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Evaluation of Water Hardness and pH on Soybean and Cotton Insecticide Efficacy

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Evaluation of Water Hardness and pH on Soybean and Cotton Insecticide Efficacy

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Abstract

Insecticide efficacy often varies by location and year. Many factors can influence an insecticide's efficacy, but an often-overlooked factor is the quality of water in a carrier solution. Water quality includes many parameters, but two important ones are water hardness and pH. Research has shown that water hardness and pH can affect some pesticides. Multiple experiments were conducted to evaluate the impact of water hardness and pH on insecticide efficacy.

Experiments were conducted to evaluate the impact of water hardness and pH on the efficacy and residual control of chlorantraniliprole for the control of corn earworm, *Helicoverpa zea* (Boddie). Leaf dip assays were conducted using 6 ng/ml concentrations of chlorantraniliprole in water samples that had three water hardness levels (11ppm, 178 ppm, 430 ppm) and three pH levels (6.5, 8.3, and 9.1). In these trials, it was observed that as water hardness and pH increased, the percent mortality decreased. Additionally, a trial was conducted in the greenhouse to determine the impact of water hardness on the residual control of chlorantraniliprole for the control of corn earworm. There were no differences observed in soft water (11ppm) and hard water (178ppm), but with very hard water (425 ppm) there was a decrease in residual after 21 days. A field trial was conducted using chlorantraniliprole, methoxyfenozide + spinetoram, emamectin benzoate, and chlorantraniliprole + lambda-cyhalothrin. No differences were observed in the field.

Tarnished plant bugs, *Lygus lineolaris* (Palisot de Beauvois), are the most economically important insect pest in Arkansas cotton, causing major losses in yield and increasing costs for growers. Multiple experiments were conducted to determine the impact of water hardness and pH on commonly used insecticides for the control of tarnished plant control. Leaf dip assays

were conducted with sulfoxaflor, acephate, thiamethoxam, and dicrotophos that were mixed with three water hardness levels (11 ppm, 178 ppm, and 430 ppm) and three pH levels (6.5, 8.0, and 9.3). A decrease in efficacy was observed for acephate as water hardness increased, however no differences were observed for the other insecticides tested regardless of water hardness or pH. A field trials were conducted to determine the impact of water hardness and pH on the efficacy of sulfoxaflor, acephate, thiamethoxam, and dicrotophos. The tarnished plant bug population was observed at 4 and 7 days after application. As pH increased dicrotophos efficacy increased 4 days after application. No other insecticides tested were impacted by water hardness of pH. Additionally, a field trial was conducted using water conditioners that were added to water with pH levels of 6.4 or 9.1 or water hardness levels of 11 ppm and 430 ppm along with dicrotophos to determine the effect of water conditioners on dicrotophos for tarnished plant bugs. No differences in efficacies were observed at 3 days but 7 days after application Diversify had an improved efficacy compared to standard water.

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Chapter I-Introduction

Factors that Influence Pesticide Efficacy

A pesticide is a product that kills, prevents, destroys, or repels a pest (EPA, 2023). Pesticides are an important component of agriculture, needed to reduce product losses, improve yield, and increase the quality of food (Tudi et al., 2021). Because of their importance, it is crucial to understand what affects pesticide efficacy. These issues include pesticide resistance, degradation, or deactivation due to various chemicals or particles in the soil or leaf surface, photodecomposition due to ultraviolet light, temperature, spray quality, and water quality of the water that is mixed with a pesticide (Cress, 1990; Klein, 2019). The degradation of a pesticide is a chemical reaction that occurs between the pesticide's active ingredient and the chemicals in the soil, leaf surface, or other places that it may touch. The faster that a pesticide degrades the less time that is will be effective and increase the risk of toxicity. Deactivation occurs when the pesticide adheres to a soil particle, other organic matter, leaf surface, or some other environmental compound, and the pesticide is no longer available. Ultraviolet light can break pesticides down so that it is no longer toxic. Because ultraviolet light is in light from the sun, it is important to understand what pesticides are subject to photodecomposition and which ones are not. Temperature can also be a major component in breaking chemicals down and rendering them useless. Spray quality consists of multiple factors such as coverage, spray volume, boom height, nozzle usage, and other environmental factors. Water used in a spray solution is another element that can impact insecticide efficacy and can be extremely detrimental if the quality is poor. Pesticides are expensive for growers and all of these factors should be considered prior to making a spray application to ensure the pesticide will be able to perform to its full potential.

In the United States agriculture is responsible for the use of about 80% of the nation’s consumptive water (Hrozencik, 2019). Water is used for irrigation, pesticide and fertilizer

applications, crop cooling, and frost control (Eaton, 2016). Most pesticides used in agriculture are required to be dissolved or suspended in water (Schilder, 2008). Water is commonly seen as a clean input and its quality is commonly overlooked. There are many parameters of water quality include turbidity, temperature, total dissolved solids, electrical conductivity, pH, alkalinity, hardness, and salinity (Omer, 2019). Hardness and pH are the two main factors that can negatively impact pesticide performance.

Water hardness is generally considered as the amount of dissolved calcium and magnesium ions that are in the water, however, a more accurate definition is the density of cations present in water. While calcium and magnesium are the most common, other cations that can increase water hardness are zinc, iron, manganese, and aluminum (Devkota, 2016). Water is generally classified as soft, hard, or very hard depending on the amount of dissolved ions in the water (Table 1). Both soft and hard water have potential to affect pesticide performance, but generally hard water is more problematic. Herbicides such as 2,4-D, dicamba, and glyphosate have been shown to be negatively affected by hard water cations. In this situation the positively charged cations attach to the negatively charged pesticides and potentially reduce the effectiveness of the pesticide (Fishel, 2019). Studies have shown that poor water quality can cause a decrease in efficacy in some families of pesticides (Whitford et al., 2009).

In order to determine actual water hardness, water samples must go through laboratory testing. A common method of evaluating a water's hardness is colorimetric titration with an EDTA solution. An idicatator is added in small increments and the water sample changes color and depending on the test the color indicates the level of hardness. A water hardness formula is also used to determine hardness that determines the mg/L (Stricklin, 2023). This formula is:

$$\text{Water Hardness (mg/L)} = \text{Ca(mg/L)} \times 2.497 + \text{Mg(mg/L)} \times 4.118$$

Ca= Calcium content

Mg= Magnesium content

However, outside of a laboratory setting total dissolved solids (TDS) is commonly used as an indicator of water hardness. TDS a measure of anything that is dissolved in water that is not an H2O molecule (Woodard, 2023). This accounts for any organic or inorganic materials, such as calcium, chloride, magnesium, potassium, zinc, aluminum, copper, lead, other metals, minerals, salts, and ions, that are dissolved in a particular volume of water. An increased TDS can be an indicator of hard water (Table 1). TDS and hardness are similar, but TDS measures more cations and anions in the solution. A high TDS with unknown matter in the water may have no effect on pesticides.

In basic terms, pH is how acidic or alkaline a solution is, but pH stands for the "power of hydrogen". The pH scale ranges from 0 to 14, with 0 being the most acidic and 14 being the most alkaline. This number is determined by the molar concentration of hydrogen and hydroxyl ions in the solution. The higher the concentration of hydrogen ions the lower the pH, and the higher the concentration of hydroxyl ions the higher the pH (Fondriest Environmental, Inc., 2014). The pH of water is a measure of the amount of hydrogen ions (H+) in a solution. This determines how acidic or alkaline a solution is. A pH of 7 is a neutral pH, with anything below 7 being acidic and a pH above 7 is alkaline (Turner, 2022). Many factors can change the pH of water including temperature, sunlight, rain, drought, and other applications to the field (UMASS, 2012). Most areas of the U.S. have water with a pH above 7, creating the potential for alkaline hydrolysis (Deer & Beard, 2001). Alkaline hydrolysis is the chemical breakdown of a compound due to the compound's reaction with water. Essentially, larger molecules break down into smaller molecules. In warm water the rate of alkaline hydrolysis increases and because mid-south

temperatures are high during the summer when many applications are being made, the potential for alkaline hydrolysis is high. This can cause pesticide degradation rendering them less or completely ineffective (Cornell, 2021). Insecticidal half–life can be affected by high pH levels (Tavares et al., 2023). Half-life is the amount of time for a quantity of a substance to be reduced to half of its original value. It is possible for water to interact with active ingredients and or the additives of a pesticide. Poor water quality can also decrease absorption by the target pests (Whitford et al., 2009). Water quality parameters can interact with the active ingredients or other ingredients in a pesticide. The pesticides acephate, carbaryl, malathion, dicamba, and paraquat have all been recorded to have a reduction in half-life when the pH of water is higher than 7. Most pesticides tend to perform best in slightly acidic water with a pH between 4-6.5. Water quality varies from location to location and is dependent on the source. It is important to test water pH and hardness before using it in a spray solution to determine if buffers and other additives are needed. Some pesticide labels will suggest what adjuvants that should be used with them. It is important to read labels to determine what actions need to be taken to maintain insecticidal efficacy prior to a spray application.

In Arkansas, water used in spray mixes has a wide range of water hardness levels and pH levels. Butts et al. (2020) conducted a water survey in 2019 and 2020 and took samples from 79 locations in 17 Arkansas counties and measured the water hardness, cation concentration, and pH of water. Approximately 72% of the water samples had a pH greater than 7, 29% had water hardness levels above 200 ppm and 22% had both a pH greater than 7 and a hardness of more than 200 ppm. Water with these pH levels and hardness has the potential to reduce pesticide efficacy. This emphasizes the importance of checking water quality before using it in a spray solution.

There are ways to improve poor water quality and to help ensure an effective pesticide application. A widely used method to combat poor water quality is adding water conditioners to a spray tank prior to mixing. Water conditioners are anything that changes the water quality. Adding a water conditioner can improve the pesticides performance and residual. The most widely used material as a water conditioner is ammonium sulfate (AMS). The sulfate ions bind with the cations in the hard water to allow the pesticide to remain unbound in the water. However, there are many water conditioners available, and some pesticide labels may be specific as to what water conditioner should be used (Whitford et al.,2009, Voight, 2017). A non-ionic surfactant in addition to AMS might improve performance of a pesticide in hard water (Tharp & Sigler, 2013). The quality of water in a pesticide carrier solution is an important component prior to making a pesticide application. It is important to know the hardness and pH of the water before beginning to mix a spray solution.

Soybean

The soybean, [*Glycine max* (L.) Merr.], is a plant native to East Asia. Soybeans are the 2nd leading crop produced globally producing approximately 114.3 billion kg of soybeans in 2022 (American Soybean Association, 2022). Approximately 85% of the crop is used for soybean meal and oil (Lee et al., 2016). Soybean meal has a high protein content and is often used for animal feed. Other products include cooking oil, animal grains, vegan foods, biodiesel, and many other industrial applications. Brazil, the United States, Argentina, and India are the top four producers of soybeans (Vorra et al., 2020). Arkansas produced approximately 4.5 billion kg of soybeans in 2022, this makes them ranked 10th in the United States for soybean production (NASS, 2022). In Arkansas, soybean is grown in 45 of the 75 counties and are used for domestic and international products (Spradley, 2005).

