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Herbicide Combinations for Effective Weed Management in Rice

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Review Article

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ABSTRACT

Rice (*Oryza sativa* L.) is the most important food crop catering half of the world's population. India being the second largest producer of rice, needs to produce around 120 million tons of rice by 2030 to feed its one and a half billion plus population. Weeds are undoubtedly a major biotic constraint to rice production in most of the rice growing areas of the world. Rice fields are very often characterized by a complex plurispecific weed flora, comprising of grasses, sedges, and broad-leaved weeds (BLWs). They usually grow faster than rice and absorb available water and nutrient earlier than the rice and suppress rice growth. Cultural and mechanical methods of weed management in general, are time consuming, cumbersome and laborious apart from being less effective because of chance of escape and regeneration of weeds from roots or rhizome that are left behind. Herbicides offer the most effective, economical and practical way of weed management. Since rice ecosystems usually harbours a variety of weeds, the use of a single herbicide cannot give satisfactory results. Moreover, continous use of such herbicides leads to the evolution of

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weeds resistant to several herbicides. Therefore, more convenient option would be single shot application of ready mix or tank mix combination of herbicide. The herbicide mixtures broaden the spectrum of weed control in single application. The ideal herbicide combinations are those that effectively target the weed species while minimizing toxicity to crops, thereby exhibiting enhanced selectivity. Using herbicide combinations allows for reduced herbicide use rates compared to using a single herbicide. Additionally, apart from providing broad-spectrum weed control, herbicide combinations reduce the herbicide load in the environment and minimize application costs. Among the various combination herbicides available, the ones having pre-emergence and post-emergence herbicides combined had shown better weed control with single shot application at reduced cost. Some of the ready-mix herbicide combinations that are gaining greater importance includes Pretilachlor + Pyrazosulfuron-ethyl, Pendimethalin + Penoxsulam and Butachlor + Penoxsulam.

Keywords: Herbicide combinations; herbicide resistance; rice; weed management.

1. INTRODUCTION

Rice (*Oryza sativa* L.), holds immense significance, being the staple food crop, nourishing almost half of the world’s population. Among all nations, India possesses the largest expanse of land dedicated to rice cultivation, covering approximately 40.10 million hectares. In the year 2020-21, India achieved a rice production of 102.36 million metric tons, with an average yield of 2.55 tons per hectare, as reported by the Government of India (GOI, 2020). However, considering the burgeoning population of over 1.5 billion, India faces the challenge of producing 120 million tons of rice by 2030 to meet its food requirements. Therefore, a comprehensive assessment of this scenario emphasizes the urgent need to enhance, intensify, and adopt cutting-edge scientific and technological advancements to augment rice productivity within the country.

Weeds are undoubtedly a significant biotic constraint to rice cultivation in most of the rice growing areas around the world, leading to approximately 33 percent of the total yield losses, surpassing the impact of insects (26 percent) and diseases (20 percent) (Saha et al. 2022). Rice fields commonly harbor a diverse weed community comprising grasses, sedges, and broad-leaved weeds (BLWs) (Kumar and Rana, 2013). These weeds tend to outgrow rice plants, deplete water and nutrients ahead of rice, and impede rice growth (Garg et al. 2020). In dry direct seeded rice (DSR), uncontrolled weed growth can cause yield reductions ranging from 96 to 100 percent (Maity and Mukherjee, 2008). Timely and effective weed control is crucial for maintaining high productivity. Implementing efficient weed management practices has resulted in an impressive 85.5 percent increase in grain yield (Mukherjee and Singh, 2005). Nevertheless, no single weed control method can effectively manage all weed species, necessitating the development and adaptation of flexible integrated weed management (IWM) strategies for sustainable long-term weed control. While various herbicides are available and commonly used, they often exhibit limited efficacy in reducing the populations of all weed types. Consequently, devising an effective weed management strategy remains a challenge for widespread adoption of DSR.

The predominant use of pre-emergence (PE) herbicides in rice cultivation typically falls short in delivering effective weed control throughout the growing season. While a single application of herbicide can effectively manage weeds initially, continuous reliance on these herbicides contributes to the development of weeds that are resistant to several herbicides. Consequently, there is a growing need for alternative post-emergence (PoE) herbicides that can offer comprehensive weed control without negatively impacting rice growth and yield. To optimize weed control effectiveness and reduce application costs, the adoption of herbicide combinations and the integration of herbicides with manual or mechanical methods have become increasingly common practices, rather than exceptions (Rana et al. 2015).

2. WEED FLORA IN RICE

Weeds pose a significant biotic limitation to the rice growth and productivity. Issues of weed infestation in rice has become increasingly challenging due to changes in rice cultivation methods, driven by factors such as labour scarcity and water availability. The adoption of direct seeding methods has gained popularity as a means to reduce labour dependency, but this has led to a more complex weed scenario. Rice fields are now dominated by a diverse mix of grassy weeds, sedges, BLWs, and aquatic weeds, influenced by various factors like agro-climatic conditions, soil types, crop establishment techniques, nutrient and water management practices, the soil weed seed bank, and the specific cropping systems employed in different rice ecologies.

Uncontrolled weed growth in paddy fields has resulted in substantial yield reductions, with dry-seeded rice, wet-seeded rice and transplanted rice experiencing a grain yield decrease of 75.8, 70.6 and 62.6 per cent respectively (Singh et al. 2005). In dry DSR, weed competition is particularly severe compared to transplanted rice due to the concurrent emergence of rice and weed seedlings and the absence of standing water to suppress weed emergence and growth during the initial stages of crop emergence, as reported by Singh et al. (2013). The direct-seeded crop can suffer heavy damage ranging from 50 to 100 percent due to weeds (Rana et al., 2014). Effective weed management practices are crucial for achieving optimal rice yields.

