule assembly |
| Faba beans, Peas | *Alopecurus myosuroides* | chlorotoluron, clodinafop-propargyl, cloransulam-methyl, iodosulfuron-methyl-Na, isoproturon, mesosulfuron-methyl, and pinoxaden | Inhibition of ACC ase, Inhibition of ALS, PSII inhibitors - Serine 264 Binders |
| Beans | *Eleusine indica* | fenoxaprop-ethyl, glyphosate, and haloxyfop-methyl | Inhibition of ACCase, Inhibition of Enolpyruvyl Shikimate Phosphate (EPSP) Synthase |
| | *Amaranthus powellii* | thifensulfuron-methyl, and tribenuron-methyl | Inhibition of Acetolactate Synthase |

| **Legumes** | **Herbicide resistant weeds** | **Herbicides** | **Mode of action** |
|---|---|---|---|
| Chickpea, faba beans, Lentils, peas | *Avena sterilis* | diclofop-methyl, fluazifop-butyl, and sethoxydim | Inhibition of Acetyl CoA Carboxylase |
| Beans | *Bromus diandrus ssp. rigidus* | clethodim, fluazifop-butyl, haloxyfop-methyl, quizalofop-ethyl, and tepraloxydim | |
| Faba beans | *Phalaris paradoxa* | clodinafop-propargyl, and fenoxaprop-ethyl | |
| Chickpea, Faba beans, Lentils, | *Avena fatua* | clethodim, clodinafop-propargyl, diclofop-methyl, and fenoxaprop-ethyl | |
| Chickpea, Lentils, Peas | *Lolium perenne ssp. multiflorum* | clodinafop-propargyl, diclofop-methyl, quizalofop-ethyl, and sethoxydim | |
| Faba beans | *Phalaris brachystachys* | clodinafop-propargyl, and fenoxaprop-ethyl | |
| Chickpea | *Avena sterilis ssp. ludoviciana* | clodinafop-propargyl, and diclofop-methyl | |
| Chickpea | *Avena sterilis ssp. ludoviciana* | glyphosate | Inhibition of Enolpyruvyl Shikimate Phosphate Synthase |
| | *Avena fatua* | | |
| Chickpea and soybean | *Ambrosia artemisiifolia* | imazamox, metsulfuron-methyl, and tribenuron-methyl | Inhibition of Acetolactate Synthase |
| Chickpea, Lentils, Peas | *Lactuca serriola* | chlorsulfuron, imazethapyr, metsulfuron-methyl, thifensulfuron-methyl, triasulfuron, and tribenuron-methyl | |
| | *Anthemis cotula* | chlorsulfuron, imazethapyr, thifensulfuron-methyl, and tribenuron-methyl | |
| | *Lolium perenne ssp. multiflorum* | clethodim, clodinafop-propargyl, diclofop-methyl, flufenacet, quizalofop-ethyl, and triasulfuron | Inhibition of Acetyl CoA Carboxylase, Inhibition of Acetolactate Synthase, Very Long-Chain Fatty Acid Synthesis inhibitors |
| Peas | *Setaria viridis* | ethalfluralin, and trifluralin | Inhibition of Microtubule Assembly |
| | *Avena fatua* | imazamethabenz-methyl | Inhibition of Acetolactate Synthase |
| | *Polygonum convolvulus* | florasulam, thifensulfuron-methyl, and tribenuron-methyl | |
| | *Lolium perenne ssp. multiflorum* | chlorotoluron, iodosulfuron-methyl-Na, and mesosulfuron-methyl | Inhibition of ALS, PSII inhibitors |
| Lentils, Peas | *Kochia scoparia* | dicamba, glyphosate, thifensulfuron-methyl, and tribenuron-methyl | Inhibition of ALS, Inhibition of EPSP synthase, Auxin Mimics |
| Faba beans, Peas | *Alopecurus myosuroides* | chlorotoluron, clodinafop-propargyl, cloransulam-methyl, iodosulfuron-methyl-Na, isoproturon, mesosulfuron-methyl, and pinoxaden | Inhibition of ACCase, Inhibition of ALS, PS-II inhibitors |
| Lentils | *Sonchus asper* | imazamox, and thifensulfuron-methyl | Inhibition of ALS |
| Soybean | *Ageratum conyzoides* | pyrithiobac-sodium, and trifloxysulfuron-Na | Inhibition of ALS |

