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An Evaluation of Novel Herbicides Pyraclonil and Metribuzin in California Rice (*Oryza sativa*)

By

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THESIS

Submitted in partial satisfaction of the requirements for the degree of

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in

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of the

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DAVIS

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2022

An Evaluation of Novel Herbicides Pyraclonil and Metribuzin in California Rice (*Oryza sativa*)

ABSTRACT

A system of permanently flooded rice and a lack of diverse weed management techniques have selected for flood-tolerant weed populations in California water-seeded rice agroecosystems. As a result of limited available herbicides in California and a system of continuous rice monocropping, herbicide resistance has developed in several weeds found in California rice fields. The rise in herbicide resistance has increased the cost and difficulty of weed management, necessitating demand for novel herbicide development to delay resistance expansion and assist the management of current herbicide-resistant weed biotypes. Greenhouse and field experiments were conducted to 1) characterize pyraclonil activity on common California rice weeds alone and in combination with currently available herbicides and 2) evaluate the differential response of rice genotypes to POST application of metribuzin at various rates. Field experiments were conducted to evaluate pyraclonil, a novel protoporphyrinogen oxidase (protox) inhibiting active ingredient under development for California rice, applied alone and in combination with other herbicides to determine grass, sedge, and broadleaf control and crop safety. These experiments indicated that pyraclonil applied alone is insufficient for broad-spectrum weed control, but, when applied in combination with currently available herbicides, provides consistently greater control of watergrass species, bearded sprangletop, ricefield bulrush, smallflower umbrellasedge, ducksalad, and redstem. Pyraclonil demonstrated no lasting injury that affected rice yields and was effective as a base treatment herbicide for incorporation into water-seeded rice weed management programs. Greenhouse experiments were conducted to evaluate the differential response of 142 California rice cultivars to foliar-applied metribuzin when rice plants were at the three- to four-leaf stage. Dose-response experiments failed to confirm a differential response for specific rice cultivars but did indicate differential responses among the different types of rice available. At tested rates, short-grain rice cultivars were more susceptible injury including stunting and biomass reductions compared to long-grain or medium-grain cultivars at the same rates. These results suggest that further research is needed to establish metribuzin's candidacy for development as a postemergence product in rice. These results are pertinent to the rice growers and pest control advisors who are concerned with the management of herbicide resistance in California rice and may contribute to the ongoing research concerning differential response of cultivars to novel chemicals.

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“The thing I can't say and never will say is that I'm self-made. To make that claim would be to commit a grave sin against all the many, many people who helped me get to where I am.” Ken Langone

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INTRODUCTION

Rice (*Oryza sativa* L.) is the major calorie source for a large proportion of the world's population and is one of the most commonly grown agricultural commodities in the world (Smith 1995). California is the second largest rice-growing state in the USA, with around 200,000 ha production, most of which is concentrated in the Sacramento Valley ([CDFA] California Department of Food and Agriculture). The majority of California's rice production consists of short- and medium-grain *japonica* varieties and a few long-grain *indica* varieties, including cultivars developed for both the local climate and a continuously-flooded cropping system, where rice is pre-germinated and seeded by airplane onto fields with a 10-15 cm standing flood (Ceseski and Al-Khatib 2021; Espino et al. 2019).

The flooded conditions in which California rice is grown favor flood-adapted, competitive grass weeds such as watergrass species (*Echinochloa* (L.) Beauv. spp.), bearded sprangletop [*Leptochloa fusca* (L.) Kunth ssp. *fascicularis* (Lam.) N. Snow], and weedy (red) rice (*Oryza sativa* (L.) f. *spontanea* Roshev.) (Brim-DeForest et al. 2017b; Ceseski et al. 2022). The continuously flooded system also promotes sedges such as ricefield bulrush [*Schoenoplectus mucronatus* (L.) Palla] and smallflower umbrellasedge (*Cyperus difformis* L.) as well as aquatic broadleaf weeds such as ducksalad [*Heteranthera limosa* (Sw.) Willd.] and redstems (*Ammannia* (L.) spp.) (Brim-DeForest et al. 2017b).

Weeds are the greatest biological constraint to rice yields, and farmer inputs towards weed management are expected to increase as herbicide resistance spreads worldwide (Brim-DeForest et al. 2017a). The potential yield lost to weed infestation is species dependent, and the practice of continuous rice monoculture in California has resulted in an abundance of highly competitive weeds that negatively impact rice yields (Fischer et al. 2000; Smith Jr. 1988; Ceseski and Al-Khatib 2021). In California rice fields, weedy grasses are the largest predictors of overall yield loss. Late watergrass [*Echinochloa phyllopogon* (Stapff). Koss] competition has caused rice yield losses as high as 59% (Brim-DeForest et al. 2016; Gibson et al. 2001). Studies in Arkansas have shown rice yield losses to be 79% from competition with barnyardgrass [*Echinochloa crus-galli* (L.) Beauv.] and 36% from bearded sprangletop competition (Smith Jr. 1968). Weedy rice densities of 30 to 40 plants m^{-2} can reduce rice yields by 60-90%, depending on the cultivar (Smith Jr. 1988; Ziska et al. 2015). In the United States Midsouth region, yield losses due to ducksalad infestations can reach 30% (Smith 1995).

Most California rice herbicides are limited in the spectrum of weeds controlled and the length of residual activity, requiring herbicide treatment plans to consist of multiple herbicides to enact weed control over a range of weeds (Espino et al. 2019). Continuous use of herbicides with the same mode of action aids in the development of herbicide resistance in a crop (Hill et al. 1994). Confirmed herbicide resistance from various populations of watergrass species (Fischer et al. 2000; Hill et al. 1994; Peterson et al. 2018) and bearded sprangletop (Driver et al. 2020) have been documented. California arrowhead (*Sagittaria montevidensis* Cham. & Schltdl.) and smallflower umbrellasedge were the first confirmed instances of herbicide resistance in rice to bensulfuron-methyl, an ALS-inhibitor, in 1993 (Busi et al. 2006). Eight other rice weed species have since been identified with resistance to commonly used herbicides, some with resistance to more than one mode of action (Heap 2022; Becerra-Alvarez and Al-Khatib, 2022). A direct result of herbicide resistance development to more than one mode of action is the necessity of using combinations of different modes of action to combat weeds in rice systems.

Permanently-flooded rice agroecosystems are limited to few available herbicides in California, largely due to ecotoxicity and strict regulatory structure (Ceseski and Al-Khatib

2021; Hill et al. 1994). As of 2019, there are 13 registered active ingredients for water-seeded rice in California and 9 modes of action registered for use (Espino et al. 2019). The rise in herbicide resistance has increased the cost and difficulty of weed management, necessitating demand for novel herbicide development to delay resistance expansion and assist the management of current herbicide-resistant weed biotypes (Driver et al. 2020). The following studies examined the crop response to chemicals not currently in use in California water-seeded rice.

CHAPTER ONE describes field studies performed in 2019 and 2021 at the Rice Experiment Station in Biggs, CA. The efficacy of pyraclonil, a protox inhibitor, was explored alone and in combination with several currently available rice herbicides against common grass, sedge, and broadleaf weeds in California rice field. Combination treatments included pyraclonil at 0.3 kg ai ha^{-1} applied the day of seeding, in combination with or followed by recommended rates of propanil, clomazone, benzobicyclon plus halosulfuron, thiobencarb, bispyribac-sodium, penoxsulam, or florpyrauxifen-benzyl at their respective recommended application timings. Rice phytotoxicity and yield in response to pyraclonil and these registered herbicides was evaluated. Pyraclonil applied alone had mixed effects on weed control, but all pyraclonil herbicide combination treatments controlled watergrass species, bearded sprangletop, ricefield bulrush, smallflower umbrellasedge, ducksalad, and redstem consistently better than pyraclonil applied alone. Pyraclonil applied alone caused minor visible rice injury that varied by year but did not reduce yields. This study determined that pyraclonil was effective as a base treatment herbicide and may prove to be a new useful tool for rice growers to incorporate into their weed management programs.

CHAPTER TWO details greenhouse studies undertaken in 2021-2022 to evaluate the response of several rice genotypes to five different rates of foliar-applied metribuzin, a Photosystem II inhibitor herbicide not currently used in California rice systems. Short-grain rice cultivars as a group were found to be more susceptible to crop phytotoxicity than the long-grain or medium-grain rice lines. Crop injury from metribuzin was correlated with biomass reductions ($r = 0.657$, $P < 0.0001$) and plant height reductions ($r = 0.727$, $P < 0.0001$). The results indicate that further research is needed to establish metribuzin's candidacy for development as a POST emergence product in rice.

This exploration of novel herbicides has characterized the activity of pyraclonil in California rice, both alone and in combination with other water-seeded rice herbicides. The efficacy of the herbicide, as well as the response of the target crop, has been identified and establishes pyraclonil as an herbicide with great potential for integration into existing rice weed management programs. The differential responses of various rice cultivars to increasing doses of foliar metribuzin has described heretofore unknown rice responses and identified areas of concentration upon which future researchers may focus. Introduction of novel herbicides and continued analysis of their activity in rice allows for development of alternate methods of sustainable weed control to contend with the rise of herbicide resistance amid the common weeds of California rice agriculture.

