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Strategies to Overcome Antagonism of Quizalofop-p-ethyl when Applied in Mixture with Other Herbicides

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STRATEGIES TO OVERCOME ANTAGONISM OF QUIZALOFOP-P-ETHYL WHEN APPLIED IN MIXTURE WITH OTHER HERBICIDES

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ABSTRACT

A field study was conducted in 2017 and 2018 at the LSU Agricultural Center H. Rouse Caffey Rice Research Station (RRS) near Crowley, LA. to evaluate the influence of different adjuvants in overcoming the antagonism of quizalofop when mixed with bispyribac in Louisiana rice production. The antagonism of quizalofop mixed with bispyribac plus HCOC at 14 DAIT was overcome with a neutral interaction observed at 28 DAIT for barnyardgrass control with an observed control of 91%, compared with an expected control of 97%. The addition of COC, SNS or HCOC into a mixture of quizalofop plus bispyribac provided synergistic or neutral interactions at 14 and 28 DAIT for CL-111, CLXL-745, and red rice control.

A field study was conducted in 2017 and 2018 at RRS in 2017 and 2018 to evaluate the impact of reduced rates of halosulfuron on quizalofop activity in Louisiana rice production. At 28 DAIT, antagonism of quizalofop for barnyardgrass control was observed when mixed with halosulfuron plus thifensulfuron at 53 g ha^{-1} with an observed control of 89%, compared with an expected control of 98%; however, this antagonism was overcome at the same evaluation date with a neutral interaction for barnyardgrass control when quizalofop was mixed with halosulfuron plus thifensufluron at 34 g ha^{-1} with an observed control of 96%.

Two Field studies were conducted in 2018 at RRS to evaluate sequential applications of quizalofop applied on previously antagonized weeds from a quizalofop plus propanil mixture to determine the time needed between antagonism and a second application of quizalofop. Quizalofop mixed with propanil followed by a sequential application of quizalofop at 7, 14, and 21 DAIT controlled barnyardgrass with an observed visual value of 97 to 98%, compared with an expected control of 95 to 98%. However, the sequential treatment of quizalofop applied at 28

DAIT to antagonized barnyardgrass resulted in 71% control, compared with an expected control of 67%.

Chapter 1.
Introduction

Red rice (*Oryza sativa* L.) is one of the most troublesome pests of cultivated rice (*O. sativa* L.) (Webster 2000), and in 1979 it was reported that red rice infestations caused a $50 million loss each year in southern United States rice (Smith 1979). The genetic similarity between red rice and cultivated rice make it difficult to selectively control using a herbicide in crop (Levy et al. 2006). In 2002, Imidazolinone-resistant (IR) rice (Clearfield® BASF, Research Triangle Park, NC 27709) became available to producers and provided growers with an effective herbicide option for red rice control (Croughan 2003; Rustom et al. 2018). Hybrid IR-rice (RiceTec, Inc. Houston, TX) was introduced in 2003.

For over 150 years, red rice has been a troublesome, conspecific pest of cultivated rice (Craigmiles 1978; De Wet and Harlan 1975; Gealy et al. 2003). Red rice infestations can reduce grain quality due to seed contamination and grain yields by competing for light, water, nutrients, and other growth requirements (Smith 1988; Smith et al. 1977). The pericarp of red rice contains anthocyanins which transmits a red color on the caryopsis and readily shatters before harvest (Pantone and Baker 1991). The red grains can be removed by extra milling; however, this can be an expensive process and can cause extensive breaking of the cultivated rice grain, reducing quality and value (Smith 1981).

Soon after the adoption of the IR-rice technology, outcrosses of IR-rice with red rice were reported (Zhang et al. 2006). Research indicates gene flow from IR-rice to naturally occurring red rice has resulted in the development of IR-red rice (Rajguru et al. 2005). When gene flow occurs, it is typically a one direction flow from the cultivated species to the weedy populations (Langevin et al. 1990). In addition to IR-red rice, hybrid IR-rice has an inherent seed dormancy characteristic with a high degree of seed shattering, and often has weedy characteristics when the F_2 is allowed to establish in succeeding growing seasons (Burgos et al. 2014; Sudianto et al. 2013). IR-red rice and subsequent generations of hybrid IR-rice are often referred to as weedy rice.

Red rice is a conspecific pest of cultivated rice production due to the nature of red rice outcompeting cultivated rice, causing severe yield loss (Gressel and Valverde 2009). Red rice is botanically classified as the same species as cultivated rice; however, there are phenotypic differences that distinguish red rice from cultivated rice (Kwon et al. 1992). The phenotypic characteristics of red rice are dark to light green leaves, superior height, awned and/or awnless seeds, and pubescent or glabrous leaves (Rustom et al. 2015, 2018). Red rice often has a competitive advantage over cultivated rice due to its ability to grow taller and produce more tillers than the cultivated rice (Diarra et al. 1985).

Smith (1988) suggested that more than 70 weed species infest drill-seeded rice production in the United States each year. Among these 70 weed species, red rice is one of the more problematic weed species due to its superior competitive ability. Fischer and Ramirez (1993) observed a 50% yield reduction when red rice infested cultivated rice at a population of 24 red rice plants m^{-2} for a duration of 40 days after emergence. Smith (1988) reported red rice caused the highest yield reduction of the grass-weed groups evaluated, and each red rice plant m^{-2} caused a reduction in rice yields of 219 kg ha^{-1}.

Another weed management issue in rice production is barnyardgrass [*Echinochloa crus-galli* (L.) P. Beauv.]. Smith (1968) reported that season-long barnyardgrass infestation reduced rough rice yield up to 79%. Barnyardgrass is a monocot weed that is glabrous, with no ligule or auricles and can survive in partially submerged conditions (Bryson and DeFelice 2009), which allows barnyardgrass to easily adapt to a flooded rice field. Barnyardgrass has been confirmed in

Arkansas, Mississippi, and Louisiana to be resistant to several herbicides with differing sites of action (SOA) (Malik et al. 2010; Riar et al. 2013).

In the 1960's, propanil was one of the first labelled herbicides to control barnyardgrass in cultivated rice production and in 1995 at least one application of propanil was applied to 98% of Arkansas rice (Carey et al. 1995). The use of propanil for control of barnyardgrass increased U.S. rice yields from 34 to 74% (Smith 1965). However, the first case of propanil-resistant barnyardgrass was recorded in 1989 in Poinsett County, AR, and in 1990 seedlings from these resistant biotypes were determined to be resistant to propanil at rates as high as 11.2 kg ha^{-1} (Baltazar and Smith 1994; Carey et al. 1995; Malik et al. 2010).

In 1992, quinclorac was introduced to cultivated rice production primarily to control propanil-resistant barnyardgrass; however, in 1999 quinclorac- and propanil-resistant barnyardgrass was found in Craighead County, AR to be resistant to 16 times the recommended rate of quinclorac or propanil (Malik et al. 2010).

Propanil- and/or quinclorac-resistant barnyardgrass led many growers to the adoption of IR-rice in the Midsouth United States; however, the adoption of IR-rice has led to barnyardgrass resistance to many acetolactate synthase (ALS) inhibiting herbicides such as imazamox, imazethapyr, penoxsulam, and bispyribac-sodium (Riar et al. 2013). The resistance of barnyardgrass to multiple herbicide SOA led BASF to develop a new herbicide-resistant rice.

In the mid-2010s, BASF began development of a new herbicide-resistant rice which confers resistance to acetyl Co-enzyme A carboxylase (ACCase) inhibiting herbicides due to IR-weedy rice and herbicide-resistant barnyardgrass. The herbicide targeted for use is the Group 1 herbicide quizalofop belonging to the aryloxyphenoxypropionate family. Quizalofop inhibits the ACCase enzyme and this enzyme catalyzes the first committed step in de novo fatty acid synthesis (Burton et al. 1989; Focke and Lichtenthaler 1987). The inhibition of de novo fatty acid synthesis prevents the formation of cell walls, which results in cell destruction causing plant death (Shaner 2014). The targeted single application rate of quizalofop in ACCase-resistant (ACCase-R) rice production is 92 to 155 g ai ha^{-1}, not to exceed 240 g ha^{-1} per year (Anonymous 2017). ACCase-R rice allows quizalofop to be applied postemergence (POST) for control of annual and perennial grasses, including IR-weedy rice and barnyardgrass. Previously, quizalofop has been used for red rice control in soybean [*Glycine max* (L.) Merr.] production at 70 g ha^{-1} and often times requires a sequential application when treating red rice at later growth stages (Askew et al. 2000).

Quizalofop does not control sedge (*Cyperus* spp.) or broadleaf weeds and other herbicides will be needed to help manage these weeds in ACCase-R rice production (Anonymous 2017; Rustom et al. 2018). Herbicides are often applied in a mixture to broaden the weed control spectrum, manage herbicide resistance, and save time and application costs (Gressel and Segel 1990; Jordan 1995; Zhang et al. 2005). Herbicide mixtures have proven to be beneficial in improving efficacy and broadening the weed control spectrum in IR-rice (Carlson et al. 2011; Fish et al. 2015, 2016; Pellerin and Webster 2004; Pellerin et al. 2003; Webster et al. 2012). Herbicide mixture interactions may result in one of three responses: antagonistic, synergistic, or additive/neutral (Berenbaum 1981; Blackshaw et al. 2006; Blouin et al. 2004, 2010; Drury 1980; Fish et al. 2015, 2016; Hatzios and Penner 1985; Morse 1978; Nash 1981; Streibig et al. 1998). When a herbicide mixture has an observed response greater than the expected response based on each herbicide applied separately, the interaction is synergistic; when the observed response is a reduction in control the interaction is deemed antagonistic

(Colby 1967). If a herbicide mixture is said to be statistically similar as the expected value the mixture is defined as neutral or additive.

Colby's method is a standard statistical linear model for analyzing the observed synergistic, antagonistic, or additive/neutral response for herbicide mixtures compared to the expected response based on each herbicide applied alone (Colby 1967). Blouin et al. (2004) suggests that a nonlinear mixed-model is needed to detect mixture interactions if the expected response based on the herbicides applied alone is defined as a multiplicative, nonlinear function of the means, rather than Colby's standard linear model for tests of hypotheses. In the study conducted by Blouin et al. (2004), a nonlinear mixed-model proved to be more sensitive and versatile than a linear mixed-model. Also, in a study conducted by Lanclos et al. (2002) evaluating glufosinate mixtures on glufosinate-resistant rice, the Blouin et al. (2004) nonlinear mixed model proved to detect more significant effects with a significance level of 0.05, compared to Colby's linear mixed-model. Blouin et al. (2010) revised his previous model into an augmented mixed-model and recommends the augmented mixed-model to be used for evaluating mixture interactions that are defined as multiplicative, nonlinear functions of the means. From this point forward, the Blouin et al. (2010) augmented mixed-model will be referred to as Blouin's Modified Colby's method.

ACCase inhibiting herbicide antagonism has historically been observed when applied in a mixture with broadleaf or sedge herbicides (Ferreira and Coble 1994; Hatzios and Penner 1985; Myers and Coble 1992; Rhodes and Coble 1984; Rustom et al. 2018; Zhang et al. 2005). Antagonism of ACCase inhibiting herbicide activity on barnyardgrass has previously been observed in Louisiana rice production when fenoxaprop activity was reduced when applied in a mixture with halosulfuron, bensulfuron, or carfentrazone; however, fenoxaprop mixtures with bentazon or molinate resulted in a neutral response (Zhang et al. 2005). Bromoxynil, pyrithiobac, and chlorimuron have been observed to antagonize quizalofop when applied in a mixture for control of broadleaf signalgrass [*Urochloa platyphylla* (Munro ex. C. Wright) R.D. Webster], johnsongrass (*Sorghum halepense* L.), and yellow foxtail (*Setaria pumila* Pior) (Bjelk and Monaco 1992; Culpepper et al. 1999; Snipes and Allen 1996).

Rustom et al. (2018) observed antagonism of quizalofop when mixed with numerous ALS inhibiting herbicides for control of either weedy rice or barnyardgrass including bispyribac, bensulfuron, halosulfuron, imazosulfuron, orthosulfuron plus halosulfuron, orthosulfuron plus quinclorac, penoxsulam, and penoxsulam plus triclopyr. Penoxsulam and bispyribac proved to be the least compatible ALS inhibiting herbicides in a mixture with quizalofop for control of weedy rice and barnyardgrass. In a separate study observing the interactions of contact herbicides mixed with quizalofop, antagonism of quizalofop was observed when applied in a mixture with propanil for control of weedy rice and barnyardgrass at all observation dates (Rustom 2017). Although neutral results were recorded for quizalofop mixed with bentazon or saflufenacil at 28 days after the initial treatment (DAIT), antagonism that occurred at 14 DAIT resulted in yield reductions. Propanil proved to be the least compatible contact herbicide in a mixture with quizalofop for control of weedy rice and barnyardgrass.

An adjuvant is a material that is added to a postemergence herbicide application or a herbicide mixture to enhance or modify the herbicide(s) (Hazen 2000). Adjuvants can enhance penetration by improving spray coverage, reducing droplet surface tension, acting as a humectant, and increasing cuticle permeability (Wanamarta et al. 1989). Adjuvants are typically comprised of surfactants, oils, solvents, polymers, salts, diluents, humectants, and water (Hazen 2000). There are two major categories of adjuvants, the utility adjuvants and the activator adjuvants. Utility adjuvants typically aid in herbicide compatibility, pH buffering, spray drift reduction, and/or de-foaming agents. However, activator adjuvants improve herbicide efficacy by lowering surface tension, increasing adherence to the leaf surface, reducing the rate of drying, and/or eliminating the natural barriers preventing uptake.