In the wet-seeded rice ecosystem, the predominant weed species include grasses such as weedy rice (*Oryza sativa f. spontanea*), *Leptochloa chinensis* and *Echinochloa stagnina.* Additionally, sedges such as *Cyperus* spp. and *Fimbristylis miliacea*, along with BLWs like *Eichhornia*, *Ludwigia perennis*, and *Limnophila heterophylla* are commonly found (Mounisha and Menon, 2020). According to IRRI (2020), the most problematic weeds documented in rice fields across Asia includes five grass species (*Oryza sativa f. spontanea, L. chinensis, Echinochloa colona, E. crus-galli, Ischaemum rugosum,*), four sedge species (*F. milacea, Cyperus difformis, C. iria, Scirpus juncoides*), and three BLWs (*Eclipta prostrata, Sphenoclea zeylanica, Ludwigia hyssopifolia*). These weed species pose significant challenges to rice cultivation in the region.

The extent of yield reduction caused by weed competition is influenced by various factors, including the composition and density of the weed flora, the duration of competition, management practices, and prevailing climatic conditions. Therefore, implementing timely and effective weed management practices is crucial to achieve optimal grain yield in rice crops. By controlling weed growth and minimizing competition, farmers can maximize the productivity and profitability of their rice fields.

3. CRITICAL PERIOD OF CROP-WEED COMPETITION

The concept of critical period for weed control (CPWC) refers to a particular phase in the crop's life cycle, when it is highly susceptible to competition from weeds. During this period, effective weed control becomes crucial to prevent significant yield losses. Understanding the CPWC is valuable for making informed decisions about the timing of weed control interventions and reducing herbicide usage. Ideally, weeds appearing before or after the CPWC should not pose a significant threat and should not result in substantial reduction in yield. Therefore, weeding during the CPWC can lead to crop yields similar to those obtained under conditions of continuous weed suppression throughout the growing season. Typically, one-third of the crop's life cycle is considered critical for weed control (Anwar et al., 2012).

Effective weed control during the initial stages of rice growth, specifically from 0 to 40 days after sowing (DAS), has been shown to enhance the productivity of dry DSR (Maity and Mukherjee, 2008). Singh *et al*. (2008) demonstrated the CPWC for DSR is from 15 to 45 DAS, while Khaliq and Matloob (2011) stated that the period from 20 to 50 DAS is critical for crop in dry DSR.

For transplanted rice, the CPWC is observed to be from 20 to 40 days after transplanting (DAT), as documented by Mukherjee et al. (2008). In wet-seeded rice, the critical period extends from 15 to 60 DAS, and about 60 percent of weeds emerge during the 7-30 DAT, exerting strong competition with rice plant (Saha and Rao, 2010). To prevent any yield losses, a weed-free period from 25-45 DAS is required for dry DSR (Singh et al. 2011).

4. WEED MANAGEMENT IN RICE

Traditional methods of weed management are often time-consuming, laborious, and less effective due to the possibility of weed regrowth from leftover roots or rhizomes. The visual similarity of certain grassy weeds with crop plant, makes hand weeding a challenging task. Manual weeding, which requires 2-3 rounds per season and significant labor input, can be costly for weed control, involving more than 80 person-days per hectare. As a result, chemical weed management using selective herbicides is considered an alternative or supplement to manual weeding, offering a more efficient and cost-effective approach to weed control in rice fields.

Herbicides are regarded as the most effective, economical, and practical method of weed management, providing superior weed control and requiring less labour compared to manual or mechanical methods (Chauhan et al. 2014). PE herbicides such as butachlor, pretilachlor, oxadiazon, pendimethalin, anilofos and oxadiargyl are recommended for control of early weed flushes. However, these herbicides have varying effects on different weed species and tend to have a narrow spectrum of control, primarily targeting annual grasses and some sedges.

To achieve higher weed control efficiency and crop yield, careful selection of herbicides, accurate timing of application, proper dosage, and appropriate application methods are crucial factors. Jacob et al. (2004) noted that one major advantage of chemical weed control is the reduction in cultivation costs. However, Mandal et al. (2011) highlighted the challenge of controlling the second weed flush at 25 to 30 DAS. Rice ecosystems typically harbours a diverse range of weeds, and relying on a single herbicide may not yield satisfactory results (Mounisha, 2020).

Controlling complex weed flora through sole application of PE or PoE herbicide is a challenging task, and prolonged use of the single herbicide may contribute to herbicide resistance in weeds. Farmers often resort to applying additional PoE herbicides or resort to manual weeding, which increases the cost and effort involved in weed management. It is advisable to encourage the use of multiple herbicides with different active ingredients for broad-spectrum weed control (Yadav et al. 2019).

5. HERBICIDE RESISTANCE AND WEED SHIFT IN RICE

Herbicide resistance (HR) is a widespread problem in agriculture. It’s the inherited ability of an individual plant to survive a herbicide application that would kill a normal population of the same species. While herbicides effectively and economically control weeds in DSR, the continuous use of the same herbicide or those with similar modes of action can lead to the development of herbicide resistance and a shift in weed species, either gradually or rapidly. Several factors contributes to the development of herbicide resistance in weeds, such as prolonged residual activity, single target site of action, specific modes of action, and high effectiveness against a wide range of weed species (Raj and Syriac, 2017). This resistance has become a major concern in weed control, jeopardizing the sustainability of rice cropping systems and impacting global food security while increasing management costs (Hicks et al. 2018).

Mahajan and Chauhan (2008) observed that the extensive use of PE herbicides such as butachlor, pretilachlor and anilofos for controlling early flushes of grassy weeds in transplanted rice led to increased instances of HR. The rapid and widespread evolution of HR weeds has disrupted weed management in commercial agriculture. This issue has escalated to epidemic proportions, resulting in higher crop production costs, reduced farm profitability, and, in some cases, forcing farmers to exit the business. Current strategies to mitigate the emergence and spread of HR weeds focus on diversifying the mechanisms of action (MOAs) of herbicides. Such efforts includes rotating and sequencing the herbicides with different MOAs across successive growing seasons or within the same season, and employing herbicide combinations which involves exposing weeds to multiple MOAs simultaneously (Beckie, 2006).