| **Legumes** | **Herbicide resistant weeds** | **Herbicides** | **Mode of action** |
|---|---|---|---|
| | *Amaranthus powellii* | aminocyclopyrachlor, dichlorprop, imazethapyr, MCPA, and mecoprop | Inhibition of ALS, Auxin Mimics |
| | *Brassica rapa* | diclosulam, glyphosate, imazapyr, and metsulfuron-methyl | Inhibition of ALS,<br>Inhibition of EPSP synthase, |
| | *Bidens pilosa* | atrazine, and imazethapyr | Inhibition of ALS,<br>PSII inhibitors - Serine 264 Binders |
| | *Conyza bonariensis* | glyphosate | Inhibition of EPSP synthase |
| | *Carduus acanthoides* | 2,4-D, and glyphosate | Inhibition of EPSP synthase, Auxin Mimics |
| | *Digitaria insularis* | fenoxaprop-ethyl, and haloxyfop-methyl | Inhibition of ACC ase |
| | *Eleusine indica* | fenoxaprop-ethyl, glyphosate, and haloxyfop-methyl | Inhibition of ACC ase,<br>Inhibition of EPSP synthase |
| | *Sorghum halepense* | clethodim, glyphosate, and haloxyfop-methyl | Inhibition of ACC ase,<br>Inhibition of EPSP synthase |
| | *Xanthium strumarium* | chlorimuron-ethyl, and imazethapyr | Inhibition of ALS |
| | Xanthium strumarium | chlorimuron-ethyl, and imazethapyr | Inhibition of ALS |
| | *Conyza sumatrensis* | 2,4-D, diuron, glyphosate, paraquat, and saflufenacil | Multiple Resistance: 5 Sites of Action<br>PSII inhibitors - Serine 264 Binders,<br>PS I Electron Diversion,<br>Inhibition of Protoporphyrinogen Oxidase,<br>Inhibition of EPSP synthase,<br>Auxin Mimics |
| Soybean, bean | *Amaranthus tuberculatus* | atrazine, glyphosate, imazethapyr, lactofen, mesotrione, and metribuzin | Multiple Resistance: 5 Sites of Action<br>Inhibition of ALS,<br>PSII inhibitors - Serine 264 Binders,<br>Inhibition of Protoporphyrinogen Oxidase<br>Inhibition of Hydroxyphenyl Pyruvate Dioxygenase,<br>Inhibition of EPSP synthase |

## 3. NEW HERBICIDE MOLECULES

Farmers are progressively adopting a novel category of herbicides characterized by low application rates, which operate by inhibiting crucial plant enzymes [20]. Referred to as Low Dosage High Efficiency (LDHE) compounds, these herbicides demonstrate exceptional effectiveness even at minimal doses. They offer several benefits compared to conventional herbicides. These innovative herbicide compounds allow for a significant reduction in chemical dosage, ranging from 100 to 1000 times less compared to conventional herbicides [21]. Despite such minimal application rates, these herbicides showcase exceptional herbicidal potency, contributing to their environmentally friendly profile.

### 3.1 Objectives for New Herbicides

Proposing clear objectives for new herbicides is essential for various reasons, spanning scientific, agricultural, economic, and environmental considerations. Following are the objectives as outlined by Kraehmer et al. [17].

- Effective against both grass and dicotyledonous weeds
- Minimal application rates
- Versatility for application both before and after emergence
- Exceptional selectivity within specific crop production systems
- High safety standards
- Compatible with herbicide rotation regimes (e.g., resistance management)
- Favorable environmental performance

## 4. RECENT PROGRESS IN DISCOVERING HERBICIDE NEW MODES OF ACTION (MOAS)

The identification of herbicides through novel targets or MOA constitutes an ultimate approach to addressing weed resistance. However, only a limited number of herbicides with innovative MOAs have surfaced in recent decades (Table 7).

The levels of $C_{14}$:0 and $C_{16}$:0 saturated fatty acids in cinmethylin- treated plants are declined, signifying that both types of FAT proteins are inhibited by the herbicide. The direct relationship between cinmethylin (herbicide) and FAT proteins was recognized through co-crystallization within the FAT enzyme and fluorescence-based thermal shift experiments [23]. Herbicides that impede Very Long-Chain Fatty Acid Elongases (VLFCAEs), such as oxyacetamides, thiocarbamates, and chloroacetanilides, are known to induce leaf twisting or curling [22].