Soybean growth can be split into two developmental stages, vegetative and reproductive. This system allows growers and researchers to discuss proper management for the different developmental stages. The original growth system was developed by W.R. Fehr and C.E. Caviness in 1977 but some developments have been made and the system that is now more commonly used is Palle Pedersons developmental stages (Pederson and Elbert 2009). These stages are:

- Vegetative Stages
  - VE Emergence; 5-21 days after planting
  - VC Unifoliate unroll; 1 node
  - V1 First trifoliate produced; 2 nodes
  - V2 Second trifoliate formed; 3 nodes
  - V3 Third trifoliate formed; 4 nodes
  - Vn These stages continue to flower and are numbered based on the nodes on the main stem that is fully developed
- Reproductive Stages
  - R1: Flowering begins, open flower on any node
  - R2: Full Flower, open flower in top 1 or 2 nodes
  - R3: Beginning pod, 3/16” pod in one of the 4 upper nodes
  - R4: Full Pod, ¾” in one of the 4 upper nodes
  - R5: Beginning Seed, 1/8” seed in pod in one of the 4 upper nodes
  - R6: Full seed, pod is full of green seeds in one of the 4 upper nodes
  - R7: Beginning Maturity, 1 pod anywhere on the plant is a mature color
  - R8: Full Maturity, 95% of pods a mature color

Soybean insect pests in Arkansas can be variable in abundance from year to year and have many factors that can change their impact on soybean. Weather, location, and production practices can have huge impacts on which pests occur and the pressure of the insect pests. Insect pests of soybeans are usually divided into groups based on what part of the plant that they feed on and the damage that is caused (Everngam and Headrick, 1994). The top three insect pests in Arkansas soybeans are the stink bug complex, corn earworm *Helicoverpa zea* (Boddie), and soybean loopers, *Chrysodeixis includens* (Walker).

The most common and visible injury to soybeans is defoliation. Defoliation is any type of injury to the leaf that reduces the total amount of leaf surface on the plant (Kogan and Turnipseed 1980). Soybean loopers are economic pests in the southern United States such as Arkansas, Texas, Georgia, South Carolina, Mississippi, and Alabama (Carter et al., 2017). They are usually foliage feeders but will occasionally feed on other parts of the plant. Soybean loopers are a late season pest that typically infest soybeans in the months of August and September. Damage is most common in the reproductive stage of soybeans because damage that occurs in the vegetative stages has the capability to compensate for the damages that occur (Haile et al., 1998). The current thresholds in Arkansas are 40% defoliation before bloom with 5 larvae present when using a drop cloth or 29 larva presents with 25 sweeps (Studebaker, 2022). After blooming the threshold is 25% defoliation with the same number of larva present in each sampling method. Some of the commonly used insecticides in the Arkansas MP144 include chlorantraniliprole, emamectin benzoate, indoxacarb, methoxyfenozide + spinetoram, and many other mixed insecticides.

Although defoliating insects are the largest group of insect pests in soybean, pod feeding insects are the most detrimental to yield. The corn earworm is the number one insect pest in

Arkansas soybean and was considered the costliest pest in Arkansas in 2022 (Musser et al., 2022). The young larva will feed on the leaves but as they grow the larva start feeding on the stem, leaves, pods, and blooms (Lorenz et al, 2000). Corn earworm damages the pod by chewing on the pods and causing holes and other damage. This can cause yield loss, pod drop, and reduced seed quality. The soybean fields are the most at risk of infestation when the soybean is at the R2 stage, in bloom. After blooming, the threshold table, which takes into account crop value and application cost, is the best to determine the level at which you need to treat (Bateman et al., 2023).

Stinkbugs are also a common pod-feeding insect pest in Arkansas soybean. Stink bugs will use their piercing-sucking mouthparts into the pods and suck the juices out of the pod. There are six economically important species of stinkbugs in Arkansas that are commonly seen. These are brown marmorated stink bug, *Halyomorpha halys (Stål, 1855)*, green, *Chinavia hilaris*, red banded stink bug, *Piezodorus guildinii* (Westwood), red shouldered stink bug, *Thyanta custator*, and southern green stink bug, *Nezara viridula* (Linnaeus), and brown stink bug, *Euschistus servus* (Say) (Musser et al., 2022). The pressure and populations of stink bug species vary year to year. Punctures can be identified by the presence of small brown on black spots. Damage that can occur from stink bugs includes a reduction in seed quality and quantity, discolored seeds, a reduced germination rate, delayed maturity, and abnormal leaflets and pods. Management decisions differ in Arkansas depending on the species of stink bugs that are found (Bateman et al., 2023). The threshold in Arkansas is when an average of 1 stinkbug per row foot is found using a shake sheet or 9 stink bugs per 25 sweeps up to the R6 growth stage. The threshold doubles from R6 to R6.5. The threshold for redbanded stink bugs is found using a sweep need

and it is 6 bugs in 25 sweeps and it is important to sweep deep into the canopy (Akin et al., 2022).

Cotton

Cotton is an important agricultural crop that provides fiber, edible oil, and animal feed (Voora et al. 2020). Fiber is derived from lint and is used for apparel, home furnishings, and industrial applications. The seeds are used for cholesterol-free oil and high protein livestock and poultry feeds. There are 50 known cotton species in the genus *Gossypium*, but only 4 species are cultivated including, *G. hirsutum, G. barbadense, G. arboretum,* and *G. herbaceum* (Wendel et al. 2010).

The top four producers of cotton are India, China, United States, and Brazil. India and China are responsible for about 45-50 percent of the worlds production and are also the top consumers of raw cotton. Worldwide, 22,679,618.5 million metric tons of cotton are produced, worth approximately $12 billion U.S. (Khan et al., 2020). *G. hirsutum,* upland cotton, compromises 97% of United States production with the remaining 3% of production is compromised by *G. barbadense,* Pima cotton (Meyer 2020). The United States is responsible for 35 percent of global cotton exports with over 70 percent of the exports traveling to other countries as raw cotton and later returns to the U.S. as finished products. In the United States there are 17 cotton producing states with the top 4 producers being Texas, Georgia, Mississippi, and Arkansas (Meyer 2020). In 2019-2020 there were approximately 20 million bales of cotton produced in the U.S., with a value of approximately $7 billion U.S.

Cotton is a woody perennial plant with an indeterminate growth habit that is grown as an annual crop (Ritchie et al., 2004). After planting the seedling will emerge in 4 to 14 days, then

two cotyledons will pull through the soil and unfold, and this will begin active vegetative growth. The main stem leaves are the first vegetative structure to form after emergence. On average a new node will form every 3 days, varying in early and late season (Main, 2012). Cotton plants have two types of branches, vegetative or fruiting. Vegetative branches are produced initially after germination with fruiting branches being produced beginning on the 5th or 6th node (Ritchie et al., 2004). Cotton fruit (squares, blooms, and bolls) are developed on the fruiting branches. The cotton "square" is a flower bud and is the first part of reproductive growth. When cotton begins squaring, it can be broken down into several different growth stages, beginning first at "pinhead" and then "matchhead" square. Squares then turn into flowers, which begins the growth stage known as bloom. Each flower begins white, then pink, and eventually red (Wilson, 2023). The flower will dry 5 to 7 days after emerging and fall off giving rise to a boll. The boll will fill and once it reaches its full size, it will dry, and the suture between the carpel walls will split, and the bolls will open (Ritchie et al. 2004).

In 2022, three of the most damaging insect pests of Arkansas cotton were tarnished plant bug *Lygus lineolaris* (Palisot de Beauvois), corn earworm, and tobacco thrips, *Frankliniella fusca* (Hinds) (Cook et al., 2022). Arkansas had a total of 630,000 acres of cotton planted and of those acres 100% was infested by tarnished plant bugs, bollworms, and thrips. Tarnished plant bugs were the costliest of the three, costing growers an average of $93.06 an acre to control with an overall yield reduction of 5%. Thrips cost an average of $15.06 an acre to control with a 1% yield reduction followed by bollworms that cost $4.99 an acre to control, not including fees for transgenes, with a 1.5% average yield reduction.

Tarnished plant bug has a wide host range, with over half of the cultivated species grown in the Unites States considered to be host plants for it (Dixon and Fasulo 2001, George et al.

2021). Tarnished plant bugs have 169 recorded host plant species across 35 families in the Mississippi Delta region alone (George et al. 2021). Some economically important crops that are hostable for tarnished plant bug include cotton, soybeans, seed alfalfa, *Medicago sativa,* and many fruit crops including apples, *Malus domestica*, cherries, *Prunus avium,* strawberries, *Fragaria x ananassa,* pears, *Pyrus communis,* and peaches, *Prunus persica*. Some non-crop hosts include shepherd's purse, *Capsella bursa-pastoris* (L.) Medicus, and henbit, *Lamium amplexicaule* (L.), which are also key winter and spring host plants that bloom from December to April that tarnished plant bugs can overwinter in. Tarnished plant bugs overwinter in dead weeds, leaf litter, tree bark, garden debris, clover, *Trifolium repens*, alfalfa, and mullein leaves, *Verbascum densiflorum*. The adults become active in early spring, feeding, and laying eggs in florets, blossoms, grasses, and weeds which will hatch in 7 to 10 days (Dixon 1989, Eaton 2016). The nymphs go through 5 instars taking 12.5 to 40 days to advance through the stage depending on the temperature, 12.5 days requires a temperature of 33.9 C and 40 days are for cooler temperatures such as 11.7 C. After molting into adults, females will lay eggs in about one week (Smith 2011). The adult tarnished plant bug ranges from 4.90 to 5.95 mm long, 2.52 to 3.01 mm wide, and is bronze with yellow and black markings (Dixon and Fasulo 2001). Tarnished plant bugs insert their mouthparts into terminals, squares, flowers, and bolls, inserting toxic saliva into the flowering structure while extracting juices and damaging the plant (Musser et al., 2009). Terminals may be deformed or killed depending on the extent of damage which may result in loss of apical dominance, also called crazy cotton (Reisig, 2022). Feeding on pinhead squares can lead to abscissions but feeding on larger squares doesn't always lead it abscissions. Damaged small squares will begin to turn yellow before turning brown then black as they abort. Feeding on larger squares results in blooms that have high potential for anther damage. Feeding on white

blooms also results in darkened anthers and petal deformities. Tarnished plant bug damage to small bolls causes external spotting, wart-like growths, stained lint, and damaged seed. (Musser et al., 2009 and Reisig, 2022). There are two sampling methods that are commonly used for tarnished plant bugs, sweep nets, and drop cloths. Sweep nets are used to monitor adult migrations into the field before peak bloom and drop cloths are used after peak bloom to monitor nymphal densities in the field. Arkansas's current threshold for tarnished plant bugs is 3 tarnished plant bugs per 1.5 row m or 8 to 12 tarnished plant bugs per 100 sweeps from early square through cutout (Bateman et al., 2023). After cutout the threshold doubles to 6 tarnished plant bugs per 5 row feet.