6. HERBICIDE COMBINATION/ MIXTURES

In intensive agriculture, it is common to apply two or more herbicides concurrently, either as pre-packaged formulations or by mixing different herbicides prior to application. This approach is employed because single herbicides often have a narrow spectrum of activity, which often fails to provide satisfactory and season-long weed control. Weed populations typically comprises of multiple species with varying degrees of sensitivity to herbicides, necessitating multiple herbicide applications or additional measures for effective weed control. However, this approach escalates the cost associated with weed control and overall crop production expenses.

The ideal herbicide combinations are those that effectively target the weed species while minimizing toxicity to crops, thereby exhibiting enhanced selectivity. Using herbicide combinations allows for reduced herbicide use rates compared to using a single herbicide. Additionally, apart from providing broad-spectrum weed control, herbicide combinations reduce the herbicide load in the environment and minimize application costs. Even at lower doses, combining different herbicides has been found to be more efficient against a wide range of weeds (Avudaithai and Veerabadran, 2000).

According to Paswan *et al*., using herbicides with distinct modes of action in combination, targets different sites in weeds, thereby preventing the development of target site resistance in susceptible species. Herbicide mixtures help to address resistance issues and the potential shifts in weed populations that can occur when relying on a single herbicide (Duary et al. 2015). Herbicides used in combination, whether applied pre-plant, pre-emergence, or post-emergence, broaden the weed control spectrum and extend the duration of residual weed control.

The superiority of tank mixtures of herbicides in reducing weed populations compared to using a single herbicide has been reported by Mahajan and Chauhan (2015), suggesting that tank mix herbicides may have a greater synergistic effect for broad-spectrum weed control. The purpose of combining herbicides aims at broadening the spectrum of weed control, ensuring that each herbicide in the mixture can target and control the weeds that might be missed by the other herbicides.

6.1 Advantages of Herbicide Combinations over Single Herbicide

Herbicide mixtures offer several advantages over using a single herbicide. These advantages highlight the practical benefits of using herbicide mixtures for effective weed management in agricultural systems. It includes:

1. Reduction in production cost: Using herbicide mixtures can help save time and labour compared to applying multiple herbicides separately. This reduces the overall cost of weed control in crop production.
2. Reduction in soil compaction: By eliminating multiple field operations needed to apply different herbicides individually, herbicide mixtures can help minimize soil compaction, which is beneficial for soil health and crop growth.
3. Increase in the spectrum of weeds controlled: Herbicide mixtures broaden the range of weed species controlled, providing more comprehensive weed management. This ensures effective control of a wider variety of weeds in the field.
4. Extension of weed control duration: Herbicide mixtures can extend the period of weed control, offering prolonged suppression or elimination of weeds throughout the growing season. This helps maintain clean fields and reduces competition between weeds and crops.
5. Improvement in crop safety: Combining minimum doses of selected herbicides, rather than applying a single high dose of one herbicide, improves crop safety. This reduces the risk of herbicide damage to crops while still achieving effective weed control.
6. Reduction in crop and soil residues: Using minimum doses of persistent herbicides in mixtures can help reduce crop and soil residues of these herbicides. This is beneficial for minimizing any potential environmental impact associated with long-lasting herbicides.
7. Delay in the appearance of HR weeds: The use of herbicide mixtures can help delay the development of HR weed species. By employing different modes of action and targeting multiple weed vulnerabilities, mixtures make it more challenging for weeds to develop resistance to the herbicides.

6.2 Types of Herbicide Interactions

The herbicide interactions in mixtures can have different effects, such as, additive, synergistic, or antagonistic interactions. These interactions impact the overall activity and effectiveness of the herbicide mixture. In the case of additive interactions, the activity of the mixture equals combined activities of each herbicide when applied separately. This means that the herbicides in the mixture work independently and their combined effect is simply additive.

Synergistic interactions occur when the activity of the mixture exceeds the combined activities of the individual herbicides. In this case, the individual herbicides enhance each other's effectiveness, resulting in a more potent weed control action. Synergistic interactions can be beneficial for achieving better control of problematic weeds. However, they may also cause problems if they result in higher herbicidal activity on crop plants.

On the other hand, antagonistic interactions happen when the activity of the mixture is less than the combined activities of the individual herbicides. Antagonism can reduce the effectiveness of the herbicide mixture and pose challenges in weed control. For instance, when a contact herbicide like glufosinate or paraquat is combined with a systemic herbicide like glyphosate, the contact herbicide rapidly damages the weed’s foliage. This damage restricts the weed’s capacity to absorb an adequate amount of the systemic herbicide, thereby lowering its effectiveness. However, in some cases, antagonism can be advantageous when it reduces herbicide activity on crops, minimizing the risk of crop damage. When antagonism occurs, higher doses of the concerned herbicide are typically needed, whereas synergism allows for reduced application rates. The effectiveness of such interactions depends on type and growth stage of the targeted weeds.

In agriculture, selecting the appropriate herbicide combinations is crucial for long-term weed control, as it reduces input costs, prevents yield losses, and minimizes environmental pollution. Further research and field trials are needed to better understand herbicide interactions and optimize their use for effective and sustainable weed management in agricultural practices.

In agriculture, selecting the appropriate herbicide combinations is crucial for long-term weed control, as it reduces input costs, prevents yield losses, and minimizes environmental pollution. It's important to note that the specific interactions between herbicides can vary depending on factors such as weed species, growth stage, environmental conditions, and formulation compatibility. Further research and field trials are needed to better understand herbicide interactions and optimize their use for effective and sustainable weed management in agricultural practices.

