Characterization of the Herbicide Pendimethalin in Water-Seeded Rice

By

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DISSERTATION

Submitted in partial satisfaction of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

Horticulture and Agronomy

in the

OFFICE OF GRADUATE STUDIES

of the

UNIVERSITY OF CALIFORNIA

DAVIS

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2024

**Acknowledgements**

First and foremost, I would like to thank Dr. Kassim Al-Khatib, who served as an outstanding PhD advisor and created an environment that allowed me to succeed. I also want to thank the various mentors I had at UC Davis and during my undergraduate at CSU Chico, which include Dr. Brad Hanson, Dr. Whitney Brim-DeForest, Dr. Alex Ceseski, and Dr. Hossein Zakeri. Thank you all for the support and advice. I am also thankful for the UC Weed Science group and the UC Rice group, past and present members, which made the time at Davis and Biggs enjoyable. Lastly, I would like to thank my family for their continuous support during my academic journey.

I would also like to acknowledge the various fellowships I received that helped fund my time as a graduate student. They include the 2021 D. Marlin Brandon Rice Research Fellowship awarded by the California Rice Research Trust, the Horticulture and Agronomy Graduate Group scholarships including the Bert and Nell Krantz Fellowship and the Jack Pickett Agricultural Scholarship, the UC Davis Department of Plant Sciences, for the GSR scholarship funded by the James Monroe McDonald Endowment, administered by UCANR, and the William G. and Kathleen Golden International Agricultural Fellowship from UC Davis.

**Abstract**

California has approximately 200,000 ha of land in rice (*Oryza sativa* L.) production centered in the Sacramento and Northern San Joaquin Valleys. Herbicide-resistant weeds are a continuing challenge in California rice which has led to the reduction of weed control from available herbicides. Our greenhouse herbicide resistance screening showed that pendimethalin controlled herbicide-resistant grass populations. Currently, there are no group 3 mode of action herbicides used in water-seeded rice; therefore, we evaluated pendimethalin for use in water-seeded rice. Three pendimethalin formulations applied at three rates and three timings were evaluated for rice response and weed control in 2020 and 2021 field studies. Additionally, rice cultivar response was examined in greenhouse studies across five common California rice cultivars to two pendimethalin formulations at two rates and application timings. The results demonstrated rice injury was reduced when pendimethalin was applied at 10 days after seeding (DAS) (3-leaf stage rice) and 15 DAS (4-leaf stage rice) compared to a 5 DAS (1-leaf stage rice) application; however, weed control was reduced up to 34% at these later timings. The cultivars demonstrated 68% reduced stand establishment when pendimethalin was applied at 5 DAS. When treated at 10 DAS, all cultivars except 'M-205' were similar to the nontreated in stand establishment and dry biomass. Cultivars with increased seedling vigor were more tolerant to the pendimethalin post-emergence applications. The reduction in weed control from a 15 DAS application compared to earlier timings in the field study led to a further field study evaluating weed control and rice response from pendimethalin applied post-emergence alone and in herbicide mixtures at 1.1, 2.3 and 4.4 kg ai ha$^{-1}$ in 2022 and 2023. When pendimethalin was applied in mixtures, grass weed control was 68% to 86% compared to pendimethalin applied alone which only control weeds 48% to 63%. All treatments resulted in less than 8% visual rice injury and tiller counts and grain yields resulted similar to the standard treatment of clomazone applied at day of rice seeding. Pendimethalin did not cause injury of concern on rice when applied at the 4- to 5-leaf stage water-seeded rice. In 2021, a study was carried out to determine pendimethalin behavior in flood water of a water-seeded rice field. In this study, three pendimethalin formulations were applied at three rates onto the water and water samples collected at 1, 3, 5, 10 and 15 days after treatment for analysis. The residue concentrations at 1 day after treatment ranged from 3.0 to 125.6 parts per billion and dissipated quickly over time. A first-order dissipation model fit the data and calculated half-lives were 2.3 to 3.5 days from the capsule suspension, 0.6 to 0.7 days from the emulsifiable concentrate and 3.5 to 6.9 days from the granule formulation. Pendimethalin did not result in residue concentrations of environmental concern. The results can assist in generating management tactics to ensure weed control activity and reduce off-target contamination. Overall, the results from this research provide supporting data to pursue registration of pendimethalin for water-seeded rice and add to the body of knowledge of rice herbicide tolerance and herbicide dissipation in water-seeded rice.

**Keywords:** Herbicide degradation; herbicide formulations; herbicide rate; herbicide mixtures; rice injury.

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# Chapter 1

## Review of Pendimethalin Characteristics

Aaron Becerra-Alvarez

## Introduction

Management of weeds is a challenge in crop production. Weeds can interfere with the cultivated crop by competing for light, water and nutrients, which can lead to reduced yields and reduced economic return on investment to the grower (Radosevich et al. 1997). The approach for integrated management of weeds consists of combined inputs from cultural, mechanical, biological and chemical control methods. Cultural practices like clean seed, clean equipment, and proper field preparation are commonly integrated with mechanical practices like tillage, mowing or cultivation for control of weeds. Biological practices are less common in weed management. Therefore, chemical control is the following option to integrate for weed management (Harker and O'Donovan 2013). Chemical practices are the use of herbicides to prevent weed emergence or to cease growth of weeds until plant death, in most cases. Herbicides continue to be important tools to integrate in weed management programs because of their cost-effectiveness, rapid action and flexibility with management, when used appropriately, which have allowed for increased crop yields to be achieved (Radosevich et al. 1997). A successful weed management program can be accomplished when cultural, mechanical and chemical management are integrated.

In the California rice production system, herbicide resistance has been a continuing challenge due to continuous rice cultivation year after year, a historically limited number of herbicides available and the overuse of the available herbicides for weed control (Hill et al. 2006). From 2015 to 2021, there were 661 suspected herbicide-resistant weed reports and nearly 53% of watergrass populations recorded multiple-resistance to up to four modes of action (Becerra-Alvarez et al. 2023). The presence of herbicide-resistant weeds leads to a reduction in weed control with the available herbicides and reduced yield. The most recent herbicides registered in California rice include pyraclonil in 2024, florpyrauxifen-benzyl in 2023, benzobicylcon in 2017, carfentrazone in 2006 and clomazone in 2004 (CA DPR 2024). However, these herbicides have varying degrees of control over different weed species and producers are limited in control options (Becerra-Alvarez et al. 2023). There is a need for new herbicide tools to maintain the viability of the current herbicides for future years by practicing herbicide rotations and mixtures (Busi et al. 2020; Becerra-Alvarez et al. 2023). However, the registration of new modes of action in a crop or region is influenced by many factors like the crop injury potential, weed control efficacy, environmental concerns or lack of economic incentive by the manufacturing companies (Duke 2012; Fennimore and Doohan 2008).

Because not many new herbicide modes of action have been developed recently (Duke and Dayan 2022) and herbicide resistance is increasing, new potential rice herbicides can be evaluated from other cropping systems or by revaluating or reformulating older chemistries. There has been success in introducing herbicides from larger agronomic crops to high value specialty crops through the Interregional Project Number 4, a US federal program (Fennimore and Doohan 2008). Similarly, evaluating older chemistries for new crops can be successful; however, the environmental effects are of greater concern because old chemistries tend to be less environmentally safe (Stewart et al. 2011). Various characteristics are important to consider when evaluating a potential herbicide for a new crop like crop safety, weed control spectrum and persistence in the environment. To ensure a greater potential for success when evaluating new herbicides, a hypothesis-driven research approach should be taken.

Pendimethalin [N-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine] is a mitotic inhibiting (Group 3) herbicide from the dinitroaniline chemistry that inhibits seedling growth shortly after germination (Appleby and Valverde 1989). Pendimethalin controlled herbicide-resistant grass populations in the greenhouse (Fischer et al. 2000) and has relatively few reports of resistant weed populations (Heap 2023). Preliminary greenhouse work indicated pendimethalin was effective in controlling several recently collected herbicide-resistant grasses from California rice fields (Personal observation). Therefore, pendimethalin could be a valuable addition for management of herbicide-resistant weedy grasses. Pendimethalin is registered for use in dry-seeded rice and commonly applied to the soil surface after drill-seeding rice relatively deep in the soil (Bond et al. 2009). In dry-seeded systems; however, rice injury from pendimethalin is influenced by soil moisture, where higher soil moisture leads to greater injury levels (Awan et al. 2016). Characterization of pendimethalin in water-seeded rice, where moisture is always present, has not been evaluated because of the perceived risk of rice injury (Fischer et al. 2000). There is no previous research that has evaluated pendimethalin formulations at different rates and timings in water-seeded rice. Therefore, the objective of these studies was to evaluate and characterize pendimethalin in water-seeded rice.

The objective of this chapter is to review the literature on pendimethalin, pendimethalin use in rice production systems and background related to characterizing pendimethalin for water-seeded rice. This review will provide greater background to the research studies outlined in the following dissertation chapters. The review will begin with a history and background of the dinitroaniline chemical family, pendimethalin use in rice, environmental fate of pendimethalin in rice production systems, and future directions for characterization in water-seeded rice.

**History and Background of the Dinitroaniline Chemical Family**

The dinitroaniline chemistries have been available herbicides since the 1960's. The first dinitroanilines were synthesized by the Eli Lilly Research Laboratories and included trifluralin, benefin, nitralin, isopropalin, oryzalin, profluralin, butralin, ethalfluralin, fluchloralin and prosulfalin (Parka and Soper 1977). Trifluralin (α,α,α,-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine) was the first commercialized compound in the US and was used in soybean and cotton as a pre-plant incorporation for grass weed control at rates of 1,000 to 2,000 g ai $ha^{-1}$ (Epp et al. 2017). The dinitroanilines are most effective in controlling annual grasses and small seeded broadleaf weeds (Shaner et al. 2014). Currently, trifluralin and pendimethalin are the most commonly used dinitroanilines in the US and worldwide for weed control in cereals, cotton, soybeans, vegetables, ornamentals and fruit and nut trees (Chen et al. 2021; Shaner et al. 2012).

Pendimethalin was developed by American Cyanamid in the 1970’s, previously named penoxalin (Helling 1976). BASF would later purchase the American Cyanamid’s agrichemical business and take possession of pendimethalin in the 2000’s. Pendimethalin was moderately less volatile than trifluralin, which lead to relatively greater soil persistence and longer weed control activity (Kennedy and Talbert 1977).

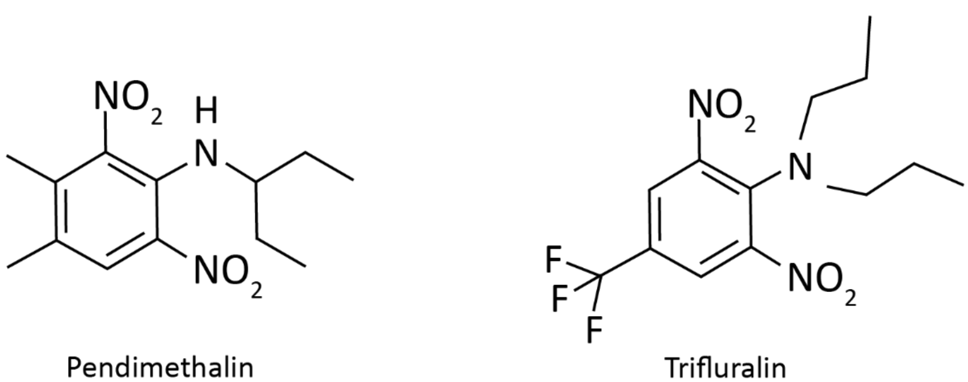


Figure 1-1. Pendimethalin and trifluralin chemical structures. Both compounds have the 2,6-dinitroaniline chemical base structure.

*Characteristics of Dinitroanilines.* The physical, chemical and biological properties of herbicides can help broadly predict their behavior in the environment, weed control efficacy and handler safety. The 2,6-dinitroaniline chemical structure is the base structure that defines the compounds in the dinitroaniline chemical group (Figure 1). The additional chemical structures on the base structures will affect the specific characteristics of each compound.

The common characteristics in all dinitroaniline compounds is a low water solubility, typically <1 parts per million (ppm), and most are soluble in organic solvents. The nitro groups decrease the water solubility by creating hydrogen bonds with alkyl groups of other compounds like soil or organic sediments, which creates lipophilic aggregates (Weber 1990). The lipophilic nature appears to make the compounds susceptible to bioaccumulation in the environment; however, they have a high affinity for organic sediments or organic matter in the soil (Koc= 80 to 471,000). Most compounds are non-ionizable, except for oryzalin (Helling 1976). These characteristics tend to lead to the classification of dinitroanilines including pendimethalin as low risk for contaminating surface or ground water and low risk to environment contamination and human health (Helling 1976; Vighi et al. 2017).

A major characteristic with dinitroanilines is volatility, with trifluralin being the most volatile because of the addition of the trifluoromethyl groups (Figure 1; Kennedy and Talbert 1977). Pendimethalin is classified as moderately volatile with a vapor pressure of 1.25 $10^{-3}$ Pa (Shaner et al. 2012). Therefore, incorporation in soil after an application is encouraged either by rainfall, irrigation or mechanical incorporation to reduce volatilization and achieve adequate weed control with pendimethalin (Shaner et al. 2014).

The soil residual carryover to the following growing season after application of pendimethalin and other dinitroaniline herbicides can be concerning when practicing crop rotations that include susceptible crop species. As mentioned, soil persistence is relatively lengthy and if the environment does not promote degradation, then the compound can be present for the following growing season. Photodegradation is observed with pendimethalin but is a minor degradation pathway (Vighi et al. 2017; Shaner et al.2014). Angeles et al. (2020) observed pre-plant herbicides, including pendimethalin, to persist in the soil longer than intended caused by cultural changes from flood irrigation to drip irrigation in processing tomato fields in the San Joaquin Valley, CA. Hanson and Thill (2001) investigated imazethapyr and pendimethalin soil persistence causing winter wheat injury after application on pea/lentil fields; however, wheat injury and yield reduction was rate and location dependent.

*Mode of Action.* Excellent reviews evaluating dinitroaniline mode of action and behavior in plants have been performed by Parka and Soper (1977), Appleby and Valverde (1989) and Chen et al. (2021).

The mode of action of pendimethalin and other dinitroanilines is inhibiting the mitotic pathway of cell division by preventing the assembly of the microtubules. Microtubules are protein-like organelles that are made up of α- and β-tubulin molecules which are heterodimers and form the mitotic spindle which orient cells and direct the cell division (Appleby and Valverde 1989). During cell division, the microtubules create the mitotic spindle by polymerizing the tubulin dimers. In the presence of the herbicides the tubulin does not polymerize. The herbicide molecule will bind to the α-tubulin, which prevents the β-tubulin from docking and polymerization cannot be continued. The polymerization inhibition leads to the halt in cell division, which cause the accumulation of incomplete cells in one area and create the anatomical feature of swollen or clubbed root tips and stunted growing points. Dinitroanilines exclusively bind to plant cells and do not bind to animal microtubules (Appleby and Valverde 1989).

There is evidence which suggests dinitroanilines also inhibit the calcium ($Ca^{2+}$) uptake in the mitochondria. Cytoplasmic calcium is a regulator of cell cycle and redistribute among the organelles and cytoplasm (Hertel and Marme 1983). Studies by Hertel and Marme demonstrated dinitroaniline compounds caused $Ca^{2+}$ to accumulate in the cytoplasm at $10^{-4}$ M nmol $mg^{-1}$ protein concentrations, which could cause interference with microtubule assembly and cell division. However, Morejohn et al. (1987) reported oryzalin to depolymerize microtubules at very low concentrations (0.1 μM). Therefore, Appleby and Valverde (1989) concluded it was unlikely that the effect of calcium regulation would depolymerize microtubules. The calcium deregulation may be a side effect of the dinitroaniline compounds that can affect plant growth when applied post-emergence, but is not the herbicidal mode of action.

Additional evidence also suggest dinitroaniline herbicides can affect guard cell functions when applied on the plant foliage in lab studies. Marcus et al. (2001) demonstrated microtubule-inhibitors prevented stomata guard cells to open, then, re-open after application of drugs that blocked the microtubule-inhibitors. Microtubules remain present in guard cells after cell differentiation and function as a guiding mechanism and signal mechanisms for the opening/closing of guard cells (Marcus et al. 2001). Marcus et al. tested fusicossin, a drug that induces guard cell opening by activation of the proton pumps, after use of microtubule-inhibitors which caused the guard cells to reopen after being signaled to close by the microtubule-inhibitors. These results may indicate the role of microtubules in signal transduction of protons like the $Ca^{2+}$ activity in guard cells which acts to open and close stomata (Marcus et al. 2001). The results support the observed regulation of $Ca^{2+}$ by Hertel and Marme (1983).

Other effects from dinitroaniline herbicide applications include oxidative cell damage by reactive oxygen species that are created in response to the stress in treated plants (Langaro et al. 2017) and reduced absorption and translocation of nutrients in treated plants (Olson et al. 1984).

However, these effects also are observed in relatively tolerant crops and do not contribute to the primary herbicidal mode of action but can be important in suppressing plant growth.

*Weed Resistance.* While resistance to dinitroaniline herbicides is limited, there have been cases reported on 12 weed species including *Alopecurus aequialis, A. myosuroides, Amaranthus palmeri, Avena fatua, Beckmannia syzgachne, Echinochloa crus-galli* var. *crus-galli, Eleusine indica, Fumaria densiflora, Lolium rigidum, Poa annua, Seteria viridis* and *Sorghum halepense* (Heap 2023). The relatively low number of resistance cases may be attributed to lack of documenting or due to the typical practice of applying dinitroanilines in combination with other herbicides. The relatively low resistance could be due to possible fitness costs associated with the resistance mechanisms (Chen et al. 2021). In most crops, dinitroanilines are used as part of an herbicide program and suspected herbicide-resistant plants are controlled with the pre-emergence herbicide mixtures applied early in the season and any surviving plant after the pre-emergence application are likely to be controlled with a post-emergence herbicide with a different mode of action later in the growing season (Chen et al. 2021).

Resistance mutations in the α-tubulin genes have been documented in dinitroaniline-resistant populations inducing target-site resistance (Chen et al. 2021). The resistance-endowing mutation, Thr-239-lle, was initially reported in *E. indica* and later also in *L. rigidum* (Chen et al. 2021). Other resistance-endowing mutations are presented and explained in the review by Chen et al. (2021). There is evidence of fitness loss from the dinitroaniline-resistance mutation Arg-243-Met resulting in a severe reduction in plant biomass accumulation (Chu et al. 2018).

Non-target site resistance mechanisms to dinitroanilines are not common; however, there is not to many research many research on the subject matter probably because of the difficulty in quantifying metabolites in plants (Chen et al. 2021). Early research demonstrated degradation of pendimethalin in tolerant plants, but no single metabolite was more abundant and in some species the parent molecule was the majority recovered residue (Appleby and Valverde 1989). However, there is some indirect evidence of metabolic pendimethalin degradation in multiple resistant populations (Han et al. 2021). The cytochrome P450 genes which Han et al. identifies as responsible for metabolic resistance have been documented to confer resistant to many herbicides and would not be surprising if they contributed to resistance mechanisms against dinitroanilines (Chen et al. 2021).