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CHAPTER 1

Characterization of Pyraclonil Activity on Common California Rice (*Oryza Sativa*) Weeds Alone and in Combination with Currently Available Herbicides

Submitted to Weed Technology

Abstract

Continuously flooded rice and a lack of diverse weed management techniques have selected for flood-tolerant weed populations in California water-seeded rice agroecosystems, necessitating introduction of novel active ingredients into existing weed control programs to allow herbicide mode of action rotation and reduce selection for herbicide resistance in weed populations. A field study was conducted at the Rice Experiment Station in Biggs, CA to evaluate pyraclonil, a novel protoporphyrinogen oxidase (protox) inhibiting active ingredient under development for California rice, applied alone and in combination with other herbicides to determine grass, sedge, and broadleaf control and crop safety. Treatments included pyraclonil at 0.3 kg ai ha^{-1} applied the day of seeding, in combination with or followed by recommended rates of propanil, clomazone, benzobicyclon plus halosulfuron, thiobencarb, bispyribac-sodium, penoxsulam, or florpyrauxifen-benzyl at their respective application timings. It was determined that pyraclonil applied alone provided 54% control of watergrass species and 24% of ricefield bulrush, which was inadequate control, but did control 86% of ducksalad and 91% of redstem. All pyraclonil combination treatments controlled watergrass species, bearded sprangletop, ricefield bulrush, smallflower umbrellasedge, ducksalad, and redstem consistently greater than pyraclonil applied alone. Pyraclonil applied alone caused visible rice injury that varied by year but did not reduce yields. Pyraclonil was effective as a base treatment herbicide and could be a new useful tool for rice growers to incorporate into their weed management programs if registered for use in California.

1.1. Introduction

Rice (*Oryza sativa* L.) is the major calorie source for a large proportion of the world's population and is one of the most commonly grown agricultural commodities in the world (Smith 1995). California is the second largest rice-growing state in the USA, with approximately 200,000 ha of rice, most of which is concentrated in the Sacramento Valley. The majority of rice in California is produced using a continuously flooded, i.e., water-seeded system, where rice is pre-germinated and aerially seeded into fields with a 10-to 15 cm existing flood (Ceseski and Al-Khatib 2021; Espino et al. 2019). The flooded conditions in which California rice is grown favor flood-adapted, competitive grass weeds such as watergrass species (*Echinochloa* (L.) Beauv. spp.) and bearded sprangletop [*Leptochloa fusca* (L.) Kunth ssp. *fascicularis* (Lam.) N. Snow] (Brim-DeForest et al. 2017b, Ceseski et al. 2022). The continuously flooded system also promotes sedges such as ricefield bulrush [*Schoenoplectus mucronatus* (L.) Palla] and smallflower umbrellasedge (*Cyperus difformis* L.) as well as aquatic broadleaf weeds such as ducksalad [*Heteranthera limosa* (Sw.) Willd.] and redstems (*Ammannia* L. spp.) (Brim-DeForest et al. 2017b).

Weeds are the greatest biological constraint to rice yields, and farmer inputs towards weed management are expected to increase as herbicide resistance spreads worldwide (Brim-DeForest et al. 2016). The potential yield lost to weed infestation is species dependent, and the practice of continuous rice monoculture in California has resulted in an abundance of highly competitive weeds that negatively impact rice yields (Smith Jr. 1988; Fischer et al. 2000; Ceseski and Al-Khatib 2021). In California rice fields, weedy grasses are the largest predictors of overall yield loss (Brim-DeForest et al. 2017a). Late watergrass [*Echinochloa phyllopogon* (Stapff). Koss] competition has caused rice yield losses as high as 59% (Brim-DeForest et al. 2017a; Gibson et al. 2001). Studies in Arkansas have shown rice yield losses to be 79% from competition with barnyardgrass [*Echinochloa crus-galli* (L.) Beauv.] and 36% from bearded sprangletop competition (Smith Jr. 1968). In the Midsouth region, yield losses due to ducksalad infestations can reach 30% (Smith 1995).

Most California rice herbicides are limited in the spectrum of weeds controlled and the length of residual activity, requiring herbicide treatment plans to consist of multiple herbicides to enact weed control over a range of weeds (Espino et al. 2019). Effective weed control in the state relies on combinations of herbicides to enact a complete spectrum of weed control (Espino et al. 2019)

Continuous use of herbicides with the same mode of action aids in the development of herbicide resistance in rice fields (Hill et al. 1994). However, due to high costs of development and registration, few additional herbicides are currently available for California rice growers, particularly herbicides that target grass weeds (Hill et al. 1994; Espino et al. 2019). As of today, there are 13 registered active ingredients for water-seeded rice in California that belong to 9 modes of action (Espino et al. 2019). The rises in herbicide resistance have made weed management more difficult and more costly to California rice growers (Driver et al. 2020).

Herbicide resistance has also been a major biological issue, with confirmed resistance from various populations of watergrass species (Fischer et al. 2000, Hill et al. 1994, Peterson et al. 2017) and bearded sprangletop (Driver et al. 2020). California arrowhead (*Sagittaria montevidensis* Cham. & Schltdl.) and smallflower umbrellasedge were the first confirmed cases of herbicide resistance in rice to bensulfuron-methyl, an ALS-inhibitor, in 1993 (Busi et al. 2006). Eight other rice weed species have since been identified with resistance to commonly used herbicides, some with resistance to more than one mode of action (Heap 2022, Becerra-

Alvarez and Al-Khatib 2022). A direct result of herbicide resistance development to more than one mode of action is the necessity of using combinations of different modes of action to combat weeds in rice systems.

Pyraclonil is a broad-spectrum herbicide with protoporphyrinogen oxidase (protox) inhibitor mode of action that is new to California. Carfentrazone, which is a currently registered protox-inhibitor, is a viable herbicide for California water-seeded rice but lacks activity on grass weeds (Sharma and Singh 2007). Pyraclonil is presently in use in Japan and has shown efficacy against sulfonylurea-resistant broadleaf biotypes of *Lindernia procumbens* (Krock.) Borbas, grasses, and sedges (Hamamura 2018). Currently, there is no record of protox inhibitor resistance in California rice weeds.

Protox inhibition takes place inside the chloroplasts of plant cells. As the last enzyme in the common tetrapyrrole biosynthesis pathway prior to heme and chlorophyll synthesis, protoporphyrinogen IX oxidase (protox) catalyzes the oxidation of protoporphyrinogen IX (protogen) to protoporphyrin IX (proto) (Matringe et al. 1992). Pyraclonil inhibits the conversion of protogen to proto by blocking protox activity. When protox is inhibited, excess protogen accumulates in the chloroplast until protogen leaks to cytoplasm (Becerril and Duke 1989, Jacobs and Jacobs 1984). In cytoplasm, leaked protogen is oxidized into proto and is unable to reenter the chloroplast (Matringe et al. 1989). When proto is exposed to light and molecular oxygen in the cytoplasm, it produces toxic oxygen species, which are responsible for lipid peroxidation and membrane disruption, resulting in overall plant death (Becerril and Duke 1989; Granick 1965; Jacobs et al. 1991; Vavilin and Vermaas 2002).

A formulation of pyraclonil has been developed by Nichino America Inc. as a preemergent granular form that is suitable for aerial application in California water-seeded rice agroecosystems.

Therefore, the objectives of this research were to determine the grass, sedge, and broadleaf control of pyraclonil alone and in partnership with other commonly used herbicides in water-seeded rice systems and determine the rice response to the granular formulation of pyraclonil.

1.2. Materials and Methods

1.2.1 Field Location and Conditions

Field experiments were conducted during the 2019 and 2021 growing seasons at the Rice Experiment Station in Biggs, CA, USA (39.46°N, 121.74°W). Soils at the study site are characterized as Esquon-Neerdobe (fine, smectitic, thermic Xeric Epiaquerts and Duraquerts) silty clay with a pH of 5.1, and 2.8% organic matter. The study site weed seedbank has been previously described in Brim-DeForest et al. (2017a, 2017b) and contains watergrass species, bearded sprangletop, ricefield bulrush, smallflower umbrellasedge, ducksalad, and redstem.

1.2.2 Experiment Materials and Design

Seeds of medium-grain rice cultivar 'M-206' were soaked in water for 24 hours for pre-germination and then drained and aerially seeded at a rate of 168 kg ha^{-1} into a 10 cm flooded field. Seeding dates were June 13, 2019, and June 1, 2021. The experiment was a randomized complete block design with four replications in both years. Plots were 3 m by 6 m and surrounded by small levees to prevent herbicide cross contamination to other plots (Figure 1.1). Pyraclonil (Nichino America, Inc., Wilmington, Delaware, USA) was applied as a granular formulation of 1.89% pyraclonil at a rate of 0.3 kg ai ha^{-1} at day of seeding (DOS) (Table 1.1). Pyraclonil was also applied in combination with propanil, clomazone, benzobicyclon plus halosulfuron, thiobencarb, bispyribac-sodium, penoxsulam, and florpyrauxifen-benzyl (Table 1.1).

Treatment applications were timed on rice emergence or development stages according to manufacturer labels. Granular herbicides were evenly broadcast by hand. Foliar applied herbicides were applied with a CO_2-pressurized boom sprayer with a 2 m boom equipped with six 8003XR flat-fan nozzles (TeeJet Technologies, Springfield, Illinois, USA) calibrated to deliver 187 L ha^{-1} at 180 kPa. For the combination treatments including propanil, the spray mixture included 2.5% v/v crop oil concentrate (COC, Prime Oil®, WinField Solutions LLC, Arden Hills, Minnesota, USA). For the combination treatment including bispyribac-sodium, the spray mixture included a multifunction adjuvant of 0.37 ml ha^{-1} (DyneAmic®, Helena Agri-Enterprises LLC, Collierville, Tennessee, USA).

Several of the contact herbicide treatments required the 10 cm permanent flood to be lowered in order to reveal the weeds. For the treatments containing propanil, bispyribac-sodium, and florpyrauxifen-benzyl, the plots were drained to reveal 70% of the weeds prior to that herbicide application and were reflooded to 10 cm 48 hours after application, according to the manufacturer labels.

1.2.3 Data collection

Visual ratings measuring weed control were conducted for watergrass species, bearded sprangletop, ricefield bulrush, smallflower umbrellasedge, ducksalad, and redstem at 14 and 42 DAT (days after treatment with pyraclonil). Ratings consisted of a 0 to 100 scale, where 0 = no weed control, and 100 = no weeds present, or full control.