Adjuvants are an integral component of weed management due to their nature of altering the physical and chemical properties of herbicides and modifying herbicide activity (Bridges 1989; McWhorter 1986). Antagonism of ACCase inhibiting herbicides when mixed with broadleaf or sedge herbicides can be overcome by using adjuvants in the mixture (Jordan 1995; Jordan and York 1989; Penner 1989). A crop oil concentrate (COC) consisting of fatty acid esters and alkoxylated alcohols-phosphate esters (Dash® label, BASF, Research Triangle Park, NC 27709) was patented in 1989 specifically for use with sethoxydim when mixed with other herbicides (Hazen 2000). The antagonism of ACCase inhibiting herbicides when mixed with ALS inhibiting herbicides has been associated with the reduced translocation of the graminicide, caused by the physiological effect of the ALS inhibiting herbicide on the grass species (Croon et al. 1989; Kammler et al. 2010). Jordan (1995) observed a reduction of sethoxydim and clethodim antagonism by bentazon when applied with a non-ionic surfactant (NIS) in comparison to a COC for control of barnyardgrass, broadleaf signalgrass [*Urochloa platyphylla* (Munro ex. C. Wright) R.D. Webster] and johnsongrass (*Sorghum halepense* L.). Zollinger (2005) observed a blend of methylated seed oil (MSO) and a NIS overcome antagonism of quizalofop in a mixture with tribenuron for control of yellow foxtail (*Setaria pumila* Pior).

Herbicide antagonism can be influenced by the rate of the herbicides used in a mixture (Blackshaw et al. 2006; Culpepper et al. 1999; Hatzios and Penner 1985; Jordan et al. 1993). Antagonism of an ACCase inhibiting herbicide can be reduced by increasing the ratio of the

ACCase inhibitor to broadleaf herbicide in a mixture. Green (1989) observed that antagonism between bentazon and quizalofop for control of barnyardgrass can be overcome by doubling the rate of quizalofop. Rhodes and Coble (1984) observed that antagonism of sethoxydim by bentazon for the control of broadleaf signalgrass [*Urochloa platyphylla* (Munro ex. C. Wright) R.D. Webster] can be overcome by increasing the rate of sethoxydim. The antagonism of sethoxydim occurred at the lower rate of 0.28 kg ha^{-1} and no antagonism was observed at the higher rate of 0.56 kg ha^{-1} when applied in a mixture with the same rate of bentazon. Grichar and Boswell (1987) observed that increasing the rate of fluazifop from 0.28 to 0.42 kg ha^{-1} overcame reductions in fluazifop activity from bentazon but not from 2,4-DB for control of Texas panicum (*Panicum texanum* Buckl.) and large crabgrass (*Digitaria sanguinalis* L.); however, reductions in sethoxydim activity were overcome by increasing the rate from 0.28 to 0.42 kg ha^{-1} when mixed with 2,4-DB. Different responses among plant families in response to herbicide interactions may be due to genetic, physiological, or morphological differences (Zhang et al. 1995).

An alternative to applying two potentially non-compatible herbicides is to apply the herbicides sequentially (Minton et al 1989). Applying two or more herbicides sequentially is a common practice to improve the spectrum of weed control, reduce production costs, and/or to prevent herbicide resistance (Zhang et al. 1995). ACCase inhibiting herbicides are often times antagonized when applied in a mixture with a broadleaf herbicide; however, in some cases a sequential application of the ACCase inhibiting herbicide applied alone can overcome the antagonism that occurred at the earlier application date (Rustom et al. 2018). Antagonism of quizalofop was observed when applied in a mixture with bispyribac, bensulfuron, halosulfuron, imazosulfuron, orthosulfuron plus halosulfuron, orthosulfuron plus quinclorac, penoxsulam, and penoxsulam plus triclopyr on either weedy rice or barnyardgrass at either 14 and/or 28 days after initial treatment (DAIT). A second application of quizalofop applied alone at 28 DAIT resulted in a neutral response at 42 DAIT for all herbicide mixtures except for penoxsulam containing mixtures.

The efficacy of a sequential herbicide application can be altered due to a prior herbicide application (Hatzios and Penner 1985). In a study evaluating sequential applications of quizalofop following an application of propanil plus thiobencarb, quizalofop activity on weedy rice and barnyardgrass was 45 to 76% when applied 0 to 3 days after propanil plus thiobencarb when evaluated at 28 days after treatment; however, by delaying quizalofop to 7 day after propanil plus thiobencarb control of weedy rice and barnyardgrass increased to 81 to 86% (Rustom 2017). Minton et al. (1989) concluded barnyardgrass control with sethoxydim or quizalofop were antagonized when imazaquin or lactofen was applied 24 hours prior to the graminicide. However, when sethoxydim or quizalofop was applied 24 hours prior to a imazaquin or lactofen application, no antagonism of the graminicides occurred for barnyardgrass control. If a graminicide and broadleaf herbicide are to be applied sequentially, it is imperative that the graminicide is applied prior to the broadleaf herbicide or after an adequate interval if applying the broadleaf herbicide first.

Herbicide mixtures are an essential component of cultivated rice production in order to broaden the spectrum of weed control, delay herbicide resistance, save time and application costs. The objective of this research was to evaluate different strategies to overcome antagonism of quizalofop for control of weedy rice and barnyardgrass when applied in a mixture with broadleaf or sedge herbicides. The methods evaluated consist of adding different adjuvants to quizalofop plus bispyribac mixtures, reducing the rate of halosulfuron in a mixture with quizalofop, and by applying quizalofop sequentially on previously antagonized weeds resulting from a mixture of quizalofop plus propanil.

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Chapter 2.
Do Adjuvants Reduce the Antagonism of Quizalofop-p-ethyl when mixed with Bispyribac-sodium

Introduction

Red rice (*Oryza sativa* L.) is one of the most troublesome pests of cultivated rice (*O. sativa* L.) (Webster 2000), and in 1979 it was reported that red rice infestations caused a $50 million loss each year in southern United States rice (Smith 1979). The genetic similarity between red rice and cultivated rice cause the selective control of this weed using a herbicide in crop to be difficult (Levy et al. 2006). In 2002, Imidazolinone-resistant (IR) rice (*O. sativa* L.) [Clearfield® BASF, Research Triangle Park, NC 27709] was first commercialized, and provided growers with an effective herbicide option for red rice control (Croughan 2003; Rustom et al. 2018). Hybrid IR-rice (RiceTec, Inc. Houston, TX) was introduced in 2003.

Soon after the adoption of the IR-rice technology, outcrosses of IR-rice with red rice were reported (Zhang et al. 2006). Research indicates gene flow from IR-rice to naturally occurring red rice has resulted in the development of IR-red rice (Rajguru et al. 2005). When gene flow occurs, it is typically a one direction flow from the cultivated species to the weedy populations (Langevin et al. 1990). In addition to IR-red rice, hybrid IR-rice has an inherent seed dormancy characteristic with a high degree of seed shattering, and often times has weedy characteristics when the F_2 is allowed to establish in succeeding growing seasons (Burgos et al. 2014; Sudianto et al. 2013). IR-red rice and subsequent generations of hybrid IR-rice are often referred to as weedy rice.

Red rice is a conspecific pest of cultivated rice production due to the nature of red rice outcompeting cultivated rice, causing severe yield loss (Gressel and Valverde 2009). Smith (1988) suggested that more than 70 weed species infest drill-seeded rice production in the United

States each year. Among these 70 weed species, red rice is one of the more problematic weed species due to its superior competitive ability compared with commercial rice. Red rice is botanically classified as the same species as cultivated rice; however, there are phenotypic differences that distinguish red rice from cultivated rice (Kwon et al. 1992). The phenotypic characteristics of red rice and weedy rice can have dark to light green leaves, superior height, awned and/or awnless seeds, and pubescent or glabrous leaves (Rustom et al. 2015, 2018). Red rice often has a competitive advantage over cultivated rice due to its ability to grow taller and produce more tillers than the cultivated rice (Diarra et al. 1985).

Another weed management issue in rice production is barnyardgrass [*Echinochloa crus-galli* (L.) P. Beauv.]. Smith (1968) reported that a season-long barnyardgrass infestation reduced rough rice yield up to 79%. Barnyardgrass has been confirmed in Arkansas, Mississippi, and Louisiana to be resistant to several herbicides with differing sites of action (Malik et al. 2010; Riar et al. 2013). Propanil was one of the first herbicides to control barnyardgrass in cultivated rice production and in 1995 at least one application of propanil was applied to 98% of Arkansas rice (Carey et al. 1995). Propanil- and/or quinclorac-resistant barnyardgrass led many growers to the adoption of IR-rice in the Midsouth United States; however, the adoption of IR-rice has led to barnyardgrass resistance to many acetolactate synthase (ALS) inhibiting herbicides such as imazamox, imazethapyr, penoxsulam, and bispyribac-sodium (Riar et al. 2013).

In the mid-2010s, BASF began development of a new herbicide-resistant rice which confers resistance to acetyl Co-enzyme A carboxylase (ACCase) inhibiting herbicides due to IR-weedy rice and herbicide-resistant barnyardgrass. This new non-transgenic rice is resistant to quizalofop, a Group 1 herbicide, in the aryloxyphenoxypropionate herbicide family. Quizalofop inhibits the ACCase enzyme, and this enzyme catalyzes the first committed step in the de novo fatty acid synthesis (Burton et al. 1989; Focke and Lichtenthaler 1987). The targeted single application rate of quizalofop for use in ACCase-resistant (ACCase-R) rice production is 92 to 155 g ai ha^{-1}, not to exceed 240 g ha^{-1} per year (Anonymous 2017). ACCase-R rice allows quizalofop to be applied postemergence (POST) for control of annual and perennial grasses, including IR-weedy rice. Previously, quizalofop was used for red rice control in soybean [*Glycine max* (L.) Merr.] production at 70 g ha^{-1}, and often requires a sequential application when treating red rice at later growth stages (Askew et al. 2000).

Herbicides are often applied in a mixture to broaden the weed control spectrum, delay herbicide resistance, and save time and application costs (Gressel and Segel 1990; Jordan 1995; Zhang et al. 2005). Herbicide mixture interactions may result in one of three responses: antagonistic, synergistic, or additive/neutral (Berenbaum 1981; Blackshaw et al. 2006; Blouin et al. 2004, 2010; Drury 1980; Fish et al. 2015, 2016; Hatzios and Penner 1985; Morse 1978; Nash 1981; Streibig et al. 1998). When a herbicide mixture has an observed response greater than the expected response based on each herbicide applied separately, the interaction is synergistic; when the observed response is a reduction in control the interaction is deemed antagonistic (Colby 1967). If a herbicide mixture is said to be statistically similar as the expected value the mixture is defined as neutral or additive.

ACCase inhibiting herbicide antagonism has historically been observed when applied in a mixture with broadleaf or sedge herbicides (Ferreira and Coble 1994; Hatzios and Penner 1985; Myers and Coble 1992; Rhodes and Coble 1984; Rustom et al. 2018; Zhang et al. 2005). Rustom et al. (2018) observed antagonism of quizalofop when mixed with numerous ALS inhibiting herbicides for control of either weedy rice or barnyardgrass including bispyribac, bensulfuron, halosulfuron, imazosulfuron, orthosulfuron plus halosulfuron, orthosulfuron plus quinclorac, penoxsulam, and penoxsulam plus triclopyr. Penoxsulam and bispyribac proved to be the least compatible in a mixture with quizalofop for control of weedy rice and barnyardgrass.

An adjuvant is a material that is added to a postemergence herbicide application or a herbicide mixture to enhance or modify the herbicide(s) (Hazen 2000). Adjuvants can enhance penetration by improving spray coverage, reducing droplet surface tension, acting as a humectant, and increasing cuticle permeability (Wanamarta et al. 1989). Adjuvants are typically comprised of surfactants, oils, solvents, polymers, salts, diluents, humectants, and water (Hazen 2000). There are two major categories of adjuvants, the utility adjuvants and the activator adjuvants. Utility adjuvants typically aid in herbicide compatibly, pH buffering, spray drift reduction, and/or de-foaming agents. However, activator adjuvants improve herbicide efficacy by lowering surface tension, increasing adherence to the leaf surface, reducing the rate of drying, and/or eliminating the natural barriers preventing uptake.

Adjuvants are an integral component of weed management due to their nature of altering the physical and chemical properties of herbicides and modifying herbicide activity (Bridges 1989; McWhorter 1986). Antagonism of ACCase inhibiting herbicides when mixed with broadleaf or sedge herbicides can be overcome by using adjuvants in the mixture (Jordan 1995; Jordan and York 1989; Penner 1989). A crop oil concentrate (COC) consisting of fatty acid esters and alkoxylated alcohols-phosphate esters (Dash® label, BASF, Research Triangle Park, NC 27709) was patented in 1989 specifically for use with sethoxydim when mixed with other herbicides (Hazen 2000). The antagonism of ACCase inhibiting herbicides when mixed with ALS inhibiting herbicides has been associated with the reduced translocation of the graminicide, caused by the physiological effect of the ALS inhibiting herbicide on the grass species (Croon et al. 1989; Kammler et al. 2010). Jordan (1995) observed a reduction of sethoxydim and clethodim antagonism by bentazon when applied with a non-ionic surfactant (NIS) in comparison to a COC for control of barnyardgrass, broadleaf signalgrass [*Urochloa platyphylla* (Munro ex. C. Wright) R.D. Webster] and johnsongrass (*Sorghum halepense* L.). Zollinger (2005) observed an adjuvant blend of methylated seed oil (MSO) and a NIS overcome antagonism of quizalofop in a mixture with tribenuron for control of yellow foxtail (*Setaria pumila* Pior).

Quizalofop activity on barnyardgrass and weedy rice is often antagonized when applied in a mixture with ALS inhibiting herbicides (Rustom et al. 2018). Past research has shown that adjuvants can aid in overcoming herbicide antagonism by enhancing herbicide penetration, improving spray coverage, and reducing surface tension (Penner 1989). The objective of this research was to evaluate the potential of different adjuvants ability to overcome or reduce the antagonism of quizalofop when applied in a mixture with the ALS inhibiting herbicide bispyribac.

Materials and Methods

A field study was conducted in 2017 and 2018 at the LSU Agricultural Center H. Rouse Caffey Rice Research Station (RRS) near Crowley, LA. to evaluate the influence of different adjuvants in overcoming the antagonism of quizalofop when mixed with bispyribac in Louisiana rice production. The soil type at the RRS is a Midland silty clay loam (Fine, smectitic, thermic Chromic Vertic Epiaqualfs) with a pH of 5.7 and 3.3% organic matter. Field preparation consisted of a fall and spring disking followed by two passes in the opposite direction with a two-way bed conditioner consisting of rolling baskets and s-tine harrows set at a depth of 6 cm. A preplant fertilizer of 8-24-24 (N-P_2O_5-K_2O) was applied at 280 kg ha^{-1} followed by a preflood application of 280 kg ha^{-1} of 46-0-0 fertilizer was applied to the study area when rice was in the four-leaf to one-tiller stage prior to permanent flood establishment. A permanent 10-cm flood was established when the ACCase-R rice reached the four-leaf to one-tiller growth stage, and was maintained until two weeks prior to harvest.