**Table 7. Novel mechanisms of actions [22]**

| New MOAs | Key enzymes | Herbicide |
|---|---|---|
| Fatty acid synthesis | Fatty acid thioesterases | Cinmethylin |
| Lipid biosynthesis | Very long chain fatty acid elongases (VLCFAE) | Chloroacetanilides (Eg: alachlor)<br>Thiocarbamates (Eg: EPTC)<br>Oxyacetamides (Eg: Flufenacet) |
| Plastoquinone biosynthesis | Solanyl disphosphate synthase (SPS) | Triketone herbicides<br>Aclonifen |
| | Homogentisate solanesyl transferase (HST) | Cyclopyrimorate<br>Haloxydine |
| Amino acid biosynthesis and protein regulation | Dihydroxy-Acid Dehydratase (DHAD) | Aspterric acid (*Aspergillusterrus*) |
| | 3-Dehydroquinate Synthase | 7-deoxy-sedoheptulose (7dSH) |
| | Serine/Threonine Protein Phosphatases (PPs) | Endothall<br>Cantharidin |
| Acetyl CoA | Pyruvate Dehydrogenase Complex (PDHc) | Cyclic methylphosphonates |
| Histidine biosynthesis | Imidazole glycerol Phosphate Dehydratase (IGPD) | Tirazole phosphonates |
| De Novo pyrimidine nucleotide biosynthesis (Orotate pathway) | Dihydroorotate dehydrogenase (DHODH) | Tetflupyrolimet |
| Plastid synthesis | Peptide deformylase | Actinonin (Actinomycetes) |

Endothall and cantharidin exhibit a gradual and irreversible inhibition of Threonine/ Serine Protein Phosphatase activities [24]. Crystallographic studies have confirmed that aclonifen binds to SPS, leading to the decolorizing of treated plants by SPS blocking [22]. Previous research established that haloxydine, serving as inhibitor of suicide that imitates the binding of homogentisate, may effectively block this enzyme. Furthermore, at a concentration of 25 uM, 7dSH significantly hampers plant development to a degree comparable to an equivalent dose of glyphosate, with 7dSH demonstrating activity in the low micromolar range [25]. Although lacking preemergence activity, 7dSH has proven valuable in post-emergence applications.

Strong Isopropylmalate dehydrogenase (IGDP) inhibitors are triazole phosphonates [26]. Additionally, 1-alkylphosphonate derivatives that have significantly stronger herbicidal activity are substituted phenoxyacetoxy. particularly substituted phenoxyacetoxy compounds, exhibit markedly stronger herbicidal activity. Their efficiency in controlling broad-leaved weeds and sedges correlates with the inhibition of Pyruvate Dehydrogenase Complex (PDHc) [27].

## 5. BIO-EFFICACY OF NEW HERBICIDE MOLECULES IN DIFFERENT LEGUMES

The cultivation of various legumes faces a significant challenge due to the pervasive issue of weed infestation, leading to a substantial reduction in yield. Major weed flora occurring in different legumes is present in Table 8.

To date, only a few studies have been conducted on the application of novel herbicides to legumes.

Fluchloralin, quizalofop ethyl, imazethapyr, and oxyfluorfen demonstrated safety in cultivation of chickpea [35]. A notably reduced dry weight of weeds was detected under pre-emergence (PE) application of oxyfluorfen at 0.120 kg ha$^{-1}$, combined with hand weeding (HW) once and inter-cultivation (IC) once at 30-35 days after sowing (DAS), as well as fluchloralin at 0.675 kg ha$^{-1}$ (PE) with imazethapyr at 0.050 kg ha$^{-1}$ (PE) [35]. Significantly higher WCE was noted by oxyfluorfen at 0.120 kg ha$^{-1}$ (PE) with one HW and inter-cultivation once at 30-35 DAS (99.01%) and fluchloralin at 0.675 kg ha$^{-1}$ (PE) with imazethapyr at 0.050 kg ha$^{-1}$ (PE) (98.54%). The treatment with oxyfluorfen at 0.120 kg ha$^{-1}$ (PE) combined with imazethapyr at 0.050 kg ha$^{-1}$ (PE) resulted in significantly HEI and lower WI. However, the performance was comparable to the treatment involving fluchloralin at 0.675 kg ha$^{-1}$ (PE) with imazethapyr at 0.050 kg ha$^{-1}$ (PE) [35].