Visual crop phytotoxicity ratings were conducted at 14 and 42 DAT on a 0 to 100 scale, where 0 = no injury and 100 = plant death, as compared to the nontreated control plots. Phytotoxicity ratings consisted of stunting and chlorosis ratings. Rice grain was harvested from each plot with a small-plot combine with a swath width of 2.3 m (Almaco, Nevada, Iowa, USA). Rice grain yield for both years was adjusted to 14% moisture.

1.2.4 Statistical analysis

There were no interactions between treatment and year for the weed control ratings; therefore, the weed control ratings were averaged across years (n = 8). The rice injury data revealed significant year-by-treatment interaction, so the data were analyzed separately by year for both chlorosis and stunting ratings. The data were tested for homogeneity of variance and analyzed using ANOVA and linear regression utilizing the *agricolae* and *emmeans* packages (Lenth 2020) in R, and with JMP® Pro16 (R Core Team 2022; JMP®, Version Pro16. SAS Institute Inc., Cary, NC, 1989–2022). Herbicide treatments, year, and time of rating were used as fixed effects and replicates as random effects. Means separation was performed using Tukey-Kramer's honestly significant difference (HSD) at 95% significance level.

1.3. Results and Discussion

1.3.1 Weed Control

The study site varied in weed population composition each year. Based on nontreated plots, watergrass species infestation in 2019, averaged 10% abundance compared with 28% in 2021 (Figure 1.2). Sedge and broadleaf pressure were similar in both years. Similar variations have been noted in this same field location and attributed to annual differences in temperature and management (Brim-DeForest et al. 2017a). In 2021, the study was seeded 12 days earlier than in 2019; the weather differences between the two years may have contributed to the difference in weed population (National Centers for Environmental Information).

Pyraclonil applied alone or with other herbicides provided 76-96% control of watergrass species at 14 DAT (Table 1.2). The efficacy of pyraclonil alone decreased as the season progressed, reaching 54% watergrass control at 42 DAT, which was less than pyraclonil applied with other herbicides. All tested herbicide combination treatments provided excellent season-long control of watergrass species. There were no differences among the pyraclonil combination treatments regarding their control of watergrass species at 14 DAT or 42 DAT; watergrass control ranged from 88-100% in treated plots by 42 DAT. Pyraclonil applied alone did not achieve season-long watergrass control and should be combined with other herbicides that express season-long activity on watergrass species.

There was no difference in sprangletop control among pyraclonil treatments at 14 DAT; however, there was a non-significant trend of 100% control of sprangletop achieved with pyraclonil followed by propanil, pyraclonil followed by thiobencarb followed by propanil, pyraclonil followed by bispyribac-sodium followed by propanil, pyraclonil followed by penoxsulam followed by propanil, and pyraclonil followed by florpyrauxifen-benzyl followed by propanil (Table 1.2). At 42 DAT, however, the herbicide programs of pyraclonil followed by propanil and pyraclonil followed by penoxsulam followed by propanil provided similarly low control of bearded sprangletop, ranging from 61-68% control. The decline in weed control from 14 DAT to 42 DAT may be attributed to the late emergence of bearded sprangletop that escaped the pyraclonil treatments (Driver et al. 2020). Bearded sprangletop requires 215 growing degree days (GDD) to achieve 90% emergence, contributing to a later emergence compared to other common weeds such as watergrass species, which require only 124 GDD for 90% emergence (Driver and Al-Khatib 2019). GDDs for June 2019 and June 2021 were estimated and used to establish 90% bearded sprangletop emergence in thermal time degree days (Izquierdo et al. 2009, National Centers for Environmental Information). However, there was no difference in the amount of GDDs between the years that the field study was conducted. The field location received 220 GDDs by 21 days after seeding in 2019, enough to reach 90% emergence of bearded sprangletop in 2019. In 2021, the field location reached 229 GDD for 90% bearded sprangletop germination 20 days after the rice was planted.

The combination of pyraclonil followed by benzobicyclon plus halosulfuron followed by propanil gave 50% control of bearded sprangletop at 14 DAT; however, at 42 DAT, no sprangletop was found in the treated plots. Benzobicyclon plus halosulfuron is applied at 1.5 rice leaf stage but exhibits long-lasting weed control through both foliar and root uptake that may account for the control of later cohorts of bearded sprangletop (McKnight et al. 2018).

Pyraclonil applied alone did not control ricefield bulrush substantially differently from the untreated plots and was insufficient for effective ricefield bulrush control; however, the pyraclonil applications followed by propanil, benzobicyclon plus halosulfuron and propanil, clomazone and propanil, thiobencarb and propanil, bispyribac-sodium and propanil, or penoxsulam and propanil achieved similar ricefield bulrush control ranging from 61-88% at 14 DAT (Table 1.2). Differences in ricefield bulrush control among the different herbicide combinations began to emerge at 42 DAT. The treatment of pyraclonil followed by benzobicyclon plus halosulfuron and propanil and pyraclonil followed by florpyrauxifen-benzyl and propanil controlled 97% of ricefield bulrush. These two treatments provided greater control over ricefield bulrush than pyraclonil followed by propanil, 48% control, and pyraclonil alone, 23% control. Benzobicyclon plus halosulfuron is a standard treatment to control ricefield bulrush in California, which explains the higher level of control resulting from this program (Fischer 2012). Later-season application of florpyrauxifen-benzyl at early-tiller stage may be timed to eliminate ricefield bulrush that are not controlled by the combination of pyraclonil and propanil, which may account for the high efficacy of this herbicide combination.

Pyraclonil applied alone and all herbicide combinations achieved greater control of smallflower umbrellasedge at 14 DAT (Table 1.2). Pyraclonil applied alone provided 65% control of smallflower umbrellasedge at 14 DAT. This level of control at 14 DAT was less than that of pyraclonil applied in combination with benzobicyclon plus halosulfuron followed by propanil and thiobencarb followed by propanil, ranged from 95 to 97% control, respectively. The following pyraclonil combinations provided greater smallflower umbrellasedge control compared to pyraclonil alone, which provided 48% control at 42 DAT: pyraclonil followed by benzobicyclon plus halosulfuron and propanil, pyraclonil followed by thiobencarb and propanil, pyraclonil followed by propanil and bispyribac-sodium, pyraclonil followed by penoxsulam and propanil, and pyraclonil followed by propanil and florpyrauxifen-benzyl. All treatments provided significantly higher levels of control than the untreated plots at 42 DAT. Pyraclonil alone was insufficient for effective season-long control of smallflower umbrellasedge; however, when partnered with other herbicides labelled for control or suppression of this weed, the level of control was excellent.

Plots treated solely with pyraclonil maintained the lowest levels of ducksalad control of the treatments tested, ranging from 85 to 86% control throughout the season (Table 1.2). All pyraclonil combinations had excellent control of ducksalad that ranged between 92 to 100% at 14 DAT. Ducksalad control remained high and ranged between 86% to 100% at 42 DAT for all herbicide combinations with no differences among treatments.

Pyraclonil applied alone provided 86% control of redstem at 14 DAT (Table 1.2). All pyraclonil combination treatments provided excellent (100%) control of redstem at 14 DAT.

Some redstem appeared at 42 DAT in plots treated with the combinations of pyraclonil followed by propanil and pyraclonil followed by clomazone followed by propanil but there was no difference between these treatments and the other treatments tested. All herbicide treatments provided effective season-long control of redstem.

1.3.2 Rice Response

Rice injury was observed as chlorosis and stunting across all treatments in both years from 7 DAT to 42 DAT. The rice injury data revealed significant year-by-treatment interaction, so the data were analyzed separately by year for both chlorosis and stunting ratings.

Several treatments caused chlorosis at 14 DAT in 2019: pyraclonil (73% chlorosis), pyraclonil followed by clomazone and propanil (71%), pyraclonil followed by thiobencarb and propanil (79%), and pyraclonil followed by propanil and bispyribac-sodium (71%) (Table 1.3). All other treatments had chlorosis ranging from 41 to 61%, with the exception of the herbicide combination of pyraclonil followed by propanil and florpyrauxifen-benzyl, which displayed 25% chlorosis. However, by 42 DAT in 2019, only pyraclonil alone exhibited chlorosis, at 4% in the treated plots (Table 1.3).

No rice chlorosis was observed in any treated plot in 2021 at 14 DAT (Table 1.4). At 42 DAT, the herbicide combination of pyraclonil followed by thiobencarb and propanil caused 19% chlorosis, which was significantly higher than other treatments. Chlorosis gradually disappeared in the treated plots. Hakim et al. (2021) also found slight rice injury including chlorosis from herbicide applications consisting of thiobencarb and propanil in non-saline soils in Malaysia.

The chlorosis ratings between 2019 and 2021 were diverse. All treated plots presented some chlorosis at 14 DAT in 2019 but recovered by 28 DAT and demonstrated negligible phytotoxicity after 42 DAT. No chlorosis was observed in any treatment until after 21 DAT in 2021. Only the combination of pyraclonil followed by thiobencarb and propanil provided any sign of chlorosis at 19% at 42 DAT in 2021. Applying thiobencarb slightly earlier than recommended on the manufacturer's label may have caused the early chlorosis, but the rice was able to recover from the early phytotoxicity.

No stunting was observed for any treatments in 2019 at 14 DAT. The combination of pyraclonil followed by thiobencarb followed by propanil caused 24% stunting by 42 DAT, which was significantly different from the five other treatments (Table 1.3). Pyraclonil alone, pyraclonil followed by propanil, pyraclonil followed by benzobicyclon plus halosulfuron and propanil, pyraclonil followed by clomazone and propanil, and pyraclonil followed by propanil and florpyrauxifen-benzyl caused rates of stunting indistinguishable from the untreated plots. There was no significant stunting from any other treatments besides the combination treatment containing thiobencarb.