6.3 Mechanisms of Herbicide Interactions

Herbicide interactions within mixtures can take place before, during, or after application of the formulation. This indicates that herbicides can engage in physical or chemical interactions within the spray solution or biological interactions within the plant. The mechanisms responsible for these interactions are broadly categorized into four groups: biochemical, physiological, chemical and competitive (Zhang *et al.* 1995). According to this classification, the herbicide interactions in mixtures can be attributed to the following:

a) Variations in the quantity of herbicide that reaches its targeted site of action, as a consequence of its absorption, translocation, or metabolism being influenced by the presence of another herbicide.
b) Interactions at the target site occurs, when one herbicide in the mixture affects the binding of the other herbicide at its specific site of action.
c) Interaction between combined herbicides can result in contrasting effects on the same physiological mechanisms in the plant or enhance the overall effect through synergy.
d) Chemical reactions occurring between the combined herbicides, can lead to the formation of inactive complexes or increase the rate of metabolism.

6.4 Factors Affecting Herbicide Interactions

- The behaviour of herbicide mixtures can be significantly influenced by where and how well the combined herbicides enter and move within the plant.
- Nature and magnitude of herbicide interactions primarily depend on the characteristics of the combined herbicides, such as their chemical composition, absorption, movement within the plant, mechanism of action, and metabolic pathways.
- The entry point and the mobility of the herbicide molecules combined, within the plant can have a notable impact on the behaviour of the herbicide mixture.
- Antagonistic interactions can arise when one herbicide undergoes increased metabolism in the presence of another herbicide.
- The nature of interactions between herbicides combined can vary, depending on the targeted plant species.
- The growth stage of weed plants often influences the degree of interactions between combined herbicides.
- Antagonistic interactions between graminicides (herbicides targeting grasses) and broadleaf herbicides arise from the morphological and physiological distinctions between grasses and BLWs.

6.5 Types of Herbicide Mixture

There are two types of herbicide mixtures:

- Factory-mix/pre-mix: These are herbicide mixtures prepared in the factory with specific proportions. Examples include Almix, Londax power, and Coreon. They are typically used when there is an immediate need for weed control in certain crops. Ready-mix herbicides that can effectively control wide range of weed species are now available in the market, reducing the need for manual tank mixing and avoiding potential compatibility issues between herbicides. It is important to determine the optimal timing for applying these new herbicides to ensure weed populations are brought below the threshold level.
- Field-mix/tank-mix: This involves mechanically mixing two or more herbicides with their required quantities in the spray tank just before application to the field. For example, atrazine + pendimethalin can be mixed together for enhanced efficacy and broad-spectrum weed control in crops where these herbicides are selective. It is crucial to follow the instructions provided on the label of each herbicides, regarding tank mixes.

The following examples illustrate the effectiveness of tank mix applications:

- Tank mix application of cyhalofop-butyl with pyrazosulfuron-ethyl at 18 DAS can effectively manage mixed weed flora in wet-seeded rice, resulting in the highest benefit-to-cost (B:C) ratio and net returns (Atheena, 2016).
- Tank mix application of cyhalofop-butyl + penoxsulam + fipronil has shown reduced incidence of dead heart, white ear, weed density, and weed biomass, while increasing weed control efficiency (WCE), grain yield, net returns, and B:C ratio (Mohapatra and Tripathy, 2017).

In the case of PE application, a tank mixture of bispyribac sodium with metsulfuron-methyl + chlorimuron ethyl has been effective in controlling weed populations and achieving higher profitability in transplanted rice. The highest net returns and B: C ratio were also recorded under the same herbicide combination (Hossain and Mondal, 2014).

7. HERBICIDE COMBINATIONS FOR WEED MANAGEMENT IN RICE

The rice ecosystem contains a diverse range of weeds, and relying on a single herbicide often fails to deliver satisfactory results. Most herbicides used in rice cultivation are specific to certain weed species, offering limited control (Mukherjee and Singh, 2005). Over the past 25 years, numerous herbicides have been tested for effective weed management in rice, utilizing different application timings such as PE, PoE, and early PoE. However, the effectiveness of PE herbicides is sometimes inadequate due to their limited control range and the requirement of continuous water stagnation in the fields. In such cases, PoE herbicides become the preferred option as they provide season-long weed control (Puniya et al. 2007). However, the application of separate PE and PoE herbicides increases the cost involved. Consequently, many farmers are increasingly adoping the use of herbicide mixtures applied in a single application to achieve comprehensive weed control in rice fields (Lap et al. 2013).

Herbicide mixtures offer the advantage of a wider range of weed control in a single application [38]. Combining herbicide effective against grasses with one that targets BLWs can address both types of weeds, while a combination of a grass effective herbicide with another that controls both BLWs and sedges can further extend the spectrum of weeds controlled (Mukherjee, 2006).

Using a broad-spectrum herbicide that includes PE and PoE herbicides is crucial for achieving effective weed control throughout the growing season and preventing the emergence of problematic weed plants or the development of HR weed biotypes (Yadav et al. 2009) Judiciously chosen combination herbicides offer more effective weed control compared to single herbicide applications (Khaliq et al. 2012). In a study conducted by Chauhan and Yadav (2013) it was revealed that using two or more herbicides may become an integral part of future integrated techniques to achieve better control of complex weed populations in DSR. Combining compatible herbicides from different chemical families, such as 2,4-D and dicamba for BLWs, can help manage specific weed populations. Herbicide combinations can also address multiple weed categories simultaneously, such as grasses and BLWs. For instance, a combination product of chlorimuron and metsulfuron effectively controls sedges and grassy weeds in rice (Choudhury et al. 2016). The use of multiple herbicides with different active ingredients is recommended for broad spectrum weed control (Mitra, 2022).

Herbicide mixtures are regarded as powerful tools for cost-effective control in intensive agriculture, and both tank mixes and proprietary mixtures expand the weed control spectrum with a single application (Damalas, 2004). In DSR, a combination of graminicides and a herbicide for sedges and BLWs has been found to be more effective for broad-spectrum weed control (Karim et al. 2004). Utilizing a grass-effective herbicide in conjunction with a herbicide designed for BLWs can effectively control both types of weeds (Mukherjee, 2006).