The most common methods for controlling tarnished plant bugs in cotton are the use foliar applied insecticides. These treatments include insecticides in the organophosphate, pyrethroids, carbamates, neonicotinoids, and sulfoximine groups. Resistance to organophosphates and pyrethroids has been documented in populations of tarnished plant bugs (Snodgrass, 1996). Common insecticides used in the mid-south include sulfoxaflor, acephate, thiamethoxam, and dicrotophos. Outside of insecticides there are several recommended cultural control practices that can be implemented to help reduce tarnished plant bug populations (Gore et al., 2015). It is important to keep cotton fields together, away from corn and early planted soybeans, and be aware of surrounding wild hosts. Any wild hosts should be eliminated before they flower to reduce the risk of colonization of tarnished plant bugs. A hairy leaf and early maturing variety should be planted in order to help reduce yield loss and pest populations. Hairy leaf varieties have been shown to provide better yield and square retention when tarnished plant bugs are present but lepidopteran pests like hairy varieties because it can help protect their eggs.

Table1. Classification Table on Water Hardness and Total Dissolved Solids

Hardness (ppm)	Classification	Total Dissolved Solids (ppm)	Classification
0-60	Soft	0- 70	Very Soft
60-120	Moderately Hard	70-150	Soft
120- 180	Hard	150-250	Slightly Hard
>180	Very Hard	250-320	Moderately Hard
		320-420	Hard
		>420	Very Hard

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Chapter II. Evaluating the Effects of Water Hardness and pH on Chlorantraniliprole and Other Soybean Insecticides for the Control of Corn Earworm, *Helicoverpa zea,* in Arkansas Soybeans

Abstract

Insecticide efficacy often varies by location and year. Many factors can influence an insecticide's efficacy, but an often-overlooked factor is the water of the carrier solution. Multiple experiments were conducted to evaluate the impact of water hardness and pH on chlorantraniliprole efficacy for control of corn earworm. In the first experiment, leaf dip assays were conducted to evaluate the effects of water pH on chlorantraniliprole. Serial dilutions were used to achieve the concentration of 6 ng/ml of chlorantraniliprole, in 3 different water samples with pH levels of 6.5, 8.0, 9.3. Leaf discs were dipped in the treatment solution and allowed to dry. Larvae were then placed on leaf discs and observed for mortality at 48 h after application. In the next experiment, leaf dip assays were conducted in the same way but with water at hardness's of 11 ppm, 178 ppm, and 430 ppm, respectively. A third experiment was conducted in the greenhouse where chlorantraniliprole (Prevathon®, FMC, Philadelphia, PA) 52.7 g ai/ha was mixed with water at the same hardness treatments as the leaf dip assays then applied to soybean plants in a spray chamber. Leaves were pulled from the soybean plants at 1, 7, 21, 28, and 35 days after application and cut into 12.7 mm leaf discs. Larvae were placed on leaf discs and checked for mortality at 48 h. A field trial was conducted using the same water hardness treatments as the leaf dip assays and were mixed with chlorantraniliprole 52.6 g ai/ha, methoxyfenozide + spinetoram 109.5 g ai/ha + 21.9 g ai/ha , emamectin benzoate 11.3 g ai/ha, and chlorantraniliprole + lambda-cyhalothrin 51.2 g ai/ha + 25.6 g ai/ha, then sprayed on soybeans and evaluated at 4, 7, and 10 days after treatment for the control of corn earworm. In the leaf dip assays, percent mortality decreased as pH and water hardness increased. No differences were observed in the greenhouse trial between soft (11 ppm) and hard (178ppm)

water but there was a significant decrease in residual control with very hard water (430 ppm). There were no differences observed in the field trial across treatments.

Introduction

In 2022, Arkansas growers harvested 1,274,760 hectares of soybeans for a total of 4,457,905,812 kilograms of soybeans (USDA NASS, 2022). In the years 2018-2021 the average yield loss to corn earworm, *Helicoverpa zea* (Boddie), was 3.35% of the total yield loss per year (Heatherly, 2022). These losses make corn earworm the number one insect pest in Arkansas soybean (Lorenz et al., 2000). Corn earworm larvae feed on the soybean plant causing reduced leaf surface area, delayed pod fill, a reduced number of seeds per pod, and lower yield. Nucleopolyhedrovirus, chlorantraniliprole, emamectin benzoate, lambda-cyhalothrin + chlorantraniliprole, and methoxyfenozide + spinetoram are some of the insecticides commonly used to control corn earworm. Insecticide efficacy often varies by location and year. There are many factors that can influence a pesticide’s efficacy, but an often-overlooked factor is the water quality of carrier solution. There are many parameters of water quality that include turbidity, temperature, total dissolved solids, electrical conductivity, pH, alkalinity, hardness, and salinity (Omer, 2019). However, the two major factors that are impacting pesticides with regards to water quality are water hardness and pH.

Water hardness is the concentration of cations such as calcium, magnesium, and iron present in water (Devkota, 2016). These minerals can reduce the effectiveness of weak acid pesticides due to the positively charged ions binding with the negatively charged ions in the pesticide (Tharp and Sigler, 2013). Hard water can cause multiple issues such as reduced pesticide uptake in the targeted pest, slower penetration, or it can cause the pesticide to become an insoluble salt. These all impact pesticide activity. Total dissolved solids are sometimes used as

a measure of water hardness, however the difference in water hardness and total dissolved solids is that hardness only measures cations and total dissolved solids measure the total of all organic and inorganic materials (Voight, 2017). These include inorganic salts like calcium, magnesium, potassium, sodium, bicarbonates, chlorides, and sulfates and some other organic matter that is dissolved in water (Woodard, 2019). Salt-formulated herbicides such as glyphosate, sethoxydim, ammonium salt of imazethapyr, and glufosinate ammonium can be adversely affected by some minerals in water (Tharp and Sigler, 2013).

A water's pH is a measurement of the amount of hydrogen and hydroxide ions present (Fishel, 2002). A pH below 7 is considered acidic, with a high amount of hydrogen ions. A pH above 7 is considered alkaline, with a high amount of hydroxide ions present. There are several things that can influence pH including the rock underlying surface soils, atmospheric deposition, the municipal water treatments, wastewater discharge, and the carbon dioxide levels (Addy et al., 2004). Most pesticides work best when mixed in water that is slightly acidic (UMASS Extension, 2012). In alkaline water pesticides can go through a process called alkaline hydrolysis. Organophosphates, synthetic pyrethroids, and carbamates, when mixed with water with a pH over 7 can break down. The alkalinity of the water and the susceptibility of the pesticide are some factors that determine the rate of breakdown. Alkaline hydrolysis breaks down the active ingredient in these pesticide formulations and reduces the effectiveness (Deer & Beard, 2001).

This study’s objective was to determine the potential effects of water hardness and pH on insecticides used to control corn earworm in soybean.

Materials and Methods

The tested water hardness and pH levels were decided upon from water samples that were collected from multiple grower farms across Arkansas. Arkansas water used in spray mixes has a wide range of hardness and pH. Samples from 10 farming locations that are commonly used for pesticide application were collected in the summer of 2021. Hardness in these samples ranged from 2.41 to 430 ppm (very soft to extremely hard) and pH from 7.22 to 8.34 (Table 1). Water samples were sent to Waypoint Analytical, Inc. and analyzed. The water report from the reverse osmosis filtration system that is the standard water for all test can be found in Appendix A. All pH water samples were tested using a pH and temperature meter (MW102, Milwaukee Instruments, Inc., Rocky Mount, NC) and calibrated before each use.

Across all trials water was mixed with magnesium chloride to adjust water hardness or sodium hydroxide to adjust pH. Water was obtained from a reverse osmosis filtration system with a hardness of 11 ppm and pH of 6.4, respectively. A 26.5 liter Aqua-Tainer was filled with filtered water then magnesium chloride was added to increase the water hardness. Magnesium chloride was added until the total dissolved solids was around 430ppm, the highest hardness needed for treatments. This was repeated to produce the water hardness needed for the other treatment. Approximately, 8.8 liters of water at 430 ppm was drained and 8.8 liters of filtered water was added to the container to reach 178 ppm. To produce the desired pH levels a 26.5 liter Aqua-Tainer was filled with filtered water then sodium hydroxide was added to increase the pH. Sodium hydroxide was added until the pH was near 9.1, the highest pH needed for treatments. This was repeated to produce the water pH needed for the other treatment. Approximately, 8.8 liters of water at 9.1 was drained and 8.8 liters of filtered water was added to the container to get

to pH 8.3. All water hardness/total dissolved solid (TDS) measurements were tested using a multifunction water quality tester (ORAPXI, China) and calibrated before each use.

Serial dilutions were used to determine the LD_{50} for chlorantraniliprole for corn earworm. Serial dilutions began using a 600ng ai/ml stock solution of chlorantraniliprole (Vantacor®, FMC, Philadelphia, PA) was made. Then 1 ml, 5 ml, 10 ml, 20 ml, or 40 ml, of each of these solutions were mixed with 1000 ml of water. Then the same steps that were conducted in the following leaf dip assays were followed. We then determined that the 1 ml solution (6ng/ml) was the LD_{50} and would produce the best results.

All corn earworm larvae were obtained from the Mississippi State Rearing Lab (Starkville, MS) and the colony was maintained at the University of Arkansas Lonoke Research and Extension Center in the Entomology lab. They were reared on a diet substrate (Southland Products Inc., Lake Village, AR) consisting of wheat and soybean germ in 29 ml insect rearing cups (Solo P100N, Lake Forest, IL). Larva were stored in an insect incubator (Percival I36VL, Percival Scientific Inc., Boone, IO) with 14:10 light: dark ratio set at 29.4°C during light hours and 25.6°C during the dark hours.

Leaf Dip Assays

All soybean leaf dip assays were conducted at the University of Arkansas Lonoke Research and Extension Center, Lonoke, AR in 2021 and 2022. Chlorantraniliprole (Vantacor®, FMC, Philadelphia, PA) at 6 ng/ml was mixed with three water samples with pH levels of 6.5, 8.3, and 9.1. The hardness leaf dips also consisted of 4 treatments including an untreated check. Leaf dip assays also were conducted with four water hardness treatments including a nontreated control. Chlorantraniliprole 6 ng/ml was mixed with three water samples with TDS of 11 (very

soft), 178 (slightly hard), and 430 ppm (very hard). Soybean seeds (P45A02X) (Pioneer, Johnston, IA) were in the greenhouse. When plants reached the V5 growth stage leaves were pulled from the plant at the third node from the top on the 120 soybean plants. The pH leaf dips consisted of 4 treatments including the untreated check. Leaf discs were cut using a circle punch with a diameter of 12.7mm then were dipped into each treatment, allowed to dry then placed in a 100mm VWR petri dish (Avantor delivered by VWR, Radnor, PA) with a damp cotton pad and a single 2nd instar corn earworm larva. The larvae were checked at 48 h for mortality. Each trial was replicated 3 times temporally with 30 replications per treatment spatially. Mortality was determined by observing movement and if the specimens could not right themselves after being turned over, they were considered dead. Percent mortality was determined by dividing the total number of dead corn earworms by the total corn earworm, then multiplied by 100. Mortality data was analyzed using (JMP®, Version 16.2, SAS Institute Inc., Cary, NC)

Greenhouse Residual Trial

Green house trials were conducted at the University of Arkansas Lonoke Research and Extension Center, Lonoke, AR in 2021 and 2022. Chlorantraniliprole at 6 ng/ml was mixed with 3 water samples with TDS levels of 11 (very soft), 178 (slightly hard), and 430 ppm (very hard), then applied to 30 V4-V5 soybean plants treatment for each. Applications were made using a Generation 4 Research Tracker Sprayer (Devries Manufacturing, Hollandale, MN) with cone spray nozzles (TeeJet TX-VK6) on 45.7cm above the plants at 93.5 L/ha and 275.6 kPa. After application plants were placed back in the greenhouse to dry for an hour. Leaves were pulled from the third node from the top of the plant at 1, 7, 21, 28, and 35 days. Leaves were placed in a 100mm VWR petri dish with a damp cotton pad and a single 2nd instar corn earworm larva. Each treatment consisted of 30 petri dishes (replicates). The larvae were checked at 48 h for mortality.