The predominant control of grassy weeds was demonstrated by clodinafop-propargyl and quizalofop-ethyl, which presents a problem in the cultivation of chickpeas since broad-leaved weeds offer a serious hazard. Nonetheless, a wide range of weeds were successfully controlled by treatments using topramezone at 13.8 g per ha and clodinafop-propargyl in combination with Na-acifluorfen at 500 g per ha, which augmented seed yield, weed control index (WCI) and WCE [28]. The study also underlined the need for additional investigation to determine the best timing and dosage for various agro-ecological circumstances.

An integrated approach involving imazethapyr at 75 g ha$^{-1}$ (PE) at 10 days after sowing (DAS) along with post-emergence (PoE) application of quizalofop ethyl at 50 g ha$^{-1}$ at 15 DAS, followed by one HW at 50 DAS, and a post-emergence tank mix application of 75 g of imazethapyr per ha along with 50 g of quizalofop ethyl per ha at 15 DAS, followed by HW once at 50 DAS, demonstrated effectiveness in diminishing weed density and their dry weight. This integrated approach resulted in higher WCE and lower WI, leading to a reduction in nutrient uptake by weeds when applied in pigeon pea [29].

According to published studies [30], among various new herbicide molecules, the sodium acifluorfen 16.5% application combined with clodinafop propargyl 8% EC at 1250 ml ha$^{-1}$ at 20 DAS exhibited superior performance, achieving WCI and WCE rates of 70.52% and 81.48%, respectively in blackgram. The treatment having similar molecules applied at reduced rate of 1000 ml ha$^{-1}$ also demonstrated significant effectiveness, with WCI and WCE rates of 63.91% and 79.42%, respectively. Overall, hand weeding two times at 20 DAS and 35 DAS showed notably better performance, followed by herbicide treatments.

Previous study in greengram [31] reported that the highest WCE (95.20%) was achieved with PoE application of sodium acifluorfen 16.5% EC and clodinafop propargyl 8% EC at 250 g ha$^{-1}$. PE application of Diclosulam 84% WDG at 26 g a.i ha$^{-1}$ showed a comparable WCE of 94.74%

**Table 8. Major weed flora in different legumes**

| Crop | Weed flora | References |
|---|---|---|
| Chickpea | *Chenopodium album* L., *Sonchus arvensis* (L.), *Rumex dentatus* (L.), *Medicago denticulata (L.). Euphorbia geniculata* (L.)., *Physalis minima* (L.), *Cirsium arvense* (L.) *Scop and Vicia hirsuta* (L.) *Gray., Paspalidium flavidum* (L.) | [28] |
| Pigeon pea | *Echinochloa colona* (L.) *Link, Celosia argentea* (L.), *Commelina benghalensis, Cyperus rotundus* (L.), *Cynodon dactylon* (L.), *Cyperus iria* (L.), *Sorghum halepense* (L.), *Eleusine indica (L.),* and *Mollugo pentaphylla* (L.) *etc.* | [29] |
| Black gram | *Chloris barbata, Cyperus rotundus, Echinochola colonum, Digitaria longiflora, Commelina benghalensis, Trianthema portulacastrum* | [30] |
| Green gram | *Alternanthera sessilis, Amaranthus viridis, Commelina benghalensis, Cyperus rotundus, Cynodon dactylon, Corchorus acutangulus, Panicum repens, Parthenium hysterophorous, Eleusine indica, Trianthema portulacastrum, Celosia argentea* and *Digera arvensis* | [31] |
| Cowpea | *Acrachne racemosa, Eleusine africana/ indica, Setaria viridis, Brachiaria spp, Cynodon dactylon, Commelina benghalensis, Cyperus rotundus, Dactyloctenium aegyptium Echinocloa crusgalli, Rottboellia cochinchinensis (exaltata), Digitaria sanguinalis, Panicum spp, Phyllanthus niruri, Parthenium hysterophorus, Solanum nigrum, Trianthema portulacasttrum, Tribulus terrestris* and *Xanthium strumarium.* | [32] |
| Soybean | *Amaranthus viridis, Digera arvensis, Eleusine indica, Digitaria sanguinalis, Cyperus rotundus, Alternanthera philoxeroides, Dactyloctanium aegyptium, Euphorbia hirta, Physalis minima, Echinochloa colonum and Phylanthus niruri,* | [33] |
| Groundnut | *Euphorbia geniculata, Alternanthera philoxeroides, Echinocloa colonum, Cynodon dactylon, Amaranthus viridis, Cyperus rotandus, Alternanthera spp., Eleusine indica, Euphorbia hirta, Dactyloctanium aegyptium, Phylanthus niruri, Parthenium hysterophorus, Convolvulus arvensis, Digera arvensis, Physalis minima, Celosia argentea, and Digitaria sanguinalis.* | [34] |