The combination of pyraclonil followed by benzobicyclon plus halosulfuron followed by propanil caused 4% stunting in 2021 at 14 DAT, which was slightly more stunting than the other treatments, but otherwise no severe stunting was observed at that early date for any treatment (Table 1.4). Pyraclonil applied alone and pyraclonil followed by benzobicyclon plus halosulfuron followed by propanil caused 7 and 8% stunting, respectively, at 42 DAT. These results agree with earlier research that noted that pyraclonil at rates ranging from 25 to 200 g ai ha^{-1} caused ≤ 8% shoot biomass reduction when applied to a commonly used rice variety in China (Liu et al. 2021). The herbicide program containing thiobencarb resulted in significantly greater stunting at 23% at 42 DAT compared to all other herbicide treatments (Figure 1.3). Baltazar and Smith Jr. (1994) found 30% stunting in rice treated with propanil and thiobencarb and noted that yields were unaffected by this early season stunting. A possible explanation for the phytotoxicity from the herbicide combination containing thiobencarb may result from the application timing. Thiobencarb was applied at 1.5 rice leaf stage in order to coincide with 2 leaf stage of the watergrass species in the field. This application timing is slightly earlier than the recommended application timing of 2 rice leaf stage (Anonymous, 2013).

The interaction of yield by years was significant; therefore, these data were presented separately. The phytotoxicity seen on the rice crop was transient and rice yields were not affected. There were no significant differences in yield among treatments in either study year. In 2019 rice yields averaged 8,796 kg ha^{-1} (Table 1.3), whereas in 2021, yields from the herbicide programs averaged 11,294 kg ha^{-1} (Table 1.4). The difference between the two years' yield may be due to the difference in planting date and weather patterns between the years this study was conducted. The difference in average yield in our study coincided with average rice yield for California. In 2019, the average yield for California rice was 8,536 kg ha^{-1}, whereas in 2021, California rice averaged 10,144 kg ha^{-1} ([CDFA] California Department of Food and Agriculture 2021).

1.4. Conclusions

Pyraclonil applied alone is less effective on watergrass species, bearded sprangletop, ricefield bulrush and smallflower umbrellasedge as compared to the combination treatments tested, but it does provide good control of ducksalad and redstem. Pyraclonil applied in combination with propanil, benzobicyclon plus halosulfuron followed by propanil, clomazone followed by propanil, thiobencarb followed by propanil, propanil followed by bispyribac-sodium, penoxsulam followed by propanil, or propanil followed by florpyrauxifen-benzyl provided excellent weed control with great safety on rice. Pyraclonil performs well as a base herbicide incorporated into a weed management program. When selecting an herbicide to accompany pyraclonil, the history of the weed composition in that field should be considered. Pyraclonil applied at 0.3 kg ai ha^{-1} at day of seeding shows low rice injury by 42 DAT and no negative effect on yield. The addition of pyraclonil for use in California rice will provide growers with a new, much needed tool for weed management options if registered for use in California.

1.5. Acknowledgements

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Tables and Figures

Table 1.1. Herbicides, rates, and application timings of the pyraclonil treatments applied on rice at Biggs, CA in 2019 and 2021.

Herbicides	Trade Name	Rate (kg ai ha^{-1})	Application Timing
Pyraclonil	Zembu ®[a]	0.3	Day of seeding (DOS)
Pyraclonil	Zembu ®[a]	0.3	DOS
Propanil	SuperWHAM!® CA[b]	6.7	5 rice-leaf stage
Pyraclonil	Zembu ®[a]	0.3	DOS
Benzobicyclon/ Halosulfuron	BUTTE®[c]	0.26	1.5 rice-leaf stage
Propanil	SuperWHAM!® CA[b]	6.7	5 rice-leaf stage
Pyraclonil	Zembu ®[a]	0.3	DOS
Clomazone	Cerano 5 MEG®[d]	0.7	DOS
Propanil	SuperWHAM!® CA[b]	6.7	5 rice-leaf stage
Pyraclonil	Zembu ®[a]	0.3	DOS
Thiobencarb	Bolero® UltraMax[e]	0.17	1.5 rice-leaf stage
Propanil	SuperWHAM!® CA[b]	6.7	5 rice-leaf stage
Pyraclonil	Zembu ®[a]	0.3	DOS
Propanil	SuperWHAM!® CA[b]	6.7	5 rice-leaf stage
Bispyribac-sodium	Regiment® CA[e]	0.02	Early rice tillering
Pyraclonil	Zembu ®[a]	0.3	DOS
Penoxsulam	Granite® GR[f]	0.26	3 rice-leaf stage
Propanil	SuperWHAM!® CA[b]	6.7	5 rice-leaf stage
Pyraclonil	Zembu ®[a]	0.3	DOS
Propanil	SuperWHAM!® CA[b]	6.7	5 rice-leaf stage
Florpyrauxifen-benzyl	Loyant®[f]	0.04	Early rice tillering

[a] Nichino America, Inc., Wilmington, Delaware, USA

[b] RiceCo LLC, Memphis, Tennessee, USA

[c] Gowan Company LLC, Yuma, Arizona, USA

[d] Wilbur-Ellis Company LLC, Fresno, California, USA

[e] Valent USA LLC, Walnut Creek, California, USA

[f] Corteva AgriScience, Wilmington, Delaware, USA

Table 1.2. Average percent weed control at 14 and 42 days after pyraclonil treatment (DAT) in 2019 and 2021.

Program	Watergrass spp.[a]		Bearded sprangletop[a]		Ricefield bulrush[a]		Smallflower umbrellasedge[a]		Ducksalad[a]		Redstem[a]	
	DAT											
	14	42	14	42	14	42	14	42	14	42	14	42
	%											
Pyraclonil	76 a	54 b	87 a	80 ab	31 a	24 b	65 a	48 b	85 a	86 a	86 a	94 a
Pyraclonil fb[b] propanil	76 a	88 a	100 a	68 ab	61 a	48 ab	80 a	68 ab	100 a	100 a	100 a	88 a
Pyraclonil fb benzobicyclon/halosulfuron fb propanil	86 a	99 a	50 a	100 a	88 a	97 a	97 a	99 a	100 a	100 a	100 a	100 a
Pyraclonil fb clomazone fb propanil	93 a	99a	80 a	99 a	71 a	69 ab	80 a	78 ab	92 a	100 a	100 a	95 a
Pyraclonil fb thiobencarb fb propanil	96 a	99a	100 a	100 a	75 a	88 a	95 a	96 a	100 a	100 a	100 a	100 a
Pyraclonil fb propanil fb bispyribac-sodium	95 a	100 a	100 a	94 ab	71 a	73 a	87 a	81 ab	100 a	89 a	100 a	100 a
Pyraclonil fb penoxsulam fb propanil	88 a	92 a	100 a	61 b	71 a	87 a	79 a	88 a	100 a	100 a	100 a	100 a
Pyraclonil fb propanil fb florpyrauxifen-benzyl	87 a	98 a	100 a	93 ab	46 a	97 a	80 a	97 a	100 a	100 a	100 a	100 a

[a] Within columns, means accompanied by the same letter do not significantly differ with Tukey's honestly significant difference (HSD) at α=0.05.
[b] followed by

Table 1.3. Rice chlorosis and stunting at 14 and 42 days after treatment with pyraclonil (DAT) and grain yield for rice as affected by pyraclonil applied alone and in combination with other herbicides in 2019.

Program	Chlorosis[a]		Stunting[a]		Yield[a]
	DAT				kg ha^{-1}
	14	42	14	42	
	%				
Untreated control	-	-	-	-	6,316 a
Pyraclonil	73 ab	4 a	0 a	0 b	7,762 b
Pyraclonil fb[b] propanil	61 ab	0 a	0 a	4 b	7,887 b
Pyraclonil fb benzobicyclon/halosulfuron fb propanil	41 ab	0 a	0 a	1 b	9,666 b
Pyraclonil fb clomazone fb propanil	71 ab	0 a	0 a	1 b	8,406 b
Pyraclonil fb thiobencarb fb propanil	79 a	0 a	0 a	24 a	9,517 b
Pyraclonil fb propanil fb bispyribac-sodium	71 ab	0 a	0 a	3 ab	8,506 b
Pyraclonil fb penoxsulam fb propanil	50 ab	0 a	0 a	11 ab	9,362 b
Pyraclonil fb propanil fb florpyrauxifen-benzyl	25 b	0 a	0 a	1 b	9,264 b

[a] Within columns, means accompanied by the same letter do not significantly differ with Tukey's honestly significant difference (HSD) at α = 0.05.

[b] fb, followed by

Table 1.4. Rice chlorosis and stunting at 14 and 42 days after treatment with pyraclonil (DAT) and grain yield for rice as affected by pyraclonil applied alone and in combination with other herbicides in 2021.

Program	Chlorosis[a]		Stunting[a]		Yield[a]
	DAT				kg ha^{-1}
	14	42	14	42	
	%				
Untreated control	-	-	-	-	3,716 a
Pyraclonil	0 a	0 b	2 a	7 b	10,292 b
Pyraclonil fb[b] propanil	0 a	0 b	1 a	4 b	10,914 b
Pyraclonil fb benzobicyclon/halosulfuron fb propanil	0 a	0 b	4 a	8 b	11,754 b
Pyraclonil fb clomazone fb propanil	0 a	0 b	0 a	3 b	11,778 b
Pyraclonil fb thiobencarb fb propanil	0 a	19 a	3 a	23 a	11,137 b
Pyraclonil fb propanil fb bispyribac-sodium	0 a	0 b	1 a	4 b	11,224 b
Pyraclonil fb penoxsulam fb propanil	0 a	0 b	1 a	5 b	11,072 b
Pyraclonil fb propanil fb florpyrauxifen-benzyl	0 a	0 b	2 a	1 b	12,179 b

[a] Within columns, means accompanied by the same letter do not significantly differ with Tukey's honestly significant difference (HSD) at α=0.05.
[b] fb, followed by

Figure 1.1. Study field site in 2021. Rice cultivar ‘M-206’ planted at 168 kg ha^{-1} into a 10 cm flooded field with herbicide treatments applied in 3 m x 6 m plots in a randomized complete block design with 4 replications.