Mortality was determined by observing movement and if the specimens could right themselves after being turned on their back. Percent mortality was determined by dividing the total number of dead corn earworms by the total number of corn earworms then multiplied by 100. These trials were replicated 3 times temporally.

Field Trial

A field trial was conducted near Stuttgart, AR at the University of Arkansas Rice Research & Extension Center in 2022. Plot size was 3.8 meters (6 rows) by 12.2 meters. Trials were arranged in a randomized complete block with 4 replications. Chlorantraniliprole (Vantacor®, FMC, Philadelphia, PA) 21.28 g ai/ha, methoxyfenozide + spinetoram (Intrepid Edge, Corteva, Indianapolis, IN) 53.20 g ai/ha, emamectin benzoate (Denim, Syngenta Crop Protection, Greensboro, NC) 9.08 g ai/ha, chlorantraniliprole + lambda-cyhalothrin (Besiege, Syngenta Crop Protection, Greensboro, NC) 31.08 g ai/ha, were each mixed with water samples with water TDS' of 11 ppm, 180 ppm, and 430 ppm, respectively, including a nontreated control check for a total of 13 treatments. All treatments were mixed and allowed to rest for 3 hours prior to application. Applications were made using a Bowman Mudmaster at 93.5 L/ha at 276 kPa using a TXVS-6 hollow cone nozzle. Plots were sampled using a sweep net at 3, 7, and 10 days after application and corn earworm larva numbers were recorded. Data were analyzed using (JMP®, Version 16.2, SAS Institute Inc., Cary, NC).

All data were analyzed using JMP 16 (1989-2007). Data for the leaf dip and greenhouse experiment were analyzed using regression analysis and were considered significant if slopes had a $P < 0.05$. For the greenhouse experiment a mixed model analysis of variance was used to analyze percent mortality for water hardness and pH. Run and replication were random factors. Differences for treatments for were considered significant if $P < 0.05$ and means were separated

using Tukey's HSD. For the field experiment a mixed model analysis of variance was used to analyze percent mortality across water hardnesses for each insecticide treatment.

Results

Leaf Dip Assays

As water pH increased, percent mortality decreased (F=29.7 df= 1,5, P=0.003); Figure 1.a). Chlorantraniliprole mixed with water with a pH of 9.4 resulted in an approximate 20% decrease in mortality as compared to water with a pH of 6.5. Mortality in the nontreated control was 0%.

As water hardness increased, percent mortality decreased (F=10.9, df=1,5, P=0.02); Figure 1.b). Chlorantraniliprole mixed with water with a hardness of 420 ppm resulted in an approximate 20% decrease in mortality as compared to water with a hardness of 11 ppm. Mortality in the nontreated control was 0.01%.

Greenhouse Trial

In the greenhouse trial, there were no differences in the residual control provided by chlorantraniliprole mixed with hard and soft water (Figure 2). However, chlorantraniliprole mixed with the very hard water provided significantly less residual control than when mixed with either soft or hard water. Chlorantraniliprole mixed with 11 ppm water, or 178 ppm water lost approximately 0.5 and 0.75 percentage points of residual control per day and chlorantraniliprole mixed with the 430 ppm water lost approximately 1.5 percentage points residual control per day (F = 8.5362, df = 2, 37, P = 0.0009).

Field Trial

In the field trials, the tested products chlorantraniliprole (F=2.5, df=1,5, P=0.2), emamectin benzoate (F=1.5, df=1,5, P=0.3), methoxyfenozide + spinetoram (F=1.5, df=1,5, P=0.3), and chlorantraniliprole + lambda-cyhalothrin (F=0.1, df=1,5, P=0.8) had no differences at four days after application as TDS increased (Figure 3). Chlorantraniliprole (F=6.0, df=1,5, P=0.1), emamectin benzoate (F=0.2, df=1,5, P=0.6), methoxyfenozide + spinetoram (F=0.3, df=1,5, P=0.6), and chlorantraniliprole + lambda-cyhalothrin (F=0.3, df=1,5, P=0.6) showed no differences seven days after application as TDS was increased (Figure 4). Chlorantraniliprole (F=0.9, df=1,5, P=0.4), emamectin benzoate (F=2.0, df=1,5, P=0.2), methoxyfenozide + spinetoram (F=0.7, df=1,5, P=0.4), and chlorantraniliprole + lambda-cyhalothrin (F=1.4, df=1,5, P=0.3) also had no differences 10 days after application as TDS increased (Figure 5).

Discussion

Water hardness and pH have been shown to reduce the efficacy of multiple insecticides, herbicides, and fungicides. In this study water hardness and pH reduced efficacy of chlorantraniliprole on soybean in the lab and the greenhouse. However, in the field trial there were no differences in chlorantraniliprole, emamectin benzoate, methoxyfenozide + spinetoram, and chlorantraniliprole + lambda-cyhalothrin efficacy as water hardness increased. There are a couple of reasons why this likely was the case. In the leaf dip study, a LD_{50} rate was used to evaluate the impact of water hardness on chlorantraniliprole efficacy. Chlorantraniliprole is extremely toxic to corn earworm and if the field rate was used it would have killed all the larvae across all treatments in the lab study. In the greenhouse study differences between water hardnesses really only became prevalent when leaves were pulled at later dates. Our leaf dip assays indicated that at least some of the chlorantraniliprole was being bound up in the very hard

water treatments and the greenhouse study indicates that reduced residual efficacy may show up in the field. We hypothesize that differences between the hard water treatments may have shown up in the field trial if it became reinfested behind the original population. The original population declined after approximately 10 days in the field and in the greenhouse study, differences only became apparent at approximately 21 days after treatment. Because chlorantraniliprole provides excellent residual control of corn earworm and exhibits high toxicity to corn earworm, differences in control between the different water hardnesses and pH's would likely only manifest at later dates.

In Arkansas it costs growers an average of $44.46 per hectare to treat corn earworm in 2022. For example, if a grower plants 100 hectares of soybeans and must treat corn earworm this on average would cost them around $4,446 total. Growers in Arkansas sprayed 45% of their acreage to control corn earworm in 2022 (Musser et al., 2022). Because reinfestation of corn earworm is common in Arkansas, insecticides with long residual control, such as chlorantraniliprole, are recommended to prevent reinfestations. By adding a spray grade ammonium sulfate (AMS) the water hardness issues can be resolved. The additionally $11.12 per hectare is the cost of adding 10.1 kg/ha of AMS to a spray mix and this can help prevent issues that might arise with water quality. According to the data in this study poor water quality can reduce residual control. Making another application can potentially double the cost of managing corn earworm for a grower. This is an expense that could potentially be avoided by testing water and adding the needed conditioners to correct water quality issues. There are more tests that need to be conducted to determine the long-term issues with water quality but testing water quality is simple thing that can help prevent these issues. These results indicate that it is important to know what quality water is being used in a spray solution.

Results from this study aim to help soybean producers understand the importance of water hardness. Water hardness and pH did impact efficacy of soybean insecticides in the lab and the greenhouse. Future studies are needed to further evaluate if the reduction in efficacy from waters with a high pH or hardness is reflected in a field situation.

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Table 1. Water Hardness and pH levels collected and tested throughout Arkansas.

Locations (County)	Hardness (ppm)	Hardness	pH
Prairie, Hazen	159	Hard	8.16
Greene	10.9	Soft	7.65
Prairie, Des Arc	182	Very Hard	7.92
White	33.9	Slightly Hard	7.16
White	193	Very Hard	7.72
Poinsett	233	Very Hard	8.34
Drew/Desha	2.41	Soft	8.11
Conway	430	Very Hard	7.22
Arkansas	359	Very Hard	7.76
Lonoke	178	Very Hard	7.38

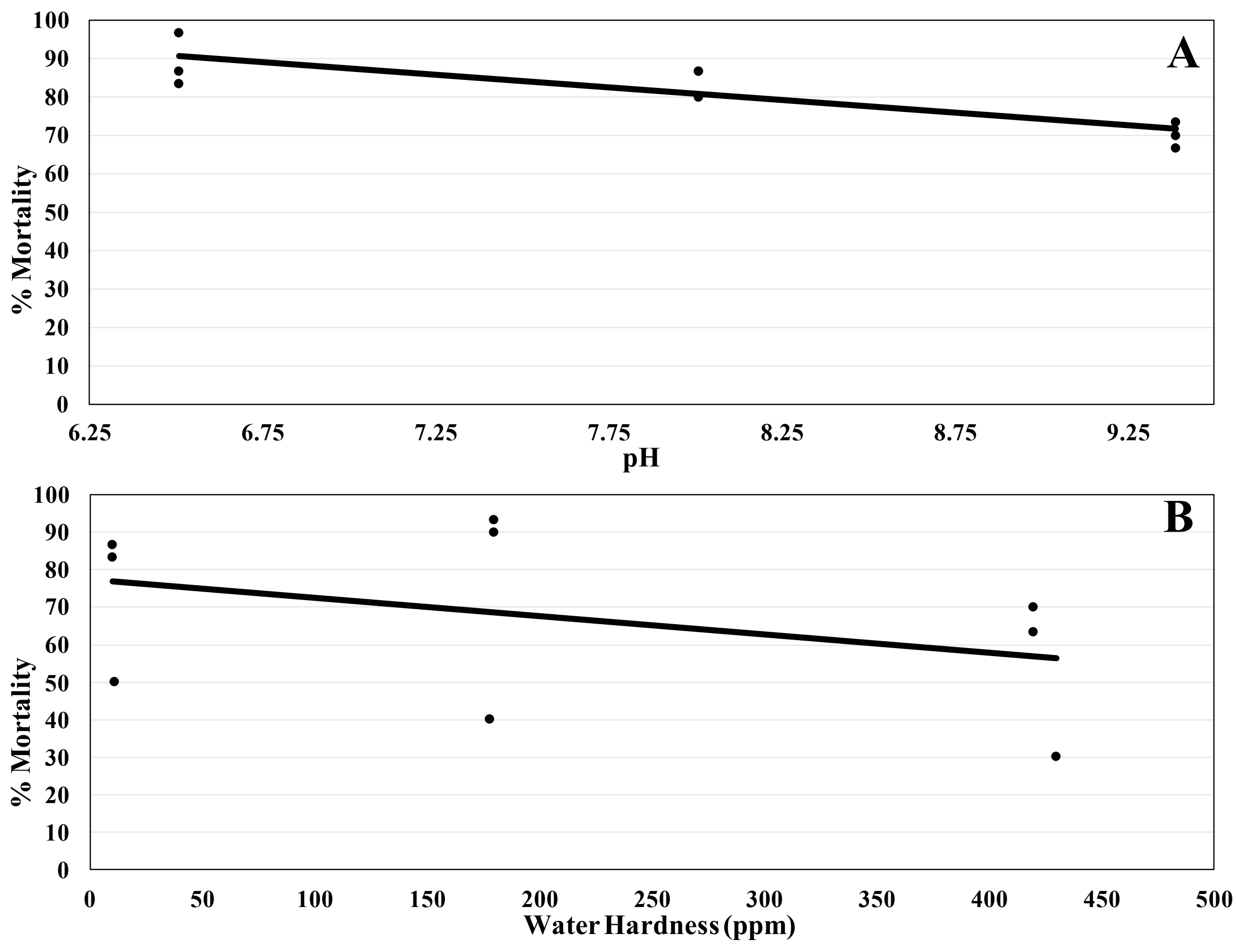

Figure 1. Percent mortality of *Helicoverpa zea* for the effects of pH (A) and water hardness (B) on chlorantraniliprole in leaf dip assays