*Crop and Weed Tolerance.* Lipid content in plant has been associated with tolerance to dinitroaniline herbicides. Hilton and Christiansen (1971) and Ndon and Harvey (1981) demonstrated that lipid content in the seed or roots of the tolerant species can bind the herbicide and prevent it from reaching the site of action. The results agree with the physico-chemical properties of the dinitroanilines, which are lipid-soluble and attracted to lipid-rich plant tissues. In general, broadleaves have greater lipid content in seeds, roots and shoots than grasses, but a positive correlation of lipid content with relative dinitroaniline herbicide tolerance has been observed in grasses such as corn, foxtail, sorghum, and oats (Ndon and Harvey 1981). The lipid binding is a major mechanism of tolerance to dinitroanilines in carrots, *Daucus carota* (Parka and Soper 1977). Safening to dinitroanilines has been demonstrated with applications of lipid type substances to seeds or soil in various plant species (Parka and Soper 1977).

Herbicide placement has been an important action for improving crop tolerance. The dinitroaniline characteristics suggests they will bind to organic matter and not be readily leached; therefore, injury occurs based on the proximity of sensitive plant parts to the herbicide (Parka and Soper 1977). The majority of dinitroaniline herbicides will remain in the upper 7.5 cm of the soil after an application (Shaner et al. 2012). The site of herbicide uptake can differ among plant species in roots and shoots (Durgesha 1994; Malefyt and Duke 1984; Parka and Soper 1977). In green foxtail, *Setaria viridis*, an application of trifluralin in the soil shoot zone caused similar injury to an application in the seed zone, and greater injury than a root zone application, indicating the early shoot herbicide absorption is important for injury on grasses (Knake et al. 1967). Planting the crop seed deeper in the soil can be a management action to prevent contact with the herbicide in the crop's sites of absorption.

**Pendimethalin in Rice Production Systems**

The use of dinitroanilines in rice production systems was not widely adopted before the 1980's because of the potential for significant rice injury (Brewer et al. 1982). However, various research efforts further expanded their potential use in rice systems (Brewer et al. 1982; Koger et al. 2006; Ahmed and Chauhan 2015; Awan et al. 2016). Koger et al. (2006) performed studies to understand effects of rice cultivar, planting depth and rainfall on crop safety after a pendimethalin application in dry-seeded rice. A cultivar effect was observed in three long-grain cultivars and was attributed to the varying mesocotyl lengths. An elongated mesocotyl may mean increased herbicide absorption on the soil surface, while a shorter mesocotyl length would reduce herbicide absorption at the seedling growing point on the soil surface. Therefore, it was observed that deeper planting led to greater crop safety to the pendimethalin. Khaliq and Matloob (2012) suggested a similar mechanism to pendimethalin tolerance in a dry-seeded system.

Awan et al. (2016) and Ahmed and Chauhan (2015) determined rice injury from pendimethalin is affected by soil moisture and application rate in dry-seeded rice. By delaying the soil saturation time up to 7 days after seeding and pendimethalin application, rice injury can be reduced; however, in comparison with other preemergence herbicides, pendimethalin caused the greatest injury levels (Awan et al. 2015). The decrease in grain yields and increased injury levels reduced adoption of pendimethalin by growers in dry-seeded rice (Awan et al. 2015).

In drill-seeded rice, pendimethalin is commonly used. The selectivity mechanism is deeper rice seed planting. Koger et al. (2006) reported that planting depth is influential in enabling crop safety to pendimethalin. When rice seeds are placed 7 to 10 cm in soil, it prevents the growing points from coming in contact with the herbicide on the soil surface, while the herbicide can control the weeds seeds emerging on the soil surface (Bond et al. 2009).

Pendimethalin has successfully been incorporated in drill-seeded rice systems of the US Mid-South. Pendimethalin has been a useful herbicide to manage propanil-resistant barnyardgrass in the Mid-South (Baltazar and Smith 1991; Norsworthy et al. 1999). Pendimethalin can be mixed well with other herbicides and is incorporated as a post-emergence application to overlay soil residual herbicide activity (Osterholt et al. 2019a; Osterholt et al. 2019b; Osterholt et al. 2021).

**Environmental Fate of Pendimethalin in Rice Production Systems**

Barrett and Lavy (1983) evaluated pendimethalin dissipation in common aerobic and nonaerobic cropping systems. The systems evaluated included soybeans (furrow-irrigated), upland rice (flush-irrigated but never continuously flooded) and lowland rice (flush-irrigated and subsequently flooded). Barrett and Lavy demonstrated soil half-lives of 3 to 7 days in lowland rice and upland rice, while half-lives were 7 days in the first year and nearly 20 days the second year in soybeans. The results indicated that soil-water content was a significant factor in pendimethalin dissipation and these results were supported by Savage (1980). Barrett and Lavy (1983) described the dissipation spectrum as rapid dissipation in lowland rice > upland rice > soybeans, which was most likely caused by the alternate wetting intervals in the rice cropping systems that accelerated the dissipation. The dry/wet soil cycles would have increased volatilization in the dry soil and reduce the concentration of pendimethalin (Weber 1990). Weber (1990) suggests volatilization decreases in anerobic or flooded conditions where pendimethalin vapor moves less readily in the wet soil compared to movement in dry soil with more open pore space.

Makkar et al. (2020) demonstrated pendimethalin soil dissipation in dry-seeded and transplanted rice fields to follow a biphasic first-order dissipation. The biphasic first-order dissipation results in a rapid initial dissipation after application followed by steady a dissipation rate. The behavior is commonly observed with other dinitroaniline herbicides (Savage and Jordan 1980). The dry-seeded rice was in non-flooded conditions and flush irrigated, while the transplanted rice was continuously under flooded conditions (Makkar et al. 2020). Similar to Barrett and Lavy (1980), Makkar et al. (2020) demonstrated total pendimethalin dissipated 1 to 2 days faster at the initial phase and about 10 days faster at the final phase in the transplanted rice field (anaerobic conditions) when compared to the dry-seeded rice field (aerobic conditions).

The pendimethalin fate in a flooded rice field is most likely binding to organic compounds in the soil (Vighi et al. 2017). Microbial and photodegradation are other important pathways that can contribute to degradation (Kulshrestha and Singh 1992; Nelson et al. 1983; Shaner et al. 2014); however, the binding action to organic matter appears to be most significant in many environments (Vighi et al. 2017).

In water-seeded rice, behavior of herbicides in the water is important to study. There are many herbicides that need to be activated with the water and perform best in the flooded conditions, while there are herbicides that are absorbed by the foliage and the flood will decrease efficacy (UCANR 2023). Additionally, downstream water quality affected by use of herbicides in water-seeded rice is of paramount concern because of the proximity to other high value crops which may use the water for irrigation and proximity to urban settlements which may use the water for consumption (Hill et al. 2006; Wagner et al. 2019). The US Environmental Protection Agency (EPA) recorded pendimethalin risk of contaminating surface waters in agricultural use to be less than 2% (USEPA 1997). There are no water quality criteria for pendimethalin; however, pendimethalin residues in surface water tributaries near agricultural regions have been documented up to 0.02 parts per billion (ppb) (1 ppb = 1 $\mu g\ L^{-1}$) (Lehotoy et al. 1998; Zimmerman et al. 2000). The US EPA documented 17.6 ppb to be the maximum level of observed pendimethalin residue in surface water, most likely contaminated by spray drift (USEPA 1997). The levels observed are not concerning in terms of environmental contamination (USEPA 1997).

Pendimethalin metabolites are formed in various soil, water and plant environments (Figure 2). The metabolites have not been labeled of environmental concern and for the most part the pendimethalin parent molecule remains intact when bound to organic matter (Vighi et al. 2017). In plants, metabolites are also not common and the majority remain as pendimethalin parent molecule when absorbed (Chen et al. 2021; Engebretson et al. 2001). The metabolites are also not documented as of concern to the environment by the US EPA (USEPA 1997; Vighi et al. 2017); however, quantifying metabolites helps in understanding the partitioning behavior of an herbicide in an agricultural or environmental system.

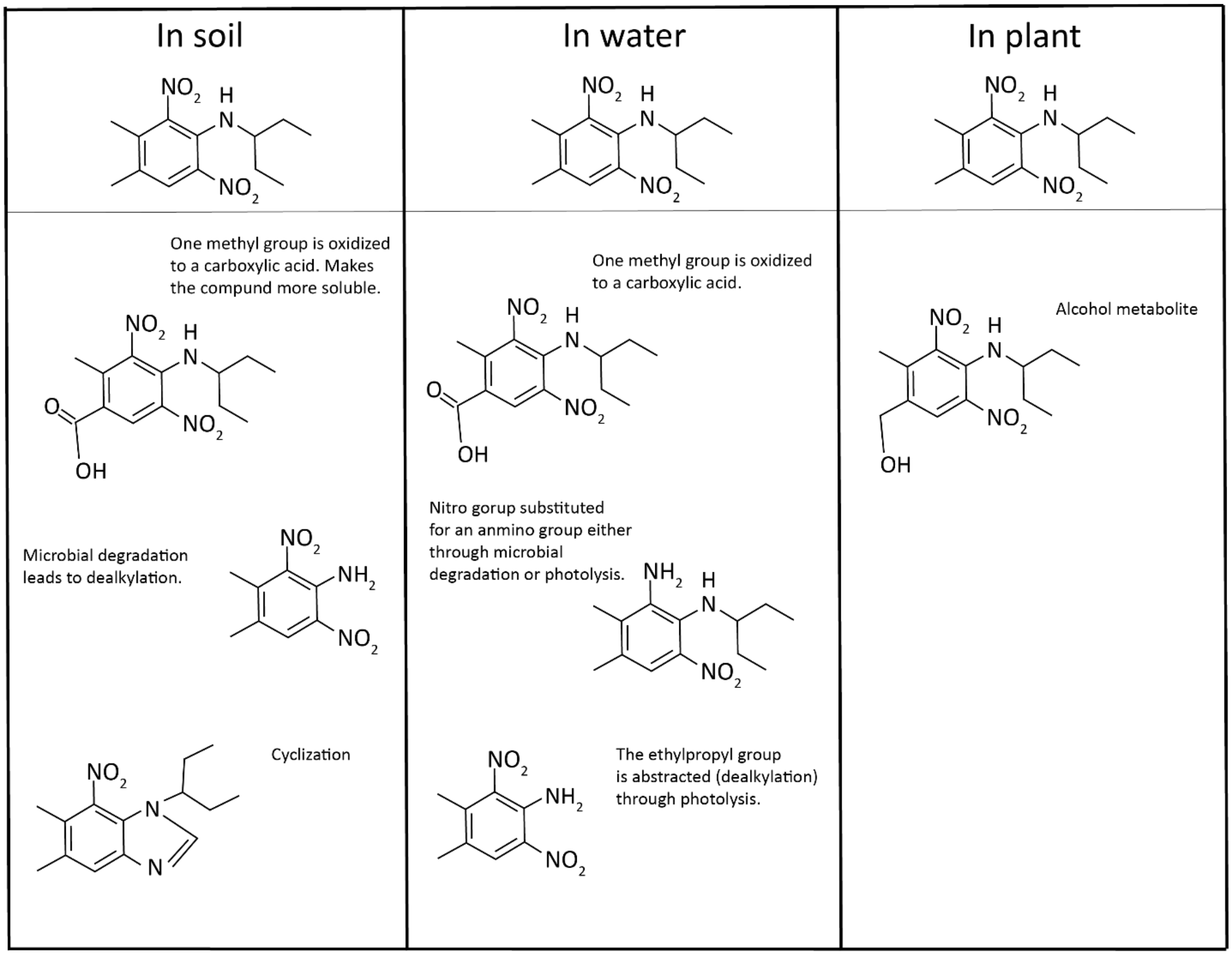


Figure 1-2. Pendimethalin metabolites in soil, water and plants. The figure is derived from the data of United States Environmental Protection Agency (1997) which identified the pendimethalin metabolites of interest.

**Characterization of Pendimethalin in Water-Seeded Rice**

In a water-seeded system, rice is pre-germinated in water for 24-36 hours and air-seeded onto flooded fields with 7-12 cm of standing water, creating an anaerobic environment. The excessive soil moisture immediately after a pendimethalin application in dry-seeded rice sowing significantly increases rice injury (Awan et al. 2016). Since water-seeded rice systems have a high-water saturation, then this makes rice seedlings prone to injury from pendimethalin.

In drill-seeded rice, rice is seeded to a depth of about 3.2 cm into the soil and the application of pendimethalin occurs on the soil surface about 1 to 3 days after seeding. The depth of the seed allows for germination and early growth of the seedling to occur before it comes into contact with the herbicide on the soil surface (Bond et al 2009). Pendimethalin has low volatility, low solubility and strongly attaches to the soil, and will only stay on the top surface layer of the soil (Makkar et al 2019). The placement of the seed provides crop safety to pendimethalin in a drill-seeded system (Bond et al. 2009). Conversely, in water-seeded rice, rice seed is placed on the soil surface and the initial seedling roots can have direct contact with the herbicide applied on the soil surface. Therefore, an application of pendimethalin later in the season after the seedling is developed and more deeply-rooted may reduce the risk of rice injury.

The herbicide formulation may also influence the risk of injury in water-seeded rice. Hatzinikolaou et al. (2004) demonstrated that greater injury to oat roots from pendimethalin occurred from the emulsifiable concentrate formulation compared to the granular and the capsule suspension formulations. Hatzinikolaou et al. (2004) suggest that the granular and the capsule suspension formulations influence the release rate of the active ingredient resulting in lower risk of crop injury. If increased soil moisture results in greater pendimethalin effectiveness and the emulsifiable concentrate pendimethalin formulation causes greater injury to grass species, then, the use of a slow-release formulation of pendimethalin will reduce rice injury and result in greater crop safety on water-seeded rice.

There is no previous research evaluating the partitioning behavior of pendimethalin in water-seeded rice. The knowledge of pendimethalin behavior in water-seeded rice will help establish proper use of the herbicide to increase herbicide efficacy and decrease off-target contamination potential. Therefore, the objectives of this research discussed in the following dissertation chapters were to evaluate pendimethalin use in water-seeded rice, optimize pendimethalin use for the water-seeded rice system and characterize pendimethalin behavior in flood water of a water-seeded rice field.

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# Chapter 2

## Water-Seeded Rice (*Oryza sativa*) Response to Pendimethalin Applied at Different Rates and Timings

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Previously submitted to Weed Technology on January 11, 2024

**Abstract**

Currently, there are a limited number of herbicides available in California water-seeded rice with wide spread resistance to most of these herbicides. Because none of the resistant grasses showed resistance to pendimethalin, a series of studies were conducted to evaluate water-seeded rice response to pendimethalin. In a field study conducted at the Rice Experiment Station at Biggs, California in 2020 and 2021, three pendimethalin formulations, a granule (GR), emulsifiable concentrate (EC) and capsule suspension (CS), were applied at 1.1, 2.3, and 3.4 kg ai $ha^{-1}$ rates, and at 5, 10, and 15 days after seeding onto water-seeded rice. In addition, a greenhouse study was conducted to examine the response of five common California rice cultivars to GR and CS formulation applications. *Echinochloa* control levels were reduced at the 15 days after seeding timing after use of EC and CS formulations compared to earlier timings. In both years, rice grain yields were greater by 3,014 kg $ha^{-1}$ after application of pendimethalin at 3.4 kg ai $ha^{-1}$ when applied at 15 days after seeding compared to 5 and 10 days after seeding, and similar to 1.1 kg ai $ha^{-1}$ applications. The GR and CS were demonstrated to be safer formulations based on a reduction in injury and greater grain yields compared to the EC. Increased seedling vigor among cultivars appeared to incur crop safety after a pendimethalin application. However, based on stand reduction and dry biomass most cultivars demonstrated tolerance to GR and CS formulation applications only after rice reached the 3-leaf stage, while an application at 1-leaf stage rice reduced stand up to 68%. Application rate, timing and formulation are important factors to consider if use of pendimethalin in water-seeded rice is to be pursued.

**Nomenclature**: Pendimethalin; rice, *Oryza sativa* L.

**Keywords:** Herbicide application timing; herbicide rate; medium-grain rice; rice injury; rice yield; short-grain rice

## Introduction

Rice (*Oryza sativa* L.) is an important staple food in many countries and produced worldwide (Chauhan et al. 2017). Water-seeded rice is a common production system in California (US), Europe, Australia and some Asian countries (Chauhan et al. 2017). The water-seeded system is useful for managing grasses, weedy rice, and other non-aquatic weeds (Hill et al. 2006; Rao et al. 2017). In California water-seeded rice, pregerminated rice seed are air-seeded onto fields with a standing flood of 7-cm to 10-cm, the field will typically be continuously flooded throughout the growing season (Hill et al. 2006).

Weeds are a major management challenge encountered in rice production (Brim-Deforest et al. 2017a). Weedy grasses in the California water-seeded rice agroecosystem include barnyardgrass [*Echinochloa crus-galli* (L.) Beauv], early watergrass (*E. oryzoides*), late watergrass [*E. phyllopogon* (Stapff) Koss], and bearded sprangletop [*Leptochloa fusca* (L.) Kunth ssp. *fascicularis* (Lam.) N. Snow]. There is potential for up to 70% rice yield loss from season-long barnyardgrass competition (Smith 1988) and up to 36% rice yield loss from competition with bearded sprangletop (Smith 1983). Therefore, weedy grasses are the most economically important weeds in rice production (Brim-Deforest et al. 2017a).

In California, herbicides continue to be an important tool for weed management in water-seeded rice, but herbicide-resistant weeds have exacerbated the issue leading to poor weed control. A high observed incidence of resistant weed populations is common (Becerra-Alvarez et al. 2023). The prevalence of resistance has developed due to the limited number of effective herbicide sites of action available and continuous rice production year after year (Hill et al. 2006). Multiple herbicide resistance in *Echinochloa* spp. has made control in rice production a significant challenge. Therefore, there is need for new tools to help implement herbicide resistance management like herbicide mode of action mixtures and herbicide mode of action rotations (Becerra-Alvarez et al. 2023).

Pendimethalin is a mitotic inhibiting herbicide from the dinitroaniline chemistry, its use is a selective pre-emergent that ceases the seedling growth shortly after germination (Appleby and Valverde 1989). Pendimethalin has activity on *Echinochloa* spp. (Fischer et al. 2000) and bearded sprangletop (McCarty et al.1995). Currently, there is no recorded resistance to pendimethalin in California rice; therefore, it has potential to be a new herbicide for water-seeded rice (Becerra-Alvarez et al. 2023; Fischer et al. 2000).