Commercial herbicide mixtures are now available in the market, and compatible herbicides can also be tank mixed before application as demonstrated by Lagator et al. 2013. Additionally, new ready-mix combinations of herbicides have been developed, eliminating the need for manual tank mixing and the potential for compatibility issues. Recently, herbicide mixtures such as bensulfuron-methyl + pretilachlor, pendimethalin + pyrazosulfuron-ethyl, penoxsulam + cyhalofop-butyl, metsulfuron-methyl + chlorimuron-ethyl, pendimethalin + penoxsulam, triafamone + ethoxysulfuron, bispyribac sodium + metamifop have shown improved efficacy in broad-spectrum weed control. The application rates and timings of these herbicide mixtures have been standardized to effectively suppress weeds during the early 5-6 weeks of rice crop establishment. These low dosage, high efficacy herbicide mixtures with a broad spectrum of weed control are expected to effectively manage weeds during the CPWC for up to 35 - 40 days after weed emergence. The combined application of appropriate PE and PoE herbicides, timed correctly according to weed growth stages, is key to crucial for effective weed management.

8. READY MIX HERBICIDE COMBINATIONS USED IN RICE

Some of the important pre-mix/ready mix herbicides utilized in rice cultivation can be categorized into different groups, outlined as follows:

8.1 Pre + Pre- Emergence Herbicides

8.1.1 Bensulfuron methyl 0.6% +pretilachlor 6%

Bensulfuron methyl 0.6% +Pretilachlor 6% (commercial names: Londax Power, Eraze) is a herbicide mixture noted for effectively managing BLWs, sedges, and grasses in rice when used as a PE or as early PoE treatment. This combination has shown to be effective against a diverse weed population in rice fields without inducing any phytotoxic effects on the crop (Sunil et al. 2010). Bensulfuron-methyl, part of the sulfonylurea herbicides family, offers broad-spectrum control of BLWs and sedges in rice field. It has been designed for selective PE and PeE management of both annual and perennial weeds and sedges. Pretilachlor, on the other hand, targets pre-emergence control of grassy weeds, particularly effective against *Echinochloa crusgalli*, although it also adversely affects broadleaf weeds (Reddy et al. 2012).

Pretilachlor is readily absorbed by the hypocotyls, mesocotyls, and coleoptiles, where it functions as a cell division inhibitor. Bensulfuron methyl is taken up by the roots and shoots of germinating weeds and acts by inhibiting the acetolactate synthase (ALS) enzyme.

Sunil et al. (2010) suggested that PE application of bensulfuron methyl combined with pretilachlor at the rate of 0.06 + 0.60 kg a.i ha^{-1}, followed by one inter cultivation at 40 DAS, resulted in a significantly lower weed population and dry weight. This treatment also achieved higher grain and straw yields (4425 kg ha^{-1} and 5020 kg ha^{-1}, respectively), along with higher net returns and B:C ratio. Similarly, the PE application of bensulfuron methyl at 60 g ha^{-1} combined with pretilachlor at 600 g ha^{-1}, applied 3 DAT, proved to be very effective in lowering the weed biomass in transplanted rice, leading to higher grain yields and net returns. This herbicide mixture effectively suppressed all predominant weeds throughout the growing season, resulting in higher WCE and grain yield. Therefore, the application of bensulfuron methyl 0.6% + pretilachlor 6% at 60 + 600 g ha^{-1} at 3 DAT could be recommended for broad-spectrum weed management and higher yield (Mishra, 2019).

8.2 Pre-emergent + Early Post Emergence

8.2.1 Pretilachlor + pyrazosulfuron-ethyl

Pyrazosulfuron ethyl combined with pretilachlor is a systemic and selective herbicide mainly used for controlling annual grasses, sedges, and BLWs in both DSR and transplanted rice. Pyrazosulfuron ethyl is absorbed by the roots and shoots of weed plants and translocated through the phloem to young meristematic areas.

After absorption, weeds exhibit chlorosis within a week, followed by necrosis. Pretilachlor, the companion herbicide, is a PE, broad-spectrum, systemic herbicide from the chloroacetamide family, that controls all types of weeds in rice. It is readily absorbed by the hypocotyls, mesocotyls, coleoptiles, and somewhat by sprouted weed roots. Pretilachlor works by affecting cell division and elongation in seedling shoots by inhibiting ALS, which is essential for amino acid synthesis. When these two ready-mix herbicides are applied together in the field, their combined efficacy becomes greater than their individual applications, resulting in significant inhibition of the diverse weed flora in transplanted rice (Mondal et al., 2018).

The ready-mix combination of pretilachlor and pyrazosulfuron-ethyl at 615 g ha^{-1}, used as a PE treatment, has been reported to be highly effective (91-96%) against the composite weed flora in transplanted rice, resulting in higher grain yield and B: C ratio (Yadav et al. 2018). When applied at 600 g ha^{-1} on 6 DAS in direct-seeded rice, this herbicide combination proved to be the most effective weed control method, delaying early crop-weed interactions by reducing the emergence of *Echinochloa crus-galli* compared to other PE herbicide doses and hand weeding (Tahir et al. 2021).

In transplanted rice, pretilachlor combined with pyrazosulfuron-ethyl at 615 g ha^{-1} provided superior control of complex weed flora (93.9% in 2013 and 94.2% in 2014) and higher grain yields (6.50 t ha^{-1} in 2013 and 5.37 t ha^{-1} in 2014) than the recommended herbicides butachlor at 1500 g ha^{-1} (85%, 6.34 t ha^{-1} in 2013) and pretilachlor at 1000 g ha^{-1} (87%, 5.05 t ha^{-1} in 2014). Additionally, Mondal et al. (2018) demonstrated that the ready-mix of pyrazosulfuron-ethyl and pretilachlor at 3.5 kg ha^{-1} given as a PE treatment was found to be very effective against composite weed flora in transplanted rice.