Figure 1.2. Untreated control plot in 2021 showing evidence of 28% abundance of watergrass species.

Figure 1.3. Rice phytotoxicity damage at 50 days after planting in plots treated with pyraclonil, thiobencarb, and propanil. Rice recovered by 90 days after planting.

CHAPTER 2

Responses of Rice Cultivars to Foliar-Applied Metribuzin

Prepared for submission to Weed Technology

Abstract

Metribuzin is a photosynthetic-inhibiting herbicide that controls several important grass and broadleaf weeds. Several crops, including soybeans, wheat, peas, and potatoes, have shown differential varietal responses to metribuzin. The increasing development of herbicide resistance in weeds found in California rice cropping systems has encouraged researchers to evaluate alternate herbicides to prevent and manage herbicide-resistant weed biotypes. To determine whether rice has differential varietal responses to metribuzin for potential utilization in a rice breeding program, greenhouse experiments were conducted to evaluate the response of 142 long-, medium-, and short-grain rice cultivars to the herbicide. Metribuzin was applied at 0, 22, 44, 88, 176, and 352 g ai ha^{-1} when rice plants were at the three- to four-leaf stage. Crop response in terms of phytotoxicity, height reduction, and biomass reduction was evaluated. Metribuzin caused significant injury to all rice lines tested but short-grain rice cultivars were on average more susceptible than medium- and long-grain rice. In general, short-grain rice cultivars had greater height reduction and produced less biomass than long-grain or medium-grain rice lines. Crop visual injury ratings were correlated with plant height reductions and biomass reductions. The results indicate that further research is needed to establish metribuzin's candidacy for development as a POST emergence product in rice. Future research into alternative methods of weed control will be essential to establish a new product for use in California rice agroecosystems.

2.1. Introduction

Rice (*Oryza sativa* L.) is one of the most commonly grown agricultural commodities in the world (Smith 1995) and contributes significantly to sources of human energy across the globe (Kondhia et al. 2015). California is the second largest rice-growing state in the USA, with approximately 200,000 ha of rice acreage in California, much of which is concentrated in the Sacramento Valley. The majority of California's rice production consists of short- and medium-grain *japonica* varieties and a few long-grain *indica* varieties, including cultivars developed for both the local climate and a continuously-flooded cropping system, where rice is pre-germinated and seeded by airplane onto fields with a 10-15 cm standing flood (Ceseski and Al-Khatib 2021; Espino et al. 2019). Decades of using this practice to suppress grass, sedge, and broadleaf weeds that would otherwise decrease yields, in addition to no crop rotation, have selected for weed species that exhibit ecological requirements and growing patterns that are similar to rice and can compete with rice resources (Hill et al. 1994). The flooded conditions in which most California rice is grown favor weedy grasses that are well-adapted to flooded conditions which include watergrass species (*Echinochloa* (L.) Beauv. spp.), bearded sprangletop [*Leptochloa fusca* (L.) Kunth ssp. *fascicularis* (Lam.) N. Snow] and weedy rice (*Oryza sativa* f. *spontanea* Rosh) (Brim-DeForest et al. 2017; Ceseski et al. 2022).

Crop yields and harvest quality face the highest biological constraints due to weed infestations, and farmer inputs towards weed management are expected to increase as herbicide resistances spreads worldwide (Brim-DeForest et al. 2016). Certain weeds and weed groups cause more yield loss than others, even at lower infestation densities (Smith Jr. 1988). In rice systems, grasses are considered the most difficult weeds to control due to the narrow selectivity between the crop and the grass weeds (Carey III et al. 1995). Rice yield losses can amount to

79% after season-long interference from barnyardgrass [*Echinochloa crus-galli* (L.) Beauv.] and have been recorded as high as 59% due to season-long competition with late watergrass [*Echinochloa phyllopogon* (Stapff). Koss] (Gibson et al. 2001; Smith Jr. 1968). Weedy rice is an increasingly problematic weed in rice-growing regions around the world causing yield loss and contamination due to the critical weedy traits of seed shattering and seed dormancy, which builds up a large soil seed reservoir for future years (Ziska et al. 2015). The weedy rice infestation threshold stands at one to three plants m^{-2} in the USA, with higher ratios causing significant yield loss; weedy rice densities of 30 to 40 plants m^{-2} can reduce rice yields by 60-90%, depending on the height of the cultivar (Smith Jr. 1988; Ziska et al. 2015). In California, six biotypes of weedy rice have thus far been identified (de Leon et al. 2019). Infestations of weedy rice cause harvest quality problems, increased production costs, and reduced yield, so an effective method of control is needed (de Leon et al. 2019).

As a result of the continually flooded conditions under which most California rice is produced, the majority of growers rely solely on herbicides and deep-water flooding for weed management (Hill et al. 2006). Permanently-flooded rice agroecosystems are limited, however, to few available herbicides in California, largely due to ecotoxicity and strict regulatory structure (Ceseski and Al-Khatib 2021; Hill et al. 1994). To date, there are 13 registered active ingredients across nine modes of action (MOA) available for use in California flooded rice, which creates few opportunities for herbicide rotation to inhibit herbicide resistance development (Espino et al. 2019).

Current herbicides in use in California rice systems include acetolactate synthase (ALS)-inhibitors, protoporphyrinogen oxidase (protox) inhibitors, carotenoid biosynthesis inhibitors, acetyl CoA carboxylase (ACCase) inhibitors, tubulin inhibitors, photosystem II (PSII) inhibitors, very long chain fatty acid (VLCFA) inhibitors, auxin-mimics, 4-hydroxyphenylpyruvate dioxygenase (HPPD) inhibitors, and 1-deoxy-D-xylulose 5-phosphate (DOXP) inhibitors (Espino et al. 2019). Most California rice herbicides are limited in the spectrum of weeds controlled, requiring proper selection in combination and sequence to provide adequate weed control. Early season grass control applications commonly consist of field rates of carotenoid biosynthesis inhibitors, HPPD inhibitors, ALS inhibitors, or VLCFA inhibitors (Brim-DeForest 2021). Late season cleanup applications often use PSII inhibitors, ALS inhibitors, or ACCase inhibitors in order to control later-emerging grasses (Brim-DeForest 2021).

The continuous use of herbicides with similar modes of action has contributed to herbicide resistance development in several weeds found in California rice systems. California arrowhead (*Sagittaria montevidensis* Cham. & Schltdl.) and smallflower umbrella sedge (*Cyperus difformis* L.) were the first confirmed cases of rice weeds with resistance to bensulfuron-methyl, an ALS-inhibitor, in 1993 (Busi et al. 2006). Since then, eight other rice weed species have been identified, some with resistance to more than one mode of action (Heap 2022; Becerra-Alvarez and Al-Khatib 2022). The rise in herbicide resistance has increased the cost and difficulty of weed management, necessitating demand for novel herbicide development to postpone resistance expansion and assist the management of current herbicide-resistant weed biotypes (Driver et al. 2020).

Metribuzin is a selective and systemic herbicide that controls many broadleaf and some grass weeds (Armendáriz et al. 2014). Metribuzin is a triazinone PSII inhibitor that binds to the Q_B binding site on the D1 protein of the Photosystem II complex in the chloroplast thylakoid membranes. Once the chemical binds to the site, electron transport from Q_A to Q_B is blocked and CO_2 fixation and ATP and $NADPH_2$ production is stopped, halting necessary resources for plant growth (Lambreva et al. 2014). Foliar-applied metribuzin is absorbed into the plant at moderate rates with apoplastic translocation.

To date, metribuzin is labelled for use in alfalfa, asparagus, cereals, field corn, garbanzo beans, lentils, peas, potatoes, sainfoin, soybeans, sugarcane, and tomatoes. There is no label for metribuzin for use in rice in California. Although information regarding the effect of metribuzin application rates and timing on weed control in rice is scant, recent studies from Mississippi have indicated that metribuzin applied post-rice-emergence at 42 g ai ha^{-1} caused 3-6% injury by 28 days after treatment (Lawrence et al. 2021). The same study found no correlation between rice injury from metribuzin and yield reduction, dry weight reduction, maturity delays, or seed germination (Lawrence et al. 2021). Mahajan and Chauhan (2022) evaluated metribuzin at rates 72 and 144 g ai ha^{-1} and were able to reduce *Echinochloa colona* biomass by 70 to 100%, respectively, compared to the untreated control.

Crop tolerance to herbicides may result from the ability of a crop to metabolize the chemical (Wright et al. 2021). Selectivity differences among cultivars depends on accumulation of a critical amount of the active ingredient at the target site of action and a sufficient differential in chemical uptake, in-plant movement, and arrival of the chemical at the correct location in the active form (Cole 1994). Although there may be several factors involved in selectivity, the most imperative function is that of resistant plants metabolizing and detoxifying herbicides rapidly and susceptible plants having reduced or no ability to do so (Cole 1994).

Differential tolerance responses of soybean cultivars to foliar-applied metribuzin have been noted (Hardcastle 1974). In rice, cultivar-specific responses to herbicide treatments have been previously identified and used to develop herbicide-resistant rice lines, such as Clearfield or FullPage (BASF) and Provisia or Max-Ace (ADAMA) rice, which confer resistance to imidazolinones and quizalofop, respectively. Differing levels of sensitivity to triclopyr (Pantone and Baker 1992) and florpyrauxifen-benzyl (Wright et al. 2021), synthetic auxin herbicides, have also been observed in various rice cultivars. The inherent genetic variability in rice cultivars may provide a resource for crop improvement through breeding.

There is a need for additional and alternative herbicide programs to complement sustainable chemical weed control in rice systems. Investigation of differential responses to a chemical can reveal susceptible and tolerant crop lines that may prove useful in breeding programs. With limited knowledge of the response of rice cultivars to metribuzin, the objectives of this research were to evaluate the response of various rice genotypes to post-rice-emergence-applied metribuzin and to determine if early-season injury symptoms from POST application of metribuzin are correlated with reduced shoot biomass.