Pendimethalin is registered for use in drill-seeded rice as a preemergence or as an early post-emergence (Osterholt et al. 2019), however, it is not available in water-seeded rice because of significant crop injury potential (Fischer et al. 2000). In drill-seeded rice, pendimethalin application is suggested to be at three to seven days after planting and rice should be seeded at depths of 3.2 cm or greater to reduce injury (Bond et al. 2009; Koger et al. 2006). A deeper planting depth allows the seedlings to grow before contacting pendimethalin on the soil surface (Bond et al. 2009). In water-seeded rice, rice seed is sown on the surface of the soil in high moisture levels, therefore, a post-emergence application may reduce injury by allowing seedlings to establish before a pendimethalin application. The 1.1 kg $ha^{-1}$ rate is the typical label rate used in drill-seeded rice for watergrass control (Bond et al. 2009). Pendimethalin degrades faster in anaerobic conditions than in aerobic conditions (Barrett and Lavy 1983). Using higher rates may still provide adequate activity in an anaerobic condition. Therefore, the 2X and 3X of the labeled rate were selected to evaluate for rice response and weed control.

Herbicide formulation and application timing can be significant factors to reduce the rice injury to acceptable levels in a water-seeded system. Hatzinikolaou et al. (2004) recorded the emulsifiable concentrate (EC) of pendimethalin had greater soil activity, but the water dispersible granule (GR) and capsule suspension formulation (CS) remained active in the soil longer, producing an extended soil residual activity. Hatzinikolaou et al. (2004) observed that the EC formulation resulted in a greater reduction in root length than GR and CS formulations, however, the GR and CS formulations also resulted in root length reduction in various plant species tested.

Tolerance to herbicides can also vary among rice cultivars. Koger et al. (2006) observed differential response to pendimethalin among three long grain rice cultivars, with the 'Wells' cultivar demonstrated greater susceptibility to pendimethalin when compared to 'Cocodrie' and 'Lemont' cultivars in a conventional tillage, dry-seeded system at different seeding depths. Bond et al. (2009) observed no differences with minimal to no rice injury, among the same three long grain cultivars in a stale seedbed dry-seeded field study. Because of differences in cultivars and production practices, it is important to examine the response from common California rice cultivars to pendimethalin to understand the practicability and limitations of its use in the water-seeded system.

Field and greenhouse studies were conducted to examine the response of water-seeded rice to a pendimethalin application. In the field study, we evaluate rice plant response to three pendimethalin formulations, GR, EC and CS, at three different application timings and three pendimethalin rates. The greenhouse study evaluated the response of five common California rice cultivars after a GR and CS pendimethalin application in a simulated water-seeded condition. The objectives of these studies were to characterize the response of water-seeded rice after a pendimethalin application and evaluate its potential use for water-seeded rice.

## Materials and Methods

### *Field Study*

The field study was conducted in 2020 and 2021 at the Rice Experiment Station in Biggs, CA. Soils at the study site are characterized as Esquon-Neerdobe (fine, smectitic, thermic Xeric Epiaquerts and Duraquerts), silty clay, made up of 27% sand, 39% silt, and 34% clay, with a pH of 5.1, and 2.8% organic matter. Following rice cultivation during the off-season winter months, the field was flooded to 10 cm above the soil after a pass with a single offset stubble disc and then drained in early spring of the following year. Field preparation in spring consisted of one pass with a chisel plow and two passes with a single offset disc, followed by a land plane to smooth the soil surface. A corrugated roller was used to pack the soil and eliminate large clods on the soil surface prior to planting. A granule fertilizer starter mixture of ammonium sulfate and potassium sulfate (34% N, 17% P, 0% K) was applied by plane at 336 kg $ha^{-1}$ prior to the corrugated roller pass.

Seeds of the rice cultivar ‘M-206’ were pregerminated in steel bins filled with water until all the seeds were completely covered. For disease control, a 5% sodium hypochlorite solution was added in the water for the first hour, then drained and refilled with only water for the remaining 24 h. The seed was then drained until dry for 12 h, and seeded by aircraft at 140 kg $ha^{-1}$ seeding rate in 2020 and 170 kg $ha^{-1}$ seeding rate in 2021 onto the field with a 10-cm standing flood. Individual 3-m wide by 6-m long plots surrounded by 2.2-m wide shared levees were made to prevent contamination from adjacent treatments in a replication. The flood was maintained the whole season and other than being temporarily lowered for application of foliar herbicides for sedge and broadleaf control. Standard agronomic and pest management practices were followed based on the University of California rice production guidelines (UCANR 2023). Seeding dates were May 23, 2020 and June 5, 2021.

The study design was in a factorial arrangement of the treatments under a randomized complete block design with four replications. The treatment factors were three formulations, three application timings, and three application rates. The pendimethalin EC formulation was BAS 455 39H (BASF, Florham Park, NJ) with 0.4 kg $L^{-1}$ of active ingredient, the CS formulation was BAS 455 48H (BASF) with 0.5 kg $L^{-1}$ of active ingredient, and the GR was BAS 455 20H (BASF) with 2% of active ingredient per weight. Application timings were 5, 10, and 15 days after seeding (DAS), corresponding to 1-, 2- to 3- and 3- to 4-leaf stage rice, respectively. The application rates were 1.1, 2.3 and 3.4 kg ai $ha^{-1}$. A nontreated control plot with no pendimethalin applied was randomly placed within each replication to serve as a reference for the assessments.

The CS and EC formulations were applied with a $CO_2$ pressurized backpack sprayer calibrated at 206 kPa to deliver 187 L $ha^{-1}$. The sprayer boom was 3-m wide equipped with six flat-fan 8003VS tips (TeeJet Technologies, Glendale Heights, IL) traveling at 4.8 km $h^{-1}$ and spraying onto the water surface. The GR formulation was spread by hand in each respective plot. Additional herbicides were applied for control of emerged grasses in 2020 and for control of other weed species not controlled by pendimethalin both years. Due to a high population of grasses surviving the pendimethalin treatment in 2020, an additional post-emergence rescue treatment cyhalofop-butyl at 0.3 kg ai $ha^{-1}$ (Clincher CA, Corteva, Indianapolis, IN) and propanil at 1.7 kg ai $ha^{-1}$ (SuperWham! CA, UPL, King of Prussia, PA) were applied at 21 DAS was applied which likely influenced the yield and weed control data to some degree. Copper sulfate crystals (Copper Sulfate Crystals MUP, Quimag Quimicos Aguila, Jalisco, MX) were applied by plane at 17 kg ha$^{-1}$ three DAS for control of algae. In 2020, a mixture of carfentrazone-ethyl at 0.1 kg ai ha$^{-1}$ (Shark H20, FMC, Philadelphia, PA) and triclopyr at 0.3 kg ai ha$^{-1}$ (Grandstand CA, Corteva) was also applied at 52 DAS for sedge and broadleaf control. In 2021, only carfentrazone-ethyl at 0.1 kg ai ha$^{-1}$ and triclopyr at 0.3 kg ai ha$^{-1}$ were applied for sedge and broadleaf control at 32 DAS.

Visual weed control of the of *Echinochloa* spp. and bearded sprangletop were recorded on 14 and 56 days after pendimethalin treatment (DAT), on a scale of 0 to 100, where 0=no control and 100=complete control. *Echinochloa* spp. counts in the nontreated were conducted 30 DAS by sampling twice in the plots within a 30-cm by 30-cm quadrat. Visual percent rice injury assessments were carried out at 20 DAT and 40 DAT by observing present symptomology, which included stand reduction and stunting, and compared to the nontreated, on a scale of 0 to 100, where 0=no injury and 100=plant death. Rice tiller counts were conducted at 75 DAS by sampling twice within 30-cm by 30-cm quadrat in each plot and data scaled to a meter squared area for presentation. Rice grain was hand harvested from two 1-m$^2$ quadrats in each plot and mechanically threshed (Large Vogel Plot Thresher, Almaco, Nevada, IA). Grain was then cleaned and weighed, and adjusted to 14% moisture.

*Greenhouse Experiment, Cultivar Response*

An experiment to compare rice cultivar response to pendimethalin was conducted at the Rice Experiment Station greenhouse in Biggs, CA. A factorial arrangement of treatments in a completely randomized design was implemented. The factors were five cultivars, two formulations, two timings and two rates. The rice cultivars consisted of ‘S-102,’ ‘M-105,’ ‘M-205,’ ‘M-206,’ and ‘M-209.’ These rice cultivars represent common short-grain and medium-grain cultivars produced in California. CS and GR formulations were applied at 5 and 10 DAS at

1.1 kg ai ha$^{-1}$ and 2.3 kg ai ha$^{-1}$. Three experimental runs were conducted separated by time. The first run was seeded on January 15, 2021, the second run on March 7, 2021 and the third run on April 20, 2021. Field soil with similar characteristics to the field site soil above, was used to fill 34-cm by 12-cm by 12-cm plastic containers, with drainage openings on the bottom, and placed inside larger 58-cm by 41-cm by 31-cm plastic containers, with no drainage. Seeds were pregerminated by placing the different cultivar seeds inside cloth bags and in five-gallon buckets completely submerged underwater for 24 h, and then seeds were air dried before sowing. Twenty seeds were sown in each smaller container by placing the seed on the soil surface in a shallow flood onto the soil surface. The larger containers were immediately filled with water up to 10-cm above the soil level and maintained at that level throughout the study. Starting after the day of seeding, each smaller container was treated as a plot and was set in a completely randomized placement and rerandomized every seven days. Copper sulfate crystals were applied by hand at 13 kg ha$^{-1}$ three DAS for control of algae in each container for each run. The emerged rice seeds were counted before the pendimethalin applications and at 21 DAT to calculate the percent rice stand survival. At 20 DAT, plant height was measured from the soil surface to the far most extended leaf end in each plot. At 21 DAT, aboveground biomass was harvested from each plot and dry biomass was recorded.

The greenhouse was maintained at 33/25 ± 2C day/night temperature. A 16-hr photoperiod was provided and natural light was supplemented with metal halide lamps at 400 µ mol m$^{-2}$ sec$^{-1}$ photosynthetic photon flux. The CS formulation was applied using a track-sprayer (Devries, Holland, MN) at 187 L ha$^{-1}$ with a single 8001EVS nozzle (TeeJet Technologies) by placing container inside the spray chamber with a height of 43 cm from the surface of the flood water to the spray nozzle. The GR formulation was spread by hand in each respective tub, calculated by the area of the larger plastic container.

### *Statistical Analysis*

All statistical analysis was conducted on R (R Development Core Team 2022) with the use of the LMERTEST and EMMEANS packages (Kuznetsova et al. 2017; Lenth et al. 2020). Data was subjected to linear mixed effects regression models and mean separation, when appropriate, with Tukey's HSD at $\alpha$=0.05. In the field study, the model consisted of the three formulations, three rates, three application timings as fixed factors, and assessment dates as repeated measure, while replications were set as random separately each year. In the greenhouse study, the model consisted of two formulations, two rates, two application timings, and five cultivars as fixed factors, while experimental runs were treated as random. Normality of distribution were visually examined with quantile-quantile plots and linearity were visually examined by plotting residuals.

## **Results and Discussion**

### *Weed Control*

There was interaction by year for *Echinochloa* spp. control (Table 1). In 2020, 330 ± 8 *Echinochloa* spp. plants $m^{-2}$ was observed in the nontreated, while in 2021, 180 ± 2 *Echinochloa* spp. plants $m^{-2}$ was observed by 56 DAT (Table 2). The field site previously recorded variations in weed species populations by year caused by differences in weather conditions and soil seedbank (Becerra-Alvarez et al. 2022; Brim-DeForest et al. 2017). The cyhalofop and propanil application influenced the grass control levels observed in 2020.

Interaction effect across formulation with timing were observed for *Echinochloa* control both years (Table 1). The interaction of formulations with timings in 2020 demonstrated a reduction in *Echinochloa* control as application timing was delayed from 5 to 15 DAS with the

EC formulation; however, the differences were not observed after application of GR and CS formulations (Table 2). In 2021, the interaction of formulations with timings demonstrated a decrease in *Echinochloa* control as application timing was delayed from 5 to 15 DAS with the EC and CS formulation, but again not with the GR formulation (Table 2). Application rates impacted grass control across timings in 2020 and across formulation in 2021 (Table 1) Interaction of rate with timing in 2020 and rate with formulation in 2021 were observed (Table 1). The *Echinochloa* control results are not consistent with Ahmed and Chauhan (2015) findings who repeatedly demonstrated an increase in grass control with an increase in pendimethalin rates in a dry-seeded rice system. In the water-seeded rice system, pendimethalin degradation will be increased compared to a dry-seeded system (Barrett and Lavy 1983); therefore, greater pendimethalin rates may be necessary to observe an effect.

Transformations on the sprangletop control data did not help meet the assumptions of normality of distribution; therefore, the data is presented as if normality was met. Only pendimethalin timing and rate appeared to affect sprangletop control (Table 1 and 3). The bearded sprangletop population is minimal and previously observed by Brim-DeForest et al. (2017). Therefore, the control results from pendimethalin may not be comparable to fields with greater sprangletop pressure and because of the population differences each year control levels are unclear. In this study, the flood was continuous and pendimethalin application was into the water. The flood may have also been a factor in suppression of sprangletop (Driver et al. 2020).

*Rice Response*

There was treatment interaction by year for visual rice injury but not across assessment dates (Table 4). Injury differed across formulation, rate and timing (Table 4). Rice treated at the 15 DAS timing had the lowest injury levels, but differed across formulations (Table 4). The results demonstrate that different formulations resulted in varying rice injury levels, which is similar to the results of Hatzinikolaou et al. (2004) who evaluated pendimethalin injury on various grass crop species.

In 2020, tiller counts ranged from 30 to 200 tillers $m^{-2}$. In 2021, however, tiller counts were higher, ranging from 200 to 500 $m^{-2}$ (Table 5). After a GR and CS application, rice tillers were similar across timings; however, after EC application at 15 DAS tillers was higher. The rice treated at 15 DAS produced similar tiller numbers when treated at 10 DAS but not when treated at 5 DAS with pendimethalin applied at the 2.3 and 3.4 kg $ha^{-1}$ from the EC formulations (Table 5). Differences in formulations by application timings was evident and resulted in varying injury levels effected by the formulation.

The greater weedy grass pressure in 2020 may have been a factor in the increase on visual rice injury and decrease in rice stands compared to 2021. Weedy grasses interfere with early season rice growth and can reduce the rice stand and tillering capacity (Smith 1988; Brim-DeForest et al. 2017b). Rice treated with pendimethalin showed increased injury with increasing rates when applied at the 5 and 10 DAS; however, at 15 DAS, injury was similar across rates, which suggests that after rice reaches the 3- to 4-leaf stage, pendimethalin injury may not impact rice development. Absorption of pendimethalin can cause greater growth disturbance at earlier seedling stages when the grass seedling coleoptile is emerging at the surface of the soil and comes in contact with the herbicide as demonstrated by Knake and Wax (1968) with the grass weed, giant foxtail. Pendimethalin remains on the upper soil surface due to its physico-chemical properties (Makkar et al. 2019); therefore, once the seedling growing points are further above the soil surface there is a potential to overcome pendimethalin injury.

An interaction in year was observed for grain yield. Interaction effect by formulation with timings were observed for grain yield (Table 6). In both years, rice grain yield was similar across timings with the GR and CS formulations, but not with the EC formulation (Table 6). Timing was most influential on grain yield with the EC. Overall, similar grain yield was achieved from rice treated with the GR across all rates and timings in 2020 and similarly in 2021 (Table 6). The GR is formulated as a slow-release of the active ingredient which results in a reduction of crop injury (Hatzinikolaou et al. 2004). These characteristics of the GR may have allowed more rice seedlings to establish by not being exposed to high concentrated levels of the active ingredient at once.

There was a rate by timing interaction for grain yield (Table 7). Rice treated with 1.1 kg $ha^{-1}$ at all timings produced similar grain yield in both years, which were similar to yield in plots when treated with 2.3 kg $ha^{-1}$ at 10 and 15 DAS, and with 3.4 kg $ha^{-1}$ at 15 DAS (Table 7). Pendimethalin applied to rice at 3.4 kg $ha^{-1}$ at 15 DAS timing had greater yield by 3,014 kg $ha^{-1}$ of grain in both years when compared to the 5 and 10 DAS timings at 3.4 kg $ha^{-1}$ (Table 7). The results demonstrate that formulation, rate and timing are important factors affecting grain yield in water-seeded rice with use of pendimethalin. An application of pendimethalin in dry-seeded rice in Bangladesh decreased grain yields by 44% to 50% when pendimethalin was applied 2 DAS compared to the weed-free check (Ahmed and Chauhan 2015). Application timing or soil saturation timing is an important influence on rice injury after a pendimethalin application in dry-seeded systems (Awan et al. 2016). In the water-seeded system, application timing is the important factor.

While not included in the analysis, the grain yields of the nontreated plots in 2020 were extremely weedy and attempts to harvest failed and yield was recorded as zero. In 2021, the nontreated plots averaged yields of 2,450 ± 340 kg ha$^{-1}$. The yields recorded in this study after pendimethalin treatment were low compared to statewide average yields (UCANR 2023) and potentially affected by the pendimethalin application.

*Greenhouse Experiment, Cultivar Response*

Stand reduction was influenced by cultivar, formulation, rate and timing (Table 8). In general, rice treated at 5 DAS resulted up to 68% stand reduction across cultivars for both CS and GR formulations (Table 8). At 5 DAS, stand was reduced after application of both formulations for 'M-105', 'M-205', 'M-206' and 'M-209' (Table 8). Only 'S-102' at the 5 DAS timing resulted in less than 54% reduction (Table 8). At 10 DAS, 'S-102' and 'M-206' did not show stand loss across rates, while 'M-105' resulted up to 21% decrease in stand after a 2.3 kg ha$^{-1}$ application compared to a 1.1 kg ha$^{-1}$ (Table 8). However, stand reduction after 10 DAS applications were zero to 29% for all cultivars (Table 8).

Koger et al. (2006) observed differential cultivar response from pendimethalin applications on long grain rice in a dry-seeded system. Relative tolerance was attributed to mesocotyl length of seedling rice which may vary by cultivar; however, planting depth is also an important factor in dry-seeded rice for achieving pendimethalin tolerance (Ceseski and Al-Khatib 2021; Ceseski et al. 2022; Koger et al. 2006). In water-seeded rice, a mesocotyl is very short on seedlings because the seeds are placed on the soil surface; however, differences in seedling vigor can be important for relative tolerance to pendimethalin. Ceseski and Al-Khatib (2021) observed 'M-205' and 'M-209' to have greater seedling vigor when compared to 'M-105' and 'M-206', when drill-seeded in a high clay soil. The cultivar vigor characteristic differences can help understand the observed relative tolerance to pendimethalin across cultivars in this study.