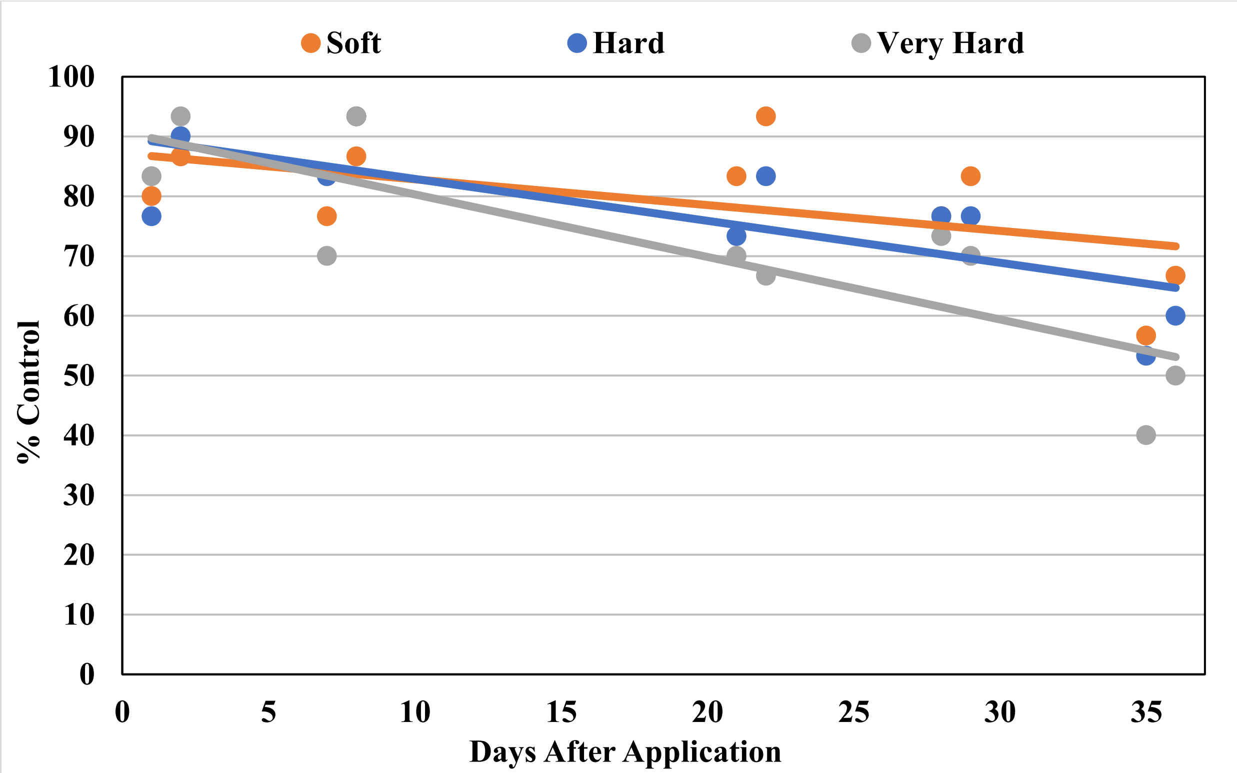

Figure 2. Greenhouse residual trial on the effects of water hardness on chlorantraniliprole

All: $F = 8.5362$, df = 2, 37, $P = <0.0009$

Soft: y = 90.98-0.4975x

Hard: y = 94.58-0.7858x

Very Hard: y = 97.09-1.5x

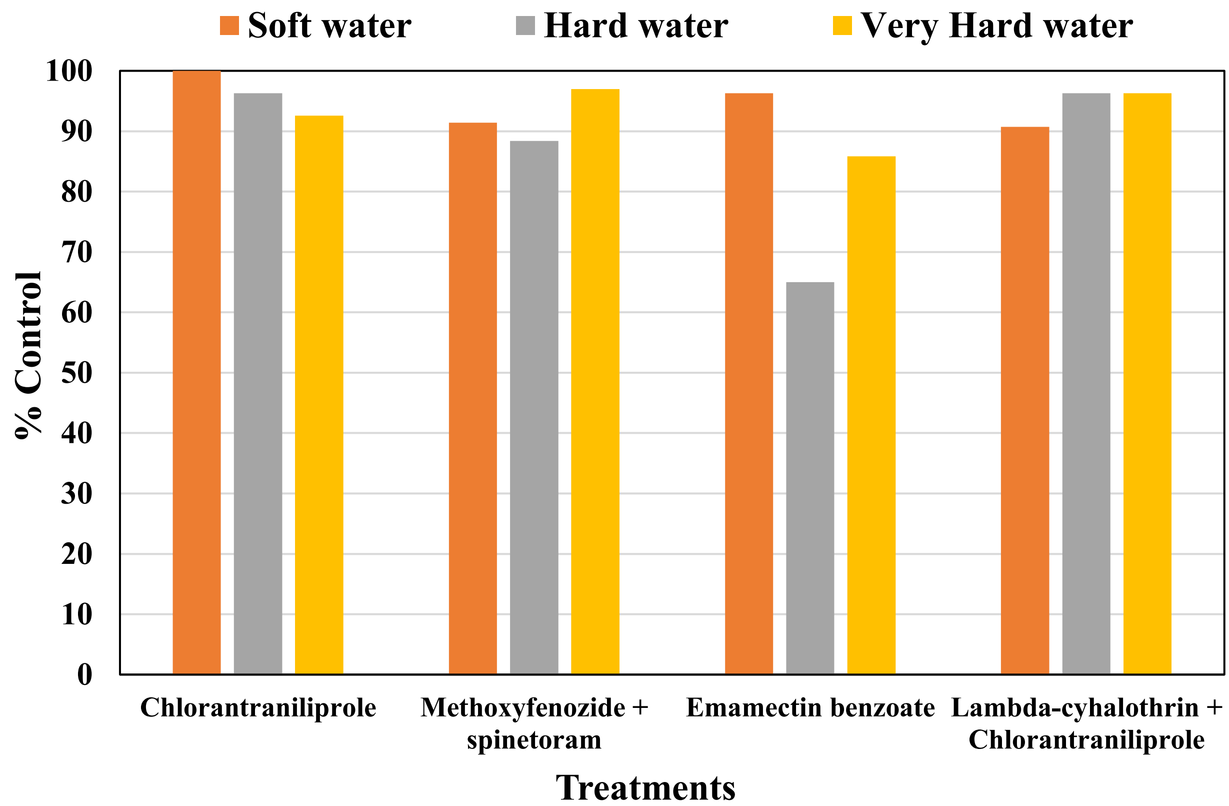

Figure 3. Percent control for the effects of water hardness on soybean insecticides 4 days after application.

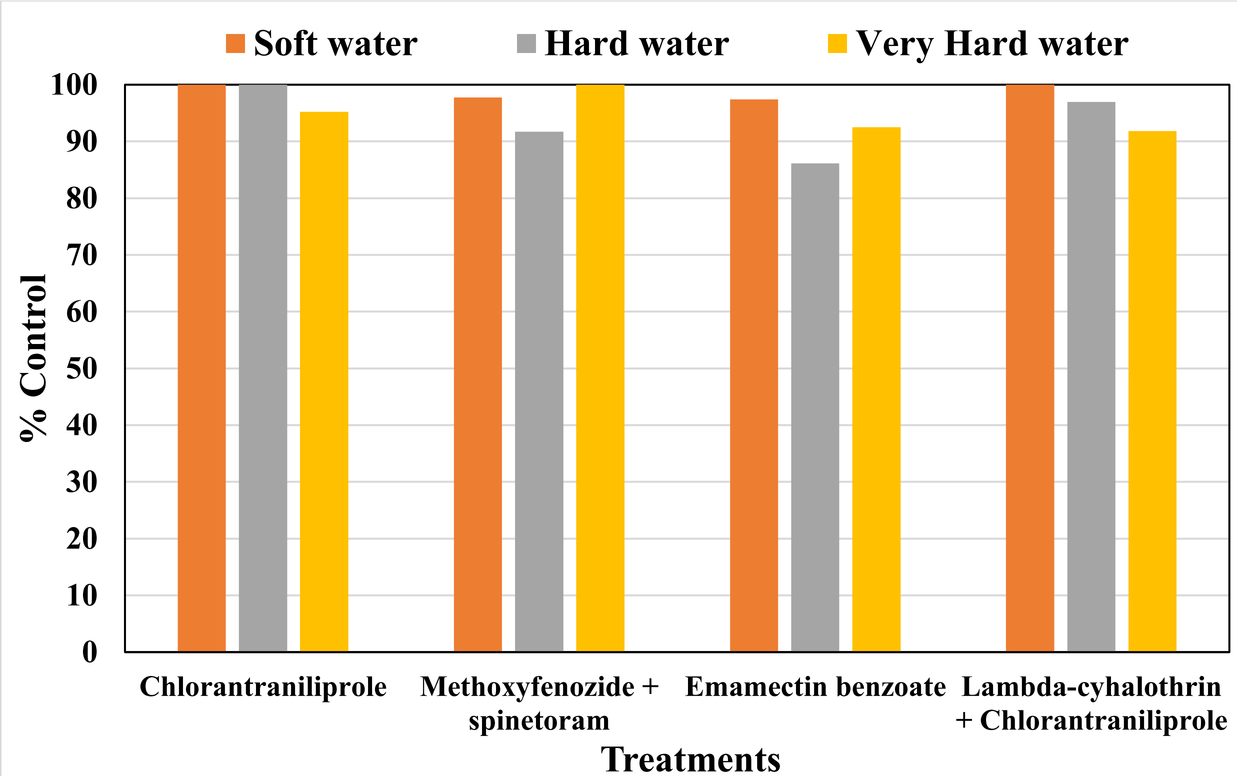

Figure 4. Percent control for the effects of water hardness on soybean insecticides 7 days after application.