2.2. Materials and Methods

2.2.1 Growing Conditions

Experiments were conducted during 2021-2022 in greenhouses at the Rice Experiment Station (RES) in Biggs, CA, USA. Plastic flats measuring 28- by 54- by 6-cm were prefilled with a Esquon-Neerdobe (fine, smectitic, thermic Xeric Epiaquerts and Duraquerts) silty clay with a pH of 5.11, and 2.8% organic matter that was sieved through a 2-cm mesh. One hundred forty-two rice lines sourced from the Rice Experiment Station representing long-grain, medium-grain, and short-grain rice were selected and fifteen seeds of each cultivar were sown in rows in the flats, with eight rice lines per flat and each row serving as a single experimental unit (Table 2.1). Flats were placed in large basins which were filled with 5 cm of standing water (Figure 2.1). Plants were grown in greenhouse conditions with average day/night temperatures of 32/18 °C and 16-hour photoperiod with supplemental light intensity of 250 mmol m^2 per second photosynthetic photon flux density.

2.2.2 Metribuzin Treatments

Rice seedlings at the three- to four-leaf stage were treated with 0, 22, 44, 88, 176, and 352 g ai ha^{-1} metribuzin (Glory 4L®, ADAMA Ltd., Raleigh, NC, USA). The treatments were applied with a research track bench sprayer (DeVries Manufacturing, Hollandale, MN, USA) equipped with a flat fan TP8001EVS TeeJet nozzle (TeeJet®Technologies, Wheaton, IL, USA) and calibrated to deliver 187 L ha^{-1} at 180 kPa (Figure 2.2). Control plants were treated with water. Each flat was sprayed at a height of 45 cm above plant canopy.

2.2.3 Data Collection

Visible rice injury was rated at 7, 14, 21, and 28 days after treatment (DAT). Visible injury ratings were based on a scale of 0, indicating no damage, to 100%, indicating plant death (Figure 2.3). Rice lines were classified as tolerant, intermediate, or susceptible if the mean 50% visible injury (ID_{50}) values were respectively higher, equivalent, or lower than 176 g ai ha^{-1}. This rate was used as the reference rate as it is a common use rate of the herbicide product in peas (Anonymous 2014). At 28 DAT, rice height was recorded by measuring the plant from top leaf to soil, and plant biomass was harvested by removing all aboveground tissue. Hand-harvested samples were dried in a greenhouse at 32 to 49 (±5) °C for 2 weeks and weighed to determine rice dry weight. Biomass and height data were reported as percent biomass and height reduction and were calculated as

$$\% \text{ reduction} = \left[\frac{\text{UTC} - \text{B}}{\text{UTC}}\right] * 100$$

where *UTC* is the mean biomass (g) or height (cm) of the untreated control for each respective rice cultivar and *B* is the biomass (g) or height (cm) of the experimental unit of interest (Ortmeier-Clarke et al. 2022).

2.2.4 Statistical Analysis

The experiment was a randomized complete block design with a split-plot arrangement of treatments, wherein each treatment was replicated three times and the experiment was conducted twice. The main plots were the rice lines, and the subplots were the herbicide rates. The experimental unit of interest was the row of plants representing each rice line in each flat. Secondary analysis based on averaged values from the rice lines combined within their respective grain types was also performed. Data from the two experimental runs and the three replications were combined as the experimental runs and replications were considered random effects. The data were fitted to the four-parameter logistic model:

$$y = a + \frac{(a - c)}{[1 + \left(\frac{x}{x_0}\right)^b]}$$

where a is the lower limit representing plant survival at increasingly large herbicide rates, c is the upper limit representing plant survival at low herbicide rates close to untreated controls, x_0 is the rate giving 50% plant response and b is the slope around x_0. Metribuzin rates that caused 50% visible injury (ID_{50}), biomass reduction (GR_{50}), and height reduction (HR_{50}) were estimated for each rice line and each grain type using the *ed* function in the *drc* package in R (Ritz et al. 2015) to create nonlinear regression models (R Development Core Team, 2022). ID_{50}, GR_{50}, and HR_{50} values were analyzed using ANOVA and means were separated using Tukey-Kramer's honestly significant difference (HSD) at 95% significance level. Correlation coefficient analysis on phytotoxicity versus height reduction and biomass reduction was estimated using JMP Pro 16 (JMP®, Version Pro16. SAS Institute Inc., Cary, NC, 1989–2022).

2.3 Results and Discussion

There was no interaction across experimental runs for rice injury, height reduction, and biomass reduction so the data were averaged over two experimental runs. Foliar application of metribuzin injured all rice cultivars at all rates. Metribuzin injury symptoms were characterized by stunting and leaf chlorosis originating at leaf margins followed by necrosis. Estimations of injury were similar to the symptoms observed from other PSII inhibiting herbicides (Smith Jr. 1965). As the study progressed, the damage symptoms became more apparent; symptoms on treated plants became more severe at 14 DAT than at 7 DAT (data not shown). Crop damage peaked at 21 DAT, with treated plants that remained alive at this rating stage showing some recovery from injury by producing new, normal growth by 28 DAT. Crop phytotoxicity from metribuzin at 352 g ai ha^{-1} was more pronounced than at the use rate of 176 g ai ha^{-1} at all rating dates.

2.3.1 Phytotoxicity

There was no significant difference among rice cultivars in metribuzin injury response at any rate tested (Table 2.2). Across all 142 rice cultivars tested, crop injury at 21 DAT ranged from 30 to 88% at the use rate of 176 g ai ha^{-1} and 53 to 100% at the 352 g ai ha^{-1} rate (data not shown).

Differing grain type (long-, short-, and medium-grain) was represented among the 142 rice lines tested. There were differences between crop injury response to metribuzin and the grain type of the rice cultivars (Figure 2.4). The average ID_{50} value for the short-grain rice lines was 136 g ai ha^{-1}, which was significantly lower than the average ID_{50} for either long-grain or medium-grain rice lines, which were 172 g ai ha^{-1} and 182 g ai ha^{-1}, respectively ($P = 0.009$) (Table 2.3). These results indicate that short-grain varieties are more susceptible to injury from foliar-applied metribuzin than long-grain or medium-grain rice lines. Differences in grain type response to metribuzin may result from inherent differences in genetic background among the different grain types. Differential response studies in soybeans have found cultivars that exhibit significant differences in crop injury from metribuzin (Barrentine et al. 1976). In a previous study, a rice gene, *HIS1*, was found to confer resistance to benzobicyclon and other β-triketone herbicides through chemical metabolism and detoxification; susceptible rice cultivars carried a defunct allele from an *indica* rice line that disabled functionality of the gene (Maeda et al. 2019). In that study, the difference in grain types resulted in a genetic difference that altered the metabolic conversion of the toxic chemical and resulted in tolerant and susceptible rice cultivars.

2.3.2 Height Reduction

Correlation coefficient analysis showed that rice phytotoxicity is highly correlated with rice cultivar height response ($r = 0.727$, $P < 0.0001$) (data not shown). There was no difference among any rice cultivar height response and rate of applied metribuzin except at the 88 g ai ha^{-1} rate ($P = 0.0407$). Of all the rice lines tested, long-grain cultivar 'RES14' displayed an average 36% height increase at 88 g ai ha^{-1} metribuzin (data not shown). This was significantly different from short-grain rice line 'RES223' and long-grain rice line 'Calmati-202', which displayed the highest amount of height reduction, 45% and 33% height reduction, respectively, at the 88 g ai ha^{-1} metribuzin rate (data not shown).

The average height HR_{50} results for the rice lines showed no difference among the grain types tested ($P = 0.002$) (Figure 2.4). Long-grain, medium-grain, and short-grain rice all required

173 to 198 g ai ha^{-1} for a 50% height reduction response (Table 2.3). These results indicate that metribuzin has an equivalent effect on height reduction across all grain types.

There were differences among the rice grain types and height reduction responses as a result of differing doses of metribuzin. At 88, 176, and 352 g ai ha^{-1} metribuzin, all three grain types had significantly different height reduction responses ($P < 0.0001$) (Table 2.4). Short-grain rice lines consistently displayed the greatest crop height reduction in response to increasing doses of metribuzin, ranging from 17 to 87% height reduction at 88, 176, and 352 g ai ha^{-1} metribuzin.

2.3.3 Biomass Reduction

Correlation coefficient analysis showed that rice phytotoxicity is moderately correlated with rice cultivar biomass response ($r = 0.657$, $P < 0.0001$) (data not shown). Reduction in plant biomass was observed for all cultivars at metribuzin rates 176 and 352 g ai ha^{-1} metribuzin (data not shown). At 176 g ai ha^{-1} metribuzin, the biomass of short-grain 'RES223' was significantly reduced by 88% of the untreated control. Long-grain lines 'RES8', 'CL271', and 'RES19' produced the least biomass reduction at 10, 8, and 4% of the untreated control, respectively. 'RES8' and 'RES19' are rice lines that were developed specifically for California water-seeded rice production. At 352 g ai ha^{-1} metribuzin, there were six rice cultivars that responded with biomass reductions ranging from 90 to 94%: 'RES223', 'RES213', 'RES226', 'RES216', 'RES230', and 'RES212', all of which were short-grain. At this rate, there were seven long-grain varieties that had biomass reductions that were less than those previously mentioned; 'L-205', 'RES36', 'L-201', 'CL271', 'RES35', 'Rex', and 'Della-2' had biomass reductions ranging from 6 to 20% at 352 g ai ha^{-1}. Of the seven long-grain rice lines that had less biomass reductions, four were developed for California rice conditions: 'L-205', 'RES36', 'L-201', and 'RES35'.

Researchers in Australia found that doses of metribuzin as low as 36 g ai ha^{-1} were required to reduce the negative effect on rice biomass (Mahajan and Chauhan 2022), so the results of the present study concur with this conclusion.