Plot size was 1.5 by 5.1 m^{-2} with eight, 19.5 cm drill-seeded rows of ACCase-R 'PVL01' (Provisia® Horizon Ag, Memphis, TN 38125) long grain rice. In order to simulate a weedy rice population, eight, 19.5 cm drill-seeded rows of 'CLXL-745' hybrid long grain IR-rice were planted perpendicular in the front third of the plot and eight, 19.5 cm drill-seeded rows of 'CL-111' long grain IR-rice were planted perpendicular in the back third of each plot. All rice lines were planted April 26, 2017 and April 12, 2018 at a rate of 84 kg ha^{-1}. Awnless red rice was also broadcast across the research area at 50 kg ha^{-1} immediately prior to planting. The research area was naturally infested with barnyardgrass.

The initial herbicide treatment was applied when ACCase-R rice was at the three- to four-leaf, mid-postemergence (MPOST), growth stage with a CO_2-pressurized backpack sprayer calibrated to deliver 140 L ha^{-1}. Red rice, CLXL-745, and CL-111 were at the three- to four-leaf growth stage and barnyardgrass was at the three- to five-leaf growth stage at the time of the initial herbicide application. The spray boom consisted of five flat-fan 110015 nozzles (Flat Fan AirMix Venturi Nozzle, Greenleaf Technologies, Covington, LA 70434) with 38-cm spacing.

The study was a randomized complete block with a three-factor factorial arrangement of treatments with four replications. Factor A consisted of MPOST applications of quizalofop at 0 or 120 g ha^{-1}. Factor B consisted of MPOST applications of bispyribac at 0 or 34 g ai ha^{-1}. Factor C consisted of no adjuvant, a COC consisting of paraffinic oil and fatty acid esters (Agri-Dex® label, Helena Chemical Company, Collierville, TN), a silicon based surfactant plus nitrogen source (SNS) consisting of a proprietary blend of alkanolamides, alkanoates, trisiloxane, and carbamides (Dyne-A-Pak® label, Helena Chemical Company, Collierville,TN), and a high concentrate COC (HCOC) consisting of fatty acid esters and alkoxylated alcohols-phosphate esters (Dash® label, BASF, Research Triangle Park, NC 27709). Sources of materials are listed in Table 2.1.

Table 2.1. Source of materials.

Product	Trade Name	Form	Rate[a]	Manufacturer
			g ai ha^{-1}	
Quizalofop	Provisia	EC	120	BASF Corporation, Research Triangle Park, NC
Bispyribac	Regiment	WP	34	Valent U.S.A. Corporation, Walnut Creek, CA
COC[b]	Agri-Dex	L	-	Helena Chemical Company, Collierville, TN
SNS	Dyne-A-Pak	L	-	Helena Chemical Company, Collierville, TN
HCOC	Dash	L	-	BASF Corporation, Research Triangle Park, NC

[a]All adjuvants were applied at 1% v v^{-1}

[b]Abbreviations: COC, crop oil concentrate; SNS, silicon based surfactant plus nitrogen source; HCOC, high concentrate crop oil concentrate

Visual evaluations for crop injury, barnyardgrass, CL-111, CLXL-745 and red rice were recorded at 14 and 28 days after the initial treatment (DAIT), on a scale from 0 to 100% where 0 = no control and 100 = plant death. A second application of quizalofop was applied alone at 120 g ha^{-1} one week after the 28 DAIT rating date to remove non-ACCase-R rice from plots not initially treated/controlled with quizalofop. Halosulfuron was applied 38 DAIT to remove any remaining broadleaf or sedge weeds. Immediately prior to harvest, ACCase-R rice plant height was recorded, measuring from the soil surface to the tip of the extended panicle. The four center rows of ACCase-R rice were harvested with a Mitsubishi VM3 combine (Mitsubishi Corporation, 3-1, Marunouchi 2- chome, Chiyoda-ky, Tokyo, Japan), to determine the rough rice yield. Grain yield was adjusted to 12% moisture content.

Rough rice yield data were analyzed using the MIXED procedure in SAS (SAS 2013). Control data was analyzed using the Blouin et al. (2010) augmented mixed method to determine synergistic, antagonistic or neutral responses for herbicide mixtures by comparing the expected control calculated based on the activity of each herbicide applied alone to an observed control (Fish et al 2015, 2016; Rustom et al. 2018). Herbicide treatments and evaluation timings represent the fixed effects for all models. The random effects were year, replication within years, and plots. The effect of different environmental conditions on herbicide activity within a year or combination of years represents the random effects of the test (Carmer et al. 1989; Hager et al. 2003; Rustom et al. 2018). Normality of effects over all evaluation dates were checked with the use of the UNIVARIATE procedure of SAS and significant normality problems were not observed (SAS 2013).

Results and Discussion

Synergistic interactions for barnyardgrass control were observed at 14 DAIT when quizalofop was applied in a mixture with all adjuvants evaluated (Table 2.2). Antagonism of quizalofop was observed for control of barnyardgrass at 14 DAIT when applied in a mixture with bispyribac plus no adjuvant, COC, SNS or HCOC with an observed control of 41, 43, 63, and 86%, respectively, compared with an expected control of 95%. These results are similar to Rustom et al. (2018) who observed antagonism of quizalofop when mixed with bispyribac plus a COC with barnyardgrass control of 60%.

Table 2.2. Barnyardgrass control with quizalofop applied alone or mixed with bispyribac and/or different adjuvants using Blouin's modified Colby's analysis, in 2017 and 2018.

		Quizalofop (g ai ha^{-1})			
		0	120		
Mixture[a]	Rate[b]	Observed	Expected	Observed[c]	P value[d]
	g ai ha^{-1}	Control %			
14 DAIT[e]					
None	—	0	—	81	—

Table 2.2. continued

		Quizalofop (g ai ha^{-1})			
		0	120		
Mixture[a]	Rate[b]	Observed	Expected	Observed[c]	P value[d]
COC	1	0	81	96+	0.0016
SNS	1	0	81	95+	0.0021
HCOC	1	0	81	95+	0.0025
Bispyribac	34	75	95	41-	0.0001
Bispyribac + COC	34+1	78	95	43-	0.0001
Bispyribac + SNS	34+1	82	95	63-	0.0001
Bispyribac + HCOC	34+1	83	95	86-	0.0352
28 DAIT					
None	—	0	—	76	—
COC	1	0	76	95+	0.0001
SNS	1	0	76	98+	0.0001
HCOC	1	0	76	97+	0.0001
Bispyribac	34	86	97	40-	0.0001
Bispyribac + COC	34+1	81	97	58-	0.0001
Bispyribac + SNS	34+1	88	97	76-	0.0001
Bispyribac + HCOC	34+1	88	97	91	0.2459

[a]Evaluation dates for each respective mixture component.

[b]Rates with a value of one represent a percentage of v v^{-1}.

[c]Observed means followed by a minus (-) are significantly different from Blouin's modified Colby's expected responses at the 5% level indicating an antagonistic response. A positive (+) indicates a synergistic response. No sign indicates a neutral response.

[d]P < 0.05 indicates an antagonistic or synergistic response, P > 0.05 indicates a neutral response.

[e]DAIT, days after initial treatment.

As with the 14 DAIT evaluation, a synergistic interaction for barnyardgrass control was observed at 28 DAIT with quizalofop plus all adjuvants evaluated (Table 2.2). Antagonism of quizalofop was observed for control of barnyardgrass at 28 DAIT when mixed with bispyribac plus no adjuvant, COC, or SNS with an observed control of 40, 58, and 76%, respectively, compared with an expected control of 97%. The antagonism of quizalofop mixed with bispyribac plus HCOC at 14 DAIT was overcome with a neutral interaction observed at 28 DAIT for barnyardgrass control with an observed control of 91%, compared with an expected control of 97%. These data indicate that the most effective broad-spectrum mixture for barnyardgrass control is quizalofop mixed with bispyribac plus HCOC.

The antagonism observed at 14 DAIT when quizalofop was mixed with bispyribac plus HCOC was probably due to a delay in the absorption of quizalofop by barnyardgrass and by 28 DAIT a neutral interaction was observed. Croon et al. (1989) concluded that more than twice as much haloxyfop remained on the leaf surface when applied in a mixture with bentazon compared with haloxyfop applied alone. This same scenario is most likely occurring with the ALS and ACCase inhibiting herbicides evaluated in this research. Zollinger (2005) suggests that some adjuvants have an increased rate of cuticular wax solubilization compared to other adjuvants, which increases the rate of absorption of herbicides into plants. These data conclude that HCOC has a higher affinity of cuticular wax solubilization on barnyardgrass than COC and SNS. HCOC is classified as a penetration agent, which is a material that enhances the ability of agrichemicals to penetrate a surface (Hazen 2000). Jordan and York (1989) concluded that substituting HCOC for COC alleviated the antagonism of sethoxydim for control of large crabgrass (*Digitaria sanguinalis* L.) when mixed with bentazon. It was also reported that adding HCOC in place of COC to a mixture of sethoxydim plus bentazon provided better control of johnsongrass (*Sorghum halepense* L.) (Finley et al. 1988).

Synergistic interactions were observed for CL-111 control at 14 DAIT when treated with quizalofop mixed with all adjuvants evaluated (Table 2.3). Antagonism of quizalofop was observed for CL-111 control at 14 DAIT when mixed with bispyribac with no adjuvant with an observed control of 61%, compared with an expected control of 86%. Synergistic interactions were observed for CL-111 control at 14 DAIT when quizalofop was mixed with bispyribac plus all adjuvants evaluated with an observed control of 91 to 95% compared with an expected control of 86%. Synergistic and/or neutral interactions were more prevalent at 14 and 28 DAIT, respectively, for control of CL-111 compared with control of barnyardgrass (Table 2.2) due to the lack of bispyribac activity on CL-111, and this influenced the expected control derived from quizalofop and bispyribac applied alone.

Table 2.3. CL-111 control with quizalofop applied alone or mixed with bispyribac and/or different adjuvants using Blouin's modified Colby's analysis, in 2017 and 2018.

		Quizalofop (g ai ha^{-1})			
		0	120		
Mixture[a]	Rate[b]	Observed	Expected	Observed[c]	P value[d]
	g ai ha^{-1}	——	Control %	——	
14 DAIT[e]					
None	—	0	—	86	—
COC	1	0	86	95+	0.0002
SNS	1	0	86	95+	0.0002
HCOC	1	0	86	95+	0.0002
Bispyribac	34	0	86	61-	0.0001
Bispyribac + COC	34+1	0	86	91+	0.0398
Bispyribac + SNS	34+1	0	86	94+	0.0023
Bispyribac + HCOC	34+1	0	86	95+	0.0005
28 DAIT					
None	—	0	—	93	—
COC	1	0	93	98	0.0501
SNS	1	0	93	98	0.0509
HCOC	1	0	93	97	0.1123
Bispyribac	34	0	93	90	0.2224
Bispyribac + COC	34+1	0	93	95	0.4274
Bispyribac + SNS	34+1	0	93	97	0.1025
Bispyribac + HCOC	34+1	0	93	98	0.0737

[a]Evaluation dates for each respective mixture component.
[b]Rates with a value of one represent a percentage of v v^{-1}.
[c]Observed means followed by a minus (-) are significantly different from Blouin's modified Colby's expected responses at the 5% level indicating an antagonistic response. A positive (+) indicates a synergistic response. No sign indicates a neutral response.
[d]$P < 0.05$ indicates an antagonistic or synergistic response, $P > 0.05$ indicates a neutral response.
[e]DAIT, days after initial treatment.

All mixtures at 28 DAIT resulted in a neutral response for control of CL-111 with an observed control of 90 to 98%, compared with an expected control of 93% (Table 2.3). These results indicate that the interaction of quizalofop mixed with bispyribac did not differ regardless of the adjuvant used. The neutral and synergistic interactions observed for CL-111 are contrasting to the antagonistic interactions observed for barnyardgrass (Table 2.2) control. Different responses among plant species in response to herbicide interactions may be due to genetic, physiological, or morphological differences (Zhang et al. 1995).

Synergistic interactions were observed at 14 DAIT for CLXL-745 control when quizalofop was mixed with all adjuvants evaluated (Table 2.4). Antagonism of quizalofop was observed at 14 and 28 DAIT when mixed with bispyribac with no adjuvant resulted in an observed control of 73 and 86%, respectively, compared with an expected control of 88 and 91%, respectively. A synergistic interaction was observed for CLXL-745 control at 14 DAIT when quizalofop was mixed with bispyribac plus HCOC with an observed control of 92%, compared with an expected control of 88%. However, at 14 DAIT, neutral interactions were observed for CLXL-745 control when quizalofop was mixed with bispyribac plus COC or SNS. Similar to the CL-111 results, neutral and synergistic interactions were commonly observed due to the lack of bispyribac activity on CLXL-745, and this directly influenced the expected control with Colby's equation (Colby 1967).

Table 2.4. CLXL-745 control with quizalofop applied alone or mixed with bispyribac and/or different adjuvants using Blouin's modified Colby's analysis, in 2017 and 2018.

		Quizalofop (g ai ha^{-1})			
		0	120		
Mixture[a]	Rate[b]	Observed	Expected	Observed[c]	P value[d]
	g ai ha^{-1}	Control %			
14 DAIT[e]					
None	—	0	—	88	—
COC	1	0	88	95+	0.0001
SNS	1	0	88	95+	0.0001
HCOC	1	0	88	95+	0.0001
Bispyribac	34	0	88	73-	0.0001
Bispyribac + COC	34+1	0	88	90	0.0858
Bispyribac + SNS	34+1	0	88	90	0.1435

Table 2.4. continued

		Quizalofop (g ai ha^{-1})			
		0	120		
Mixture[a]	Rate[b]	Observed	Expected	Observed[c]	P value[d]
Bispyribac + HCOC	34+1	0	88	92+	0.0018
28 DAIT					
None	—	0	—	91	—
COC	1	0	91	97+	0.0001
SNS	1	0	91	97+	0.0001
HCOC	1	0	91	97+	0.0002
Bispyribac	34	0	91	86-	0.0001
Bispyribac + COC	34+1	0	91	93	0.1913
Bispyribac + SNS	34+1	0	91	95+	0.0059
Bispyribac + HCOC	34+1	0	91	97+	0.0001

[a]Evaluation dates for each respective mixture component.