at 30DAS. This trend persisted at 45 DAS (97.68% and 96.37%, respectively) and at harvest (92.15% and 90.59%, respectively). They were followed closely by tank mix application of imazethapyr 10% SL and quizalofop ethyl 5% EC at 125 g a.i ha$^{-1}$ at 20 DAS (PoE) and tank mix application of pendimethalin 30% EC with imazethapyr 2% EC at 960 g a.i ha$^{-1}$ (PE). The study concluded that diclosulam effectively controlled weeds until harvest because of its extended half-life, while imazethapyr and quizalofop ethyl decreased weed density through their dual mode of action. Imazethapyr targeted broad-leaved weeds by inhibiting ALS (acetolactate synthase) enzyme, and quizalofop ethyl aimed grass density by ACCase inhibition, causing weed death.

Weed management treatments resulted in higher dehydrogenase activity when compared to the weedy check at 30 DAS in cowpea. The treatment involving stale seedbed and dry banana leaf mulching at 10 t ha$^{-1}$ followed by quizalofop-p-ethyl at 50 g ha$^{-1}$ (PoE) at 25 DAS exhibited the highest dehydrogenase activity, while the treatment with a normal seedbed + no weeding recorded the lowest dehydrogenase enzyme activity. This could be attributed to the reduced substrate obtainability caused by season-long weed invasion. Furthermore, diclosulam (PE) at 12.5 g ha$^{-1}$ subsequently application of quizalofop-p-ethyl at 50 g ha$^{-1}$ (PoE) at 25 DAS noted the highest urease enzyme activity, which was comparable to diclosulam (PE) at 12.5 g ha$^{-1}$ followed by hand weeding once at 25 DAS and dry banana leaf mulching at 10 t ha$^{-1}$. They were followed by quizalofop-p-ethyl at 50 g ha$^{-1}$ at 25 DAS. The observed differences in urease enzyme activity among treatments could be related to changes in the soil's pH and temperature [36].

Combined chemical treatments, specifically UPH-203 at different rates (60.0, 80.0 and 100 g ha$^{-1}$) along with Na-Acifluorfen 10% SL at corresponding rates (123.7, 165, and 206.2 g ha$^{-1}$), demonstrated improved WCE compared to the application of individual chemical treatments in Soybean. The reason for this improved performance is because weed species recovered more quickly after times when a single herbicide application was made. In terms of net production value (NPV), UPH-203 at 100 g ha$^{-1}$ and Na-Acifluorfen 10% SL at 206.2 g ha$^{-1}$ attained the maximum value at 1.15, followed by double hand weeding (1.10). Remarkably, none of the treatments showed any signs of phytotoxicity, including stunted growth, hyponasty/epinasty, yellowing of the leaves, necrosis, wilting, *etc.* [33].

Among various herbicidal treatments, higher WCE of 72.71%, and a favorable B:C ratio of 1.75 were recorded with Imazethapyr + Propaquizafop at 75 + 62.5 g ha$^{-1}$ applied at 20 DAS in soybean. This was followed by Imazethapyr at 100 g ha$^{-1}$, which resulted in a WCE of 70.76% and a B:C ratio of 1.57. Another effective treatment was Imazethapyr + Bentazone at 75 + 75 g ha$^{-1}$, which displayed a WCE of 68.38% and a B:C ratio of 1.60 at 45 days after application (DAA) [37].

In groundnut cultivation, diclosulam (PE) at 20 g ha$^{-1}$ followed by HW once at 40 DAS resulted in a significantly decreased density and dry weight of total weeds, along with higher WCE. This was followed by another effective treatment, involving diclosulam (PE) at 20 g ha$^{-1}$ followed by PoE application of cycloxydim at 100 g ha$^{-1}$ at 20 DAS. This trend also interpreted a higher B:C ratio because of the reduced weeding costs and an increase in both pod and haulm yield [34].