Biomass GR_{50} values were varied among the rice grain types tested in this study (Figure 2.4). The average GR_{50} for the medium-grain rice lines was 94 g ai ha^{-1}, which was significantly lower than the GR_{50} for long-grain rice lines, which averaged 114 g ai ha^{-1} ($P < 0.0001$) (Table 2.3). These results would indicate that medium-grain varieties are more susceptible to rice biomass reduction at a lower dose of foliar-applied metribuzin than long-grain rice lines. These findings are similar to results from research that showed differential responses of annual ryegrass cultivars to foliar-applied metribuzin and atrazine (Ma et al. 2020). The differential response of annual ryegrass cultivars to metribuzin may have been due to differences in metabolism of the foliar-absorbed herbicide. Annual ryegrass cultivars that were more tolerant to foliar-applied metribuzin metabolized metribuzin twice as quickly as the more sensitive cultivars (Ma et al. 2020).

There were differences between the rice grain types and the rate of biomass reduction as a result of differing doses of metribuzin. At 88, 176, and 352 g ai ha^{-1} metribuzin, all three grain types produced different biomass responses ($P < 0.0001$) (Table 2.4). Short-grain rice cultivars continually exhibited higher biomass reduction in response to increasing doses of metribuzin as compared to the other two grain types. Biomass reduction values for the short-grain cultivars averaged 73 to 87% reduction at 88, 176, and 352 g ai ha^{-1} metribuzin.

2.4. Conclusions

At all tested rates, short-grain rice cultivars were more susceptible to metribuzin than long-grain or medium-grain rice lines. In general, short-grain rice cultivars had greater height reduction and produced less biomass than long-grain or medium-grain rice lines. Crop injury from metribuzin was moderately correlated with biomass reductions and highly correlated with plant height reductions. However, further research is required to verify the extent of crop injury and resiliency from foliar-applied metribuzin under field conditions. Additional research will focus on the effect of early season foliar metribuzin application on rice yields and grain quality.

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Tables and Figures

Table 2.1. Rice line and grain type for 142 cultivars[a] used in the greenhouse study to evaluate the differential rice response to post-emergence foliar-applied metribuzin.

Grain Type							
Long-grain			Medium-grain			Short-grain	
A-201	RES6	RES31	M-105	RES159	RES333	RES209	RES245
A-202	RES7	RES32	M-205	RES160	RES340	RES212	RES247
Calaroma-201	RES8	RES34	M-206	RES161	RES341	RES213	RES251
Calmati-201	RES9	RES35	RES107	RES167	RES342	RES214	RES256
Calmati-202	RES10	RES36	RES110	RES171	RES344	RES216	RES257
Cheniere	RES11	RES37	RES111	RES172	RES358	RES218	RES259
CL271	RES12	RES38	RES114	RES173	RES359	RES220	RES261
Cocodrie	RES13	RES39	RES117	RES174	RES360	RES221	S-102
Della-2	RES14	RES40	RES119	RES175		RES223	S-201
Jazzmin-2	RES15	RES41	RES120	RES176		RES226	S-301
L-201	RES16	RES42	RES121	RES179		RES227	
L-202	RES17	RES43	RES125	RES183		RES228	
L-203	RES19	RES44	RES130	RES185		RES230	
L-204	RES20	RES45	RES131	RES187		RES233	
L-205	RES21	RES46	RES135	RES190		RES236	
L-206	RES22	RES324	RES140	RES199		RES237	
RES1	RES24	Rex	RES142	RES200		RES238	
RES2	RES25	Rondo	RES146	RES201		RES241	
RES3	RES28	Titan	RES153	RES204		RES242	
RES4	RES29		RES154	RES205		RES243	
RES5	RES30		RES157	RES329		RES244	

[a]Plant material sourced from the California Rice Experiment Station, Biggs, CA, USA

Table 2.2. Estimated metribuzin rate required to cause 50% visible injury (ID_{50}), height reduction (HR_{50}), and biomass reduction (GR_{50}) for 142 rice cultivars. Plants were treated at the three- to four-leaf stage. Visible injury was assessed at 21 days after treatment (DAT) and heights were recorded and dry weights were collected 28 DAT.

Cultivar	Grain type[a]	ID_{50}	HR_{50}	GR_{50}
			g ai ha^{-1}	
RES12	LG	354	350	71
RES13	LG	354	110	123
RES9	LG	328	138	155
RES227	SG	323	172	50
RES159	MG	320	260	93
RES17	LG	319	428	172
Cocodrie	LG	308	288	175
RES4	LG	306	95	113
RES190	MG	297	183	69
RES114	MG	288	251	78
RES41	LG	286	97	122
RES205	MG	281	193	56
RES171	MG	268	202	63
RES8	LG	266	102	234
RES342	MG	263	260	42
RES2	LG	262	182	144
RES19	LG	252	45	149
RES32	LG	246	123	43
RES3	LG	238	338	48
RES125	MG	237	276	140
RES14	LG	236	129	36

RES28	LG	229	445	63
RES46	LG	225	193	109
RES175	MG	218	162	120
RES221	SG	217	189	79
RES111	MG	217	196	176
RES160	MG	216	253	57
Calaroma-201	LG	214	157	149
RES344	MG	213	304	94
RES333	MG	210	200	124
RES161	MG	208	222	104
RES29	LG	206	194	121
RES21	LG	202	62	67
RES216	SG	202	250	123
RES200	MG	200	201	159
L-204	LG	199	224	51
RES119	MG	198	140	142
RES167	MG	198	297	196
L-203	LG	188	172	133
RES131	MG	187	230	86
RES130	MG	186	192	81
RES40	LG	185	128	79
RES16	LG	184	226	83
L-201	LG	183	183	111
RES360	MG	182	282	135
RES174	MG	182	232	56

RES22	LG	181	329	56
RES20	LG	179	198	99
RES241	SG	178	293	109
RES176	MG	174	185	73
RES185	MG	174	220	125
RES121	MG	173	196	84
M-105	MG	172	195	88
RES117	MG	170	259	104
A-202	LG	169	130	80
M-205	MG	169	199	83
S-201	SG	169	145	126
RES359	MG	169	251	147
S-301	SG	168	189	53
RES204	MG	167	231	100
RES5	LG	167	97	43
RES146	MG	167	167	125
Jazzmin-2	LG	166	CF[a]	73
RES15	LG	166	186	137
RES226	SG	166	99	119
Calmati-201	LG	164	207	213
RES154	MG	163	416	83
RES107	MG	163	209	79
RES120	MG	162	185	129
RES199	MG	160	182	223
RES11	LG	160	173	65

RES247	SG	160	151	101
RES259	SG	160	160	123
RES44	LG	158	168	118
RES172	MG	157	273	102
RES45	LG	152	141	133
RES142	MG	151	192	98
RES37	LG	151	141	103
RES341	MG	149	295	120
RES110	MG	148	238	77
RES153	MG	148	225	119
RES157	MG	146	178	61
Cheniere	LG	146	181	79
RES256	SG	145	172	122
RES43	LG	144	274	65
RES35	LG	143	158	94
RES358	MG	143	193	42
RES31	LG	143	183	97
RES183	MG	142	186	60
RES135	MG	142	224	170
RES187	MG	142	292	93
RES7	LG	142	139	90
RES340	MG	140	189	79
RES10	LG	138	157	92
RES230	SG	135	185	131
RES140	MG	134	237	84

RES329	MG	132	278	115
RES251	SG	132	127	98
L-206	LG	131	109	41
RES173	MG	130	210	132
RES179	MG	129	230	127
RES213	SG	128	119	99
RES212	SG	128	174	148
Titan	LG	127	159	141
CL271	LG	127	212	60
RES214	SG	126	198	53
RES218	SG	125	95	134
RES280	MG	124	295	158
RES261	SG	122	160	82
RES236	SG	121	172	83
RES233	SG	118	87	117
Rex	LG	118	145	45
Della-2	LG	117	148	107
RES25	LG	116	138	109
RES209	SG	116	88	89
RES39	LG	113	111	95
A-201	LG	113	122	194
RES238	SG	110	163	81
RES24	LG	109	413	79
RES245	SG	108	152	85
RES201	MG	107	164	253

RES220	SG	103	158	102
RES244	SG	98	142	158
RES228	SG	97	103	115
RES243	SG	96	170	101
RES237	SG	95	147	87
S-102	SG	95	91	123
RES223	SG	94	84	96
RES38	LG	93	89	31
RES30	LG	92	91	86
Calmati-202	LG	92	60	41
RES42	LG	90	86	71
RES257	SG	89	121	103
Rondo	LG	88	86	55
RES242	SG	86	126	81
RES6	LG	86	102	103
L-205	LG	86	68	56
RES1	LG	86	109	145
L-202	LG	85	92	46
RES36	LG	73	74	235
RES34	LG	66	32	26
RES324	LG	55	57	53

[a]abbreviations: LG= long-grain; SG = short-grain; MG = medium-grain; CF = convergence failure

Table 2.3. Average metribuzin rate required to cause 50% visible injury (ID_{50}), height reduction (HR_{50}), and biomass reduction (GR_{50}) in the 142 rice grain types studied. Plants were treated at 3-4 leaf stage. Visible injury information was recorded at 21 days after treatment (DAT) and dry weight and heights were collected at 28 DAT.

Grain Type[b]	ID_{50}[a]	HR_{50}[a]	GR_{50}[a]
		g ai ha^{-1} (± standard error)	
SG	136 b (± 11)	198 a (± 15)	95 ab (± 8)
LG	172 a (± 8)	186 a (± 10)	114 a (± 5)
MG	182 a (± 9)	173 a (± 11)	94 b (± 6)

[a]Within columns, means accompanied by the same letter do not significantly differ with Tukey's honestly significant difference (HSD) at α=0.05.
[b]SG = short-grain, 31 cultivars; LG = long-grain, 61 cultivars; MG = medium-grain, 50 cultivars

Table 2.4. Average rice height reduction and biomass (%) for each grain type at 28 days after foliar applied metribuzin at varying rates. Positive numbers indicate percent reduction as compared to the nontreated control plants and negative numbers indicate percent increase as compared to the nontreated control plants.