8.2.2 Pendimethalin + pyrazosulfuron-ethyl

Pendimethalin 38.4% + pyrazosulfuron ethyl 0.85% ZC is a selective PE herbicide used for effectively controlling grasses, BLWs, and sedges in transplanted rice. The combination of pendimethalin and pyrazosulfuron ethyl effectively manages the composite weed flora in rice fields. Pendimethalin is effective against annual grasses and certain BLWs, while pyrazosulfuron ethyl effectively controls sedges, resulting in comprehensive weed control (Singh et al. 2005). The PE application of pendimethalin aids in managing BLWs without inflicting any phytotoxic effects on rice. On the other hand, pyrazosulfuron ethyl controls grasses and sedges during the CPWC in rice, reducing weed competition pressure and thereby leading to higher crop yields (Ghosh et al. 2018).

In a study conducted by Kaur et al. (2019), it was found that pendimethalin combined with pyrazosulfuron at 1125 + 25 g ha^{-1} recorded the lowest weed density of *Echinochloa* spp. at 45 DAT, outlining it to be the most effective chemical treatment for controlling grassy weeds. A similar trend was observed for BLWs, where the same dosage of pendimethalin and pyrazosulfuron significantly reduced the population of BLWs such as *Ammania baccifera* and *Eclipta alba*. The highest WCE among the herbicidal treatments was recorded at 76.2% and 86.2% during 2015 and 2016, respectively, with the pendimethalin + pyrazosulfuron combination at 1125 + 25 g ha^{-1}. Additionally, this treatment achieved the maximum B: C ratio of 2.25.

8.3 Post Emergence +post Emergence Herbicide

8.3.1 Penoxsulam 1.02 % + Cyhalofop Butyl 5.1 %

Penoxsulam 1.02% + cyhalofop-butyl 5.1% is a new ready-mix PoE herbicide designed for broad-spectrum weed control in transplanted rice (Kailkhura et al. 2015). This unique premix formulation is an oil dispersion with an integrated adjuvant. The combination includes penoxsulam, a broad-spectrum herbicide from the triazolpyrimidine sulphonamide group that inhibits the ALS enzyme in susceptible species, and cyhalofop-butyl, a grass-effective herbicide from the aryloxyphenoxypropionate chemical group that inhibits the activity of acetyl coenzyme-A carboxylase (ACCase), an enzyme crucial for fatty acid metabolism. According to Lap et al. (2013), products combining penoxsulam and cyhalofop-butyl have been shown to enhance rice productivity in DSR, water-seeded, and transplanted rice production systems.

Yao et al. (2013), found out that the PoE foliar application of the ready-mix formulation of penoxsulam and cyhalofop-butyl at 10 to 15 DAT provided excellent control of weeds such as *Echinochloa crus-galli, L. chinensis, Paspalum distichum, C. difformis, C. iria, Scirpus juncoides,* *Monochoria vaginalis, M. korsakowi, Sagittaria* spp., *Alisma plantago-aquatica*, and *Rotala indica* [56]. Applying penoxsulam + cyhalofop-butyl 6% OD at 135 g ha^{-1} at 15 DAT resulted in superior weed control and higher grain yield (6640 kg ha^{-1}) compared to hand weeding twice (6266 kg ha^{-1}) in transplanted rice. This treatment effectively eliminated the biomass of grassy weeds, which might be attributed to the combined broad-spectrum activity of penoxsulam and cyhalofop-butyl (Ramachandra et al. 2015).

As reported by Raj and Syriac (2015), the readymix formulation of cyhalofop-butyl + penoxsulam was found effective in bringing down the weed density and dry matter at 30, 45, and 60 DAS, enhancing crop growth and grain yield in rice. Similar results were observed by Reddy and Ameena (2021), who reported that when penoxsulam and cyhalofop-butyl applied together at 20 DAS *fb* hand weeding, effectively suppressed grasses, BLWs, and sedges during the initial stages of crop growth in wet-seeded rice.

8.3.2 Metsulfuron methyl 10% + chlorimuron ethyl 10%

Metsulfuron methyl combined with chlorimuron ethyl is a sulfonylurea herbicide formulation effective against grasses and BLWs at lower application rates. This ALS inhibitor is highly efficient in controlling BLWs and sedges when applied at 4 g a.i. ha^{-1} between 15 and 25 DAS and works by inhibiting the ALS activity (Kumar and Ladha, 2011). It is a broad-spectrum urea herbicide with PoE action, formulated as a wettable powder containing 10% chlorimuron ethyl and 10% metsulfuron methyl.

Applied at a very low dosage of 8 g per acre, this herbicide can be used both pre-emergence and post-emergence and is referred to as a micro herbicide due to its minimal required dosage compared to other herbicides. It acts through both contact and residual soil activity, providing effective long-term weed management in rice. Commercially, it is formulated and sold under names such as Almix, Pimix, Topmix, and Dharrmix.

Mahbub et al. (2017) reported that applying chlorimuron ethyl 10% + metsulfuron methyl 10% at 20 g ha^{-1} during the one to two leaf stage of weeds effectively controlled all BLWs in transplanted rice, significantly enhancing grain yield and maximizing WCE. Additionally, metsulfuron-methyl + chlorimuron-ethyl when applied along with ethoxysulfuron have been found effective in controlling BLWs and sedges in rice (Umkhulzum et al. 2018).

8.3.3 Triafamone 20 % + Ethoxysulfuron 10%

Triafamone 20% + Ethoxysulfuron 10% WG (commercially known as Council® activ) is a cutting-edge PoE herbicide for rice that provides highly effective weed control, leading to increased productivity and reduced time and labour costs. It is suitable for use in both transplanted and wet DSR. This herbicide is absorbed by weed leaves and metabolized into N-demethylation, which strongly inhibits ALS activity. When applied at the recommended rate, it is safe for rice crops, offering control over grasses, sedges, and BLWs with a superior residual effect and excellent crop safety. A single application provides season long weed control (Phukan, 2021).

Early PoE application of the readymix triafamone + ethoxysulfuron is highly effective against complex weed flora in transplanted rice (Yadav et al. 2019). Menon (2019) found that at 60 DAS, the triafamone + ethoxysulfuron treatment significantly reduced weed growth in rice, resulting in the lowest weed count and weed dry matter, with a highest WCE of 92%.