Rice biomass was affected by pendimethalin rate and timing (Table 9). The higher rate was an important factor in decreasing biomass for 'S-102' at the 5 DAS from CS and GR applications at 2.3 kg $ha^{-1}$ (Table 9). Dry biomass was reduced by 77% at 5 DAS compared to the 10 DAS timing averaged across formulations, rates, and cultivars. However, biomass reduction was minimal and not significant at 10 DAS, except for 'M-205' at 2.3 kg $ha^{-1}$ GR formulation (Table 9).

Awan et al. (2016) observed a decrease in rice seedling biomass in dry-seeded rice when pendimethalin was applied at 2.0 kg $ha^{-1}$, but not at 1.0 kg $ha^{-1}$. Similarly, in this study biomass reduction was rate-dependent for 'M-205'. Plant height was no different among treatments and were similar to the nontreated by time of biomass harvest (data not shown). Awan et al. did observe a decrease in plant height from pendimethalin treated plots in a dry-seeded system with no recovery by the final evaluation.

**Practical Implications**

Pendimethalin is currently not available for water-seeded rice; however, these results support the introduction of pendimethalin in California water-seeded rice. The CS and GR formulations are most appropriate for water-seeded rice. These results indicate rice injury is reduced with a post-emergence application after the 3- to 4-leaf stage rice in a water-seeded system compared to an application at 1- to 2-leaf stage. Pendimethalin is not a stand-alone herbicide and will need to be accompanied with other available herbicides to achieve season-long weed control. In general, most rice cultivars tested were relatively tolerant to pendimethalin when treated after the 3-leaf stage rice; furthermore, cultivars with lower seedling vigor scores may become more injured from a pendimethalin post-emergence application. The results provide supporting data for registration of pendimethalin in water-seeded rice and provide a base knowledge from which further work should be conducted to enhance its use in this system.


**Acknowledgments**

The authors would like to acknowledge the California Rice Research Board and BASF for providing funding for this project, the California Rice Experiment Station for their support in field management, and the various past and present lab members who assisted with this project, in particular Saul Estrada and Dr. Alex R. Ceseski. The authors also acknowledge the D. Marlin Brandon Rice Research Fellowship by the California Rice Research Trust, the Horticulture and Agronomy Graduate Group scholarships including the Bert and Nell Krantz Fellowship and the Jack Pickett Agricultural Scholarship, and the Department of Plant Sciences, UC Davis for the award of a GSR scholarship funded by endowments, particularly the James Monroe McDonald Endowment, administered by UCANR, which supported the student.


**Competing Interests**

Competing interests: The authors declare none.

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Table 2-1. Significance of main effects of formulation, timing, rate and interactions among the main effects for grass weed control in 2020 and 2021 field study on water-seeded rice planted in Biggs, California[a].

| Effect | 2020 *Echinochloa* control | 2020 Sprangletop control[b] | 2021 *Echinochloa* control | 2021 Sprangletop control[b] |
|---|---|---|---|---|
| | P value | | | |
| Formulation | 0.040 | 0.007 | 0.137 | 0.642 |
| Timing | 0.282 | 0.012 | 0.005 | 0.003 |
| Rate | 0.002 | 0.009 | 0.012 | <0.001 |
| Formulation x Timing | <0.001 | <0.001 | 0.002 | 0.053 |
| Formulation x Rate | 0.162 | 0.750 | 0.003 | 0.348 |
| Rate x Timing | 0.005 | 0.089 | 0.503 | 0.373 |
| Formulation x Timing x Rate | 0.464 | 0.489 | 0.408 | 0.920 |

[a]Transformations of the sprangletop control data did not help meet the assumptions of normality of distribution and data is presented as if normality was met.

Table 2-2. *Echinochloa* control as affected by the application of pendimethalin formulations applied at different times, averaged over rates in 2020 and 2021 field study on water-seeded rice planted in Biggs, California[abc]

| Assessment | Formulations | Timing | 2020 | 2021 |
|---|---|---|---|---|
| | | | *Echinochloa* control | |
| | | DAS | % | |
| 14 DAT | GR | 5 | 34 abc | 94 abc |
| 14 DAT | GR | 10 | 37 abc | 82 abc |
| 14 DAT | GR | 15 | 31 abc | 84 abc |
| 14 DAT | EC | 5 | 61 a | 99 a |
| 14 DAT | EC | 10 | 68 ab | 92 abc |
| 14 DAT | EC | 15 | 32 bc | 83 bc |
| 14 DAT | CS | 5 | 20 c | 97 ab |
| 14 DAT | CS | 10 | 28 bc | 85 abc |
| 14 DAT | CS | 15 | 30 bc | 80 c |
| 56 DAT | GR | 5 | 74 a | 84 ab |
| 56 DAT | GR | 10 | 72 a | 84 ab |
| 56 DAT | GR | 15 | 73 a | 71 b |
| 56 DAT | EC | 5 | 78 a | 96 a |
| 56 DAT | EC | 10 | 79 a | 87 ab |
| 56 DAT | EC | 15 | 75 a | 75 b |
| 56 DAT | CS | 5 | 71 a | 94 a |
| 56 DAT | CS | 10 | 67 a | 85 ab |
| 56 DAT | CS | 15 | 72 a | 70 b |

[a]Means with the same letter within each column do not significantly differ by Tukey's HSD $\alpha=0.05$, averaged over the three rates.

[b]In 2020, 330 ± 8 *Echinochloa* spp. plants $m^{-2}$ were present in the nontreated. In 2021, 180 ± 2 *Echinochloa* spp. plants $m^{-2}$ were present in the nontreated.

[c]DAS, days after seeding; DAT, days after treatment; GR, granule; EC, emulsifiable concentrate; CS, capsule suspension.

Table 2-3. Sprangletop control as affected by application of three pendimethalin formulations and three timings averaged over rates in 2020 and 2021 on water-seeded rice planted in Biggs, California[ab]

| | | | 2020 | | 2021 | |
|---|---|---|---|---|---|---|
| Assessment | Formulations | Timing | Sprangletop control | | | |
| | | DAS | % | | | |
| 14 DAT | GR | 5 | 32 | d | 94 | ab |
| 14 DAT | GR | 10 | 83 | ab | 4 | b |
| 14 DAT | GR | 15 | 77 | ab | 2 | b |
| 14 DAT | EC | 5 | 55 | c | 15 | ab |
| 14 DAT | EC | 10 | 91 | a | 8 | b |
| 14 DAT | EC | 15 | 69 | bc | 4 | b |
| 14 DAT | CS | 5 | 24 | d | 54 | a |
| 14 DAT | CS | 10 | 75 | ab | 10 | b |
| 14 DAT | CS | 15 | 76 | ab | 3 | b |
| 56 DAT | GR | 5 | 74 | a | 87 | a |
| 56 DAT | GR | 10 | 84 | a | 82 | a |
| 56 DAT | GR | 15 | 79 | a | 83 | a |
| 56 DAT | EC | 5 | 85 | a | 93 | a |
| 56 DAT | EC | 10 | 77 | a | 91 | a |
| 56 DAT | EC | 15 | 80 | a | 84 | a |
| 56 DAT | CS | 5 | 76 | a | 88 | a |
| 56 DAT | CS | 10 | 74 | a | 90 | a |
| 56 DAT | CS | 15 | 80 | a | 83 | a |

[a]Means with the same letter within each column do not significantly differ by Tukey's HSD $\alpha$=0.05, averaged over the three rates.

[b]DAS, days after seeding; DAT, days after treatment; GR, granule; EC, emulsifiable concentrate; CS, capsule suspension.

Table 2-4. Visual rice injury as affected by the application of three pendimethalin formulations at three rates, and three timings in 2020 and 2021 field study on water-seeded rice planted in Biggs, California[abc]

| Formulation | Rate | Timing | 2020 | | 2021 | |
|---|---|---|---|---|---|---|
| | | | Visual injury | | | |
| | kg ha$^{-1}$ | DAS | % | | | |
| GR | 1.1 | 5 | 51 | f-l | 35 | f-l |
| GR | 2.3 | 5 | 71 | b-j | 56 | b-j |
| GR | 3.4 | 5 | 89 | a-e | 74 | a-e |
| GR | 1.1 | 10 | 41 | j-l | 26 | j-l |
| GR | 2.3 | 10 | 48 | h-l | 33 | h-l |
| GR | 3.4 | 10 | 67 | c-k | 51 | c-k |
| GR | 1.1 | 15 | 34 | kl | 18 | kl |
| GR | 2.3 | 15 | 36 | kl | 20 | kl |
| GR | 3.4 | 15 | 42 | g-l | 26 | g-l |
| EC | 1.1 | 5 | 99 | a-d | 83 | a-d |
| EC | 2.3 | 5 | 100 | a | 88 | a |
| EC | 3.4 | 5 | 100 | a | 90 | a |
| EC | 1.1 | 10 | 76 | a-h | 60 | a-h |
| EC | 2.3 | 10 | 95 | ab | 79 | ab |
| EC | 3.4 | 10 | 97 | ab | 81 | ab |
| EC | 1.1 | 15 | 37 | i-l | 21 | i-l |
| EC | 2.3 | 15 | 51 | f-l | 36 | f-l |
| EC | 3.4 | 15 | 60 | e-l | 45 | e-l |
| CS | 1.1 | 5 | 48 | f-l | 32 | f-l |
| CS | 2.3 | 5 | 95 | a-e | 79 | a-e |
| CS | 3.4 | 5 | 100 | a-c | 85 | a-c |
| CS | 1.1 | 10 | 36 | j-l | 21 | j-l |
| CS | 2.3 | 10 | 75 | a-g | 60 | a-g |
| CS | 3.4 | 10 | 80 | a-f | 64 | a-f |

| | | | | |
|---|---|---|---|---|
| CS | 1.1 | 15 | 33 kl | 17 kl |
| CS | 2.3 | 15 | 38 i-l | 23 i-l |
| CS | 3.4 | 15 | 35 i-l | 20 i-l |

[a]Interaction by year, P=0.016, was observed for the visual injury. Model output recorded differences across formulations, P<0.001, rates, P<0.001, application timings, P<0.001, formulations x rates, P<0.001, formulations x application timings, P<0.001, rates x application timings, P<0.001, and formulations x rates x application timings, P<0.001. There was no observed interaction across the two assessment dates of 20 and 40 days after treatment, P=0.644, therefore the data was presented as averaged over assessments.

[b]Means with the same letter within each column do not differ by Tukey's HSD α=0.05.

[c]GR, granule; EC, emulsifiable concentrate; CS, capsule suspension; DAS, days after rice seeding.

Table 2-5. Rice tiller counts as affected by the application of three pendimethalin formulations at three rates, and three timings in 2020 and 2021 field study on water-seeded rice planted in Biggs, California[abcd]

| | | 2020 | | 2021 | |
|---|---|---|---|---|---|
| Formulation | Timing | Tiller count | | | |
| | DAS | —— $m^2$ —— | | | |
| GR | 5 | 88 | ab | 410 | ab |
| GR | 10 | 149 | a | 472 | a |
| GR | 15 | 164 | a | 486 | a |
| EC | 5 | 0 | c | 240 | c |
| EC | 10 | 3 | bc | 326 | bc |
| EC | 15 | 129 | ab | 452 | ab |
| CS | 5 | 6 | bc | 329 | abc |
| CS | 10 | 81 | abc | 403 | abc |
| CS | 15 | 145 | ab | 468 | ab |

[a]Results presented are averaged over the three rates. Counts conducted 75 days after application.

[b]There was interaction by year, P=<0.001. Significance observed across formulations, P=0.011, rates, P=0.007, application timings, P=0.006, formulations X rates, P=0.314, formulations X application timings, P=<0.001, rates X application timings, P=0.089, and formulations X rates X application timings, P=0.687.

[c]Means with the same letter within each column do not differ by Tukey's HSD α=0.05.

[d]GR, granule; EC, emulsifiable concentrate; CS, capsule suspension; DAS, days after rice seeding.

Table 2-6. Rice grain yield as affected by the application of three pendimethalin formulations averaged over three rates at three timings in 2020 and 2021 field study on water-seeded rice planted in Biggs, California[abcd]

| Formulation | Timing | 2020 Grain yield | | 2021 Grain yield | |
|---|---|---|---|---|---|
| | DAS | kg ha$^{-1}$ | | | |
| GR | 5 | 2,170 | abc | 6,191 | abc |
| GR | 10 | 2,436 | ab | 6,457 | ab |
| GR | 15 | 3,485 | a | 7,506 | a |
| EC | 5 | 0 | d | 2,770 | d |
| EC | 10 | 216 | cd | 4,236 | cd |
| EC | 15 | 2,465 | ab | 6,486 | ab |
| CS | 5 | 656 | bc | 4,677 | bc |
| CS | 10 | 1,972 | abc | 5,992 | abc |
| CS | 15 | 2,572 | ab | 6,593 | ab |

[a]Results presented are averaged over the three rates.

[b]Interaction by year was observed, P<0.001. Model output recorded differences across formulations, P<0.001, rates, P<0.001, application timing, P=0.002, rates x application timing, P<0.001, and formulation x application timing, P=0.011. No differences were observed for formulation x rate, P=0.066, and formulations x rates x application timing, P=0.315.

[c]Means with the same letter within each column do not differ by Tukey's HSD α=0.05.

[d]GR, granule; EC, emulsifiable concentrate; CS, capsule suspension; DAS, days after seeding.

Table 2-7. Rice grain yield as affected by the application of three pendimethalin rates averaged over three formulations at three timings in 2020 and 2021 field study on water-seeded rice planted in Biggs, California[abcd]

| Application rate | Timing | 2020 | | 2021 | |
|---|---|---|---|---|---|
| | | Grain yield | | | |
| kg ai $ha^{-1}$ | DAS | kg $ha^{-1}$ | | | |
| 1.1 | 5 | 2,214 | ab | 6,235 | ab |
| 1.1 | 10 | 2,440 | a | 6,460 | a |
| 1.1 | 15 | 2,746 | a | 6,767 | a |
| 2.3 | 5 | 200 | cd | 4,221 | cd |
| 2.3 | 10 | 1,694 | abc | 5,715 | abc |
| 2.3 | 15 | 2,272 | abc | 6,293 | abc |
| 3.4 | 5 | 0 | d | 3,182 | d |
| 3.4 | 10 | 490 | bcd | 4,511 | bcd |
| 3.4 | 15 | 3,504 | a | 7,525 | a |

[a]Results presented are averaged over the three formulations.

[b]Interaction by year was observed, $P<0.001$. Model output recorded differences across formulations, $P<0.001$, rates, $P<0.001$, application timing, $P=0.002$, rates x application timing, $P<0.001$, and formulation x application timing, $P=0.011$. No differences were observed for formulation x rate, $P=0.066$, and formulations x rates x application timing, $P=0.315$.

[c]Means with the same letter within each column do not differ by Tukey's HSD $\alpha=0.05$.

[d]DAS, days after seeding.

Table 2-8. Percent stand reduction of five rice cultivars after application of two pendimethalin formulations at two rates and two application timings in a controlled water-seeded environment[ab]

| | Rice stand survival | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | GR | | | | CS | | | |
| | kg ai ha$^{-1}$ | | | | | | | |
| | 1.1 | 2.3 | 1.1 | 2.3 | 1.1 | 2.3 | 1.1 | 2.3 |
| Cultivar | 5 DAS | | 10 DAS | | 5 DAS | | 10 DAS | |
| | % Reduction of the nontreated | | | | | | | |
| S-102 | 1 | 39 | 0 | 0 | 0 | 54 | 0 | 0 |
| M-105 | 37 | 68 | 0 | 21 | 61 | 41 | 17 | 7 |
| M-205 | 37 | 46 | 4 | 29 | 40 | 51 | 4 | 23 |
| M-206 | 43 | 62 | 0 | 7 | 49 | 35 | 0 | 0 |
| M-209 | 45 | 66 | 5 | 26 | 44 | 75 | 0 | 13 |

Tukey's HSD α=0.05

application timings, 37

cultivar, 18

cultivar X formulation, 18

cultivar X rates, 23

rates X application timings, 10

[a]Means with differences above Tukey's HSD are significant when compared across the appropriate factors and interactions. Model output demonstrated differences across cultivar, P<0.001, application timings, P<0.001, cultivar X formulation, P=0.045, cultivar X rates, P<0.001, rates X application timings, P<0.05. No differences were observed across formulations, P=0.131, rates, P=0.277, cultivar X application timings, P=0.223, formulations X rates, P=0.152, formulations X application timings, P=0.469, cultivar X formulations X rates X application timings, P=0.06.

[b]GR, granule; CS, capsule suspension; DAS, days after seeding.

Table 2-9. Dry aboveground biomass reduction three weeks after treatment of five rice cultivars after application of two pendimethalin formulations at two rates and two application timings in a controlled water-seeded environment[ab]

| | Dry biomass | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | GR | | | | CS | | | |
| | kg ai $ha^{-1}$ | | | | | | | |
| | 1.1 | 2.3 | 1.1 | 2.3 | 1.1 | 2.3 | 1.1 | 2.3 |
| Cultivar | 5 DAS | | 10 DAS | | 5 DAS | | 10 DAS | |
| | % Reduction of the nontreated | | | | | | | |
| S-102 | 12 | 62 | 0 | 12 | 21 | 78 | 0 | 0 |
| M-105 | 55 | 72 | 0 | 21 | 62 | 52 | 34 | 0 |
| M-205 | 58 | 63 | 28 | 46 | 43 | 78 | 17 | 23 |
| M-206 | 53 | 72 | 5 | 6 | 54 | 69 | 4 | 0 |
| M-209 | 54 | 83 | 25 | 35 | 46 | 93 | 1 | 8 |
| Tukey's HSD α=0.05 | | | | | | | | |
| rates, 15 | | | | | | | | |
| application timing, 46 | | | | | | | | |
| cultivar X rate, 23 | | | | | | | | |
| rates X application timing, 26 | | | | | | | | |

[a]Means with differences above Tukey's HSD are significant when compared across the appropriate factors and interactions. Model output demonstrated differences across rates, P=0.008, application timings, P<0.001, cultivar X rate, P=0.006, rate X application timing, P=0.004, and formulation X application timing, P<0.05. No differences were observed across cultivar, P=0.181, formulations, P=0.614, cultivar X formulation, P=0.337, cultivar X application timings, P=0.481, formulation X rate, P=0.755, and cultivar X formulation X rate X application timings, P=0.159.

[b]GR, granule; CS, capsule suspension; DAS, days after seeding.