	Height Reduction[a]			Biomass Reduction[a]		
	Dose (g ai ha^{-1})					
Grain Type[b]	88	176	352	88	176	352
	% (± standard error)					
SG	17 a (± 3)	42 a (± 3)	69 a (± 4)	73 a (± 3)	78 a (± 3)	87 a (± 2)
LG	4 b (± 1)	25 b (± 2)	36 c (± 3)	26 b (± 2)	46 b (± 2)	54 c (± 2)
MG	-2.2 c (± 2)	13 b (± 2)	55 b (± 2)	32 b (± 4)	53 b (± 3)	76 b (± 2)

[a]Within columns, means accompanied by the same letter do not significantly differ with Tukey's honestly significant difference (HSD) at α=0.05.
[b]SG = short-grain, 31 cultivars; LG = long-grain, 61 cultivars; MG = medium-grain, 50 cultivars

Figure 2.1. Fifteen seeds of each rice cultivar were sown into rows within the flats, with 8 rice lines per flat, with 3 replications. Flats were placed in basins filled with 5 cm of standing water.

Figure 2.2. Metribuzin at varying doses was applied with a research track bench sprayer (DeVries Manufacturing, Hollandale, MN, USA) equipped with a flat fan TP8001EVS TeeJet nozzle (TeeJet®Technologies, Wheaton, IL, USA) and calibrated to deliver 187 L ha^{-1}).

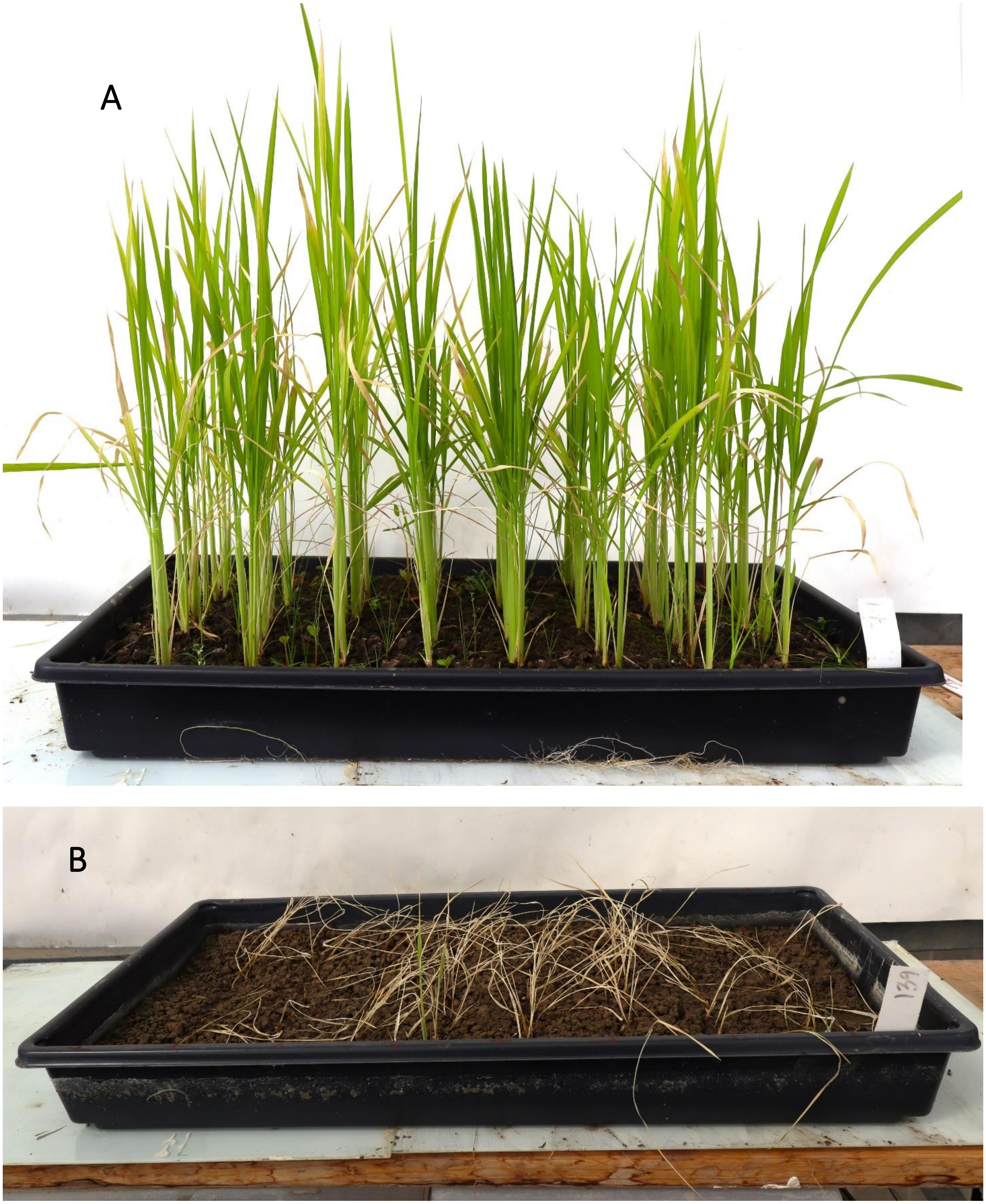

Figure 2.3. Flats containing rice lines that were classified as 0%, no damage (A) or 100%, plant death (B) as a result of foliar applied metribuzin applied 21 days previously.

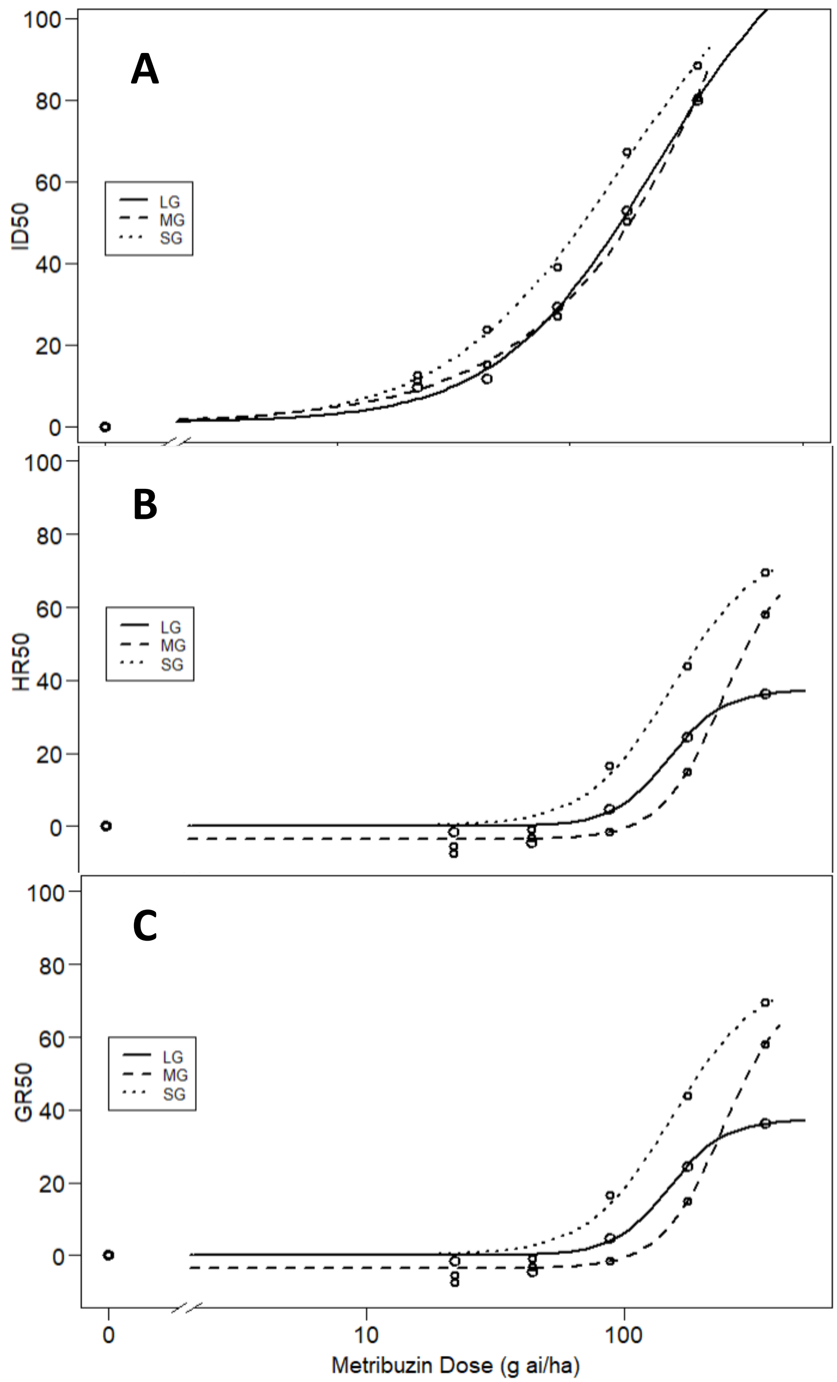

Figure 2.4. Rice phytotoxicity, height reduction, and biomass reduction as a result of increasing doses of metribuzin on 61 long-grain, 50 medium-grain and 31 short-grain rice lines are shown as ID_{50} (A), HR_{50} (B), and GR_{50} (C). The data are averaged from two experimental runs with three replicates. Curves represent four-parameter logistic regression. Equation: $Y = a + (a - c) / [1+(x/x_0)^b]$, where *a* and *d* are the maximum and minimum estimated values, *b* is the relative slope of regression about x_0, and x_0 is the rate giving 50% plant response.