8.3.4 Bispyribac sodium + Metamifop 14% SE

Bispyribac sodium is a PoE systemic herbicide from the pyrimidinyl carboxy class that works by disrupting the production of ALS, which is essential for synthesizing the branched-chain amino acids valine, leucine, and isoleucine. Metamifop, a grass-effective PoE herbicide is a part of the aryloxyphenoxy propionic acid family, and is employed to control a wide range of annual grassy weeds in many of the cereal crops, including rice. It inhibits the action of ACCase, an enzyme crucial for the first committed step in de novo fatty acid biosynthesis (McCullough et al. 2016). Herbicide combination of bispyribac sodium and metamifop has gained wide recognition as an effective solution for controlling a broad spectrum of weeds with a single application.

Multilocation trials conducted by DRR (2003) revealed that bispyribac sodium + metamifop at 70 g ha^{-1}, combined with PIW - 111 wetter, was more effective and produced better results than when applied individually. Raj and Syriac (2016) observed that, among different doses of bispyribac sodium + metamifop, its application at

90 g ha^{-1} produced the highest grain yield and net returns This was statistically on par with lower doses of 80 and 70 g ha^{-1}, all registering the same B: C ratio of 2.32. Consequently, considering economics and WCE, bispyribac sodium + metamifop at 70, 80, and 90 g ha^{-1} can be recommended for broad-spectrum weed control in wet DSR.

8.3.5 Florpyrauxifen-benzyl + Cyhalofop-butyl

Cyhalofop-butyl, a well-known PoE herbicide in rice from the aryloxyphenoxy propionate group with ACCase inhibitor mode of action, has been combined with a new herbicide, florpyrauxifen-benzyl, from the arylopicolinate class of synthetic auxin herbicides that disrupt plant cell growth. This combination offers broad-spectrum weed control in DSR and is effective against difficult-to-control weeds, making it a potential source for early PoE weed control in rice (Mounisha, 2020).

Mahapatra et al. (2020) observed that, the highest grain yield in rice was achieved with the application of herbicide combination florpyrauxifen-benzyl + cyhalofop butyl at 150 g ha^{-1}, and was comparable to a weed-free condition, without exhibiting any adverse effects on the soil environment, thus ensuring sustainability in wet DSR. Sreedevi et al. (2020) concluded that rice weeds grown under aerobic conditions could be controlled with an early PoE pre-mix herbicide combination of florpyrauxifen-benzyl + cyhalofop butyl at 150 to 180 g ha^{-1}, with no residual toxicity. This treatment provided excellent control of grasses, sedges, and BLWs and was considered the best available herbicide.

Mounisha et al. (2021) reported that among various herbicide treatments, the lowest nitrogen removal (3.52 kg ha^{-1}) at 60 DAS was observed with the application of florpyrauxifen-benzyl + cyhalofop-butyl at 12 DAS, which was comparable with pendimethalin + penoxsulam applied at 5 DAS, and cyhalofop-butyl + penoxsulam and florpyrauxifen benzyl + cyhalofop butyl, both applied at 18 DAS. The same pre-mix herbicide treatment also resulted in the lowest phosphorus and potassium removal.

8.4 Pre-emergence + Post Emergence Herbicide

8.4.1 Pendimethalin+ Penoxsulam

Penoxsulam is an ALS inhibitor herbicide used for PoE control of annual grasses, sedges, and BLWs in rice cultivation but is ineffective against *Leptochloa chinensis* (Jabusch and Tjeerdema, 2005). Pendimethalin, on the other hand is a herbicide from the nitroaniline class which prevents plant cell division and is commonly applied as a PE spray in dry-seeded rice.

Uraon (2019) reported that application of a combination of pendimethalin + penoxsulam (240+10 g L^{-1}) SE at 2400 + 100 g a.i. ha^{-1} at 7 DAS resulted in maximum yields and effective weed control in DSR. In a study conducted by Uraon and Shrivastava (2018) it was reported that this herbicide combination achieved the highest returns and B: C ratio, as well as the best growth characteristics in rice, such as plant height, dry matter, number of tillers, leaf area, leaf area index, and crop growth rate. Kumar et al. (2018) concluded that the PE application of the herbicide combination pendimethalin + penoxsulam at 4-7 DAT provided the highest B: C ratio compared to other treatments.

8.4.2 Penoxsulam 0.97% w/w + Butachlor 38.8%

Penoxsulam 0.97% w/w + Butachlor 38.8% is a broad-spectrum, systemic herbicide combination for early PoE control of key grasses, BLWs, and sedges in transplanted rice by inhibiting ALS. Penoxsulam 24% SC, an early PoE herbicide, when applied 8-12 DAT is effective against complex weed flora, particularly BLWs and sedges. However, issues with spraying this herbicide early due to standing water and small rice seedlings limit its practical field use. Similarly, butachlor is highly effective herbicide against *Echinochloa* but slightly less against some BLWs and sedges. The combination of penoxsulam 0.97% w/w + butachlor 38.8% can be applied 0-7 DAT, unlike conventional Butachlor, which is used as a PE herbicide in rice. This combination offers superior residual control of economically important weeds.

According to Yadav et al. (2019), Penoxsulam combined with butachlor 41% SE at 820 g ha^{-1}, when sprayed in 300 L water ha^{-1} at 0-7 DAT under saturated field conditions (with re-irrigation 24 hours after spraying), effectively controlled the composite weed flora in transplanted rice, resulting in higher grain yields.

9. EFFECT OF HERBICIDE MIXTURES ON WEED SEED BANK

Weed seed bank refers to the collection of of viable weed seeds found on the soil surface and dispersed throughout the soil profile (Singh et al. 2012). It is the primary reason for the persistent presence of weeds in agricultural fields and serves as an indicator of the weed population in the soil (Dhawan, 2007).