Hand weeding produced higher weed-related measures in the study at 20 and 45 DAS in groundnut. Compared to other herbicide treatments, acifluorfen 16.5% (PoE) + clodinafop-propargyl 8% EC (206.25 + 100 g ha$^{-1}$) had substantially better WCE, Weed Management Index (WMI), and HEI values of 90.22%, 1.37, and 10.64, respectively, and a lower WI of 4.07. Lower weed dry weight and increased pod yield from these treatments were linked to the higher HEI [38].

## 6. PHYTOTOXICITY EFFECT OF NEW HERBICIDE MOLECULES IN DIFFERENT LEGUMES

The application of flumioxazin resulted in a 59% reduction in crop stands, while fomesafen + S-metolachlor led to an 11% decrease. Sulfentrazone-based programs exhibited variability, with pre-plant treatments typically showing fewer plants compared to pre-emergence treatments. Stunting was observed across various programs, with injury levels exceeding 20%. The flumioxazin programmes caused substantial crop damage, reaching 86% and 91%. Crop damage was exacerbated by excessive rains around planting time, which seeped the pesticide into the seed zone. However, the injury had largely reduced to less than 10 per cent by midseason. Injury from several sulfentrazone treatments *i.e.,* fomesafen + S-metolachlor, and both flumioxazin treatments persevered into midseason, surpassing 20%. Although higher damage in flumioxazin treatments raised concerns, the crop eventually recovered. The study also concluded that heavy rainfall had an adverse impact on the efficacy of residual herbicides [39].

As reported earlier [40], for groundnut cultivation, treatments using twice the recommended doses of fenoxaprop-p-ethyl at 875 ml ha$^{-1}$ and 1750 ml ha$^{-1}$ did not show any phytotoxicity. A number of signs were included in the assessment, including leaf epinasty, chlorosis, vein clearing, resetting, tip burning, wilting, and necrosis.

According to Pankaja and Dewagan [41], no phytotoxic effects were observed on blackgram at 3, 5, 7, and 15 DAA (days after application) of quizalofop-ethyl at 37.5 g ha$^{-1}$ and fenoxaprop-p-ethyl at 100 g ha$^{-1}$. The study found that these herbicides were completely safe for the crop, as evidenced by the absence of phytotoxic symptoms such as epinasty, vein clearing, necrosis, hyponasty, and wilting. Additionally, there was no residual effect on the soil.

Assessing the phytotoxicity of herbicides using epinasty and chlorosis revealed that treatments with imazethapyr at 50 g ha$^{-1}$, imazethapyr + imazamox at 40 g ha$^{-1}$, and imazethapyr + imazamox at 60 g ha$^{-1}$ exhibited phytotoxicity at 15 DAA [28]. These treatments resulted in bushy growth with narrow leaves, and due to the herbicides' greater toxic impact, chickpea plants did not recover well from the phytotoxic effects, which persisted until the blossoming stage. While the remaining treatments showed some degree of phytotoxicity, it was minimal, and the crop exhibited satisfactory recovery and growth.

In groundnut, diclosulam (PE) at 20 g ha$^{-1}$ and subsequently application of cycloxydim at 100 g ha$^{-1}$ at 20 DAS demonstrated superiority in suppressing growth of weeds during the early stages of fodder sorghum. This effectiveness was attributed to the extended herbicidal activity of diclosulam and a reduction in the weed seed bank. Crucially, no herbicide tested showed any negative effects on the dry fodder production, growth characteristics, or germination of the residual fodder sorghum crop [34].

## 7. RESIDUAL EFFECT OF NEW HERBICIDE MOLECULES IN DIFFERENT LEGUMES

Forage sorghum, mung beans, and cowpeas that were planted after the wheat crop showed no signs of fenoxaprop's 100 g ha$^{-1}$ residual activity [42]. This indicates that the fenoxaprop application did not have a lingering impact that negatively affected the subsequent growth and development of these crops.

In white bean cultivation, crop injury tended to increase with the dose of imazethapyr. Specifically, when imazethapyr induced up to 62% observable injury when administered at a higher rate of 300 g ha$^{-1}$. This higher dose also led to a reduction in various growth parameters, including plant height, shoot and root dry weight and yield (32, 48, 20 and 77%, respectively), compared to the application of imazethapyr as pre-emergence at a lower rate of 50 g ha$^{-1}$ [43].