[b]Rates with a value of one represent a percentage of v v^{-1}.

[c]Observed means followed by a minus (-) are significantly different from Blouin's modified Colby's expected responses at the 5% level indicating an antagonistic response. A positive (+) indicates a synergistic response. No sign indicates a neutral response.

[d]P < 0.05 indicates an antagonistic or synergistic response, P > 0.05 indicates a neutral response.

[e]DAIT, days after initial treatment.

Synergistic interactions were observed at 28 DAIT for CLXL-745 control when quizalofop was mixed with all adjuvants evaluated (Table 2.4). At 28 DAIT, a neutral interaction was observed for CLXL-745 control when quizalofop was mixed with bispyribac plus COC. Synergistic interactions were observed at 28 DAIT for CLXL-745 control when quizalofop was mixed with bispyribac plus SNS or HCOC with an observed control of 95 and 97%, respectively, compared with an expected control of 91%. Similar to the results for barnyardgrass, HCOC proved to be the most consistent adjuvant for the mixture of quizalofop plus bispyribac for control of CLXL-745, with a synergistic response at 14 and 28 DAIT. These results support results concluded by Jordan and York (1989) which stated that HCOC outperforms COC when added to a mixture of sethoxydim plus bentazon in regards to large crabgrass control.

As with barnyardgrass (Table 2.2), CL-111 (Table 2.3), and CLXL-745 (Table 2.4) a synergistic interaction was observed at 14 DAIT for red rice control with quizalofop plus all adjuvants evaluated (Table 2.5). Antagonism of quizalofop was observed at 14 DAIT for red rice control when mixed with bispyribac with no adjuvant with an observed control of 67% compared with an expected control of 88%. A neutral interaction was observed at 14 DAIT for red rice control when quizalofop was mixed with bispyribac plus COC; however, a synergistic interaction occurred with quizalofop mixed with bispyribac plus SNS or HCOC with an observed control of 92 and 95%, respectively, compared with an expected control of 88%. These results are similar to the results observed for CL-111 (Table 2.3) and CLXL-745 (Table 2.4) control with neutral and synergistic interactions.

Table 2.5. Red rice control with quizalofop applied alone or mixed with bispyribac and/or different adjuvants using Blouin's modified Colby's analysis, in 2017 and 2018.

		Quizalofop (g ai ha^{-1})			
		0	120		
Mixture[a]	Rate[b]	Observed	Expected	Observed[c]	P value[d]
	g ai ha^{-1}	Control %			
14 DAIT[e]					
None	—	0	—	88	—
COC	1	0	88	97+	0.0001
SNS	1	0	88	95+	0.0001
HCOC	1	0	88	94+	0.0014
Bispyribac	34	0	88	67-	0.0001
Bispyribac + COC	34+1	0	88	91	0.0519
Bispyribac + SNS	34+1	0	88	92+	0.0177
Bispyribac + HCOC	34+1	0	88	95+	0.0002
28 DAIT					
None	—	0	—	97	—
COC	1	0	97	98	0.3331
SNS	1	0	97	98	0.5183
HCOC	1	0	97	97	0.7959
Bispyribac	34	0	97	93	0.0628
Bispyribac + COC	34+1	0	97	95	0.5188
Bispyribac + SNS	34+1	0	97	98	0.4780
Bispyribac + HCOC	34+1	0	97	99	0.3026

[a]Evaluation dates for each respective mixture component.
[b]Rates with a value of one represent a percentage of v v^{-1}.

[c]Observed means followed by a minus (-) are significantly different from Blouin's modified Colby's expected responses at the 5% level indicating an antagonistic response. A positive (+) indicates a synergistic response. No sign indicates a neutral response.
[d]$P < 0.05$ indicates an antagonistic or synergistic response, $P > 0.05$ indicates a neutral response.
[e]DAIT, days after initial treatment.

Similar to CL-111 (Table 2.3) control, all bispyribac containing mixtures at 28 DAIT were neutral for red rice control with an observed control of 93 to 99%, compared with an expected control of 97% (Table 2.5). These results indicate that regardless of the adjuvant used, neutral interactions were observed for all mixtures at 28 DAIT. The results of red rice are similar to previous results of CL-111 (Table 2.3) which demonstrate synergistic interactions at 14 DAIT for quizalofop mixed with bispyribac plus SNS or HCOC with a neutral interaction at 28 DAIT.

Crop injury did not exceed 5% across all herbicide treatments and evaluation dates (data not shown). A uniform standard treatment of quizalofop plus COC was applied one week after the 28 DAIT rating date to eliminate any remaining rice lines so the rough rice yield would not be impacted by the other rice lines infesting the plot area. ACCase-R rice yielded 3620 kg ha^{-1} when treated with quizalofop plus bispyribac with no adjuvant. ACCase-R rice treated with a mixture of quizalofop plus bispyribac plus either COC, SNS, or HCOC yielded 4530 to 4700 kg ha^{-1} (Table 2.6). However, ACCase-R rice treated with quizalofop applied with COC, SNS, or HCOC without the addition of bispyribac yielded 3890 to 4010 kg ha^{-1}. The decrease in yield was due to the lack of early season broadleaf control without the presence of bispyribac. This yield reduction is a direct result of broadleaf weeds competing with the ACCase-R rice for essential growth requirements including light, space, and nutrients prior to the application of halosulfuron at 38 DAIT. Similar yield reductions exist when quizalofop was not applied due to barnyardgrass and weedy rice competing with the ACCase-R rice prior to the second application of quizalofop. These decreases in yield demonstrate the necessity of herbicide mixtures for broad-spectrum weed control.

Table 2.6. Rough rice yields of ACCase-resistant rice treated with quizalofop and respective mixtures in 2017 and 2018.[a]

		Quizalofop (g ai ha^{-1})	
Mixture[b]	Rate	0	120
	g ai ha^{-1}	kg ha^{-1}	
None	—	200 e	3380 c
COC	1	0 e	3890 bc
SNS	1	90 e	4010 bc
HCOC	1	0 e	4010 bc
Bispyribac	34	260 e	3620 c
Bispyribac + COC	34+1	2400 d	4540 ab
Bispyribac + SNS	34+1	3460 c	4530 ab
Bispyribac + HCOC	34+1	3480 c	4700 a

[a]Means followed by a common letter are not significantly different at P = 0.05 with the use of Fisher's protected LSD

[b]Respective mixture component.

In conclusion, it is essential to incorporate an adjuvant when applying quizalofop alone and when applying quizalofop in a mixture with bispyribac. At 14 DAIT, synergistic interactions were observed when quizalofop was mixed with either adjuvant evaluated for barnyardgrass and all rice lines evaluated. Herbicides are often applied in a mixture to broaden the weed control spectrum, delay herbicide resistance, save time and application costs (Gressel and Segel 1990; Jordan 1995; Zhang et al. 2005). Since quizalofop does not have any activity on broadleaf weeds, a herbicide with broadleaf activity may be needed in a mixture. Bispyribac, a common broadleaf herbicide used in Louisiana rice production, can antagonize quizalofop when applied in a mixture (Rustom et al. 2018).

These results indicate that the antagonism of quizalofop when mixed with bispyribac plus HCOC at 14 DAIT was overcome at 28 DAIT with a neutral interaction for barnyardgrass control. The addition of COC, SNS or HCOC into a mixture of quizalofop plus bispyribac provided synergistic or neutral interactions at 14 and 28 DAIT for CL-111, CLXL-745, and red rice control. However, HCOC probably promotes increased uptake and translocation of quizalofop in barnyardgrass and weedy rice at a higher volume than COC and SNS (Penner 1989). These results are similar to that of Wanamarta et al. (1989) where the active ingredient in HCOC overcame antagonism of sethoxydim from bentazon compared with a COC. It was reported that the active ingredient of HCOC greatly increased sethoxydim absorption when compared with over 190 surfactants evaluated. Young et al. (1996) concluded that utilizing HCOC instead of COC will improve the efficacy of sethoxydim by increasing foliar absorption. These results suggest that incorporating HCOC into a mixture of quizalofop plus bispyribac will offer the most beneficial mixture for broad-spectrum weed control including barnyardgrass and weedy rice in ACCase-R rice production.

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Chapter 3.
Can Reduced Rates of Halosulfuron Limit Antagonism of Quizalofop-p-ethyl

Introduction

Red rice (*Oryza sativa* L.) is taxonomically classified in the same genus and species as cultivated rice (*O. sativa* L.) (Rajguru et al. 2005), and Gealy et al. (2000) reported 65% of the rice in Louisiana was infested with red rice in 2000. Red rice can grow taller and produce more tillers than cultivated rice resulting in a competitive advantage, which can lead to yield reduction (Estorninos et al. 2005; Gressel and Valverde 2009). Prior to 2002 in Louisiana, approximately 80% of rice grown was water-seeded in order to reduce losses due to red rice (Gealy et al. 2000). However, in 2002 the commercialization of imidazolinone-resistant (IR) rice (Clearfield® BASF, Research Triangle Park, NC 27709) provided growers with an effective red rice control option (Croughan 2003; Harrell and Saichuk 2014; Webster and Masson 2001). Since the adoption of IR-rice technology, drill-seeded rice production systems have become more prevalent in Louisiana (Harrell and Saichuk 2014).

In 2003, Hybrid IR-rice (RiceTec, Inc. Houston, TX) was introduced. Hybrid IR-rice has an inherent seed dormancy characteristic with a high degree of seed shattering, and often times has weedy characteristics when the F_2 is allowed to establish in succeeding growing seasons (Burgos et al. 2014; Sudianto et al. 2013). Also, growing IR-rice in close proximity with sexually compatible relatives such as red rice promotes gene flow from IR-rice to the naturally occurring red rice resulting in IR-red rice (Gealy et al. 2003). IR-red rice and subsequent generations of hybrid IR-rice are often referred to as weedy rice.

Barnyardgrass [*Echinochloa crus-galli* (L.) P. Beauv.] is one of the most troublesome weeds infesting rice fields (Dowler 1997) and is capable of reducing rough rice yields up to 79% with season-long competition (Smith 1968). Propanil was first commercialized in the 1960s for control of barnyardgrass, and by 1995, 98% of Arkansas rice received at least one application of propanil (Carey et al 1995). The discovery of propanil- and quinclorac-resistant barnyardgrass in 1989 and 1999, respectively, and the development of IR-weedy rice led to the development of new herbicide resistant rice technologies (Malik et al. 2010).

In the mid-2010s, BASF began development of a new herbicide-resistant rice which confers resistance to acetyl Co-enzyme A carboxylase (ACCase) inhibiting herbicides due to IR-weedy rice and herbicide-resistant barnyardgrass. This new non-transgenic rice is resistant to quizalofop, a Group 1 herbicide, in the aryloxyphenoxypropionate herbicide family. Quizalofop inhibits the ACCase enzyme, and this enzyme catalyzes the first committed step in the de novo fatty acid synthesis (Burton et al. 1989; Focke and Lichtenthaler 1987). The targeted single application rate of quizalofop in ACCase-resistant (ACCase-R) rice production is 92 to 155 g ai ha^{-1}, not to exceed 240 g ha^{-1} per year (Anonymous 2017). ACCase-R rice allows quizalofop to be applied postemergence (POST) for control of annual and perennial grasses, including IR-weedy rice. Previously, quizalofop was used for POST control of red rice in soybean [*Glycine max* (L.) Merr.] production at 70 g ha^{-1} and often requires a sequential application when treating red rice at later growth stages (Askew et al. 2000).

Quizalofop does not have activity on sedge (*Cyperus* spp.) or broadleaf weeds and other herbicides will be needed to help manage these weeds in ACCase-R rice production (Anonymous 2017; Rustom et al. 2018). Herbicides are often applied in a mixture to broaden the weed control spectrum, delay herbicide resistance, and save time and application costs (Gressel and Segel 1990; Jordan 1995; Zhang et al. 2005). Herbicide mixtures have proven to be beneficial in improving efficacy and broadening the weed control spectrum in IR-rice (Carlson et al. 2011; Fish et al. 2015, 2016; Pellerin and Webster 2004; Pellerin et al. 2003; Webster et al.

2012). Herbicide mixture interactions may result in one of three responses: antagonistic, synergistic, or additive/neutral (Berenbaum 1981; Blackshaw et al. 2006; Blouin et al. 2004, 2010; Drury 1980; Fish et al. 2015, 2016; Hatzios and Penner 1985; Morse 1978; Nash 1981; Streibig et al. 1998). When a herbicide mixture has an observed response greater than the expected response based on each herbicide applied separately, the interaction is synergistic; when the observed response is a reduction in control the interaction is deemed antagonistic (Colby 1967). If a herbicide mixture is said to be statistically similar as the expected value the mixture is defined as neutral.

ACCase inhibiting herbicide antagonism has historically been observed when applied in a mixture with broadleaf or sedge herbicides (Ferreira and Coble 1994; Hatzios and Penner 1985; Myers and Coble 1992; Rhodes and Coble 1984; Rustom et al. 2018; Zhang et al. 2005). Antagonism of ACCase herbicide activity on barnyardgrass has previously been observed in Louisiana rice production when fenoxaprop activity was reduced when applied in a mixture with halosulfuron (Zhang et al.2005). Rustom et al. (2018) observed antagonism of quizalofop when mixed with numerous ALS herbicides for control of either weedy rice or barnyardgrass including bispyribac, bensulfuron, halosulfuron, imazosulfuron, orthosulfuron plus halosulfuron, orthosulfuron plus quinclorac, penoxsulam, and penoxsulam plus triclopyr.