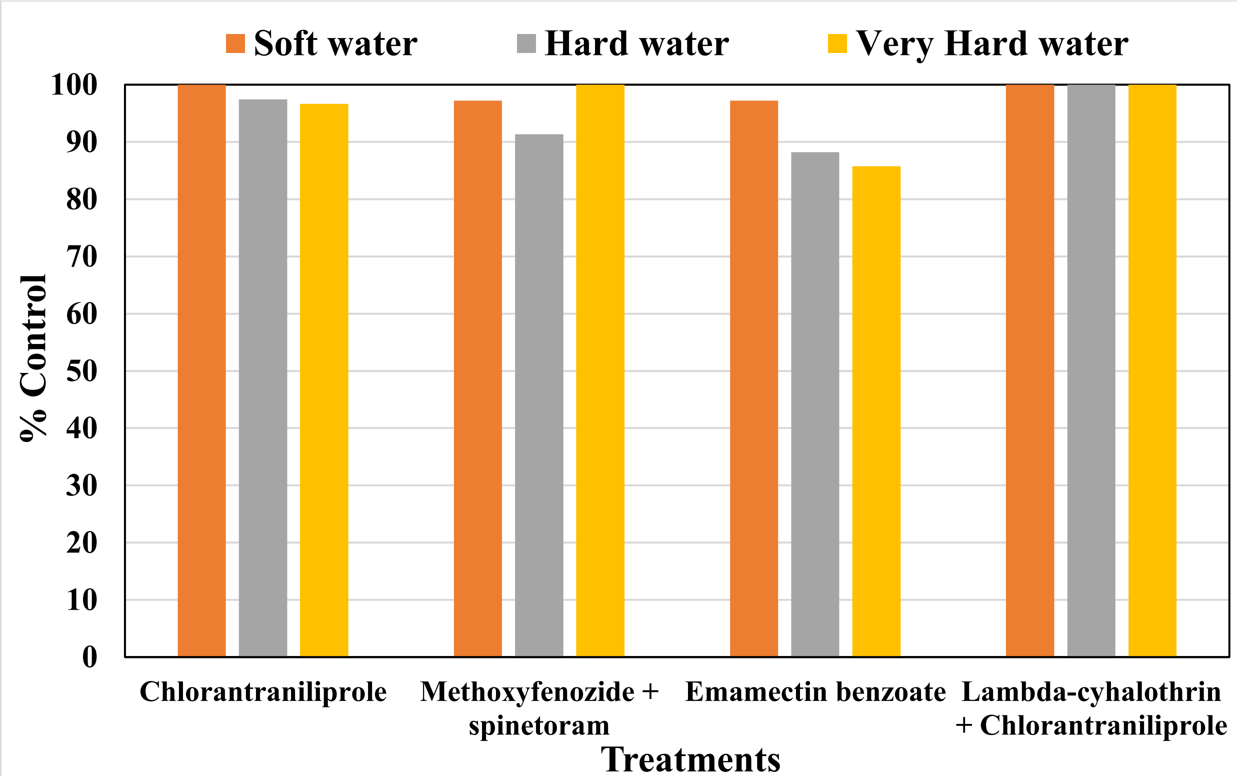

Figure 5. Percent control for the effects of water hardness on soybean insecticides 10 days after application.

Chapter III: Evaluating the Effects of Water Hardness and pH on Cotton Insecticides for the Control of Tarnished Plant Bugs, *Lygus lineolaris (Beauvois)* in Arkansas Cotton

Abstract

There are many factors that can influence an insecticide's efficacy, but an often-overlooked factor is the water quality used in an insecticide solution. Multiple lab and field experiments were conducted to evaluate the impact of water quality on insecticide efficacy for tarnished plant bug, *Lygus lineolaris* (Palisot de Beauvois). Leaf-dip assays were conducted with sulfoxaflor, acephate, thiamethoxam, and dicrotophos which were each mixed in water with hardness levels of 11, 178, and 430 ppm or with water with pH's of 6.5, 8.0, and 9.3. Leaf discs were then dipped in each solution, dried, and placed in petri dishes with a moist cotton pad. Adult plant bugs were then placed in the Petri dishes and mortality was assessed 48 h after infestation. Field trials were conducted with the same rates, insecticides, and pH and hardness treatments to evaluate their impact on tarnished plant bug control. Additionally, a field trial was conducted on multiple water conditioners with dicrotophos to determine the effectiveness on ph and water hardness. The water conditioners ammonium sulfate, Quest, Smoke, Diversify, and HM1895 were combined with water with a hardness of 430ppm or a pH of 9.27. Dicrotophos was added to each water treatment then applied to cotton to determine the impact of each water conditioner on dicrotophos's efficacy on tarnished plant bugs. These treatments were checked against dicrotophos mixed with water with a hardness of 10.9ppm or water with a pH of 6.47 and an untreated check. The water hardness leaf dip data suggests that acephate efficacy decreased as water hardness increased. No differences were observed for the other insecticides tested. There were no differences observed for the tested insecticides as pH increased in the pH leaf dip. In the water hardness field trials dicrotophos efficacy increased at water hardness increased at 4 days after applications and the other tested insecticides were not affected. There were no differences

observed at 7 days after application across treatments. There were no differences between any treatments in the pH field trials at 3 or 7 days after application.

Introduction

Water hardness is a measurement of the density of cations present in water, specifically calcium and magnesium (Devkota, 2016). While calcium and magnesium are the most common, other cations that can increase water hardness are zinc, iron, manganese, and aluminum. Water hardness increases when there is an addition of one of or both of these cations.

A water's pH is a measurement of the amount of hydrogen and hydroxide ions present (Fishel, 2002). A pH below 7 is considered acidic, with a high amount of hydrogen ions. A pH above 7 is considered alkaline, with a high amount of hydroxide ions present. Many pesticides perform best in slightly acidic water with a pH of 4-6.5 (Whitford et al., 2009). Water that has an alkaline pH increases the risks of alkaline hydrolysis (Seaman & Reidl, 1986). Alkaline hydrolysis is the chemical breakdown of a compound due to the reaction with water. It divides the large molecules into smaller molecules. Insecticides are more susceptible to alkaline hydrolysis than fungicides, herbicides, and growth regulators (Deer & Beard, 2001). The most susceptible insecticides include organophosphates, carbamates, and pyrethroids. Alkaline hydrolysis takes the active ingredients and breaks them down to reduce its effectiveness. The loss of effectiveness depends on the water's alkalinity and its temperature (Whitford et al., 2009). Temperature can influence the rate that chemical and biological reactions occur. At temperatures increase the effects of pH on a pesticide usually happens quicker.

It is important to know the water hardness and pH of a carrier solution before mixing pesticides. Knowing the water hardness and pH can help determine the necessity of a water

conditioner. Herbicides, including mesotrione, glufosinate, 2,4-D, dicamba, and glyphosate decrease in effectiveness when the water hardness is above 200 ppm and pH is increased above 7 (Devkota et al., 2016). Flumioxazin is a commonly used herbicide for broadleaf weeds. In a pH of 5 the mixture will maintain its stability for several days (Fishel & Ferrell, 2007). If the pH is increased to 7 the half-life of this product decreases to 24 hours. As the pH is increased above 9 the half-life is reduced to 15 minutes. Captan is a fungicide that is widely used to combat many diseases and is strongly impacted by water pH. At a pH of 7, it has a half-life of 8 hours, compared to a pH of 8 and 9, the half-life is reduced to 10 and 2 minutes, respectively.

To maximize pesticide efficacy, it is important to choose a water conditioner based on the pesticide to be used and the issues present in the water (Schilder, 2008). There are commercial acidifiers and buffers offered. Buffers will stabilize the spray solution and keep it at a predetermined pH. Ammonium Sulfate (AMS) is one of the most widely used water conditioners to combat hard water with success in weak acid herbicides (Voight, 2017). The sulfate ions in AMS will bind with the hard water minerals (cations). It is important to add conditioners to the spray solution before adding pesticide. Adding a water conditioner before the pesticide will adjust the hard water and pH to prevent alkaline hydrolysis. The pesticide will already be broken down if the conditioner is added after the pesticide and will be unnecessary (Interagro, 2023).

In the mid-south cotton producers rely on foliar insecticide applications to protect the crop from tarnished plant bugs which can be difficult and costly to control (Snodgrass et al., 2009). In 2022, Arkansas had 100% of hectares infested with lygus and 99% of those hectares were treated with an average of 3.9 applications per hectare of cotton (Cook et al., 2022). This is the most economically damaging pest of cotton with losses + costs totaling $110,571,300 U.S. Tarnished plant bugs have been documented to be resistant to pyrethroids, organophosphates,

and cyclodiene insecticides. The University of Arkansas MP 144 2023 current recommendations for control of tarnished plant bugs include acephate, dicrotophos, imidacloprid, thiamethoxam, and sulfoxaflor. The objective of this research was to determine the impact of water hardness and pH on commonly used insecticides for tarnished plant control in cotton.

Materials and Methods

Across all trials water was mixed with magnesium chloride to adjust water hardness or sodium hydroxide to adjust pH. Water was obtained from a Columbia Water Technology reverse osmosis filtration system with a hardness of 11 ppm and pH of 6.4, respectively. A 26.5 liter Aqua-Tainer was filled with filtered water then magnesium chloride was added to increase the water hardness. Magnesium chloride was added until the hardness was near 430ppm, the highest hardness needed for treatments. This was repeated to produce the water hardness needed for the other treatment. Approximately 8.8 liters of water at 430 ppm was drained and 8.8 liters of filtered water was added to the container to get to 178 ppm. To produce the desired pH levels a 26.5 liter Aqua-Tainer was filled with filtered water then sodium hydroxide was added to increase the pH. Sodium hydroxide was added until the pH was around 9.1, the highest pH needed for treatments. This was repeated to produce the water pH needed for the other treatment. Approximately, 8.8 liters of water at 9.1 was drained and 8.8 liters of filtered water was added to the container to get to 8.3.

The tested water hardness and pH levels were decided upon from water samples that were collected from multiple grower farms across Arkansas. Arkansas water used in spray mixes has a wide range of hardness and pH. Samples from 10 farming locations that are commonly used for pesticide application were collected in the summer of 2021. Water samples were sent to Waypoint Analytical, Inc. and analyzed. All pH water samples used in leaf dip assays and field

tests were tested using a pH and temperature meter (MW102, Milwaukee Instruments, Inc., Rocky Mount, NC) and calibrated before each use. All water hardness/total dissolved solid (TDS) measurements were tested using a multifunction water quality tester (ORAPXI) and calibrated before each use.