In rice fields, numerous weed species can produce a large number of small seeds and vegetative propagules to withstand the pressure of weed control methods (Munhoz and Felfli, 2006). These seeds may either remain on the soil surface or get buried after dispersal through biotic and abiotic agents, forming a potential seed bank that serves as the main source of weeds in cropping fields. The primary goal of any weed management strategies should be to lower the weed seed bank in the soil, allowing the crop to be more competitive by either delaying weed emergence or suppressing the weed growth. Weeds are a symptom of the underlying problem, which is the weed seed bank. Therefore, an effective weed management programme should focus on reducing the weed seed bank so as to enable rice crops to be more competitive (Raj and Syriac, 2017).

Research has shown that herbicide mixtures can be more effective in depleting the weed seed bank compared to individual herbicide applications. Herbicide mixtures such as penoxsulam + cyhalofop-butyl and bispyribac-sodium + metamifop were more effective at depleting the weed seed bank than the sole applications of bispyribac-sodium and penoxsulam. Their results also showed that penoxsulam + cyhalofop-butyl was more effective than bispyribac-sodium + metamifop in depleting the weed seed bank in DSR (Raj and Syriac, 2018).

10. EFFECT OF HERBICIDE MIXTURES ON SOIL HEALTH

Soil microflora and soil enzymes are widely recognized as biological indicators of soil health. Soil microbial biomass, including bacteria, fungi, and actinomycetes, is essential for carbon cycling, litter decomposition and nutrient dynamics thereby influencing soil fertility and plant growth (Bamboo et al. 2013). Maintaining a healthy microbial population is essential for ecosystem stability, as any changes in their abundance or activity can impact nutrient cycling and soil functions, ultimately affecting soil productivity and fertility (Wang et al. 2008).

Soil enzymes are key catalysts in biological processes crucial for soil health and environmental quality. Enzymes such as dehydrogenase, urease, and phosphatase are particularly important as they drive various soil biological activities (Nannipieri et al., 2002). Dehydrogenase activity, for instance, is often used as an indicator of overall soil biological activity. Most of the combination herbicides have been shown to have no adverse effects on soil microbial communities and enzyme activities, supporting their environmentally safe use in agriculture. Raj et al. (2015), revealed that application of bispyribac sodium + metamifop at the rates of 60 to 90 g a.i. ha^{-1} had no detrimental effects on soil microbial populations or enzyme activities (specifically dehydrogenase, phosphatase, and urease) [82]. This indicates that bispyribac sodium + metamifop can be considered environmentally safe as it does not negatively impact soil health indicators.

In another study by Priya et al. (2017), it was found that combinations of herbicides, bispyribac sodium 4% SE + metamifop 10% SE applied at rates of 70, 56, and 42 g a.i. ha^{-1} along with a wetting agent at 100 ml ha^{-1}, resulted in maximum dehydrogenase activity. The microbial populations in plots treated with herbicides were similar to those in untreated controls, suggesting that these herbicide treatments did not harm soil health at the specified doses.

11. COMPATABILITY OF HERBICIDE MIXTURES WITH BENEFICIAL ORGANISMS

In sustainable agriculture, soil is often considered as a fragile and living medium that requires protection and nurturing to maintain its long term productivity and stability. The popularity of sustainable agriculture is growing tremendously owing to its reduced environmental impact, achieved by using chemical inputs such as fertilizers, pesticides, fungicides, and herbicides in an economically viable and ecofriendly ways, while promoting the use of biocontrol agents and biofertilizers whenever possible.

Some herbicides used in agriculture can adversely affect the growth of beneficial organisms due to differences in their mode of action, concentration, or chemical group. Evaluating herbicide mixtures for their compatibility with bio-fertilizer organisms helps rice growers select compatible options.

Raj et al. (2017) evaluated the compatibility of herbicide mixtures with biocontrol agents and nitrogen-fixing organisms and it was found that the application of PE herbicide mixture, bispyribac sodium + metamifop, is highly compatible with beneficial bacteria such as *Pseudomonas fluorescens, Azospirillum lipoferum*, and *Azotobacter chroococcum*, even at higher doses up to 110 g ha^{-1}. The study also demonstrated the compatibility of bispyribac sodium + metamifop with the antagonistic fungus *Trichoderma viride*, showing no harm within the range of 60 to 90 g ha^{-1}. These compatibility findings support the use of bispyribac sodium + metamifop at recommended doses (70, 80, or 90 g ha^{-1}) for effective weed control, while allowing for the management of bacterial and fungal diseases with *P. fluorescens*/ *T. viride* and reducing nitrogen fertilizer use with *A. lipoferum* in rice, all in a single application and with environmental safety in mind.

12. CONCLUSIONS

Chemical weed management is often recognized as an effective and economical method for controlling weeds in intensive agriculture. However, some grassy weeds, BLWs, and sedges are not adequately controlled by a single application of these herbicides. While broad-spectrum herbicides can handle most weeds, some tolerant species require specific herbicides. Using weed-specific herbicides in sequence to manage all types of weeds is neither practical nor economical. Herbicide mixtures offer a more practical solution, as they can be applied in a single operation, saving time.

However, several factors can influence the effectiveness of herbicide mixtures in practice. Selecting the most appropriate herbicide combinations requires considerable knowledge regarding the properties of the herbicides and the species to be controlled. Additionally, the effectiveness of weed control depends on the weed species present, which is influenced by climate, soil, and environmental conditions.

Several new pre-mix herbicides having the potential to manage weed populations effectively are now available, but their efficacy has been less studied. It is essential to identify the most effective herbicide combinations that can be recommended to smallholder farmers. Enhanced efficiency in predicting herbicide interactions can be achieved by combining computer models with a deeper understanding of herbicide behavior in plants, whether applied alone or in mixtures. Additionally, research on the interactions of herbicides with other agrochemicals and soil bio-amendments are scarce. Further investigation is needed into the persistence and dissipation of these herbicide mixtures in soil and the major microorganisms involved in their degradation.

DISCLAIMER (ARTIFICIAL INTELLIGENCE)

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc) and text-to-image generators have been used during writing or editing of this manuscript.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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