Herbicide antagonism can be influenced by the rate of the herbicides used in a mixture (Blackshaw et al. 2006; Culpepper et al. 1999; Hatzios and Penner 1985; Jordan et al. 1993). Antagonism of an ACCase inhibiting herbicide can be reduced by increasing the ratio of the ACCase inhibitor to broadleaf herbicide in a mixture. Green (1989) observed that antagonism between bentazon and quizalofop for control of barnyardgrass can be overcome by doubling the rate of quizalofop. Rhodes and Coble (1984) observed that antagonism of sethoxydim by bentazon for the control of broadleaf signalgrass [*Urochloa platyphylla* (Munro ex. C. Wright) R.D. Webster] can be overcome by increasing the rate of sethoxydim. The antagonism of sethoxydim occurred at the lower rate of 0.28 kg ha^{-1} and no antagonism was observed at the higher rate of 0.56 kg ha^{-1} when applied in a mixture with the same rate of bentazon. Grichar and Boswell (1987) observed that increasing the rate of fluazifop from 0.28 to 0.42 kg ha^{-1} overcame reductions in fluazifop activity from bentazon but not from 2,4-DB for control of Texas panicum (*Panicum texanum* Buckl.) and large crabgrass (*Digitaria sanguinalis* L.); however, reductions in sethoxydim activity were overcome by increasing the rate from 0.28 to 0.42 kg ha^{-1} when mixed with 2,4-DB. Different responses among plant families in response to herbicide interactions may be due to genetic, physiological, or morphological differences (Zhang et al. 1995).

ACCase-R rice is a tool that provides growers with an effective control option for IR-weedy rice and barnyardgrass; however, antagonism of quizalofop often times occurs when applied with a broadleaf or sedge (*Cyperus* spp.) herbicide. Research conducted by Rustom et al. (2018) concluded that quizalofop mixed with halosulfuron at the full labeled rate of 53 g ha^{-1} can result in an antagonistic interaction for weedy rice and barnyardgrass control. Often times growers in Louisiana apply halosulfuron at a reduced rate for control of broadleaf and sedge weeds. Therefore, by reducing the rate of halosulfuron and holding the quizalofop rate at 120 g ha^{-1} would effectively increase the quizalfop to halosulfuron ratio in a mixture. The objective of this research was to determine if reduced rates of halosulfuron in a mixture with quizalofop would result in a neutral interaction for weedy rice and barnyardgrass control.

Materials and Methods

A field study was conducted in 2017 and 2018 at the LSU Agricultural Center H. Rouse Caffey Rice Research Station (RRS) near Crowley, LA. to evaluate the impact of reduced rates of halosulfuron on quizalofop activity in Louisiana rice production. The soil type at the RRS is a Midland silty clay loam (Fine, smectitic, thermic Chromic Vertic Epiaqualfs) with a pH of 5.7 and 3.3% organic matter. Field preparation consisted of a fall and spring disking followed by two passes in the opposite direction with a two-way bed conditioner consisting of rolling baskets and s-tine harrows set at a depth of 6 cm. A preplant fertilizer of 8-24-24 (N-P_2O_5-K_2O) was applied at 280 kg ha^{-1} followed by a preflood application of 280 kg ha^{-1} of 46-0-0 fertilizer was applied to the study area when rice was in the four-leaf to one-tiller stage immediately prior to permanent flood establishment. A permanent 10-cm flood was established when the ACCase-R rice reached the four-leaf to one-tiller growth stage, and was maintained until two weeks prior to harvest.

Plot size was 1.5 by 5.1 m^{-2} with eight, 19.5 cm drill-seeded rows of ACCase-R ‘PVL01’ (Provisia® Horizon Ag, Memphis, TN 38125) long grain rice. In order to simulate a weedy rice population, eight, 19.5 cm drill-seeded rows of ‘CLXL-745’ hybrid long grain IR-rice were planted perpendicular in the front third of the plot and eight, 19.5 cm drill-seeded rows of ‘CL-111’ long grain IR-rice were planted perpendicular in the back third of each plot. All rice lines were planted April 26, 2017 and April 12, 2018 at a rate of 84 kg ha^{-1}. Awnless red rice was also broadcast across the research area at 50 kg ha^{-1} immediately prior to planting. The research area was naturally infested with barnyardgrass.

The study was a randomized complete block with a two-factor factorial arrangement of treatments with four replications. Factor A consisted of MPOST applications of quizalofop at 0 or 120 g ha^{-1}. Factor B consisted of MPOST applications of halosulfuron at 0, 17, 35, or 53 g ha^{-1} or a pre-packaged mixture of halosulfuron plus thifensulfuron at 34 or 53 g ha^{-1}. Sources of materials are listed in Table 3.1.

Table 3.1. Source of materials.

Herbicide[a]	Trade Name	Form	Manufacturer
Quizalofop	Provisia	EC	BASF Corporation, Research Triangle Park, NC
Halosulfuron	Permit	WDG	Gowan Company, Yuma, AZ
Halosulfuron + thifensulfuron	Permit Plus	WDG	Gowan Company, Yuma, AZ

[a]All treatments contained a crop oil concentrate (Agri-Dex® label, Helena Chemical Company, Collierville, TN) at 1% v v^{-1}.

The initial herbicide treatment was applied when ACCase-R rice was at the three- to four-leaf, mid-postemergence (MPOST), growth stage with a CO_2-pressurized backpack sprayer calibrated to deliver 140 L ha^{-1}. Red rice, CLXL-745, and CL-111 were at the three- to four- leaf growth stage and barnyardgrass was at the three- to five-leaf growth stage at the time of the initial herbicide application. The spray boom consisted of five flat-fan 110015 nozzles (Flat Fan AirMix Venturi Nozzle, Greenleaf Technologies, Covington, LA 70434) with 38-cm spacing.

Visual evaluations for crop injury, barnyardgrass, CL-111, CLXL-745 and red rice were recorded at 14, 28, and 56 days after the initial treatment (DAIT), on a scale of 0 to 100% where 0 = no control and 100 = plant death. A second application of quizalofop was applied alone at 120 g ha^{-1} one week after the 28 DAIT rating date to remove non-ACCase-R rice from plots that were not initially treated/controlled with quizalofop, and to determine if reduced grass control due to antagonism could be controlled with a second application. 38 DAIT, halosulfuron was applied at 53 g ha^{-1} in order to eliminate any remaining broadleaf or sedge (*Cyperus* spp.). Immediately prior to harvest, ACCase-R rice plant height was recorded, measuring from the soil surface to the tip of the extended panicle. The four center rows of ACCase-R rice were harvested with a Mitsubishi VM3 combine (Mitsubishi Corporation, 3-1, Marunouchi 2- chome, Chiyoda-ky, Tokyo, Japan), to determine the rough rice yield. Grain yield was adjusted to 12% moisture content.

Rough rice yield data were analyzed using the MIXED procedure in SAS (SAS 2013). Control data was analyzed using the Blouin et al. (2010) augmented mixed method to determine synergistic, antagonistic or neutral responses for herbicide mixtures by comparing the expected control calculated based on the activity of each herbicide applied alone to an observed control (Fish et al 2015, 2016; Rustom et al. 2018). Herbicide treatments and evaluation timings represent the fixed effects for all models. The random effects were year, replication within years, and plots. The effect of different environmental conditions on herbicide activity within a year or combination of years represents the random effects of the test (Carmer et al. 1989; Hager et al. 2003; Rustom et al. 2018). Normality of effects over all evaluation dates were checked with the use of the UNIVARIATE procedure of SAS and significant normality problems were not observed (SAS 2013).

Results and Discussion

Quizalofop applied alone controlled barnyardgrass 98% at 14 DAIT (Table 3.2). At 14 DAIT, all herbicide mixtures resulted in antagonistic interactions for barnyardgrass control with an observed control of 79 to 87%, compared with an expected control of 98%. These results are similar to Rustom et al. (2018) who observed 85% control of barnyardgrass when quizalofop was mixed with halosulfuron resulting in antagonism of quizalofop at 14 DAIT. Antagonism for barnyardgrass control at 14 DAIT was observed when quizalofop was mixed with halosulfuron plus thifensulfuron at the full labeled rate of 53 g ha^{-1} with an observed control of 79%, compared with an expected control of 98%. The reduced rate of halosulfuron plus thifensulfuron, 34 g ha^{-1}, antagonized quizalofop control of barnyardgrass at 14 DAIT with an observed control of 84%. At 14 DAIT, quizalofop mixed with any rate of halosulfuron plus thifensulfuron controlled barnyardgrass 79 and 84%, compared with quizalofop mixed with any rate of halosulfuron which controlled barnyardgrass 86 to 87%, these data could be due to the fact that there are two ALS inhibiting herbicides in the mixture when quizalofop is mixed with halosulfuron plus thifensulfuron.

Table 3.2. Barnyardgrass control with quizalofop applied alone or mixed with various rates halosulfuron or halosulfuron plus thifensulfuron using Blouin's modified Colby's analysis, 2017 and 2018.

		Quizalofop (g ai ha^{-1})			
		0	120		
Mixture[a]	Rate	Observed	Expected	Observed[b]	P value[c]
	g ai ha^{-1}	— % of control —			
14 DAIT[d]					
None	—	0	—	98	—
Halosulfuron	53	0	98	86-	0.0001
Halosulfuron	35	0	98	86-	0.0001
Halosulfuron	17	0	98	87-	0.0001
Halosulfuron + thifensulfuron	53	0	98	79-	0.0001
Halosulfuron + thifensulfuron	34	0	98	84-	0.0001
28 DAIT					
None	—	0	—	98	—
Halosulfuron	53	0	98	97	0.5631
Halosulfuron	35	0	98	96	0.2161
Halosulfuron	17	0	98	95	0.1381
Halosulfuron + thifensulfuron	53	0	98	89-	0.0001
Halosulfuron + thifensulfuron	34	0	98	96	0.2835
56 DAIT					
None	—	0	—	97	—
Halosulfuron	53	0	98	98	0.6860
Halosulfuron	35	0	98	98	0.5382
Halosulfuron	17	0	97	97	0.9495
Halosulfuron + thifensulfuron	53	0	97	98	0.6950
Halosulfuron + thifensulfuron	34	0	97	98	0.6233

[a]Evaluation dates for each respective mixture component.

[b]Observed means followed by a minus (-) are significantly different from Blouin's modified Colby's expected responses at the 5% level indicating an antagonistic response. A positive (+) indicates a synergistic response. No sign indicates a neutral response.

[c]P < 0.05 indicates an antagonistic or synergistic response, P > 0.05 indicates a neutral response.

[d]DAIT, days after initial treatment.

Quizalofop applied alone controlled barnyardgrass 98% at 28 DAIT (Table 3.2). All rates of halosulfuron mixed with quizalofop resulted in a neutral interaction with 95 to 97% control. At 28 DAIT, antagonism of quizalofop for barnyardgrass control was observed when mixed with halosulfuron plus thifensulfuron at 53 g ha^{-1} with an observed control of 89%, compared with an expected control of 98%; however, this antagonism was overcome at the same evaluation date with a neutral interaction for barnyardgrass control when quizalofop was mixed with halosulfuron plus thifensufluron at 34 g ha^{-1} with an observed control of 96%. At 56 DAIT, all mixtures were neutral for barnyardgrass control due to the second application of quizalofop applied at 120 g ha^{-1}, 35 DAIT.

These results are supported by previous research conducted by Grichar and Boswell (1987) who observed that increasing the ratio of fluazifop to bentazon in a mixture overcame the reduced fluazifop control of Texas panicum (*Panicum texanum* Buckl.) and large crabgrass (*Digitaria sanguinalis* L.) due to bentazon. It was also reported that increasing the ratio of sethoxydim to 2, 4-DB in a mixture overcame the reduced sethoxydim control of Texas panicum and large crabgrass due to 2, 4-DB. Green (1989) also reported that increasing the ratio of quizalofop to bentazon in a mixture overcame antagonism of quizalofop for control of barnyardgrass. These data indicate that quizalofop can be mixed with reduced rates of halosulfuron or halosulfuron plus thifensulfuron by increasing the ratio of quizalofop to the halosulfuron containing herbicides for barnyardgrass control.

Quizalofop applied alone resulted in 96% control of CL-111 at 14 DAIT (Table 3.3). As with barnyardgrass (Table 3.2), all mixtures evaluated resulted in antagonistic interactions for CL-111 control with an observed control of 83 to 90%, compared with an expected control of 96%. Although quizalofop mixed with the low rates of halosulfuron at 17 g ha^{-1} or halosulfuron plus thifensulfuron at 34 g ha^{-1} did not overcome antagonism at 14 DAIT for CL-111 control, the lower rates provided observed control of 90 and 87%, respectively. These results are comparable to the results concluded by Grichar and Boswell (1987) who observed that increasing the fluazifop to bentazon ratio will increase control from 52 to 83% for annual grass species.

Table 3.3. CL-111 control with quizalofop applied alone or mixed with various rates of halosulfuron or halosulfuron plus thifensulfuron using Blouin's modified Colby's analysis, 2017 and 2018.

		Quizalofop (g ai ha^{-1})			
		0	120		
Mixture[a]	Rate	Observed	Expected	Observed[b]	P value[c]
	g ai ha^{-1}	———	% of control	———	
14 DAIT[d]					
None	—	0	—	96	—
Halosulfuron	53	0	96	87-	0.0001
Halosulfuron	35	0	96	85-	0.0001
Halosulfuron	17	0	96	90-	0.0001
Halosulfuron + thifensulfuron	53	0	96	83-	0.0001
Halosulfuron + thifensulfuron	34	0	96	87-	0.0001
28 DAIT					
None	—	0	—	98	—
Halosulfuron	53	0	98	96	0.0743
Halosulfuron	35	0	98	95-	0.0051
Halosulfuron	17	0	98	95-	0.0246
Halosulfuron + thifensulfuron	53	0	98	85-	0.0001
Halosulfuron + thifensulfuron	34	0	98	90-	0.0001
56 DAIT					
None	—	0	—	97	—
Halosulfuron	53	0	98	98	0.6186
Halosulfuron	35	0	96	97	0.6784
Halosulfuron	17	0	97	98	0.8397
Halosulfuron + thifensulfuron	53	0	96	98	0.3438
Halosulfuron + thifensulfuron	34	0	96	98	0.3627

[a]Evaluation dates for each respective mixture component.

[b]Observed means followed by a minus (-) are significantly different from Blouin's modified Colby's expected responses at the 5% level indicating an antagonistic response. A positive (+) indicates a synergistic response. No sign indicates a neutral response.

[c]$P < 0.05$ indicates an antagonistic or synergistic response, $P > 0.05$ indicates a neutral response.

[d]DAIT, days after initial treatment.