## Chapter 3

**Weeds and Rice Response to Post-Emergence Applications of Pendimethalin Alone and in Herbicide Mixtures in Water-Seeded Rice**

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In preparation for submission to Crop Protection

**Abstract**

Herbicides are an important tool for weed management in water-seeded rice (*Oryza sativa* L.), but the reduced efficacy from available herbicides and the lack of new herbicides have encouraged research on new use of older herbicides for this production system. This research evaluated weed control and water-seeded rice response to pendimethalin applied post-emergence. Pendimethalin was applied alone and in herbicide mixtures at 1.1, 2.3 and 4.4 kg ai $ha^{-1}$ with three graminicide or broad-spectrum foliar herbicides to rice at the 4- to 5-leaf stage. A greenhouse study was conducted to evaluate rice response to pendimethalin applied at 1.1 and 2.3 kg ai $ha^{-1}$ at the 4- to 5-leaf stage grown under 5-cm and 10-cm flood depth conditions. Grass weed control at 14 days after treatment was 68% to 86% when pendimethalin was applied in herbicide mixtures and 48% to 63% when applied alone. The mixtures with bispyribac-sodium and propanil provided broad spectrum control of grass, sedge and broadleaf weeds unlike the mixture with cyhalofop-butyl, a graminicide herbicide. All treatments resulted up to 8% of visual rice injury. Rice tiller counts and grain yield were not affected by pendimethalin. The 5-cm and 10-cm flood depth affected shoot length, root length, and root biomass but not shoot biomass averaged among pendimethalin applications; however, rice was normal by 14 or 21 days after treatment. Only shoot length was reduced by 12% at 21 days after treatment at 3.4 kg ai $ha^{-1}$ of pendimethalin. The results from these studies demonstrate pendimethalin can be a potential herbicide for water-seeded rice and does not cause injury of concern on rice when applied at the 4- to 5-leaf stage rice.

**Keywords:** Flood depth; herbicide mode of action mixtures; rice injury

## Introduction

Rice (*Oryza sativa* L.) is a staple crop produced worldwide of cultural and economic value (Chauhan et al. 2017). The export exchange of rice has become a prominent market for many countries worldwide (Chauhan et al. 2017; USDA 2023). In the US, the export value rice production was nearly 1.7 billion USD in 2022 (USDA 2023). Therefore, worldwide rice production must be upheld to current or superior standards to continuously fulfill the global rice demands.

There are various common rice production systems used worldwide like transplanted paddies, dry-seeded seasonally flooded and continuously flooded systems (Chauhan et al. 2017). Water-seeded rice is not common worldwide but is the primary method in some geographical areas such as the Sacramento Valley of California (Chauhan et al. 2017; Hill et al. 2006). Water-seeded rice is the practice of seeding pregerminated seeds onto fields with a 7- to 15-cm flood, then, typically continuously flooded for the remaining of the season. The water-seeded rice production is popular in areas with ample water for irrigation or where early flood occurrence and poor drainage lead to continuously flooded fields (Chauhan et al. 2017). The flood in water-seeded rice helps to control weedy rice, weedy grasses and non-aquatic weed species (Chauhan et al. 2017; Hill et al. 2006). However, flood-adapted and herbicide-resistant weeds have further intensified the weed management challenges in many rice fields (Unan et al. 2024; Becerra-Alvarez et al. 2023).

Historically, there has been a limited number of herbicide modes of action available for water-seeded rice (Chauhan et al. 2017; Hill et al. 2006). Continuous rice cultivation is common in many growing regions because of soil types and economic limitations (Chauhan et al. 2017; Rosenburg et al. 2022; Salvato et al. 2024). Overuse of the same herbicides and continuous rice cultivation have selected for herbicide-resistant weeds which reduce weed control with the currently available herbicides. To support herbicide resistance management, additional herbicides would be beneficial for growers to practice herbicide mode of action rotations (Becerra-Alvarez et al. 2023).

Pendimethalin is a mitotic inhibiting pre-emergence herbicide from the dinitroaniline chemistry that halts seedling growth shortly after germination (Appleby and Valverde 1989). In previous surveys and preliminary greenhouse work, pendimethalin has been successful in controlling herbicide-resistant grass populations (Fischer et al. 2000; personal observation). Therefore, pendimethalin was evaluated for rice response in water-seeded rice to understand its applicability in this system (Becerra-Alvarez and Al-Khatib 2024; chapter 2). Results from Becerra-Alvarez and Al-Khatib, in chapter 2 of this dissertation, demonstrated rice injury from pendimethalin was reduced in a post-emergence application at the 4-leaf stage rice and in a capsule suspension formulation within 1.1 to 3.4 kg ai $ha^{-1}$. However, at the suggested rice stage timing, many grasses have already emerged and control with pendimethalin is reduced. Therefore, if applied post-emergence in herbicide mixtures to control the emerged grasses, then, greater season-long weed control can be achieved. Additionally, herbicide mode of action mixtures are important strategies for herbicide resistance management which help delay resistance development and can control herbicide-resistant populations (Busi et al. 2020; Beckie and Reboud 2009).

It is hypothesized that the residual pendimethalin soil activity when applied post-emergence at 4-leaf stage water-seeded rice could assist in control of late-emerging grasses. Economically important late-emerging grasses in California rice include bearded sprangletop [*Leptochloa fusca* (L.) Kunth ssp. *fascicularis* (Lam) N. Snow] and watergrass (*Echinochloa* spp.) populations. Bearded sprangletop is characterized as a late-emerging grass weed when compared to barnyardgrass [*E. crus-galli* (L.) Beauv] (Driver et al. 2024). While the majority of watergrass will emerge early in the season, there are subpopulations that can emerge later and are characterized as prolonged emergence throughout the season (Bagavathiannan et al. 2011). Populations of multiple-resistant late watergrass [*E. phyllopogon* (Stapff) Koss] have demonstrated evidence of biphasic emergence with the majority emerging early in the season followed by late-emerging cohorts within the population (Brim-Deforest et al. 2022). There is potential benefit from a pendimethalin post-emergence application for control of late-emerging grasses in water-seeded rice.

Preliminary field studies evaluating water-seeded rice response were conducted on a continuous 10-cm flood with application onto the water and demonstrated timing after the 3- to 4-leaf stage reduced injury (Becerra-Alvarez and Al-Khatib 2024; chapter 2). However, some growers lower the flood depth to encourage rice seedling establishment, or when irrigation water is limited that year. Decreasing the flood depths can influence pre-emergence herbicide rice injury in water-seeded rice as observed with available herbicides (Becerra-Alvarez et al. 2022; UCANR 2023). Therefore, knowledge of rice response as affected by pendimethalin applications at different flood depths in water-seeded rice is important to develop appropriate application methods and recommendations.

The objective of the field study was to evaluate the weed control and rice response of a post-emergence application of pendimethalin alone and in mixtures with currently available herbicides. The objective of the greenhouse study aimed to characterize rice response from pendimethalin applications at two flood depths.

## Materials and Methods

*Field Site*

The study was conducted at the Rice Experiment Station in Biggs, CA (39°27′8.0964″ N, 121°43′14.6532″ W) in 2022 and 2023. The field soil is characterized as an Esquon-Neerdobe (fine, smectitic, thermic Xeric Epiaquerts and Duraquerts), silty clay, made up of 27% sand, 39% silt, and 34% clay, with a pH of 5.1, and 2.8% organic matter. During the off-season months, the field stubble was burned in spring 2022 prior to a pass with a single offset stubble disc. Field preparation for both years consisted of one pass with a chisel plow to dry the upper soil surface and then two passes with a single offset disc, followed by a land plane to smooth the soil surface. A granule fertilizer starter mixture application of ammonium sulfate and potassium sulfate (34% N, 17% P, 0% K) was applied at 336 kg $ha^{-1}$. Then, a corrugated roller was used to pack the soil and eliminate large clods on the soil surface. Individual 3-m wide by 6-m long plots surrounded by 2.2-m wide shared levees were made after fertilizing and prior to flooding to prevent contamination from adjacent treatments in a replication.

Seeds of the rice cultivar 'M-209' were pregerminated in water. For disease control, a 5% sodium hypochlorite solution was used for the first hour, then drained and refilled with only water for the remaining 24 hours. The seed was then drained until dry up to 12 hours, and seeded at 170 kg $ha^{-1}$ both years onto the field with a 10-cm standing flood. The flood was maintained the whole season with the exception of a temporary lowering for the post-emergence herbicide treatments but was reflooded back to 10 cm 48 hours after the application. Copper sulfate crystals (Copper Sulfate Crystals MUP, Quimag Quimicos Aguila, Jalisco, MX) were applied by plane at 17 kg $ha^{-1}$ three days after seeding for control of algae. Standard agronomic and pest management practices were followed based on the University of California rice production guidelines (UCANR 2023). Seeding dates were May 23, 2022 and May 31, 2023.

The herbicides and adjuvants used in the field study are outlined in Table 1. Pendimethalin with 0.4 kg $L^{-1}$ of active ingredient, was applied alone and in mixture with foliar active herbicides at the four-leaf stage rice. The pendimethalin application rates were 1.1, 2.3 and 4.6 kg ai $ha^{-1}$. The selection of these rates was based on preliminary studies on pendimethalin rates and timings, where 1.1 and 2.3 kg $ha^{-1}$ were most appropriate rates for water-seeded rice as a post-emergence application (Becerra-Alvarez and Al-Khatib 2024; chapter 2). The 4.4 kg $ha^{-1}$ rate was included in this study to provide rice response data at 2X of the proposed rate for water-seeded rice. The treatment herbicide mixtures with each pendimethalin rate were propanil, cyhalofop-butyl (cyhalofop), and bispyribac-sodium (Table 2). The applications were carried out with a $CO_2$ backpack sprayer calibrated to deliver 187 L $ha^{-1}$ at 206 kPa traveling at 4.8 km $h^{-1}$. The sprayer boom was 3-m wide equipped with six flat-fan 8003VS tips (TeeJet Technologies, Glendale Heights, IL). At time of herbicide applications, the flood water was lowered 24 hours before treatment and reflooded back to 10 cm 48 hours after the treatment. A nontreated control and a grower standard treatment of clomazone applied at day of rice seeding were included for comparison (Table 2). The treatments were arranged in a randomized complete block design with four replications both years. A follow-up herbicide application of propanil plus triclopyr was applied for sedge and broadleaf control at the midway of full tiller formation rice stage (mid-tiller rice) on all treatments except the nontreated (Table 2). The treatments with pendimethalin alone had a follow-up treatment of cyhalofop plus florpyrauxifen-benzyl at the mid-tiller stage to control all remaining weeds after the initial assessment date (Table 2).

Visual weed control was recorded for *Echinochloa* spp., bearded sprangletop, ricefield bulrush [S*choenoplectus. mucronatus* (L.) Palla], smallflower umbrella sedge (*Cyperus difformis* L.), ducksalad (*Heteranthera limosa* L.), water hyssop (*Bacopa* spp.) and redstem (*Ammannia* spp.) on 14, 24 and 56 days after pendimethalin treatment (DAT), on a scale of 0 to 100, where 0=no control and 100=complete control. Weed density counts for *Echinochloa* spp., sedges and broadleaves were conducted 30 DAT by sampling twice in each plot with a 30-cm by 30-cm quadrat and data scaled to a meter squared area for presentation. Bearded sprangletop counts were conducted for the whole plot after heading of the grass due to a relatively low population density in the field. Visual rice injury assessments were conducted at 20 DAT and 40 DAT by observing present symptomology, which included chlorosis and stunting on a scale of 0 to 100, where 0=no injury and 100=plant death. Rice tiller counts were conducted at 75 days after seeding (DAS) by sampling twice in each plot with a 30-cm by 30-cm quadrat and data scaled to a meter squared area for presentation. Plant height was recorded at 100 DAS. Rice grain yield was collected both years and adjusted to 14% moisture. The rice grain was harvested from a 2-m by 6-m area in the plots with a small-plot combine on November 2, 2022 (SPC40, ALMACO, Nevada, IA, USA) and October 30, 2023 (SWECO 324 Custom, SWECO Products Inc., Sutter, CA, USA).

*Greenhouse Study*

A greenhouse study was conducted at the Rice Experiment Station in Biggs, CA to characterize rice growth as affected by two flood depths after a pendimethalin application. The greenhouse study allowed more accurate management of flood depths than feasible in the field study and direct side by side treatment comparison. Plastic containers with 34-cm by 20-cm by 12-cm dimensions, with openings for drainage were filled with soil from the field study and placed inside larger 58-cm by 41-cm by 31-cm plastic containers, with no drain holes. 'M-206' rice seeds were pregerminated by placing the seeds inside cloth bags, and submerging in five-gallon buckets for 24 hr. Then, the seeds were air-dried and ten seeds were placed on the soil surface of each smaller container, which would later be thinned to five evenly spaced plants per plot. Two experimental runs were carried out, seeded on April 1, 2022 and May 5, 2022. Pendimethalin applications were made at the four-leaf stage rice on April 21, 2022 and May 18, 2022. At this stage, rice could tolerate the pendimethalin application as observed in preliminary field and greenhouse studies. Before the application, pots were maintained at moist soil to shallow flood to encourage seedling establishment. Pots were then flooded maintained to 5-cm or 10-cm water depth above the soil surface after seedling establishment (about ten days after seeding) and the target water depth continuously maintained throughout the study by adding water as needed every 24 h. These two flood depths were selected because 10 cm is the recommended flood depth and occasionally growers may lower water depths to decrease water use (UCANR 2023).

The study was arranged in a factorial randomized complete block design with four replications at each experimental run. Pendimethalin was applied at 0, 2.3 and 3.4 kg ai $ha^{-1}$ onto the respective pots. Pendimethalin was applied with a track-sprayer (Devries, Holland, MN) equipped with a single 8001EVS nozzle and calibrated to deliver 187 L $ha^{-1}$. A 16-hr photoperiod was provided and natural light was supplemented with metal halide lamps at 400 µ mol $m^{-2}$ $sec^{-1}$ photosynthetic photon flux when necessary. The greenhouse was maintained at 30 ± 2 /25 ± 2 C day/night temperature. Rice seedlings were sampled at 7, 14, and 21 DAT from each pot in the greenhouse study. Shoot length, root length and dry biomass of both shoots and roots were collected at each sampling date. The studies were terminated three weeks after the herbicide treatment.

*Data Analysis*

Statistical analysis of the field data was carried out using R v.4.2.1 (R Core Team 2023) with mixed model regression analysis for the visual ratings and rice grain yield data (Kuznetsova et al. 2017). A generalized linear model with a gaussian function was implemented for weed and rice tiller count data (Stroup 2015). Mean separation with Tukey's HSD at α=0.05 was implemented where appropriate. Greenhouse study data were subjected to mixed model regression analysis and mean separation with Tukey's HSD at α=0.05, when appropriate using R v4.1.2 (Kuznetsova et al. 2017). Data transformations were performed as needed by visually assessing the models with quantile-quantile plots and plotting residuals.

**Results**

*Field Study*

*Grass control.* Pendimethalin applied alone at 1.1 kg $ha^{-1}$ caused the lowest *Echinochloa* control at 14 DAT; however, increasing pendimethalin rates to 2.3 and 4.4 kg $ha^{-1}$ did provide greater control levels (Table 2). The grass control demonstrates that pendimethalin cannot be a stand-alone herbicide; however, when rates were greater than 2.3 kg $ha^{-1}$ grass control was increased.

The foliar active herbicides in the mixtures provided good grass control for *Echinochloa* control and no antagonistic effect was observed. An additive trend was observed with the pendimethalin rate of 4.4 kg $ha^{-1}$ adding greater value to the overall control compared to the lower pendimethalin rates (Table 2). Cyhalofop and bispyribac-sodium are excellent *Echinochloa* herbicides, while propanil has suppression activity on *Echinochloa* (Ntanos et al 2000; Damalas et al. 2008). Despite the differences in *Echinochloa* populations by year, *Echinochloa* counts in the pendimethalin mixture treatments were similar to the standard treatment of clomazone followed by propanil plus triclopyr in both years (Table 2).

Bearded sprangletop populations in the field site are low and typically controlled with the continuous 10-cm to 15-cm flood level (Driver et al. 2020). The nontreated had four emerged sprangletop per plot and no treatment decreased the number of emerged sprangletop (data not shown). Cyhalofop is the only post-emergence herbicide used in the study with activity on sprangletop (UCANR 2023) and it is not surprising that cyhalofop treatments had excellent sprangletop control. It is difficult to conclude that there was any benefit from pendimethalin application for sprangletop control in this study.

*Sedge and Broadleaf control.* Pendimethalin does not have activity on sedges observed in this study. The herbicide mixtures and follow-up treatment provided greater than 91% control of smallflower umbrella sedge and ricefield bulrush by 56 DAT (Table 3). The sedge density in the pendimethalin alone treatments were 143 $m^{-2}$ and similar to the nontreated which demonstrated a density of 99 $m^{-2}$ (data not shown).

Ducksalad and water hyssop were the most dominant broadleaf species at this site. *Ammannia* spp. was present in the field but at low population presence with observed 95% control or greater over all treatments, most likely the *Ammannia* spp. were outcompeted by the crop and other weeds (data not shown). Pendimethalin does not have activity on the broadleaves present in this study. Ducksalad control levels were greater than 38% control after application of pendimethalin plus bispyribac-sodium and pendimethalin plus propanil treatments early in the growing season (data not shown). After the follow-up treatment at the mid-tiller rice timing, broadleaf control increased to 89% in 2022 but not in 2023 (Table 4). In 2023, the bispyribac-sodium mixtures resulted in the greatest broadleaf weed control (Table 4).

*Rice Response.* Rice injury was minimal, only up to 8% visual injury was observed at 20 DAT (Table 5). Rice root growth inhibition injury on the nodal root growing region was observed early in the growing season caused by pendimethalin; however, rice recovered from this injury and appeared normal by 40 DAT (data not shown).

There was a decrease in tiller number after the pendimethalin alone treatments (Table 5). The reduced tillers were most likely caused by increase of weed pressure during the early rice growth stage which was managed with the mid-tiller rice application later in the growing season and not caused by pendimethalin injury (Becerra-Alvarez and Al-Khatib 2024; chapter 2). Otherwise, tiller counts were similar across treatments and comparable to the standard treatment (Table 5). There was no difference in plant height across treatments (data not shown).

Grain yields were similar across the treatments where pendimethalin was applied in herbicide mixtures resulting in 6,186 to 8,263 kg $ha^{-1}$ (Table 5). The pendimethalin alone treatments pendimethalin plus cyhalofop resulted in similar yields to the nontreated (Table 5).

*Greenhouse Study*

Results from the greenhouse study demonstrated differences across experimental runs from the response levels measured (Table 6). The second experimental run generally resulted in 1.4 times greater shoot length and is probably because at the time of the study solar radiation increases in the Northern Hemisphere and the seedlings may have received greater natural light than the previous run (UCANR 2023).

Shoot length was generally similar across treatments and similarly increased throughout the sampling dates. Only the 3.4 kg $ha^{-1}$ pendimethalin rate did cause 8% to 12% reduction in shoots when compared to the nontreated on both experimental runs by 14 and 21 DAT (Table 7).

Shoot biomass was not different among treatments at all sampling dates and both runs (Table 6). These results demonstrate that pendimethalin applied to four-leaf stage rice can result in shoot reduction and the level of injury is rate dependent. Root length was reduced 15% only at the 7 DAT at the 10-cm flood depth compared to the 5-cm flood depth in the first run but not the second run (data not shown). However, there were no differences in root length observed by 21 DAT. In general, root biomass was not affected by the two flood depths; however, only at 7 DAT at the first run root biomass was greater at the 5-cm than the 10-cm flood depth averaged over rates but no difference by 14 DAT (data not shown). The 3.4 kg $ha^{-1}$ pendimethalin application reduced root biomass, averaged over flood depths, by 54% in the first run at 14 DAT and no reduction by 21 DAT and in the second run (data not shown).