Leaf Dip Assays

Cotton leaf dip assays were conducted at the University of Arkansas Lonoke Research and Extension Center, Lonoke, AR in 2022. The assays consisted of 13 treatments each including a nontreated control. Sulfoxaflor (Transform WG, Dow AgroSciences, Indianapolis, IN) 52 g ai/ha , acephate (Orthene 90 SP, Amvac Chemical Corporation, Los Angeles, CA) 819.2 g ai/ha, thiamethoxam (Centric 40WG, Syngenta Crop Protection, Greensboro, NC) 55.99 g ai/ha , and dicrotophos (Bidrin® 8E, Amvac Chemical Corporation, Newport Beach, CA) 56.7 g ai/ ha, were each mixed in three water samples with hardness levels of 10.9, 178, and 430 ppm, to determine the impact water hardness had on efficacy. The same insecticides and rates were also mixed in water samples with either a pH of 6.47, 8.03, or 9.27 to determine the impact of pH on efficacy. Cotton leaf discs with a diameter of 12.7 mm were dipped for 10 seconds in each treatment. The leaves were allowed to dry and placed in 100 mm petri dishes with a damp cotton pad and a tarnished plant bug adult. Mortality ratings were taken 48 h after infestation, and tarnished plant bugs were considered dead if the specimens were not able to turn themselves over after being turned on their back, they were considered dead. Tarnished plant bugs were collected using sweep nets from weedy host in Marianna, AR. Percent mortality was determined by dividing the total number of dead tarnished plant bugs by the total tarnished plant bugs then multiplied by 100. This was replicated 3 times spatially.

Field trials

All field experiments were conducted in Marianna, AR at the Lon Mann Cotton Research Station in 2021 and 2022. Plot size was 3.8 m (4 rows) by 12.2 m. Trials were arranged as randomized complete block design with 4 replications. All treatments were mixed and allowed to rest for 3 hours prior to application. Applications were made using a Bowman Mudmaster at 93.5 L/ha at 276 kPa using a TXVS-6 hollow cone nozzle. Plots were sampled 3 and 7 days after applications using a shake sheet (76 cm x 91 cm), conducting two shakes per plot sampled from rows 2 and 3. Tarnished plant bug nymphs and adults were counted. Data analyzed using (JMP®, Version 16.2, SAS Institute Inc., Cary, NC).

Two cotton field trials were conducted that consisted of 13 treatments each including an nontreated control. Sulfoxaflor (Transform WG, Dow AgroSciences, Indianapolis, IN) 52 g ai/ha , acephate (Orthene 90 SP, Amvac Chemical Corporation, Los Angeles, CA) 819.2 g ai/ha, thiamethoxam (Centric 40WG, Syngenta Crop Protection, Greensboro, NC) 55.99 g ai/ha , and dicrotophos (Bidrin® 8E, Amvac Chemical Corporation, Newport Beach, CA) 56.7 g ai/ ha, were each mixed in three water samples with hardness levels of 10.9, 178, and 430 ppm, to determine the impact water hardness has on efficacy. The same insecticides and rates were also mixed in water samples with r a pH of 6.47, 8.03, and 9.27 to determine the impact of pH on efficacy. Each trial had 4 replications spatially and was repeated 3 times temporally.

Two field trials were conducted with water conditioners on hard water and high pH. These trials consisted of 7 treatments. Dicrotophos along with AMS, Quest, Smoke, Diversify, and HM1895 were combined with water with a TDS of 430 ppm and pH of 9.27, with one treatment of 6.47 and an untreated check. Each experiment had 4 replications and was repeated 2 times. Data analyzed using (JMP®, Version 16.2, SAS Institute Inc., Cary, NC).

Water conditioner field trials were conducted with 5 water conditioners that were combined with dicrotophos (Bidrin® 8E, Amvac Chemical Corporation, Newport Beach, CA) 56.7 g ai/ ha and water samples with high hardness (430 ppm), high pH (9.3), and a standard water (11ppm, 6.5). AMS, Quest (Helena Agri-Enterprises, Collierville, TN), Smoke (Helena Agri-Enterprises, Collierville, TN), Diversify (Helena Agri-Enterprises, Collierville, TN), and HM1895 (Helena Agri-Enterprises, Collierville, TN) were the water conditioners used in this trial (Table 2). Each experiment had 4 replications and was repeated 2 times.

All data were analyzed using JMP 16 (1989-2007). Data for the leaf dip and field experiments experiment were analyzed using regression analysis and were considered significant if slopes had a $P < 0.05$. Run and replication were random factors.

Results

Leaf Dip Assay

In the water hardness leaf dip assay acephate was the only product tested that decreased in efficacy as water hardness increased ($F=32.4$, $df=1, 6$, $P<.01$; Figure 2.a). Efficacy was not impacted by water hardness for any other tested products, dicrotophos ($F=0.1$, $df=1,6$, $p=.7$), thiamethoxam ($F=0.4$, $df=1,6$, $P=0.5$), or sulfoxaflor ($F=0.9$, $df=1,7$, $P= 0.4$). Similarly, no impact on efficacy was observed for any insecticide tested for differing levels of pH acephate ($F=2.2$, $df=1,6$, $P=0.2$), dicrotophos ($F=0.04$, $df=1,6$, $P=0.8$), thiamethoxam ($F=0.2$, $df=1,6$, $P=0.6$), and sulfoxaflor ($F=0.03$, $df=1,6$, $P=0.9$) (Figure 2.b).

Field Trials

In the water hardness field trials, dicrotophos was the only product tested that increased in efficacy as water hardness increased at 4 days after application ($F=5.2$, $df=1,27.8$, $P<.05$;

Figure 3.a). For acephate (F=2.0, df=1,29, P=0.2), thiamethoxam (F=0.6, df=1,29.3, P=0.5), and sulfoxaflor (F=0.1, df=1,29.1, P=0.7), efficacy was not impacted by water hardness 4 days after application. Efficacy was not impacted for any product at 7 days after application, acephate (F=1.3, df=1,28.1, P=0.3), dicrotophos (F=2.9, df=1,29, P=0.1), thiamethoxam (F=0.5, df=1,29, P=0.5), sulfoxaflor (F=1.2, df=1,29, P=0.3) (Figure 3.b).

In the field pH trials none of the products tested, acephate (F=0.1, df=1,40.8, P=0.7), dicrotophos (F=0.5, df=1, 40.6, P=0.5), thiamethoxam (F=0.2, df=1,41.5, P=0.6), and sulfoxaflor (F=.03, df=1, 41.2, P=0.6) were impacted by pH 4 days after application. The treatments acephate (F=0.5, df=1, 41.1, P=0.5), dicrotophos (F=0.01, df=1,41.1, P=0.9), thiamethoxam (F=0.0, df=1,40.1, P=1.0), and sulfoxaflor (F=3.8, df=1, 35.5, P=0.1) were also not impacted by pH 7 after application. (Figure 3.d).

The tested products used in the hardness water conditioner trials provided no significant difference in tarnished plant bug populations 3 days after application (F=2.2, df=1,6, P=0.1; Table 3). At 7 days after application Diversify provided better control than the water solution from the standard water (F=2.5, df =1,6, P=0.1; Table 3). All other treatments: Quest, hard water (430 ppm), smoke, HM1895, and AMS, provided the same control at 7 days after application.

The water conditioner pH trial, there were no differences among treatments at 3 days after application (F=0.8, df=1,6, P=0.6; Table 3). At 7 days after HM1895 and 9.3 treatments had better control than Smoke (F=1.2, df=1,6, P=0.3; Table 3).

Discussion

Most insecticides are required to be dissolved or suspended in water (Schilder, 2008). Generally, applicators tend to assume if water looks clean, then it is suitable for pesticide

applications. However, this is not always true; water hardness and pH have the potential to affect some pesticides.

In the field trials, water hardness had no impact on sulfoxaflor, acephate, or thiamethoxam. Devkota and Johnson found that as water hardness increases to 800 mg L^{-1}, approximately 800ppm, the control of dicamba and glyphosate decreases (Devkota & Johnson, 2020). The current studies did not reach this level of water hardness. Future research on insecticides at higher rates of hardness is needed. It was also observed that pH had no effects on sulfoxaflor, acephate, thiamethoxam, and dicrotophos efficacy. Devkota and Johnson observed that a carrier water with a pH of 4 had increased efficacy for dicamba and glyphosate for common ragweed, *Ambrosia artemisiifolia,* and horseweed, *Erigeron canadensis*, than water with a pH of 9. The result from the current studies is comparable to previous work on fungicides (Stacy, 2018). In these studies, common fungicides formulation has no significant reduction in efficacy at the pH's of 5, 7, and 9 in most cases. These cases both show different results. Water quality can impact different pesticides in different ways.

It is important for growers to test their water that is used for spray solutions. The water tests need to be conducted at least once a year before spraying (Whitford et al., 2009). This helps determine what water conditioners are needed or not needed. This can help reduce extra costs by using unnecessary products and help determine when to use them. Based on the data of these trials there is potential for acephate to have some decreased efficacy. Sulfoxaflor, thiamethoxam, and dicrotophos showed no differences in efficacy as the water hardness increases or decreases, but the potential for decreased efficacy could still be present if the water has greater hardness than what was tested here.

Tarnished plant bugs are a major pest in cotton in Arkansas and the mid-south. Resistance to many chemistries used to control tarnished plant bugs have been observed. It is a possibility that resistance to pyrethroids, or other insecticides might not be the only issue. Pyrethroids has been documented and observed since at least 1994 (Parys et al., 2018). These issues that are seen in pyrethroids and in other insecticides might not only come down to resistance, but bad coverage, weather, or other observed issues. Water quality has become a prominent issue across the United States in many pesticides. Future research and this research are an important discovery in helping our growers. Research can help determine when a water conditioner is needed, what pesticides can be affected by water with high pH or hard water, and in finding out the issue of the decline in efficacy of many insecticides.

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Table 1. Water Hardness and pH levels collected and tested throughout Arkansas.

Locations (County)	Hardness (ppm)	Hardness	pH
Prairie, Hazen	159	Hard	8.16
Greene	10.9	Soft	7.65
Prairie, Des Arc	182	Very Hard	7.92
White	33.9	Slightly Hard	7.16
White	193	Very Hard	7.72
Poinsett	233	Very Hard	8.34
Drew/Desha	2.41	Soft	8.11
Conway	430	Very Hard	7.22
Arkansas	359	Very Hard	7.76
Lonoke	178	Very Hard	7.38

Table 2. The description of products used in the surfactant cotton field trials with their rates.