Quizalofop applied alone resulted in 98% control of CL-111 at 28 DAIT (Table 3.3). Quizalofop mixed with halosulfuron at 53 g ha^{-1} resulted in a neutral interaction; however, quizalofop mixed with halosulfuron reduced rates of 17 or 35 g ha^{-1} resulted in antagonistic interactions. Although the lower rates of halosulfuron proved to antagonize quizalofop for control of CL-111, observed control was 95%, compared with an expected control of 98%. Antagonistic interactions were observed at 28 DAIT when quizalofop was mixed with halosulfuron plus thifensulfuron at 34 or 53 g ha^{-1} for control of CL-111. Quizalofop mixed with halosulfuron plus thifensulfuron at 53 g ha^{-1} at 14 and 28 DAIT provided observed control of 83 and 85%, respectively, for control of CL-111. Neutral interactions were observed for all mixtures at 56 DAIT with the quizalofop applied at 35 DAIT.

At 14 DAIT, quizalofop applied alone controlled CLXL-745 97% (Table 3.4). Antagonistic interactions were observed for all mixtures at 14 DAIT for CLXL-745 control with an observed control of 82 to 89%, compared with an expected control of 97%. These results were comparable to the control of barnyardgrass (Table 3.2) and CL-111 (Table 3.3). Halosulfuron at 53 g ha^{-1} antagonized quizalofop for control of CLXL-745 with an observed control of 82%, compared with an expected control of 97% at 14 DAIT. These results are comparable to Rustom et al. (2018) who observed an antagonistic interaction at 14 DAIT for control of CLXL-745 when quizalofop was mixed with halosulfuron.

Table 3.4. CLXL-745 control with quizalofop applied alone or mixed with various rates of halosulfuron or halosulfuron plus thifensulfuron using Blouin's modified Colby's analysis, 2017 and 2018.

		Quizalofop (g ai ha^{-1})			
		0	120		
Mixture[a]	Rate	Observed	Expected	Observed[b]	P value[c]

Table 3.4. continued

Mixture[a]	Rate	Quizalofop (g ai ha^{-1}) 0 Observed	120 Expected	120 Observed[b]	P value[c]
	g ai ha^{-1}	% of control			
14 DAIT[d]					
None	—	0	—	97	—
Halosulfuron	53	0	97	82-	0.0001
Halosulfuron	35	0	97	89-	0.0001
Halosulfuron	17	0	97	88-	0.0001
Halosulfuron + thifensulfuron	53	0	97	82-	0.0001
Halosulfuron + thifensulfuron	34	0	97	88-	0.0001
28 DAIT					
None	—	0	—	98	—
Halosulfuron	53	0	98	96	0.0850
Halosulfuron	35	0	98	92-	0.0001
Halosulfuron	17	0	98	92-	0.0001
Halosulfuron + thifensulfuron	53	0	98	86-	0.0001
Halosulfuron + thifensulfuron	34	0	98	93-	0.0002
56 DAIT					
None	—	0	—	97	—
Halosulfuron	53	0	98	98	0.7003
Halosulfuron	35	0	98	98	1.0000
Halosulfuron	17	0	98	97	0.4012
Halosulfuron + thifensulfuron	53	0	97	98	0.4502
Halosulfuron + thifensulfuron	34	0	97	98	0.7330

[a]Evaluation dates for each respective mixture component.

[b]Observed means followed by a minus (-) are significantly different from Blouin's modified Colby's expected responses at the 5% level indicating an antagonistic response. A positive (+) indicates a synergistic response. No sign indicates a neutral response.

[c]$P < 0.05$ indicates an antagonistic or synergistic response, $P > 0.05$ indicates a neutral response.

[d]DAIT, days after initial treatment.

At 28 DAIT quizalofop applied alone controlled CLXL-745 98% (Table 3.4). As with CL-111 (Table 3.3), at 28 DAIT a neutral interaction was observed when quizalofop was mixed with halosulfuron at 53 g ha^{-1}; however, quizalofop mixed with halosulfuron at 17 or 35 g ha^{-1} resulted in antagonistic interactions with an observed control of 92%, compared with an expected control of 98%. Similar to CL-111 (Table 3.3), halosulfuron plus thifensulfuron at 34 or 53 g ha^{-1}

antagonized quizalofop control of CLXL-745 at 28 DAIT. Conventional wisdom may suggest that CLXL-745 is more difficult to control due to the fact that CLXL-745 is more robust in growth, produces more tillers, and is pubescent (Oard et al. 2000, Zhang et al. 2006), but previous research conducted by Rustom et al. (2018) suggests that CL-111 is more difficult to control than CLXL-745. At 56 DAIT, all mixtures were neutral for CLXL-745 control due to an application of quizalofop applied at 35 DAIT.

Quizalofop applied alone resulted in 99% control of red rice (Table 3.5) at 14 DAIT. As with barnyardgrass (Table 3.2), CL-111 (Table 3.3), and CLXL-745 (Table 3.4), all mixtures evaluated resulted in antagonistic interactions for red rice control with an observed control of 82 to 88%, compared with an expected control of 99%. These results are supported by previous research conducted by Rustom et al. (2018) who observed 86% control of red rice at 14 DAIT when quizalofop was mixed with halosulfuron at 53 g ha^{-1}.

Table 3.5. Red rice control with quizalofop applied alone or mixed with various rates of halosulfuron or halosulfuron plus thifensulfuron using Blouin's modified Colby's analysis, 2017 and 2018.

		Quizalofop (g ai ha^{-1})			
		0	120		
Mixture[a]	Rate	Observed	Expected	Observed[b]	P value[c]
	g ai ha^{-1}	——— % of control ———			
14 DAIT[d]					
None	—	0	—	99	—
Halosulfuron	53	0	99	87-	0.0001
Halosulfuron	35	0	99	88-	0.0001
Halosulfuron	17	0	99	88-	0.0001
Halosulfuron + thifensulfuron	53	0	99	82-	0.0001
Halosulfuron + thifensulfuron	34	0	99	86-	0.0001
28 DAIT					
None	—	0	—	98	—
Halosulfuron	53	0	98	96	0.1102

Table 3.5. continued

Mixture[a]	Rate	Quizalofop (g ai ha^{-1}) 0 Observed	120 Expected	120 Observed[b]	P value[c]
Halosulfuron	35	0	98	94-	0.0008
Halosulfuron	17	0	98	95-	0.0112
Halosulfuron + thifensulfuron	53	0	98	91-	0.0001
Halosulfuron + thifensulfuron	34	0	98	94-	0.0032
56 DAIT					
None	—	0	—	97	—
Halosulfuron	53	0	98	98	0.8488
Halosulfuron	35	0	98	98	0.7584
Halosulfuron	17	0	98	97	0.7763
Halosulfuron + thifensulfuron	53	0	98	98	0.8493
Halosulfuron + thifensulfuron	34	0	99	98	0.2317

[a]Evaluation dates for each respective mixture component.

[b]Observed means followed by a minus (-) are significantly different from Blouin's modified Colby's expected responses at the 5% level indicating an antagonistic response. A positive (+) indicates a synergistic response. No sign indicates a neutral response.

[c]$P < 0.05$ indicates an antagonistic or synergistic response, $P > 0.05$ indicates a neutral response.

[d]DAIT, days after initial treatment.

At 28 DAIT quizalofop applied alone controlled red rice (Table 3.5) 98%. Similar to CL-111 (Table 3.3) and CLXL-745 (Table 3.4), a neutral interaction was observed at 28 DAIT for red rice control when quizalofop was mixed with halosulfuron at the full labeled rate of 53 g ha^{-1}. Antagonistic interactions were observed for red rice control at 28 DAIT when quizalofop was mixed with reduced rates of halosulfuron at 17 or 35 g ha^{-1} with an observed control of 95 and 94%, respectively, compared with an expected control of 98%. As with CL-111 (Table 3.3) and CLXL-745 (Table 3.4), antagonistic interactions were observed for red rice control at 28 DAIT when quizalofop was mixed with halosulfuron plus thifensulfuron at 34 or 53 g ha^{-1}. Quizalofop mixed with halosulfuron plus thifensulfuron at the high rate of 53 g ha^{-1} controlled red rice at 14 and 28 DAIT 82 and 91%, respectively.

Crop injury did not exceed 5% across all herbicide treatments and evaluation dates (data not shown). A uniform standard treatment of quizalofop was applied one week after the 28 DAIT rating date to eliminate any remaining rice lines so rough rice yield would not be impacted by the other rice lines infesting the plot area. No yield differences were observed when quizalofop was mixed with any rate of halosulfuron or halosulfuron plus thifensulfuron and rough rice yields were 4680 to 5090 kg ha^{-1} (Table 3.6). A decrease in ACCase-R rice yield to 3960 kg ha^{-1} was observed when neither halosulfuron nor halosulfuron plus thifensulfuron were mixed with quizalofop in the initial herbicide application. This yield reduction is a result of broadleaf weeds competing with the ACCase-R rice for essential growth requirements including light, space, and nutrients prior to the application of halosulfuron at 38 DAIT. ACCase-R rice yielded 3300 to 3780 kg ha^{-1} when an initial herbicide application of halosulfuron or halosulfuron plus thifensulfuron was applied alone. A uniform standard treatment of quizalofop was applied 35 DAIT in order to control any remaining rice lines in order to prevent yield influences from non-ACCase-R rice and grass weeds. It is essential to have early season broad-spectrum weed control program to reduce intra- and interspecific competition, which often leads to yield reduction.

Table 3.6. Rough rice yields of ACCase-resistant rice treated with quizalofop and respective mixtures in 2017 and 2018.[a]

		Quizalofop (g ai ha^{-1})	
Mixture[b]	Rate	0	120
	g ai ha^{-1}	kg ha^{-1}	
None	—	3440 bc	3960 b
Halosulfuron	53	3300 c	5090 a
Halosulfuron	35	3730 bc	4870 a
Halosulfuron	17	3420 c	4680 a
Halosulfuron + thifensulfuron	53	3730 bc	4800 a
Halosulfuron + thifensulfuron	34	3780 bc	4920 a

[a]Means followed by a common letter are not significantly different at P = 0.05 with the use of Fisher’s protected LSD

[b]Respective mixture component.

In conclusion, these data suggest that applying quizalofop in a mixture with reduced rates of halosulfuron or halosulfuron plus thifensulfuron can be used for barnyardgrass control in

ACCase-R rice production. The most common method to overcome herbicide antagonism is to increase the ratio of the herbicide being antagonized to the mixture herbicide (Green 1989). In the case of barnyardgrass, quizalofop mixed with halosulfuron plus thifensulfuron at the lower rate of 34 g ha^{-1} was able to overcome the antagonism compared with the higher rate of 53 g ha^{-1}. These results are supported by the findings of Green (1989) who concluded that increasing the ratio of quizalofop to bentazon in a mixture overcame antagonism of quizalofop for barnyardgrass control. Antagonism between graminicides and broadleaf herbicides can be rate dependent and by increasing the ratio of graminicide to broadleaf herbicide in a mixture can overcome antagonism (Holshouser and Coble 1990).

Increasing the ratio of graminicide to broadleaf herbicide in a mixture can alleviate antagonism of the graminicide (Rhodes and Coble 1984); however, this is not always the case. Quizalofop mixed with the higher rate of halosulfuron provided a neutral interaction at 28 DAIT for CL-111, CLXL-745, and red rice control; although, the lower rates of halosulfuron antagonized quizalofop, control was 92 to 95%. Different responses among plant families in response to herbicide interactions may be due to genetic, physiological, or morphological differences (Zhang et al. 1995).

Across all species evaluated, it was observed that quizalofop mixed with halosulfuron plus thifensulfuron at 53 g ha^{-1} provided 79 to 83% control, compared with quizalofop mixed with halosulfuron at 53 g ha^{-1} which provided 82 to 87% control. This is probably a result of having two broadleaf/sedge herbicides in the mixture to antagonize quizalofop versus one broadleaf/sedge herbicide in the mixture. This research suggests that mixing quizalofop with halosulfuron plus thifensulfuron especially at the higher rate of 53 g ha^{-1} should be avoided.

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Chapter 4.
Sequential Applications of Quizalofop-p-ethyl on Antagonized Weeds

Introduction

In addition to red rice (*Oryza sativa* L.), barnyardgrass [*Echinochloa crus-galli* (L.) P. Beauv.] is one of the most troublesome weeds in rice production (Dowler 1997; Webster 2000), and a season-long infestation of barnyardgrass can cause up to a 79% yield reduction of cultivated rice (Smith 1968). Barnyardgrass is a monocot weed that is glabrous, with no ligule or auricles and can survive in partially submerged conditions (Bryson and DeFelice 2009), which allows barnyardgrass to easily adapt to a flooded rice field (Snipes and Street 1987). Barnyardgrass is a major pest of rice due to simultaneous germination allowing barnyardgrass to compete with rice in the early growing season (Smith 1968). Also, barnyardgrass and rice both have fibrous roots systems, allowing barnyardgrass roots to grow adjacent to rice roots and compete for nutrients, space, and moisture.

In the 1960's, propanil was one of the first labeled herbicides to control barnyardgrass in cultivated rice production, and in 1995 at least one application of propanil was applied to 98% of Arkansas rice (Carey et al. 1995). The repeated use of the same chemistry has led to the buildup of propanil resistance. Barnyardgrass has been confirmed in Arkansas, Mississippi, and Louisiana to be resistant to propanil and quinclorac (Malik et al. 2010; Riar et al. 2013). Propanil- and/or quinclorac-resistant barnyardgrass led many growers to the adoption of imidazolinone resistant (IR) rice in the Midsouth United States; however, the adoption of IR-rice has led to barnyardgrass resistance to many acetolactate synthase (ALS) inhibiting herbicides such as imazamox, imazethapyr, penoxsulam, and bispyribac-sodium (Riar et al. 2013).

In the mid-2010s, BASF began development of a new herbicide-resistant rice which confers resistance to acetyl Co-enzyme A carboxylase (ACCase) inhibiting herbicides due to IR-weedy rice and herbicide-resistant barnyardgrass. The herbicide targeted for use is the Group 1 herbicide quizalofop, belonging to the aryloxyphenoxypropionate family. Quizalofop inhibits the ACCase enzyme, and this enzyme catalyzes the first committed step in de novo fatty acid synthesis (Burton et al. 1989; Focke and Lichtenthaler 1987). The targeted single application rate of quizalofop in ACCase-resistant (ACCase-R) rice production is 92 to 155 g ai ha^{-1}, not to exceed 240 g ha^{-1} per year (Anonymous 2017). ACCase-R rice allows quizalofop to be applied postemergence (POST) for control of annual and perennial grasses, including IR-weedy rice. Previously, quizalofop has been used for red rice control in soybean [*Glycine max* (L.) Merr.] production at 70 g ha^{-1} and often requires a sequential application when treating red rice at later growth stages (Askew et al. 2000).