The initial quizalofop-P-tefuryl residue concentrations in the plant and soil samples were 0.41 to 1.41 mg kg$^{-1}$ and 0.95 to 2.3 mg kg$^{-1}$, respectively. The results indicated that the half-life values were 4.1 to 4.14 days for soil and 0.47 to 0.64 days for plants. The average recoveries were plant (85.33%), field soil (89%), and seed (86.33%), respectively. Importantly, residues were found to be less than the noticeable limit in all the harvested plant, seed, and soil samples regardless of treatments, suggesting that the use of quizalofop-P-tefuryl was considered completely safe for the blackgram crop in this study [44].

The LOQ (limit of quantification) for quizalofop-p-ethyl, imazethapyr, and pendimethalin was 5.0 μg kg$^{-1}$, while for oxyfluorfen, it was 10.0 μg kg$^{-1}$. Less than 11% separated the enlarged uncertainty for these herbicides' presence in peanuts. Importantly, the residues for these herbicides were less than the detection levels, indicating that they were not present or present at very low concentrations in the peanut samples [45].

Imazethapyr residues were found in the soybean grain samples with amounts ranged from 0.006 to 0.018 g g$^{-1}$ in all five different locations of a soybean field where the herbicide was sprayed (PoE) at a rate of 100 g ha$^{-1}$ for weed control. However, residues were identified in the soil at one place having above 0.0015 μg g$^{-1}$ and in other four locations it was below 0.0010 μg g$^{-1}$. Comparing the soil residues to the plant samples, they were generally lower. This research suggests that after applying imazethapyr to soybean crops, a pre-harvest period of 90-102 days is appropriate [46]. Additionally, the average imazethapyr recovery in grain, straw and soil of soybean was reported as 80%, 83% and 79%, respectively.

In a study using Ultrasonic Bath Assisted Extraction (USBE), the mean quizalofop ethyl recovery at different levels of fortification was determined to be 87.2% (soil), 83.4% (groundnut haulm), and 82.7% (kernel), respectively [43]. Based on the residues of quizalofop ethyl found in soil, groundnut haulm, and kernels at varying harvest times, the study also came to the conclusion that, in South India's tropical climate, the molecule can be used safely in groundnut to control grassy weeds at a dose of 50 g ha$^{-1}$, with a recommended pre-harvest interval of 110 days [47].

Plots that received quizalofop ethyl at 100 g ha$^{-1}$ had the highest concentration of its residue in the soil; these were followed by treatments that received 75 g and 50 g of ai ha$^{-1}$. Across the various treatments, the mean concentration of residues ranged from 0.012 to 0.0384 μg g$^{-1}$ in the soil. The decrease in the application dose resulted in a decrease in quizalofop ethyl residue concentration in the soil. Moreover, regardless the dosage of quizalofop applied, the concentration in groundnut haulm and kernel samples taken at harvest (110 DAA) was below the quantitative limit of 0.01 μg g$^{-1}$. Significantly, it was discovered that the residues were less than MRL (Maximum Residue Limit) *i.e.,* 0.05 μg g$^{-1}$ set for crops including sugar beet and soybean. Additionally, even when the highest dose of quizalofop ethyl was administered *i.e.,*100 g ha$^{-1}$, the residues in groundnut kernels and haulm were substantially less than the MRL of 0.1 mg kg$^{-1}$ [47].

## 8. CONCLUSION

Weed resistance to many of the herbicides now in use has grown widely, creating a need for novel herbicides with distinct Modes of Action (MOAs). Recent discoveries of promising herbicide targets and related herbicides offer potential solutions for managing resistant weeds. However, it is anticipated that weed evolution will lead to resistance against these new herbicides in the future. Therefore, the continuous development of herbicides with unique MOAs having high selectivity, slow resistance growth, and eco-friendliness is crucial for addressing both emerging and current herbicide resistance challenges. Having a diverse set of formulations and methods in the form of herbicides is fundamental for effective weed management. This necessitates ongoing efforts in researching and developing new herbicide molecules. The application of these novel herbicides in legumes holds promise for sustainable cultivation through efficient weed management. However, extensive research is essential to optimize the dosage and timing of these new herbicide molecules under various agro-ecological conditions specific to legume crops to ensure the sustainable and effective use of these tools in weed control for legume cultivation.

## COMPETING INTERESTS

Authors have declared that no competing interests exist.

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