Product	Description	Rate
Ammonium Sulfate	Ammonia based, mild acidifier, can bind with hard water cations, can be highly corrosive	9#/100 (read on pesticide labels)
Quest	Ammonia based, strong acidifier (minimum pH 3-3.5), will bind with hard water cations, low corrosivity, buffered ammonium system with sequestrants and corrosion inhibitors	0.25% v/v
Smoke	Non-ammonia based, mildly, strong acidifier (minimum pH 4), will bind to hard water cations, non-corrosive, 1-aminomethanamide dihydrogen tetraoxosulfate (AMADS) based buffering system	0.25% v/v
Diversify	Non- ammonia based, mild acidifier (minimum pH 5-5.5), effectively binds with hard water cations, very low corrosion, hydroxypropane tricarboxylates + amino carboxylates-based system	0.25% v/v
HM1895	Non- ammonia based, mildly, strong acidifier (minimum pH 3.5-4), will bind to hard water cations, non-corrosive, AMADS based buffering system	0.25% v/v

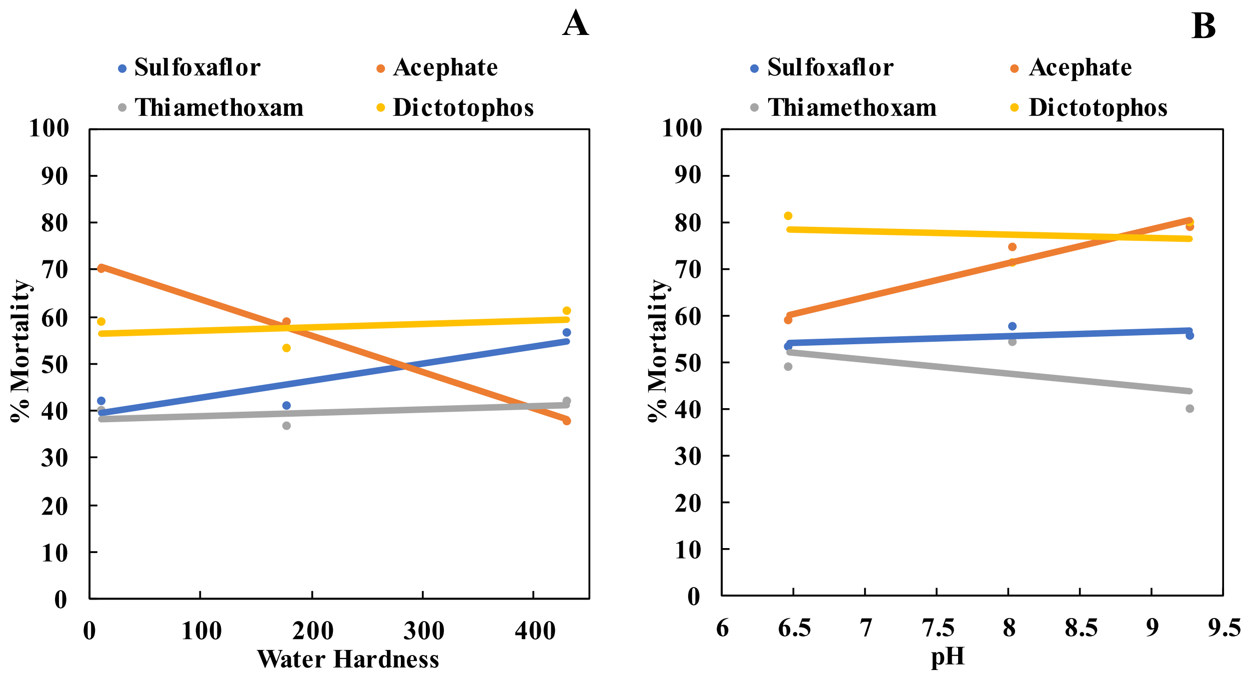

Figure 2. Percent mortality for the effects of water hardness (A), and of pH (B) on insecticide efficacy for tarnished plant bugs 48 hours after treatment for leaf dip assays.

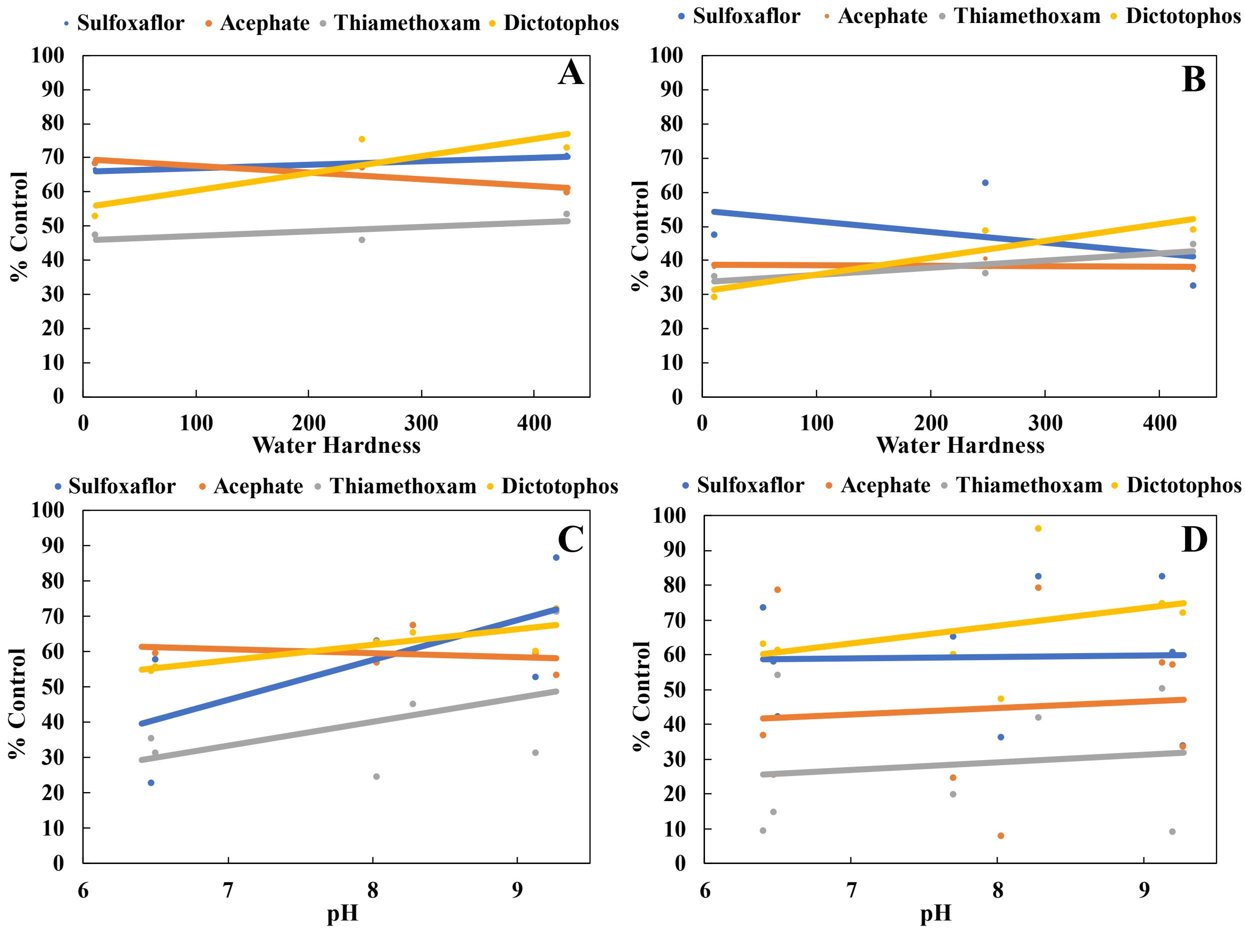

Figure 3. Percent control for the effects of water hardness on cotton insecticides 4 days after application (A) and 7 days after application (B). Percent control for the effects of pH on cotton insecticides 4 days after application (C) and 7 days after application (D).

Table 3. Percent control for the effects of surfactants with Bidrin on hardness and pH 3 and 7 days after application. Treatments with the same lowercase letters are not significantly different according to All pairs, Tukey HSD Test (α=0.05) to separate means.

Treatment	Hardness 3DAA	Hardness 7DAA	pH 3DAA	pH 7DAA
HM1895	78.3	63.7	47.3	78.8
30 ppm	71.2	73.3	71.6	78.2
Quest	62.5	75.0	69.7	76.5
AMS	57.5	61.4	69.6	69.5
Diversify	55.7	81.5	70.3	69.7
Smoke	38.2	72.2	48.4	59.2
Standard	30.7	51.6	72.8	77.5
	(F=2.2, df=6, 17.1, P=0.1)	(F=2.5, df =6, 17, P=0.1)	(F=0.8, df=6, 45, P=0.6)	(F=1.2, df=6, 45, P=0.3)

Chapter IV- Conclusion

The goal of this research was to evaluate the effects of water hardness and pH on corn earworm insecticide efficacy in soybean and tarnished plant bug insecticide efficacy in cotton. The first chapter experiments were conducted to evaluate the effects of water hardness and pH on insecticides used to control corn earworms. Results from leaf dips indicated that chlorantraniliprole efficacy decreased as water hardness and pH increased. The greenhouse study indicated that increasingly hard water reduced the residual control of chlorantraniliprole. In the field experiment Intrepid Edge, Besiege, Vantacor, and Denim were evaluated in soft, hard, and very hard water. There were no differences in any of the tested insecticides efficacy as water hardness increased. This data indicates that the initial control provided by chlorantraniliprole will likely not be impacted by poor water quality, but residual control may be reduced from increasingly poor water.

In the second chapter experiments were conducted to determine the impact of water hardness and pH on commonly used tarnished plant bugs insecticides in cotton. In the water hardness and pH leaf dip assays Transform, Centric, Bidrin, and Acephate efficacy was evaluated in waters of different hardness and pH's. Acephate was the only insecticide that had reduced control as water hardness increased. In the pH leaf dip trial, no differences were observed. In the field trial dicrotophos efficacy increased as water hardness increased, but no other difference was observed at 4 and 7 days after application.

The third objective in this study was to determine how water conditioners affected dicrotophos when mixed with very hard waters and water with a pH of 9.27. Water conditioners did not impact insecticide efficacy at 3 days after treatment, but 7 days after treatment, diversify with dicrotophos had better efficacy than the greenhouse water alone.

This research showed evidence of water hardness and pH having a negative impact on soybean and cotton insecticides. More research needs to be conducted to further our knowledge of how exactly they are affected, and more insecticides need to be tested to determine their impacts.

APPENDIX A

WATER SAMPLE FROM LONOKE RESEARCH AND EXTENSION CENTER

ENTOMOLOGY GREENHOUSE ANALYIZED BY WAYPOINT ANALYTICAL, INC.

Appendix Table 1. Water Sample Analysis from Waypoint Analytical, Inc. for the Standard water used in all trials.

Cations	**mg/L**	**meq/L**
Sodium (Na)	34.7	1.51
Calcium (Ca)	0.123	0.01
Magnesium (Mg)	0.256	0.02
Potassium (K)	0.100	0.00
Ammonium NH4	1	0.05
Ammonium NH4 -N	0.664	
Sum of Cations	1.59	
Anions	**mg/L**	**meq/L**
Chloride (Cl)	13.0	0.37
Sulfate (SO4)	0.300	0.01
Sulfate (S)	0	
Bicarbonate (HCO3)	66.5	1.09
Carbonate (CO3)	0	0.00
Nitrate (NO3)	1	0.02
Nitrate (NO3 – N)	0.216	
Phosphate (PO4)	0.385	0.01
Phosphate (P)	0.125	
Sum of Anions	1.50	
Hydrogen Ion Activity (pH)	6.9	
Equilibrium Reaction (pHc)	8.92	
Electrical Conductivity (ECw)	0.142 dS/m	
Total Dissolved Solids (TDS)	90.9 ppm	
Adj Na Adsorption Ratio (SARadj)	7.75	
Sodium Adsorption Ratio (SAR)	12.33	
Hardness	1.36	
Copper (Cu)	0.008 mg/L	
Zinc (Zn)	0.050 mg/L	
Manganese (Mn)	0.010 mg/L	
Iron (Fe)	0.100 mg/L	
Boron (B)	0.053 mg/L	
Fluoride (F)		
Aluminum (Al)	0.100 mg/L	
Molybdenum (Mo)	0.010 mg/L	