Quizalofop does not control sedge (*Cyperus* spp.) or broadleaf weeds and other herbicides will be needed to help manage these weeds in ACCase-R rice production (Anonymous 2017; Rustom et al. 2018). Herbicides are often applied in a mixture to broaden the weed control spectrum, manage herbicide resistance, and save time and application costs (Gressel and Segel 1990; Jordan 1995; Zhang et al. 2005). Herbicide mixtures have proven to be beneficial in improving efficacy and broadening the weed control spectrum in IR-rice (Carlson et al. 2011; Fish et al. 2015, 2016; Pellerin and Webster 2004; Pellerin et al. 2003; Webster et al. 2012). Herbicide mixture interactions may result in one of three responses: antagonistic, synergistic, or additive/neutral (Berenbaum 1981; Blackshaw et al. 2006; Blouin et al. 2004, 2010; Drury 1980; Fish et al. 2015, 2016; Hatzios and Penner 1985; Morse 1978; Nash 1981; Streibig et al. 1998). When the herbicide mixture has an observed response greater than the expected response based on each herbicide applied separately, the interaction is synergistic; when the observed response is a reduction in control the interaction is deemed antagonistic

(Colby 1967). If a herbicide mixture is said to be statistically similar as the expected value the mixture is defined as neutral or additive.

An alternative to applying two potentially non-compatible herbicides is to apply the herbicides sequentially (Minton et al 1989). Applying two or more herbicides sequentially is a common practice to improve the spectrum of weed control, reduce production costs, and/or to prevent herbicide resistance (Zhang et al. 1995). ACCase inhibiting herbicides are often times antagonized when applied in a mixture with a broadleaf herbicide; however, in some cases a sequential application of the ACCase inhibiting herbicide applied alone can overcome the antagonism that occurred at the earlier application date (Rustom et al. 2018). Antagonism of quizalofop was observed when applied in a mixture with bispyribac, bensulfuron, halosulfuron, imazosulfuron, orthosulfuron plus halosulfuron, orthosulfuron plus quinclorac, penoxsulam, and penoxsulam plus triclopyr on either weedy rice or barnyardgrass at either 14 and/or 28 days after initial treatment (DAIT). A second application of quizalofop applied alone at 28 DAIT resulted in a neutral response at 42 DAIT for all herbicide mixtures except for penoxsulam containing mixtures.

The efficacy of a sequential herbicide application can be altered due to a prior herbicide application (Hatzios and Penner 1985). In a study evaluating sequential applications of quizalofop following an application of propanil plus thiobencarb, quizalofop activity on weedy rice and barnyardgrass was 45 to 76% when applied 0 to 3 days after propanil plus thiobencarb when evaluated at 28 days after treatment; however, by delaying quizalofop to 7 day after propanil plus thiobencarb control of weedy rice and barnyardgrass increased to 81 to 86% (Rustom 2017). Minton et al. (1989) concluded barnyardgrass control with sethoxydim or quizalofop were antagonized when imazaquin or lactofen was applied 24 hours prior to the graminicide. However, when sethoxydim or quizalofop was applied 24 hours prior to a imazaquin or lactofen application, no antagonism of the graminicides occurred for barnyardgrass control. If a graminicide and broadleaf herbicide are to be applied sequentially, it is imperative that the graminicide is applied prior to the broadleaf herbicide or after an adequate interval if applying the broadleaf herbicide first.

ACCase-R rice is a tool to provide growers with an effective control option for IR-red rice and barnyardgrass. Due to the high frequency of quizalofop antagonism when applied in a mixture with a broadleaf herbicide, a sequential application of quizalofop may be needed to eliminate any remaining antagonized weeds from an initial quizalofop plus broadleaf herbicide application. Research conducted by Rustom et al. (2018) suggests that barnyardgrass is the most frequently antagonized grass species compared with IR-weedy rice. It was reported that barnyardgrass was controlled 49% when quizalofop was mixed with propanil plus thiobencarb; however, weedy rice was controlled 73% with the same mixture. It is imperative to determine an acceptable interval for sequential applications of quizalofop on previously treated and/or antagonized barnyardgrass, and the objective of this research was to evaluate sequential applications of quizalofop applied at different intervals following a quizalofop plus propanil application.

Materials and Methods

Two Field studies were conducted in 2018 at the LSU Agricultural Center H. Rouse Caffey Rice Research Station (RRS) near Crowley, LA. to evaluate sequential applications of quizalofop applied on previously antagonized weeds from a quizalofop plus propanil mixture to determine the time needed between antagonism and a second application of quizalofop. Field preparation consisted of a fall and spring disking followed by two passes in the opposite direction with a two-way bed conditioner consisting of rolling baskets and s-tine harrows set at a depth of 6 cm. A preplant fertilizer of 8-24-24 (N-P_2O_5-K_2O) was applied at 280 kg ha^{-1} followed by a preflood application of 280 kg ha^{-1} of 46-0-0 fertilizer was applied to the study area when rice was in the four-leaf to one-tiller stage.

Plot size was 1.5 by 5.1 m^{-2} with eight, 19.5 cm drill-seeded rows of ACCase-R 'PVL01' (Provisia® Horizon Ag, Memphis, TN 38125) long grain rice. PVL01 rice was planted March 22 on a Crowley silt loam (fine smectic, thermic Typic Albaqualfs) with a pH of 6.5 and 2.3% organic matter and April 12, 2018 on a Midland silty clay loam (Fine, smectitic, thermic Chromic Vertic Epiaqualfs) with a pH of 5.7 and 3.3% organic matter. PVL01 rice was planted at a rate of 84 kg ha^{-1}. The research area was naturally infested with barnyardgrass at 80 to 100 plants m^{-2}. A permanent 10-cm flood was established when the ACCase-R rice achieved the four-leaf to one-tiller growth stage, and was maintained until two weeks prior to harvest. The initial herbicide treatment was applied when ACCase-R rice was at the three- to four-leaf, mid-postemergence (MPOST), growth stage with a CO_2-pressurized backpack sprayer calibrated to deliver 140 L ha^{-1}. Sequential applications of quizalofop were applied 7, 14, 21, and 28 DAIT. Barnyardgrass was at the three- to five-leaf growth stage at the time of the initial herbicide application. Barnyardgrass plants at the time of the sequential applications of quizalofop at 7, 14, 21, and 28 DAIT were at the one- to two-tiller, two- to three-tiller, three- to four-tiller, and four- to five-tiller growth stages, respectively. The spray boom consisted of five flat-fan 110015 nozzles (Flat Fan AirMix Venturi Nozzle, Greenleaf Technologies, Covington, LA 70434) with 38-cm spacing.

The study was a randomized complete block with a two-factor factorial arrangement of treatments with four replications. Factor A consisted of 1) no herbicide application, 2) a MPOST application of quizalofop at 120 g ha^{-1}, 3) a mixture of quizalofop at 120 g ha^{-1} plus propanil at 4484 g ha^{-1}. Factor B consisted of either no sequential application of quizalofop or quizalofop at 120 g ha^{-1} at 7, 14, 21, or 28 days after the Factor A/MPOST application. Sequential applications of quizalofop began at 7 DAIT due to previous research conducted by Rustom (2017) that indicated quizalofop should be applied no earlier than 7 days after a propanil containing application. Sources of materials are listed in Table 4.1.

Table 4.1. Source of materials.

Herbicide[a]	Trade Name	Form	Rate	Manufacturer
			g ai ha^{-1}	
Quizalofop	Provisia	EC	120	BASF Corporation, Research Triangle Park, NC
Propanil	Stam M4	EC	4484	RiceCo, Memphis, TN

[a]All treatments contained a crop oil concentrate (Agri-Dex® label, Helena Chemical Company, Collierville, TN) at 1% v/v.

Visual evaluations for crop injury and barnyardgrass were recorded at 14 and 28 days after the sequential treatment (DAST), on a scale of 0 to 100% where 0 = no control and 100 = plant death. Immediately prior to harvest, PVL01 rice plant height was recorded measuring from the soil surface to the tip of the extended panicle. The four center rows of PVL01 rice were harvested with a Mitsubishi VM3 combine (Mitsubishi Corporation, 3-1, Marunouchi 2- chome, Chiyoda-ky, Tokyo, Japan), to determine the rough rice yield. Grain yield was adjusted to 12% moisture content.

Control data was analyzed using the Blouin et al. (2010) augmented mixed method to determine synergistic, antagonistic or neutral responses for herbicide mixtures by comparing the expected control calculated based on the activity of each herbicide applied alone to an observed control (Fish et al 2015, 2016; Rustom et al. 2018). In this case, Factor A applications were considered the herbicide applied alone at 120 g ha^{-1} and quizalofop plus propanil at 120 and 4484 g ha^{-1}. Herbicide treatments and evaluation timings represent the fixed effects for all models. The random effects were year, replication within years, and plots. Rough rice yield data and plant height data were analyzed using the MIXED procedure in SAS (SAS 2013). The effect of different environmental conditions on herbicide activity within a year or combination of years represents the random effects of the test (Carmer et al. 1989; Hager et al. 2003; Rustom et al. 2018). Normality of effects over all evaluation dates were checked with the use of the UNIVARIATE procedure of SAS and significant normality problems were not observed (SAS 2013).

Results and Discussion

All herbicide application timing interactions for barnyardgrass control at 14 DAST were neutral (Table 4.2). At 14 DAST, quizalofop applied alone followed by a sequential application of quizalofop at 7, 14, 21, and 28 DAIT controlled barnyardgrass with an observed control of 97 to 98%, compared with an expected control of 99%. Quizalofop applied alone controlled barnyardgrass 98% at 14 DAIT; however, barnyardgrass treated with quizalofop plus propanil was controlled 30% at the same rating interval. Quizalofop mixed with propanil followed by a sequential application of quizalofop at 7, 14, and 21 DAIT controlled barnyardgrass with an observed visual value of 97 to 98%, compared with an expected control of 95 to 98%. However, the sequential treatment of quizalofop applied at 28 DAIT to antagonized barnyardgrass resulted in 71% control, compared with an expected control of 67%. In all situations the interaction was deemed neutral by Blouin's Modified Colby's; however, the control of the antagonized barnyardgrass was less than 75%. The difficulty to control antagonized barnyardgrass 28 DAIT is most likely due to the size of the barnyardgrass at the time of the sequential application. Herbicides are most effective when applied to barnyardgrass no larger than the 2-leaf stage, and larger barnyardgrass plants are frequently more difficult to control (Stauber et al. 1991).

All herbicide application timing interactions for barnyardgrass control at 28 DAST were neutral. Quizalofop mixed with propanil controlled barnyardgrass 26% at 28 DAIT, compared with quizalofop applied alone which controlled barnyardgrass 92%, and this is similar to the 14 DAIT evaluation timing (Table 4.2). Quizalofop applied alone followed by a sequential application of quizalofop at 7, 14, 21, and 28 DAIT controlled barnyardgrass with an observed control of 97 to 98% at 28 DAST, compared with an expected control of 97 to 99%. At 28 DAST, quizalofop mixed with propanil followed by a sequential application of quizalofop at 7, 14, and 21 DAIT controlled barnyardgrass with an observed control of 98%, compared with an expected control of 94 to 98%. However, barnyardgrass control of 73% was observed when a sequential application of quizalofop was applied 28 DAIT of quizalofop plus propanil. Herbicide activity can be altered due to prior herbicide applications (Hatzios and Penner 1985); however, these results are most likely influenced by barnyardgrass as large as four- to five-leaf tillers at the 28 DAIT application timing. These results are supported by Snipes and Street (1987) who concluded that barnyardgrass is best controlled at earlier growth stages.

Rice treated with quizalofop followed by a sequential application of quizalofop resulted in PVL01 rice plant heights of 101 to 103 cm (Table 4.3). A mixture of quizalofop plus propanil without a sequential application of quizalofop resulted in PVL01 rice plant height of 92 cm due to season-long competition from antagonized barnyardgrass. An increase in ACCase-R rice plant heights to 100 to 102 cm was observed when the mixture of quizalofop plus propanil was followed by a sequential application of quizalofop 7, 14, and 21 DAIT due to the increased barnyardgrass control observed at 14 and 28 DAST (Table 4.2). A reduction in PVL01 rice plant height, 95 cm, occurred when a sequential application of quizalofop was delayed to 28 DAIT of quizalofop plus propanil (Table 4.3). This reduction in plant height is a result of the observed

Table 4.2 Barnyardgrass control with quizalofop applied alone or mixed with propanil with or without a sequential application of quizalofop using Blouin's modified Colby's analysis, both locations in 2018.

	Quizalofop (g ai ha^{-1})				Quizalofop plus Propanil (g ai ha^{-1})		
	0	120			120 + 4484		
Sequential Quizalofop Application[a]	Observed	Expected	Observed[b]	P value[c]	Expected	Observed	P value
	— % of control —				— % of control —		
14 DAST[d]							
No quizalofop	0	—	98[e]	—	—	30[e]	—
7 DAIT	96	99	98	0.6108	97	98	0.8368
14 DAIT	97	99	97	0.5723	98	98	0.9879
21 DAIT	93	99	98	0.6732	95	97	0.7139
28 DAIT	53	99	97	0.6781	67	71	0.3856
28 DAST							
No quizalofop	0	—	92[f]	—	—	26[f]	—
7 DAIT	97	99	98	0.6635	98	98	0.9964
14 DAIT	98	99	97	0.5799	98	98	0.8841
21 DAIT	92	99	98	0.7882	94	98	0.3604
28 DAIT	66	97	98	0.7763	74	73	0.7168

[a]All quizalofop were applied at 120 g ai ha^{-1}.

[b]Observed means followed by a minus (-) are significantly different from Blouin's modified Colby's expected responses at the 5% level indicating an antagonistic response. A positive (+) indicates a synergistic response. No sign indicates a neutral response.

[c]P < 0.05 indicates an antagonistic or synergistic response, P > 0.05 indicates an additive response.

[d]Abbreviations: [c]DAST, days after sequential treatment; DAIT, days after initial treatment.