**Discussion**

Pendimethalin applied alone did not provide adequate weed control. Therefore, herbicide mixtures would need to be incorporated into a successful weed management program. The results from the field study show no antagonistic effect from these particular herbicide mixtures with pendimethalin and the importance of herbicide combinations to manage the different weed species in the field is emphasized. Osterholt et al. (2019a) also demonstrated pendimethalin to have no antagonistic effect on quizalofop control of emerged barnyardgrass when applied as a tank mix on dry-seeded rice.

In this study, it was difficult to observe a grass control benefit from pendimethalin in the herbicide mixtures. However, the study demonstrated reduced rice injury from pendimethalin as a post-emergence application and similar grain yields to the standard treatment. Different fields have different weed populations (Bagavathiannan et al. 2011). Further work is needed to incorporate pendimethalin in water-seeded rice and understand uses and benefits for weed control in the water-seeded system across different sites.

The pendimethalin alone treatment followed by cyhalofop plus florpyrauxifen-benzyl resulted in lower control of sedges because at the time of application the sedges may have been too large (UCANR 2023). In addition, an antagonistic effect resulting in mixing cyhalofop with florpyrauxifen-benzyl cannot be ignored (UCANR 2023). The broadleaves present in this study are typically easily controlled with bispyribac-sodium, propanil and florpyrauxifen-benzyl; however, differences in the population density each year can be a factor to the observed reduced control the second year in the field study (UCANR 2023).

The yield decrease caused by pendimethalin plus cyhalofop may be due to lack of sedge and broadleaf weed control. The herbicides bispyribac-sodium and propanil have broad spectrum activity on *Echinochloa*, sedges and broadleaves (UCANR 2023). The yield decrease observed in the pendimethalin alone treatments most likely was caused because of the late application not controlling emerged grasses and other weeds (Becerra-Alvarez and Al-Khatib 2024; chapter 2). The grasses not controlled increased the interference time with the rice which would explain the reduction in tillers and grain yield (Brim-DeForest et al. 2017).

Pendimethalin is not highly water soluble, non-ionizable and not hydrolyzed in water; however, it has a high affinity for organic matter (Vighi et al. 2017). Therefore, the flood depth may have minimal effect on the molecule's activity. These characteristics can be the reason why no effect was observed from the different flood depths, since the pendimethalin molecule will tend to readily attract to the soil surface with no lateral or vertical movement (Vighi et al. 2017; Weber 1990). The greenhouse study results demonstrate a reduction in shoot length but not shoot or root biomass or root length after a pendimethalin application in water-seeded rice at a four-leaf stage application and no consistent effect from the two flood depths tested.

## Conclusions

The application of pendimethalin alone did not result in weed control greater than 63%; however, control was increased when pendimethalin was applied in herbicide mixtures. Pendimethalin should be used in conjunction with other herbicides. Pendimethalin did not cause substantial injury when applied at 4- to 5-leaf stage rice even at the 4.4 kg $ha^{-1}$ rate application. The rice recovered from minor early-season injury and grain yields across treatments with pendimethalin in mixtures were comparable to the standard treatment. In general, the results suggest that flood depths are not likely to have an effect on the level of rice injury from a pendimethalin application. Therefore, pendimethalin can be incorporated with reduced injury to water-seeded rice as a post-emergence application.

## Acknowledgements

These studies were funded by the California Rice Research Board. The authors would like to acknowledge the California Rice Experiment Station for providing the field site, greenhouse and assisting with the field management. The authors acknowledge the various lab members and technicians that helped with carrying out the studies. The authors also acknowledge the D. Marlin Brandon Rice Research Fellowship by the California Rice Research Trust, the Horticulture and Agronomy Graduate Group scholarships including the Bert and Nell Krantz Fellowship and the Jack Pickett Agricultural Scholarship, the William G. and Kathleen Golden International Agricultural Fellowship, and the Department of Plant Sciences, UC Davis for the award of a GSR scholarship funded by endowments, particularly the James Monroe McDonald Endowment, administered by UCANR which supported the student.

## Competing Interests

The authors have no competing interests to declare.

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Table 3-1. Herbicides and adjuvants used in the field study[a]

| Active Ingredient | Trade Name | Mode of Action | Manufacturer |
|---|---|---|---|
| Pendimethalin | Prowl H2O | Mitosis-inhibitor | BASF, Florham Park, NJ |
| Propanil | SuperWham! CA | PSII-inhibitor | UPL, King of Prussia, PA |
| Cyhalofop-butyl | Clincher CA | ACCase-inhibitor | Corteva, Indianapolis, IN |
| Bispyribac-sodium | Regiment CA | ALS-inhibitor | Valent LLC, San Ramon, CA |
| Triclopyr | Grandstand CA | Synthetic auxin | Corteva |
| Florpyrauxifen-benzyl | Loyant CA | Synthetic auxin | Corteva |
| Crop oil concentrate | MOR-ACT | Adjuvant | Wilbur-Ellis, San Francisco, CA |
| Methylated seed oil | Noble | Adjuvant | Winfield United, Arden Hills, MN |
| Methylated seed oil | Dyne-Amic[b] | Adjuvant | Helena Agri-Enterprises, LLC, Collierville, TN |
| Non-ionic surfactant | Preference | Adjuvant | Winfield United |

[a]PSII, photosystem II; ACCase, acetyl-CoA carboxylase; ALS, acetolactate synthase.

[b]For use with bispyribac-sodium only

Table 3-2. *Echinochloa* spp. control from a post-emergence pendimethalin application in water-seeded rice in 2022 and 2023[abc]

| Treatments | Rates | Timing | *Echinochloa* Control | | | *Echinochloa* Counts | |
|---|---|---|---|---|---|---|---|
| | kg ai ha$^{-1}$ | Rice stage | 14 DAT | 28 DAT | 56 DAT | 30 DAT | |
| | | | | | | 2022 | 2023 |
| | | | | % | | no. m$^{-2}$ | |
| Pendimethalin | 1.1 | 4- to 5-LS | 48 e | 62 e | 70 e | 66 b | 44 b |
| Cyhalofop | 0.31 | Mid-till | | | | | |
| Florpyrauxifen-benzyl | 0.04 | | | | | | |
| MSO | 0.5%v/v | | | | | | |
| Pendimethalin | 2.3 | 4- to 5-LS | 61 de | 61 de | 83 de | 11 b | 0 b |
| Cyhalofop | 0.31 | Mid-till | | | | | |
| Florpyrauxifen-benzyl | 0.04 | | | | | | |
| MSO | 0.5%v/v | | | | | | |
| Pendimethalin | 4.4 | 4- to 5-LS | 63 cde | 63 cde | 85 cde | 33 bc | 11 bc |
| Cyhalofop | 0.31 | Mid-till | | | | | |
| Florpyrauxifen-benzyl | 0.04 | | | | | | |
| MSO | 0.5%v/v | | | | | | |
| Pendimethalin | 1.1 | 4- to 5-LS | 68 bcd | 82 bcd | 90 bcd | 33 bc | 11 bc |
| Propanil | 3.4 | | | | | | |
| COC | 1%v/v | | | | | | |
| Propanil | 5.6 | Mid-till | | | | | |
| Triclopyr | 0.3 | | | | | | |
| NIS | 0.25%v/v | | | | | | |
| Pendimethalin | 1.1 | 4- to 5-LS | 86 a | 100 a | 100 a | 11 c | 0 c |
| Cyhalofop | 0.3 | | | | | | |
| COC | 2.5%v/v | | | | | | |
| Propanil | 6.75 | Mid-till | | | | | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Triclopyr | 0.3 | | | | | | |
| NIS | 0.25%v/v | | | | | | |
| Pendimethalin | 1.1 | 4- to 5-LS | 79 abc | 93 abc | 100 abc | 33 bc | 11 bc |
| Bispyribac-Sodium | 0.05 | | | | | | |
| MSO* | 0.25%v/v | | | | | | |
| Propanil | 6.75 | Mid-till | | | | | |
| Triclopyr | 0.3 | | | | | | |
| NIS | 0.25%v/v | | | | | | |
| Pendimethalin | 2.3 | 4- to 5-LS | 76 abcd | 76 abcd | 97 abcd | 33 bc | 11 bc |
| Propanil | 3.4 | | | | | | |
| COC | 1%v/v | | | | | | |
| Propanil | 5.6 | Mid-till | | | | | |
| Triclopyr | 0.3 | | | | | | |
| NIS | 0.25%v/v | | | | | | |
| Pendimethalin | 2.3 | 4- to 5-LS | 86 a | 86 a | 100 a | 11 c | 0 c |
| Cyhalofop | 0.3 | | | | | | |
| COC | 2.5%v/v | | | | | | |
| Propanil | 6.75 | Mid-till | | | | | |
| Triclopyr | 0.3 | | | | | | |
| NIS | 0.25%v/v | | | | | | |
| Pendimethalin | 2.3 | 4- to 5-LS | 77 abcd | 77 abcd | 99 abcd | 44 bc | 22 bc |
| Bispyribac-Sodium | 0.05 | | | | | | |
| MSO* | 0.25%v/v | | | | | | |
| Propanil | 6.75 | Mid-till | | | | | |
| Triclopyr | 0.3 | | | | | | |
| NIS | 0.25%v/v | | | | | | |
| Pendimethalin | 4.4 | 4- to 5-LS | 71 abcd | 71 abcd | 93 abcd | 22 bc | 22 bc |
| Propanil | 3.4 | | | | | | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| COC | 1%v/v | | | | | | |
| Propanil | 5.6 | Mid-till | | | | | |
| Triclopyr | 0.3 | | | | | | |
| NIS | 0.25%v/v | | | | | | |
| Pendimethalin | 4.4 | 4- to 5-LS | 79 abc | 79 abc | 100 abc | 11 c | 0 c |
| Cyhalofop | 0.3 | | | | | | |
| COC | 2.5%v/v | | | | | | |
| Propanil | 6.75 | Mid-till | | | | | |
| Triclopyr | 0.3 | | | | | | |
| NIS | 0.25%v/v | | | | | | |
| Pendimethalin | 4.4 | 4- to 5-LS | 80 ab | 80 ab | 100 ab | 22 c | 0 c |
| Bispyribac-Sodium | 0.05 | | | | | | |
| MSO* | 0.25%v/v | | | | | | |
| Propanil | 6.75 | Mid-till | | | | | |
| Triclopyr | 0.3 | | | | | | |
| NIS | 0.25%v/v | | | | | | |
| Clomazone | 0.6 | DOS | 86 a | 86 a | 100 a | 11 c | 0 c |
| Propanil | 6.75 | Mid-till | | | | | |
| Triclopyr | 0.3 | | | | | | |
| NIS | 0.25%v/v | | | | | | |
| Nontreated | - | - | - | - | - | 198 a | 176 a |

[a]The 4- to 5-LS applications were 15 days after seeding and the Mid-till applications were 32 days after seeding.

[b]Means with the same letter within each column are not different by Tukey's HSD α=0.05

[c]LS, leaf stage; Mid-till, approximately half-way to maximum tiller formation rice stage; DOS, day of seeding; DAT, days after treatment.

Table 3-3. Sedge control from a post-emergence pendimethalin application in water-seeded rice in 2022 and 2023[abc]

| Treatments | Rates | Timing | Smallflower Umbrella sedge Control | | | Ricefield Bulrush Control | | |
|---|---|---|---|---|---|---|---|---|
| | kg ai ha$^{-1}$ | Rice stage | 14 DAT | 28 DAT | 56 DAT | 14 DAT | 28 DAT | 56 DAT |
| | | | % | | | | | |
| Pendimethalin | 1.1 | 4- to 5-LS | 0 d | 45 d | 54 d | 0 e | 49 e | 59 e |
| Cyhalofop | 0.31 | Mid-till | | | | | | |
| Florpyrauxifen-benzyl | 0.04 | | | | | | | |
| MSO | 0.5%v/v | | | | | | | |
| Pendimethalin | 2.3 | 4- to 5-LS | 3 d | 57 d | 66 d | 6 de | 83 bc | 71 de |
| Cyhalofop | 0.31 | Mid-till | | | | | | |
| Florpyrauxifen-benzyl | 0.04 | | | | | | | |
| MSO | 0.5%v/v | | | | | | | |
| Pendimethalin | 4.4 | 4- to 5-LS | 2 d | 55 d | 64 d | 3 e | 83 bc | 67 e |
| Cyhalofop | 0.31 | Mid-till | | | | | | |
| Florpyrauxifen-benzyl | 0.04 | | | | | | | |
| MSO | 0.5%v/v | | | | | | | |
| Pendimethalin | 1.1 | 4- to 5-LS | 45 abc | 99 abc | 100 abc | 44 abc | 98 abc | 100 abc |
| Propanil | 3.4 | | | | | | | |
| COC | 1%v/v | | | | | | | |
| Propanil | 5.6 | Mid-till | | | | | | |
| Triclopyr | 0.3 | | | | | | | |
| NIS | 0.25%v/v | | | | | | | |
| Pendimethalin | 1.1 | | 29 bc | 83 bc | 91 bc | 28 bcd | 82 bcd | 92 bcd |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Cyhalofop | 0.3 | 4- to 5-LS | | | | | | |
| COC | 2.5%v/v | | | | | | | |
| Propanil | 6.75 | Mid-till | | | | | | |
| Triclopyr | 0.3 | | | | | | | |
| NIS | 0.25%v/v | | | | | | | |
| Pendimethalin | 1.1 | 4- to 5-LS | 51 a | 100 a | 100 a | 50 a | 100 a | 100 a |
| Bispyribac-Sodium | 0.05 | | | | | | | |
| MSO* | 0.25%v/v | | | | | | | |
| Propanil | 6.75 | Mid-till | | | | | | |
| Triclopyr | 0.3 | | | | | | | |
| NIS | 0.25%v/v | | | | | | | |
| Pendimethalin | 2.3 | 4- to 5-LS | 48 abc | 100 abc | 100 abc | 47 abc | 100 abc | 100 abc |
| Propanil | 3.4 | | | | | | | |
| COC | 1%v/v | | | | | | | |
| Propanil | 5.6 | Mid-till | | | | | | |
| Triclopyr | 0.3 | | | | | | | |
| NIS | 0.25%v/v | | | | | | | |
| Pendimethalin | 2.3 | 4- to 5-LS | 28 c | 81 c | 90 c | 29 bc | 83 bc | 93 bc |
| Cyhalofop | 0.3 | | | | | | | |
| COC | 2.5%v/v | | | | | | | |
| Propanil | 6.75 | Mid-till | | | | | | |
| Triclopyr | 0.3 | | | | | | | |
| NIS | 0.25%v/v | | | | | | | |
| Pendimethalin | 2.3 | 4- to 5-LS | 45 abc | 98 abc | 100 abc | 44 abc | 97 abc | 100 abc |
| Bispyribac-Sodium | 0.05 | | | | | | | |
| MSO* | 0.25%v/v | | | | | | | |
| Propanil | 6.75 | Mid-till | | | | | | |
| Triclopyr | 0.3 | | | | | | | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| NIS | 0.25%v/v | | | | | | | |
| Pendimethalin | 4.4 | 4- to 5-LS | 45 abc | 99 abc | 100 abc | 44 abc | 98 abc | 100 abc |
| Propanil | 3.4 | | | | | | | |
| COC | 1%v/v | | | | | | | |
| Propanil | 5.6 | Mid-till | | | | | | |
| Triclopyr | 0.3 | | | | | | | |
| NIS | 0.25%v/v | | | | | | | |
| Pendimethalin | 4.4 | 4- to 5-LS | 28 c | 81 c | 90 c | 27 cd | 81 cd | 91 cd |
| Cyhalofop | 0.3 | | | | | | | |
| COC | 2.5%v/v | | | | | | | |
| Propanil | 6.75 | Mid-till | | | | | | |
| Triclopyr | 0.3 | | | | | | | |
| NIS | 0.25%v/v | | | | | | | |
| Pendimethalin | 4.4 | 4- to 5-LS | 50 ab | 100 ab | 100 ab | 49 ab | 100 ab | 100 ab |
| Bispyribac-Sodium | 0.05 | | | | | | | |
| MSO* | 0.25%v/v | | | | | | | |
| Propanil | 6.75 | Mid-till | | | | | | |
| Triclopyr | 0.3 | | | | | | | |
| NIS | 0.25%v/v | | | | | | | |
| Clomazone | 0.6 | DOS | 29 bc | 83 bc | 91 bc | 27 bcd | 81 bcd | 91 bcd |
| Propanil | 6.75 | Mid-till | | | | | | |
| Triclopyr | 0.3 | | | | | | | |
| NIS | 0.25%v/v | | | | | | | |

[a]The 4- to 5-LS applications were 15 days after seeding and the Mid-till applications were 32 days after seeding.

[b]Means with the same letter within each column are not different by Tukey's HSD α=0.05

[c]LS, leaf stage; Mid-till, approximately half-way to maximum tiller formation rice stage; DOS, day of seeding; DAT, days after treatment.

Table 3-4. Broadleaf control from a post-emergence pendimethalin application in a water-seeded rice herbicide program in 2022 and 2023[abc]

| Treatments | Rates | Timing | Broadleaf Control | |
|---|---|---|---|---|
| | kg ai ha$^{-1}$ | Rice stage | 30 DAT | |
| | | | 2022 | 2023 |
| | | | % | |
| Pendimethalin | 1.1 | 4- to 5-LS | 89 ab | 100 a |
| Cyhalofop | 0.31 | Mid-till | | |
| Florpyrauxifen-benzyl | 0.04 | | | |
| MSO | 0.5%v/v | | | |
| Pendimethalin | 2.3 | 4- to 5-LS | 99 a | 100 a |
| Cyhalofop | 0.31 | Mid-till | | |
| Florpyrauxifen-benzyl | 0.04 | | | |
| MSO | 0.5%v/v | | | |
| Pendimethalin | 4.4 | 4- to 5-LS | 100 a | 100 a |
| Cyhalofop | 0.31 | Mid-till | | |
| Florpyrauxifen-benzyl | 0.04 | | | |
| MSO | 0.5%v/v | | | |
| Pendimethalin | 1.1 | 4- to 5-LS | 99 a | 44 cde |
| Propanil | 3.4 | | | |
| COC | 1%v/v | | | |
| Propanil | 5.6 | Mid-till | | |
| Triclopyr | 0.3 | | | |
| NIS | 0.25%v/v | | | |
| Pendimethalin | 1.1 | 4- to 5-LS | 98 a | 75 abc |
| Cyhalofop | 0.3 | | | |
| COC | 2.5%v/v | | | |
| Propanil | 6.75 | Mid-till | | |
| Triclopyr | 0.3 | | | |
| NIS | 0.25%v/v | | | |

| | | | | |
|---|---|---|---|---|
| Pendimethalin | 1.1 | 4- to 5-LS | 99 a | 81 ab |
| Bispyribac-Sodium | 0.05 | | | |
| MSO* | 0.25%v/v | | | |
| Propanil | 6.75 | Mid-till | | |
| Triclopyr | 0.3 | | | |
| NIS | 0.25%v/v | | | |
| Pendimethalin | 2.3 | 4- to 5-LS | 99 a | 31 def |
| Propanil | 3.4 | | | |
| COC | 1%v/v | | | |
| Propanil | 5.6 | Mid-till | | |
| Triclopyr | 0.3 | | | |
| NIS | 0.25%v/v | | | |
| Pendimethalin | 2.3 | 4- to 5-LS | 99 a | 56 bcde |
| Cyhalofop | 0.3 | | | |
| COC | 2.5%v/v | | | |
| Propanil | 6.75 | Mid-till | | |
| Triclopyr | 0.3 | | | |
| NIS | 0.25%v/v | | | |
| Pendimethalin | 2.3 | 4- to 5-LS | 100 a | 56 bcd |
| Bispyribac-Sodium | 0.05 | | | |
| MSO* | 0.25%v/v | | | |
| Propanil | 6.75 | Mid-till | | |
| Triclopyr | 0.3 | | | |
| NIS | 0.25%v/v | | | |
| Pendimethalin | 4.4 | 4- to 5-LS | 99 a | 19 ef |
| Propanil | 3.4 | | | |
| COC | 1%v/v | | | |
| Propanil | 5.6 | Mid-till | | |
| Triclopyr | 0.3 | | | |

| | | | | |
|---|---|---|---|---|
| NIS | 0.25%v/v | | | |
| Pendimethalin | 4.4 | 4- to 5-LS | 96 a | 31 def |
| Cyhalofop | 0.3 | | | |
| COC | 2.5%v/v | | | |
| Propanil | 6.75 | Mid-till | | |
| Triclopyr | 0.3 | | | |
| NIS | 0.25%v/v | | | |
| Pendimethalin | 4.4 | 4- to 5-LS | 99 a | 69 abc |
| Bispyribac-Sodium | 0.05 | | | |
| MSO* | 0.25%v/v | | | |
| Propanil | 6.75 | Mid-till | | |
| Triclopyr | 0.3 | | | |
| NIS | 0.25%v/v | | | |
| Clomazone | 0.6 | DOS | 99 a | 81 abc |
| Propanil | 6.75 | Mid-till | | |
| Triclopyr | 0.3 | | | |
| NIS | 0.25%v/v | | | |

[a]The 4- to 5-LS applications were 15 days after seeding and the Mid-till applications were 32 days after seeding. Broadleaves included ducksalad and water hyssop. In 2022, broadleaf cover in the nontreated was 32%, while in 2023, the nontreated averaged 176 plants $m^{-2}$. Data is presented as percent control from the nontreated by the sampled percent cover in 2022 and counts in 2023.

[b]Means with the same letter within each column are not different by Tukey's HSD α=0.05

[c]LS, leaf stage; Mid-till, approximately half-way to maximum tiller formation rice stage; DOS, day of seeding; NS, not significant

Table 3-5. Rice visual injury, tiller numbers and grain yield from a post-emergence pendimethalin application in water-seeded in 2022 and 2023[abcd]

| Treatments | Rates | Timing | Visual injury | | Tiller counts | Rice grain yield |
|---|---|---|---|---|---|---|
| | kg ai ha$^{-1}$ | Rice stage | 20 DAT | 40 DAT | 55 DAT | |
| | | | —— % —— | | no. m$^{-2}$ | kg ha$^{-1}$ |
| Pendimethalin | 1.1 | 4- to 5-LS | 4 abc | 2 abc | 396 bcd | 5,468 abc |
| Cyhalofop | 0.31 | Mid-till | | | | |
| Florpyrauxifen-benzyl | 0.04 | | | | | |
| MSO | 0.5%v/v | | | | | |
| Pendimethalin | 2.3 | 4- to 5-LS | 4 abc | 2 abc | 396 bcd | 6,186 abc |
| Cyhalofop | 0.31 | Mid-till | | | | |
| Florpyrauxifen-benzyl | 0.04 | | | | | |
| MSO | 0.5%v/v | | | | | |
| Pendimethalin | 4.4 | 4- to 5-LS | 8 a | 4 a | 374 cd | 5,008 bc |
| Cyhalofop | 0.31 | Mid-till | | | | |
| Florpyrauxifen-benzyl | 0.04 | | | | | |
| MSO | 0.5%v/v | | | | | |
| Pendimethalin | 1.1 | 4- to 5-LS | 4 abc | 2 abc | 594 a | 7,425 ab |
| Propanil | 3.4 | | | | | |
| COC | 1%v/v | | | | | |
| Propanil | 5.6 | Mid-till | | | | |
| Triclopyr | 0.3 | | | | | |
| NIS | 0.25%v/v | | | | | |
| Pendimethalin | 1.1 | 4- to 5-LS | 4 abc | 2 abc | 572 a | 6,897 abc |
| Cyhalofop | 0.3 | | | | | |
| COC | 2.5%v/v | | | | | |
| Propanil | 6.75 | Mid-till | | | | |
| Triclopyr | 0.3 | | | | | |

| | | | | | | |
|---|---|---|---|---|---|---|
| NIS | 0.25%v/v | | | | | |
| Pendimethalin | 1.1 | 4- to 5-LS | 2 bc | 1 bc | 649 a | 7,893 a |
| Bispyribac-Sodium | 0.05 | | | | | |
| MSO* | 0.25%v/v | | | | | |
| Propanil | 6.75 | Mid-till | | | | |
| Triclopyr | 0.3 | | | | | |
| NIS | 0.25%v/v | | | | | |
| Pendimethalin | 2.3 | 4- to 5-LS | 4 abc | 2 abc | 550 abc | 7,484 ab |
| Propanil | 3.4 | | | | | |
| COC | 1%v/v | | | | | |
| Propanil | 5.6 | Mid-till | | | | |
| Triclopyr | 0.3 | | | | | |
| NIS | 0.25%v/v | | | | | |
| Pendimethalin | 2.3 | 4- to 5-LS | 4 abc | 2 abc | 539 ab | 7,602 ab |
| Cyhalofop | 0.3 | | | | | |
| COC | 2.5%v/v | | | | | |
| Propanil | 6.75 | Mid-till | | | | |
| Triclopyr | 0.3 | | | | | |
| NIS | 0.25%v/v | | | | | |
| Pendimethalin | 2.3 | 4- to 5-LS | 2 abc | 1 abc | 638 a | 8,263 a |
| Bispyribac-Sodium | 0.05 | | | | | |
| MSO* | 0.25%v/v | | | | | |
| Propanil | 6.75 | Mid-till | | | | |
| Triclopyr | 0.3 | | | | | |
| NIS | 0.25%v/v | | | | | |
| Pendimethalin | 4.4 | 4- to 5-LS | 4 abc | 2 abc | 550 ab | 7,447 ab |
| Propanil | 3.4 | | | | | |
| COC | 1%v/v | | | | | |
| Propanil | 5.6 | Mid-till | | | | |

| | | | | | | |
|---|---|---|---|---|---|---|
| Triclopyr | 0.3 | | | | | |
| NIS | 0.25%v/v | | | | | |
| Pendimethalin | 4.4 | 4- to 5-LS | 7 ab | 4 ab | 506 abc | 6,378 abc |
| Cyhalofop | 0.3 | | | | | |
| COC | 2.5%v/v | | | | | |
| Propanil | 6.75 | Mid-till | | | | |
| Triclopyr | 0.3 | | | | | |
| NIS | 0.25%v/v | | | | | |
| Pendimethalin | 4.4 | 4- to 5-LS | 3 abc | 1 abc | 594 a | 8,250 a |
| Bispyribac-Sodium | 0.05 | | | | | |
| MSO* | 0.25%v/v | | | | | |
| Propanil | 6.75 | Mid-till | | | | |
| Triclopyr | 0.3 | | | | | |
| NIS | 0.25%v/v | | | | | |
| Clomazone | 0.6 | DOS | 2 c | 1 c | 616 a | 7,772 ab |
| Propanil | 6.75 | Mid-till | | | | |
| Triclopyr | 0.3 | | | | | |
| NIS | 0.25%v/v | | | | | |
| Nontreated | - | - | | | 297 d | 4,271 c |

[a]The 4- to 5-LS applications were 15 days after seeding and the Mid-till applications were 32 days after seeding.

[b]Total visual injury included chlorosis on leave surfaces and growth stunting of rice plants. Visual injury data was log+1 transformed and back transformed for presentation.

[c]Means with the same letter within each column are not different by Tukey's HSD α=0.05

[d]LS, leaf stage; Mid-till, approximately half-way to maximum tiller formation rice stage; DOS, day of seeding; DAT, days after treatment.

Table 3-6. Significance levels across rice seedling response after an application of pendimethalin into two flood levels and at two application rates[a]

| | Shoot length | Shoot biomass | Root length | Root biomass |
|---|---|---|---|---|
| Factors | | P value | | |
| Application rate | <0.001*** | 0.284 | 0.073 | 0.001** |
| Flood depth | <0.001*** | 0.814 | 0.034* | 0.01* |
| Sampling date | <0.001*** | <0.001*** | <0.001*** | <0.001*** |
| Run | <0.001*** | <0.001*** | <0.001*** | 0.017* |
| Application rate x flood depth | 0.523 | 0.941 | 0.402 | 0.611 |
| Application rate x sampling date | <0.001*** | 0.821 | 0.888 | 0.835 |
| Flood depth x sampling date | 0.007** | 0.594 | 0.770 | 0.440 |
| Application rate x flood depth x sampling date | 0.344 | 0.826 | 0.279 | 0.538 |

[a]Shoot biomass and root biomass data were log transformed to fulfill data heterogeneity and linearity.

Table 3-7. Rice shoot length response from two pendimethalin rates applied into two flood depths at the four-leaf stage rice in water-seeded rice[a]

| Rates | Flood depth | Shoot length | | | | | |
|---|---|---|---|---|---|---|---|
| kg ai $ha^{-1}$ | cm | Run 1 | | | Run 2 | | |
| | | 7 DAT | 14 DAT | 21 DAT | 7 DAT | 14 DAT | 21 DAT |
| | | mm | | | | | |
| 0 | 5 | 300 b | 484 cd | 590 ab | 561 | 728 bc | 848 a |
| 2.3 | 5 | 305 ab | 478 de | 566 ab | 556 | 711 cd | 816 ab |
| 3.4 | 5 | 289 b | 455 e | 525 c | 551 | 699 e | 785 bc |
| 0 | 10 | 330 ab | 535 ab | 608 a | 562 | 749 ab | 837 a |
| 2.3 | 10 | 346 a | 509 bc | 561 bc | 568 | 714 cd | 780 bc |
| 3.4 | 10 | 322 ab | 485 cd | 545 bc | 554 | 701 e | 776 bc |
| | | | | | NS | | |

[a]DAT, days after treatment; NS, not significant; cm, centimeter; mm, millimeter; Means with the same letter within each row do not significantly differ with Tukey's HSD α=0.05.

# Chapter 4

## Dissipation of Pendimethalin in a Water-Seeded Rice Field and Implications for Water Management

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Published in Agrosystems, Geosciences and Environment 7:e20475

https://doi.org/10.1002/agg2.20475

Accepted on January 19, 2024. The formatting of chapter 4 is in conformity with the journal.

**Abstract**

Water-seeded rice (*Oryza sativa* L.) in California is produced near growing urban centers and a variety of neighboring high value crops which make water quality a paramount concern because of potential herbicide residue contamination in downstream surface waters. Pendimethalin is a potential herbicide for use in California water-seeded rice. A study was conducted to characterize pendimethalin's dissipation in water of a water-seeded rice field. A capsule suspension (CS), emulsifiable concentrate (EC) and granule (GR) pendimethalin were applied onto flooded rice plots at 1.1, 2.3 and 3.4 kg ai $ha^{-1}$ rates. Water samples were collected periodically and analyzed with an LC-MS/MS system for residues. Pendimethalin dissipation differed across formulations. The initial sampled concentrations recorded values from 3.0 to 125.6 parts per billion (ppb). First-order dissipation resulted with half-lives for the CS from 2.3 to 3.5 days, the EC from 0.6 to 0.7 days and the GR from 3.5 to 6.9 days. Pendimethalin use in water-seeded rice is at low risk of contaminating downstream surface waters, however, early sampled residue concentrations could be concerning. The results can assist in generating management tactics like water-holding periods to avoid potential downstream off-target effects and ensure herbicidal activity in the applied area after a pendimethalin application in a water-seeded rice field.

**Abbreviations**

CS, capsule suspension; DAT, days after treatment; EC, emulsifiable concentrate; GR, granule; LC-MS/MS, high pressure liquid chromatography tandem mass spectrometry; ppb, parts per billion; ppm, parts per million.

## 1. Introduction

Rice (*Oryza sativa* L.) is a major crop, valued for its nutritious components as a food crop and produced worldwide (Rao et al. 2017). In the US, rice production is centered in Arkansas, California, Louisiana, Texas and Mississippi producing nearly two million metric ton of grain for the export market in 2022 (USDA 2023). Weed management is a major challenge to achieve economically viable production levels. Cultural practices to achieve an integrated weed management program in California rice include use of certified seed, proper land preparation, and water management (UCANR 2023). However, to reach the economically viable rice yields, herbicides are necessary to control weeds (Brim-DeForest et al. 2017; Hill et al. 2006).

The limited number of available herbicides and continuous rice cultivation year after year in California have selected for herbicide-resistant weeds and have caused a reduction in weed control from the available herbicides (Hill et al. 2006; Becerra-Alvarez et al. 2023). The lack of crop rotations makes water management and herbicide use the most important tools to manage weeds (UCANR 2023). Therefore, new herbicide modes of action are needed to help manage herbicide-resistant weed populations.

California rice is uniquely different from the other US rice producing states because nearly 90% of the production is medium-grain rice and produced in a water-seeded system (UCANR 2023). The water-seeded production system in California is a common method to suppress weedy grasses and non-aquatic weed species. In California, pregerminated rice seed is air-seeded onto fields with a 10- to 15-cm standing flood and the fields are typically maintained continuously flooded throughout the growing season (Hill et al. 2006).

The California rice cropping system is again unique because of its presence near growing urban communities and a variety of neighboring high value crops. Surface water used for rice production is mainly derived from reservoirs that capture water in the Cascade Mountain Range and Sierra Nevada from the Sacramento River and the Feather River, respectively (UCANR 2023; Hill et al. 2006). Much of that reservoir water also goes toward municipal potable water and irrigation for other crops in the area. There is potential for contamination of drinking water and water for wildlife by herbicide use in California rice fields, which has historically been documented with the rice herbicides thiobencarb and molinate (Hill et al. 2006; Wagner et al. 2019). Production lands further away from the water sources will also use drainage water downstream as irrigation (Hill et al. 2006). Many neighboring crops can be susceptible to pesticide residues at low concentrations and this can be of concern if herbicide residues are present in the irrigation water (Starner et al. 2005).

Historically, regulatory agencies and the California rice industry have collaborated to implement successful programs to manage and reduce off-target pesticide effects by mandating report of pesticide use, monitoring water quality, and water-holding periods after chemical applications (Hill et al. 2006; Wagner et al. 2019). Pesticide use reporting and monitoring encourage stewardship of chemical use among agencies and applicators (Wagner et al. 2019). Water-holding periods prevent the pesticide active ingredient from becoming runoff in the tail water and contaminating non-target areas and organisms. The water-holding period can differ among pesticides based on their physico-chemical properties and degradation pathways (UCANR 2023). Therefore, it is important to understand the behavior of herbicide active ingredients in the water-seeded system to successfully characterize them in support of sustainable stewardship and efficacious use of chemicals.

Herbicide products can be developed in various formulations to assist with weed control, for instance, to achieve longer soil residual activity, reduce crop injury, affect dissipation or for applicator safety (Hatzinikolaou et al. 2004; Daneshvari et al. 2021). Formulation is also suggested to influence the potential of the active ingredient to contaminate surface waters (Michael and Neary 1993).

Pendimethalin is a mitotic inhibiting herbicide from the dinitroaniline chemistry, it is a selective pre-emergent that ceases seedling growth shortly after germination of susceptible plants (Appleby and Valverde 1989). Physico-chemical properties of pendimethalin are presented in Table 1. Pendimethalin has been proposed for use in water-seeded rice, since it controlled herbicide-resistant grass populations and if labeled would provide an additional tool for management over herbicide-resistant grasses in California rice. However, there has been no work characterizing pendimethalin's behavior in water from a water-seeded rice field. It is hypothesized, based on the physico-chemical properties, that pendimethalin will not persist in surface water, however, product formulation could affect dissipation in water. Therefore, the objectives of this study were to evaluate the dissipation behavior of pendimethalin across three formulations in rice flood water after an application in a water-seeded rice field.

## 2. Materials and Methods

### 2.1. Field Site

A field study was carried out at the Rice Experiment Station in Biggs, CA (39°27′8.0964″ N, 121°43′14.6532″ W). Because of scrupulous quality assurance for each experimental unit to meet regulatory standards, which led to extensive costs associated with the analysis and labor, the study was only conducted in 2021 with three replications. Individual plots were arranged in a randomized complete block design across the field. Soils at the site are characterized as Esquon-Neerdobe (fine, smectitic, thermic Xeric Epiaquerts and Duraquerts), silty clay, made up of 27% sand, 39% silt, and 34% clay, with a pH of 5.1, and 2.8% organic matter. Irrigation waters at the research site on average have a pH of 7.81 and electrical conductivity of 0.12 ds/m. Individual 3-m wide by 6-m long plots surrounded by 2.2-m wide shared levees were made to prevent contamination from adjacent treatments. Water temperature, when delivered from the irrigation canal, can average as low as 13°C, and in the field, it is recommended for the water to not be below 18°C for appropriate rice growth and development (UCANR 2023). Irrigation water was first delivered on June 2, 2021 into a warming field basin, where it circulated before traveling to the field basin with the plots. To move water inside each individual plot, 5-cm diameter by 1.5-cm length single bend aluminum siphon irrigation tubes (Empire Irrigation Inc., Greeley, CO) were placed over the 2.2-m wide levees. The plots were flooded to 4-inch by June 4, 2021 and maintained at that depth for the duration of the study. ‘M-206’ rice was air-seeded at a rate of 170 kg $ha^{-1}$ onto the field with a standing flood on June 5, 2021.