[e]Observed control 14 DAIT

[f]Observed control 28 DAIT

control of 71 and 73%, of barnyardgrass at 14 and 28 DAST, respectively, due to the delay of the sequential application of quizalofop to 28 DAIT (Table 4.2).

Table 4.3. Heights of ACCase-resistant rice treated with quizalofop and respective mixtures in 2017 and 2018.[a]

Sequential Quizalofop Application[b]	Quizalofop (g ai ha^{-1}) 0	Quizalofop (g ai ha^{-1}) 120	Quizalofop + Propanil (g ai ha^{-1}) 120 + 4484
	cm		
No quizalofop	75 c	101 a	92 b
7 DAIT[c]	101 a	102 a	102 a
14 DAIT	102 a	101 a	100 a
21 DAIT	92 b	103 a	101 a
28 DAIT	79 c	102 a	95 b

[a]Means followed by a common letter are not significantly different at P = 0.05 with the use of Fisher's protected LSD.

[b]All quizalofop applications were applied at 120 g ai ha^{-1}.

[c]Abbreviation: WAIT, weeks after initial treatment.

Crop injury did not exceed 5% across all herbicide treatments and evaluation dates (data not shown). A uniform standard treatment of halosulfuron was applied 56 DAIT to eliminate any remaining broadleaf or sedge weeds. No yield differences occurred when two applications of quizalofop were applied alone at any interval with PVL01 rough rice yield, 4830 to 5560 kg ha^{-1} (Table 4.4). Rough rice yield of 3980 kg ha^{-1} occurred when PVL01 was treated with a mixture of quizalofop plus propanil with no sequential application of quizalofop. This yield is a result of antagonized barnyardgrass competing with the PVL01 rice throughout the growing season. PVL01 rice yield was 4800 to 4990 kg ha^{-1} when rice was treated with a mixture of quizalofop plus propanil followed by quizalofop at 7, 14, and 21 DAIT. However, PVL01 rice yield was reduced to 3730 kg ha^{-1} when the sequential application of quizalofop was delayed to 28 DAIT. This yield reduction is most likely due to the size of the barnyardgrass at the time of the sequential application, which was at the four- to five-tiller growth stage resulting in reduced control (Table 4.2) and extended competition from antagonized barnyardgrass.

Table 4.4. Rough rice yields of ACCase-resistant rice treated with quizalofop and respective mixtures in 2017 and 2018.[a]

Sequential Quizalofop Application[b]	Quizalofop (g ai ha^{-1}) 0	Quizalofop (g ai ha^{-1}) 120	Quizalofop + Propanil (g ai ha^{-1}) 120 + 4484
	kg ha^{-1}		
No quizalofop	0 e	5220 ab	3980 bc
7 DAIT[c]	5040 ab	4830 ab	4930 ab
14 DAIT	5400 a	5030 ab	4800 ab
21 DAIT	4040 bc	4900 ab	4990 ab
28 DAIT	1260 d	5560 a	3730 c

[a]Means followed by a common letter are not significantly different at P = 0.05 with the use of Fisher's protected LSD.
[b]All quizalofop applications were applied at 120 g ai ha^{-1}.
[c]Abbreviation: DAIT, days after initial treatment.

In conclusion, it is essential to apply a second application of quizalofop within three weeks of quizalofop antagonism for the management of barnyardgrass. However, research conducted by Rustom (2017) suggests that a sequential application of quizalofop should be applied no earlier than 7 days after an application of propanil plus thiobencarb. Minton et al. (1989) concluded that sethoxydim or quizalofop control of barnyardgrass was antagonized when imazaquin or lactofen was applied 24 hours before the graminicide; however, antagonism of sethoxydim or quizalofop did not occur if applied prior to the two broadleaf herbicides. Quizalofop mixed with propanil followed by a sequential application of quizalofop 28 DAIT resulted in 71 and 73% control of barnyardgrass at 14 and 28 DAST, respectively (Table 4.2). This resulted in a reduction of PVL01 rice plant height to 95 cm (Table 4.3) and a reduction in ACCase-R rice yield, 3730 kg ha^{-1}, due to barnyardgrass competition (Table 4.4). These data along with results reported by Rustom (2017) suggest that if quizalofop is antagonized for barnyardgrass control then a sequential application of quizalofop should be applied no earlier than 7 DAIT and no later than 21 DAIT.

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Chapter 5.
Summary

Red rice (*Oryza sativa* L.) and barnyardgrass [*Echinochloa crus-galli* (L.) P. Beauv.] are some of the most troublesome pests of cultivated rice (*O. sativa* L.) (Dowler 1997; Webster 2000). Although phenotypically similar, red rice often has a competitive advantage over cultivated rice due to its ability to grow taller and produce more tillers than the cultivated rice (Diarra et al. 1985). Red rice has also been reported to outcross with imidazolinone resistant (IR) rice (Clearfield® BASF, Research Triangle Park, NC 27709), resulting in IR-red rice (Rajguru et al. 2005). In addition to IR-red rice, shortly after hybrid IR-rice (RiceTec, Inc. Houston, TX) was introduced in 2003, it was reported that hybrid IR-rice has an inherent seed dormancy characteristic with a high degree of seed shattering, and often has weedy characteristics when the F_2 is allowed to establish in succeeding growing seasons (Burgos et al. 2014; Sudianto et al. 2013). IR-red rice and subsequent generations of hybrid IR-rice are often referred to as weedy rice.

IR-weedy rice and barnyardgrass resistant to multiple modes of action prompted BASF to develop an acetyl Co-enzyme A carboxylase (ACCase) resistant (ACCase-R) rice. The herbicide targeted for use is the Group 1 herbicide quizalofop, belonging to the aryloxyphenoxypropionate family. ACCase-R rice is a tool that gives growers the ability to control IR-weedy rice and herbicide resistant barnyardgrass. Due to the lack of broadleaf activity, ACCase herbicides are often applied in a mixture to broaden the weed control spectrum, manage herbicide resistance, and save time and application costs (Gressel and Segel 1990; Jordan 1995; Zhang et al. 2005). However, ACCase inhibiting herbicides have a long history of being antagonized when applied in a mixture with a broadleaf or sedge herbicide (Ferreira and Coble 1994; Hatzios and Penner 1985; Myers and Coble 1992; Rhodes and Coble 1984; Rustom et al. 2018; Zhang et al. 2005).

The objective of this research was to evaluate different strategies to overcome antagonism of quizalofop when applied in a mixture with a broadleaf or sedge herbicide. The first strategy was to evaluate the ability of different adjuvants in overcoming bispyribac antagonism of quizalofop for weedy rice and barnyardgrass control. The second strategy was to evaluate reduced rates of halosulfuron in a mixture with quizalofop to determine if quizalofop antagonism could be minimized. The third and final strategy was to evaluate sequential applications of quizalofop applied on previously antagonized barnyardgrass resulting from a mixture of quizalofop plus propanil.

A field study was conducted in 2017 and 2018 at the LSU Agricultural Center H. Rouse Caffey Rice Research Station (RRS) near Crowley, LA. to evaluate the influence of different adjuvants in overcoming the antagonism of quizalofop when mixed with bispyribac in Louisiana rice production. In order to simulate a weedy rice population, eight, 19.5 cm drill-seeded rows of 'CLXL-745' hybrid long grain IR-rice were planted perpendicular in the front third of the plot and eight, 19.5 cm drill-seeded rows of 'CL-111' long grain IR-rice were planted perpendicular in the back third of each plot. Awnless red rice was also broadcast across the research area at 50 kg ha^{-1} immediately prior to planting and the research area was naturally infested with barnyardgrass. A crop oil concentrate (COC) consisting of paraffinic oil and fatty acid esters, a silicon based surfactant plus nitrogen source (SNS) consisting of a proprietary blend of alkanolamides, alkanoates, trisiloxane, and carbamides, and a high concentrate COC (HCOC) consisting of fatty acid esters and alkoxylated alcohols-phosphate esters were evaluated in a mixture of quizalofop at 120 g ha^{-1} plus bispyribac at 34 g ha^{-1}. All adjuvants were applied at 1% v v^{-1}. Visual evaluations for barnyardgrass, CL-111, CLXL-745 and red rice were recorded at 14 and 28 days after the initial treatment (DAIT), on a scale from 0 to 100% where 0 = no control and 100 = plant death. At the conclusion of the study, rough rice yields were obtained and adjusted to 12% moisture.

Antagonistic interactions were observed at 14 DAIT for all weed species evaluated when quizalofop was mixed with bispyribac with no adjuvant, which demonstrates to necessity of incorporating an adjuvant in to a herbicide application, especially a herbicide mixture. Antagonism of quizalofop mixed with bispyribac plus HCOC observed at 14 DAIT was overcome with a neutral interaction observed at 28 DAIT for barnyardgrass control with an observed control of 91%, compared with an expected control of 97%. The addition of COC, SNS or HCOC into a mixture of quizalofop plus bispyribac provided synergistic or neutral interactions at 14 and 28 DAIT for CL-111, CLXL-745, and red rice control. These results suggest that incorporating HCOC into a mixture of quizalofop plus bispyribac will offer the most beneficial mixture for broad-spectrum weed control including barnyardgrass and weedy rice in ACCase-R rice production. These results are supported by the findings of Jordan and York (1989) who concluded that substituting HCOC for COC alleviated the antagonism of sethoxydim for control of large crabgrass (*Digitaria sanguinalis* L.) when mixed with bentazon. It was also reported that adding HCOC in place of COC to a mixture of sethoxydim plus bentazon provided better control of johnsongrass (*Sorghum halepense* L.) (Finley et al. 1988).

A field study was conducted in 2017 and 2018 at RRS to evaluate the impact of reduced rates of halosulfuron on quizalofop activity in Louisiana rice production. In order to simulate a weedy rice population, eight, 19.5 cm drill-seeded rows of ‘CLXL-745’ hybrid long grain IR-rice were planted perpendicular in the front third of the plot and eight, 19.5 cm drill-seeded rows of ‘CL-111’ long grain IR-rice were planted perpendicular in the back third of each plot. Awnless red rice was also broadcast across the research area at 50 kg ha^{-1} immediately prior to planting and the research area was naturally infested with barnyardgrass. Reduced rates of halosulfuron at 17, 35, or 53 g ha^{-1} and reduced rates of halosulfuron plus thifensulfuron at 34 or 53 g ha^{-1} were applied in a mixture with quizalofop at 120 g ha^{-1} to evaluate the potential to overcome antagonism of quizalofop. Visual evaluations for barnyardgrass, CL-111, CLXL-745 and red rice were recorded at 14 and 28 DAIT, on a scale from 0 to 100% where 0 = no control and 100 = plant death. At the conclusion of the study rough rice yields were obtained and adjusted to 12% moisture.

At 14 DAIT, antagonistic interactions were observed for control of all weed species evaluated regardless of the rate of halosulfuron or halosulfuron plus thifensulfuron mixed with quizalofop. At 28 DAIT, antagonism of quizalofop for barnyardgrass control was observed when mixed with halosulfuron plus thifensulfuron at 53 g ha^{-1} with an observed control of 89%, compared with an expected control of 98%; however, this antagonism was overcome at the same evaluation date with a neutral interaction for barnyardgrass control when quizalofop was mixed with halosulfuron plus thifensufluron at 34 g ha^{-1} with an observed control of 96%. Quizalofop mixed with the higher rate of halosulfuron provided a neutral interaction at 28 DAIT for CL-111, CLXL-745, and red rice control; although, the lower rates of halosulfuron antagonized quizalofop, control was 92 to 95%. These data suggest that applying quizalofop in a mixture with reduced rates of halosulfuron or halosulfuron plus thifensulfuron can be used for barnyardgrass control in ACCase-R rice production. These results are supported by the findings of Green (1989) who concluded that increasing the ratio of quizalofop to bentazon in a mixture overcame antagonism of quizalofop for barnyardgrass control.

Two Field studies were conducted in 2018 at RRS to evaluate sequential applications of quizalofop applied on previously antagonized weeds from a quizalofop plus propanil mixture to determine the time needed between antagonism and a second application of quizalofop. In order to simulate a weedy rice population, eight, 19.5 cm drill-seeded rows of 'CLXL-745' hybrid long grain IR-rice were planted perpendicular in the front third of the plot and eight, 19.5 cm drill-seeded rows of 'CL-111' long grain IR-rice were planted perpendicular in the back third of each plot. Awnless red rice was also broadcast across the research area at 50 kg ha^{-1} immediately prior to planting and the research area was naturally infested with barnyardgrass. Sequential applications of quizalofop at 120 g ha^{-1} at 7, 14, 21, and 28 DAIT were evaluated for control of previously antagonized barnyardgrass from a mixture of quizalofop at 120 g ha^{-1} plus propanil at 4484 g ha^{-1}. Visual evaluations for barnyardgrass were recorded at 14 and 28 days after the sequential treatment (DAST), on a scale from 0 to 100% where 0 = no control and 100 = plant death. At the conclusion of the study rough rice yields were obtained and adjusted to 12% moisture.

At 28 DAST, quizalofop mixed with propanil followed by a sequential application of quizalofop at 7, 14, and 21 DAIT controlled barnyardgrass with an observed control of 98%, compared with an expected control of 94 to 98%. However, barnyardgrass control of 73% was observed when a sequential application of quizalofop was applied 28 DAIT of quizalofop plus propanil. These data along with results reported by Rustom (2017) suggest that if quizalofop is antagonized for barnyardgrass control then a sequential application of quizalofop should be applied no earlier than 7 DAIT and no later than 21 DAIT.

ACCase-R rice is a tool that provides growers with the ability to control IR-weedy rice and barnyardgrass. It is essential to maximize control of IR-weedy rice and barnyardgrass to prevent yield loss from antagonized weeds competing with the cultivated rice. The strategies to overcome antagonism of quizalofop evaluated in this research will be economically beneficial to growers as well as aid in preserving the ACCase-R rice technology. The recommended stewardship program for ACCase-R rice is a three-year rotation between ACCase-R rice, soybeans, and IR-rice. This rotational stewardship program will prolong the life of ACCase-R rice by preventing/delaying herbicide resistance. In addition to prolonging the ACCase-R rice production system, this rotational stewardship program will allow growers to once again use the IR-rice production system on land that imidazolinone herbicides are currently not effective.

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Vita

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