### 2.2. Herbicide Applications

BAS 455 48H (BASF, Florham Park, NJ), a capsule suspension (CS) with 0.46 kg $L^{-1}$ of active ingredient, BAS 455 39H (BASF), an emulsifiable concentrate (EC) with 0.40 kg $L^{-1}$ of active ingredient and BAS 455 20H (BASF), a granule (GR) with 2% of active ingredient per weight were applied onto the flooded plots at three- to four-leaf stage rice on June 15, 2021. The application rates for each treatment were 1.1, 2.3 and 3.4 kg ai $ha^{-1}$. The selected rates are within the range of the appropriate field rates used in dry-seeded rice (Bond et al. 2009). The CS and EC were applied at 187 L $ha^{-1}$ onto the flood with a 3-m boom sprayer equipped with a CO2 backpack at 206 kPa and six flat-fan 8003VS tips (TeeJet Technologies, Glendale Heights, IL). The GR was evenly spread by hand onto the flooded plots.

### 2.3. Sample Collection

Rice flood water was sampled at 1, 3, 5, 10 and 15 days after treatment application (DAT) for each plot and replication separately. At each individual plot, a composite water sample was collected with a glass beaker from four areas in each plot near the center and quickly homogenized in a ~1-L plastic container (Ngim and Crosby 2001a). Then, 3 oz were poured in a 4-oz tight seal jar and placed in storage at 0°C immediately until delivered inside the lab within four hours. For each individual plot, new containers were used to sample each time. In the lab, water samples were cleaned and 50 mL were allocated from the filtered sample and placed in storage at -20°C until analysis.

Daily temperature, relative humidity and solar radiation data were obtained from the California Irrigation Management Information System (CIMIS), Biggs, CA weather station number 244 (CDWR 2023).

### 2.4. Residue and Data Analysis

Liquid-liquid extraction methods were modified from USEPA (USEPA 2013). High pressure liquid chromatography tandem mass spectrometry (LCMS/MS) was employed to analyze for residue in water samples. A standard for pendimethalin, were obtained as a reference to quantify residue in samples. The recovery in water samples was on average 79%. See supplementary material (Supplemental Material 1) for details on method.

Data analysis were performed using R v4.1.2 (R Core Team 2022). Linear regression analysis and analysis of variance was used to determine associations on the concentrations across formulations, rates and sampling time with LMERTEST R package (Kuznetsova et al. 2017). Means separation with Tukey's honestly significant difference at $\alpha$=0.05 was then used where appropriate with EMMEANS R package (Lenth et al. 2018). The data was log transformed to fulfill homogeneity and linearity requirements for a linear regression (Kuznetsova et al. 2017). Furthermore, pendimethalin dissipation for each formulation at each rate was fitted to the first-order kinetic equation:

$$C_t = C_0 e^{-kt}$$

Where $C_t$ is the concentration at time $t$, $C_0$ is the initial concentration, $t$ is time, and $k$ is the rate constant. The NLS: NONLINEAR LEAST SQUARES R package was used to fit the data and create models, then, the NLSTOOLS R package was used to evaluate and select the most appropriate model (Baty et al. 2015). Half-lives ($T_{1/2}$) were calculated from the equation:

$$T_{1/2} = \frac{\ln 2}{k}$$

Where $T_{1/2}$ is the time for 50% of the herbicide concentration to dissipate and $k$ is the rate constant.

## 3. Results and Discussion

There were differences in concentrations recovered from water samples across rates ($p$<0.001), sampling time ($p$<0.001), and formulation by sampling time ($p$<0.001). At 1 DAT sampling, the EC had the highest concentrations at 73.0 parts per billion (ppb) (1 ppb = 1 $\mu g\ L^{-1}$) averaged over rates (Table 2). The CS and EC formulations maintained similar concentrations throughout sampling times after the 1 DAT (Table 2). The GR maintained the greatest concentrations at 10 and 15 DAT compared to the CS and EC (Table 2).

The differences in dissipation across formulations could be attributed to the formulation properties. The EC is constructed of an oil-water-emulsion with organic solvents, while the CS encapsulates the active ingredient in layers of water-soluble polymers (Rao et al. 2021). As an oil-based formulation, the EC would make pendimethalin persist in suspension on the water at higher concentrations early on because of the inactive carriers being not water soluble. The encapsulating polymers in the CS would allow the compound to be water soluble and extend the amount of time the compound is suspended in water (Rao et al. 2021). These characteristics can explain the higher concentrations early on from the EC formulation compared to the other two formulations.

GR herbicide formulations tend to have the active ingredient adsorbed to inert material, allowing slow and continuous release of the active ingredient (Hatzinikolaou et al. 2004). This characteristic of the GR formulation may help explain the increases of concentration in water three days after the application of the 3.4 kg $ha^{-1}$ rate (Figure 1). The delayed increase in concentration was rate dependent, however. Similarly, Ngim and Crosby (2001b) observed formulation affected dissipation of the insecticide fipronil in water-seeded rice, with the granule formulation being most persistent. A GR pendimethalin application onto a water-seeded rice field may need a longer water-holding period than the liquid formulations.

Dissipation generally followed first-order kinetics (Figure 1). The GR demonstrated half-lives up to 6.9 days. The CS had half-lives three to four days less than GR and the EC had half-lives nearly seven days less (Table 3). The average daily temperature for the duration of the study was 25°C with a low of 16°C and high of 34°C. Daily solar radiation averaged 346 Watts $m^2$ with a low of 341 Watts $m^2$ and high of 366 Watts $m^2$. Relative humidity averaged at 50% with a low of 30% and high of 80%. These are the typical conditions during the early rice growing season in California and are important to note as factors that can affect the pendimethalin degradation.

Half-lives of pendimethalin in water were reduced in this study probably due to greater degradation occurring in a field environment stimulated by microorganisms, photolysis degradation and partitioning onto organic sediments from the soil (Vighi et al. 2017). Pendimethalin residue half-lives in water have been previously reported at 12.7 and 13.7 days after an application of an EC pendimethalin formulation at 0.5 parts per million (ppm) and 1.0 ppm (1 ppm = 1 mg $L^{-1}$), respectively, onto irrigation canal water (Chopra et al. 2015).

Degradation pathways can be inferred based on the physico-chemical properties of pendimethalin. The pendimethalin molecule is not high water soluble, non-ionizable and not hydrolyzed in water and possesses a high affinity for organic matter (Table 1); therefore, sediment partition is most likely the significant degradation pathway. Partitioning of pendimethalin onto sediment in water/sediment investigations in dark demonstrated to be within 0.4 to 1.6 days for 50% allocation onto sediments (Vighi et al. 2017). Pendimethalin is moderately volatile and volatilization is an important dissipation pathway in dry and moist soil, however, as soil moisture increases over soil field capacity, volatilization decreases due to lower movement of the vapor phase in wetter soils (Barrett and Lavy 1983; Weber 1990). Solar radiation was high in the study area and can be a significant degradation pathway. Both photolysis and sediment partitioning are most likely the important pathways of pendimethalin degradation. While this study negates the pendimethalin metabolites, it is important to note there are three metabolites that can form in water (USEPA 2013). Nevertheless, the pendimethalin residues in the water indicate the importance of holding flood water in the field after an application to allow the herbicide molecule to settle on the soil surface when applied onto a flooded rice field.

## 4. Practical implications

The US EPA has recorded an observed maximum level of pendimethalin in surface water at 17.6 ppb, probably contaminated by spray drift, and expressed the risk of pendimethalin contaminating surface waters to be less than 2% (USEPA 1997). While there is no water quality criteria level for pendimethalin, residues of pendimethalin have been observed in surface water tributaries near agricultural regions with concentrations up to 0.02 ppb (Lehotoy et al. 1998;

Zimmerman et al. 2000). Additionally, pendimethalin residues as low as 30.0 ppb in soil have shown to cause injury on tomato (*Solanum lycopersicum* L.), a common crop grown near California rice fields (Angeles et al. 2020). Despite observed concentrations above these levels from the EC and CS formulations early on, pendimethalin dissipated quickly below levels of concern (Figure 1).

Apart from preventing potential herbicide runoff, water-holding periods can be useful for increasing herbicide efficacy. Some pesticides currently used need the water for activation or to evenly distribute in the field and holding water in the field is common practice for California growers when using granule pesticides in rice (UCANR 2023; Ngim and Crosby 2001a; Ngim and Crosby 2001b). The concentrations observed from this study also suggest pendimethalin could benefit from a water-holding period to increase the efficacy when applied onto the flood. However, an increase in efficacy can also develop greater rice crop injury and should be balanced through application rates and timings. The rates used in this study were the typical use rates in dry-seeded rice, which are known to provide adequate weed control. This study did not focus on weed control but ongoing work is examining this aspect to enable efficacious and safe use of pendimethalin for water-seeded rice.

Pendimethalin did not persist to levels of concern in the surface-water of a water-seeded rice field and was detected at very low concentrations, in general. The results from this study can assist regulatory agencies and registrants in articulating a water-holding period for pendimethalin in water-seeded rice, which can help prevent potential contamination to municipal drinking waters, prevent damage to downstream high value crops and ensure efficacious use, therefore, promoting responsible stewardship of chemical use in California rice.

## Supplemental Material

Supplemental Material 1. Extraction and analysis method for detection of pendimethalin residue in water samples after an application onto a water-seeded rice field.

## Acknowledgments

The authors acknowledge partial funding by the California Rice Research Board, BASF and UC Davis Jastro Research Award. The authors also acknowledge the California Rice Experiment Station for providing the site and assisting with field management, the Multi-User Analytical Lab in Clemson University which performed the analytical analysis and Ekrem Uludag who assisted with the water sampling in the field. The authors also acknowledge the D. Marlin Brandon Rice Research Fellowship by the California Rice Research Trust, and the Department of Plant Sciences, UC Davis for the award of a GSR scholarship funded by endowments, particularly the James Monroe McDonald Endowment, administered by UCANR, which supported the student during the time of this study.

## Conflict of Interest

The authors have no financial or conflict of interest to declare.

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Table 4-1. Physico-chemical properties of pendimethalin[a]

| Properties | Value |
|---|---|
| Molecular formula | $C_{13}H_{19}N_3O_4$ |
| Molecular weight (g mole$^{-1}$) | 281.31 |
| Water Solubility (mg L$^{-1}$) | 0.275 |
| Vapor pressure (Pa) | 1.25 x $10^{-3}$ |
| $pK_a$ | Non-ionizable |
| Log $K_{OC}$ | 4.11 |
| Log $K_{OW}$ | 5.20 |
| Henry's Law constant (atm m$^3$ mol$^{-1}$) 25° C | 2.68 x $10^{-5}$ |

[a]From Vighi et al. (2017) and Shaner et al. (2014)

Table 4-2. Pendimethalin residue concentration in water after an application onto a water-seeded rice field as effected by formulation and sampling time averaged over three application rates[a]

| Formulation | Sampling time DAT | Concentration ppb |
|---|---|---|
| Capsule Suspension | 1 | 10.9 b |
| | 3 | 6.4 bcd |
| | 5 | 4.3 cd |
| | 10 | 0.6 fg |
| | 15 | 0.3 h |
| Emulsifiable Concentrate | 1 | 73.0 a |
| | 3 | 8.2 bc |
| | 5 | 3.3 d |
| | 10 | 0.3 gh |
| | 15 | 0.1 i |
| Granule | 1 | 4.2 cd |
| | 3 | 4.8 cd |
| | 5 | 4.8 cd |
| | 10 | 1.3 e |
| | 15 | 0.8 ef |

[a]Means with the same letter do not differ by Tukey's $\alpha$=0.05. Data was log-transformed for analysis and back-transformed for presentation. 1 ppb = 1$\mu$g $L^{-1}$; DAT, days after treatment.

Table 4-3. First-order dissipation kinetics and time until 50% dissipation of pendimethalin in flood water after an application on a water-seeded rice field across three formulations and three rates[a]

| Formulation | Application Rate kg ai $ha^{-1}$ | $C_0$ ppb | Dissipation Rate constant k $day^{-1}$ | $T_{1/2}$ days |
|---|---|---|---|---|
| Capsule Suspension | 1.1 | 8.5 ± 1.8 | 0.3 ± 0.1 | 2.3 |
| | 2.3 | 22.1 ± 2.5 | 0.3 ± 0.1 | 2.3 |
| | 3.4 | 19.2 ± 2.3 | 0.2 ± 0.04 | 3.5 |
| Emulsifiable Concentrate | 1.1 | 75.7 ± 15.9 | 1.0 ± 0.2 | 0.7 |
| | 2.3 | 353.0 ± 71.9 | 1.2 ± 0.2 | 0.6 |
| | 3.4 | 360.1 ± 133.8 | 1.0 ± 0.3 | 0.7 |
| Granule | 1.1 | 4.0 ± 0.6 | 0.1 ± 0.03 | 6.9 |
| | 2.3 | 6.3 ± 0.9 | 0.1 ± 0.03 | 6.9 |
| | 3.4 | 18.3 ± 5.1 | 0.2 ± 0.1 | 3.5 |

[a]$C_0$, Initial concentration; ± Standard error; $T_{1/2}$, time for 50% of initial concentration of the herbicide to dissipate; ppb, parts per billion; 1 ppb = 1 μg $L^{-1}$

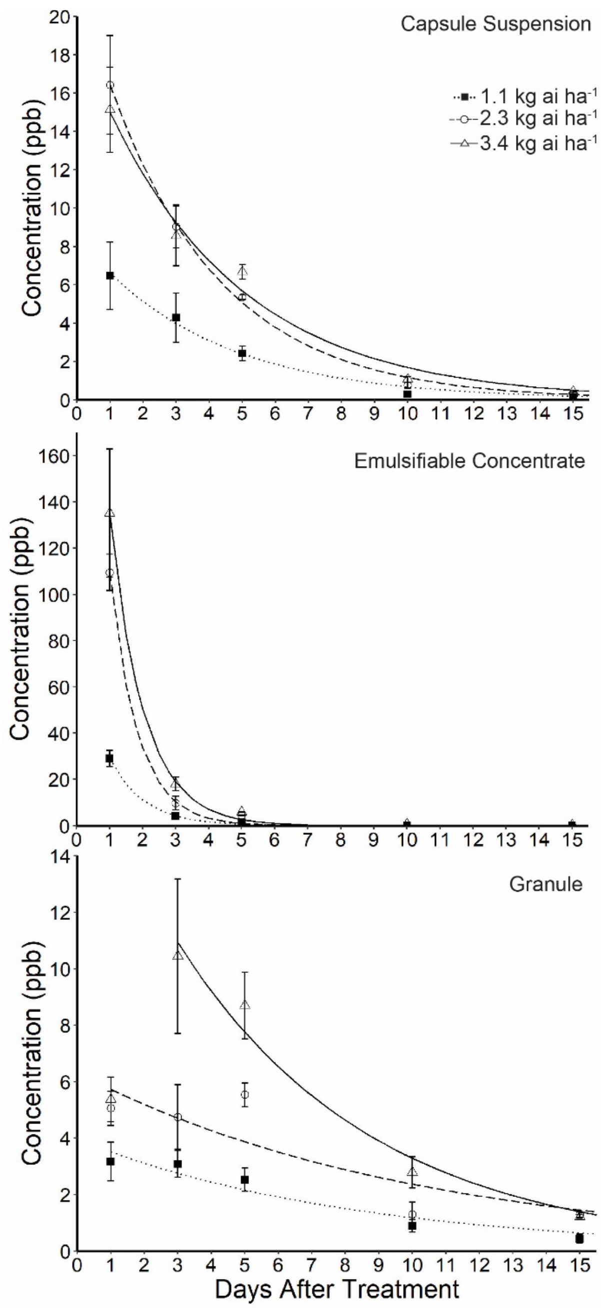


Figure 3-1. Dissipation of pendimethalin in capsule suspension (top), emulsifiable concentrate (middle) and granule (bottom) in water after applications onto a flooded water-seeded rice field at 1.1, 2.3 and 3.4 kg ai $ha^{-1}$ rates. The first-order dissipation equation $C_t = C_0\, e^{-kt}$ was fit to the data, where $C_t$ is the concentration at time t, $C_0$ is the initial concentration, t is time, and k is the rate constant. 1 parts per billion (ppb) = 1 µg $L^{-1}$. Error bars are standard error.

**Supplemental Material 1: Extraction and Analysis Method**

Dissipation of Pendimethalin in a Water-Seeded Rice Field and Implications for Water Management. Aaron Becerra-Alvarez and Kassim Al-Khatib

In the lab, water samples were cleaned from debris by periodically pouring the 90 mL sample through a funnel with filter paper of 11 µm Whatman 1 of 90 mm diameter outlining the inside the funnel's wall. The water flowed by way of gravity into a 125 mL beaker, leaving debris behind. Filter papers were changed periodically as needed. Then, 50 mL were allocated from the filtered sample and placed in storage at -20° C until analysis.

A standard for pendimethalin, ACS-grade hexane and MS-grade acetonitrile were obtained from Fisher Scientific. Liquid-liquid extraction methods were modified from USEPA (USEPA 2013). High pressure liquid chromatography tandem mass spectrometry (LCMS/MS) was employed to analyze for residue in water samples. Fifteen mL samples were extracted three times with 3 mL of hexane and placed on a rotary platform shaker for 5 minutes, then set aside for 15 minutes. Hexane extracts were pooled and 3 mL were then dried under a nitrogen gas stream. Then, volumes of 500 µL acetonitrile were added to the dried sample and vortexed. Volumes of 500 µL 0.4% formic acid was then added and vortexed for a final concentration factor of 15.

A Shimadzu LCMS-8040 triple quadrupole mass spectrometer was used equipped with electrospray ionization on positive mode. The desolvation line temperature and heat block temperature were 250° and 400° C, respectively. Nebulizing gas and drying gas were set at a flow of 3 L min$^{-1}$ and 15 L min$^{-1}$, respectively. The mobile phase flow rate was 0.4 mL min$^{-1}$ and an injection volume of 10 µL. The C18 column was Phenomenex Kinetex polar, 100 by 3.0 mm and 2.6 µm particle size. The multiple reaction monitoring ion transitions for the quantifier ion were 282.0 > 212.1 m/z (precursor ion > product ion) in a dwell time of 10 ms and for the qualifier ions were 282.2 > 43.1 m/z and 282.2 > 194 m/z in a dwell time of 5 ms.

The limit of detection was 0.006 µg $L^{-1}$ and the limit of quantification was 0.008 µg $L^{-1}$. Multiple calibration curves were implemented for the low concentration range and for the high concentration range using Shimadzu LabSolutions and MacCoss Skyline software for small molecules. Method recovery was performed by spiking five nontreated collected water samples with 0.20 µg $L^{-1}$ of pendimethalin before extraction (USEPA 2013). A low concentration of pendimethalin below 0.05 µg $L^{-1}$ was present in the collected nontreated samples, therefore, the peak areas of the control samples without standard spiking were subtracted from the spiked samples. The recovery in water samples was on average 79%.

Reference

[USEPA] United States Environmental Protection Agency (2013) Pendimethalin and Metabolites in Water-MRID 49221401. United States Environmental Protection Agency Environmental Chemistry Methods Index. Accessed from https://www.epa.gov/pesticide-analytical-methods/pendimethalin-metabolites-water-mrid-49221401 on July 15, 2021