INFLUENCE OF HIGH SURFACTANT OIL CONCENTRATE ADJUVANTS AND OIL RATE RESPONSE TO SPRAY VOLUME ON HERBICIDE EFFICACY

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ABSTRACT

There is limited research on High surfactant oil concentrates (HSOC), so studies were conducted for their evaluation. Multiple MSO-based (HSMOC) and POC-based (HSPOC) HSOCs were tested with glyphosate plus dicamba or glyphosate plus tembotrione. The addition of HSMOCs provided greater indicator species control HSPOCs when added to either herbicide tank-mix. When multiple experimental oil to surfactant ratios were added to glyphosate plus dicamba or glyphosate plus tembotrione, there were no differences among experimental HSOC ratios when added to either tank-mix by 28 days after application. Since oil adjuvant rates can be based on either treated area or percent of spray solution, oils were added to either dicamba or tembotrione to evaluate rate methods. There were few differences in species control when oils were added to dicamba. Quinoa and amaranth control were more consistent when using the percent volume-based rates with tembotrione.

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RATIONALE/SIGNIFICANCE

Herbicide spray applications commonly contain a tank-mix of multiple herbicides with adjuvants to improve weed control. Adjuvants, like herbicide active ingredients, have specific effects that can be attributed to their chemical and physical properties. Adjuvants are used to modify herbicidal activity or application characteristics to improve herbicide performance (Shaner 2014). For example, utility adjuvants can be used to stabilize herbicide formulations (Hazen 2000), improve the spray application process, and can indirectly influence herbicide efficacy (McMullan 2000). Activator adjuvants increase spray retention on leaf surfaces and absorption into the plant through the leaf cuticle (Anderson 1984; Penner 2000).

Tank-mixing multiple herbicides with glyphosate [N-(phosphonomethyl) glycine] is a common practice due to a rise in glyphosate-resistant weeds and volunteer glyphosate-resistant crops. For instance, tembotrione (2-[2-chloro-4-(methylsulfonyl)-3-[(2,2,2-trifluoroethoxy0 methyl] benzoyl]-1,3-cyclohexanedione) is a common post-emergence tank-mix partner with glyphosate in corn (*Zea mays* L.) applications to control potential glyphosate-resistant weeds such as Palmer amaranth (*Amaranthus palmeri* L.), kochia (*Bassia scoparia* L.), common ragweed (*Ambrosia artemisiifolia* L.), giant ragweed (*Ambrosia trifida* L.), waterhemp (*Amaranthus tuberculatus* L.), goosegrass (*Eleusine indica* L.), and johnsongrass (*Sorghum halepense* L.). (Anonymous 2007). Tembotrione is a lipophilic herbicide that is generally recommended to be paired with an oil adjuvant. Zollinger and Reis (2007) reported weed control increased by 54 percentage points when a high surfactant oil concentrate (HSOC) adjuvant at 0.5% v v^{-1} was added to tembotrione at 31 g ha^{-1} plus 28% urea ammonium nitrate (UAN) at 2.5% w v^{-1} when compared to tembotrione plus 28% UAN. Likewise, weed control was increased by 43 and 36 percentage points when a methylated seed oil (MSO) adjuvant at 1% v v^{-1} was added and when a petroleum oil concentrate (POC) adjuvant at 1% v v^{-1} was added to tembotrione plus 28% UAN, respectively. Adding a nonionic surfactant (NIS) adjuvant at 0.25% v v^{-1} to tembotrione plus 28% UAN also increased weed efficacy but less that the addition of an HSOC, MSO, or POC adjuvant. Conversely, glyphosate is a hydrophilic herbicide that is antagonized by oil adjuvants (Nalewaja and Matysiak 1993). Wheat injury was reduced by 32 to 40 percentage points when glyphosate applied at 150 g ha^{-1} was tank-mixed with oil adjuvants at 2.3 L ha^{-1} compared to when no adjuvant was added to glyphosate. However, glyphosate weed control can be optimized by surfactant adjuvants. The addition of NIS adjuvants at 0.5% v v^{-1} to multiple rates of glyphosate increased weed efficacy by 9 to 22 percentage points compared to glyphosate alone (Singh and Singh 2005).

Dicamba (3,6-dichloro-2-methoxybenzoic acid) was historically used primarily in rangeland and cereal crops. However, with the release of dicamba and glyphosate-resistant soybean (*Glycine max* L.) and cotton (*Gossypium hirsutum* L.), dicamba is now commonly tank-mixed with glyphosate to control many glyphosate-resistant weeds such as Palmer amaranth, kochia, common ragweed, giant ragweed, waterhemp, and horseweed (*Erigeron canadensis* L.) (Anonymous 1987). Dicamba is a hydrophilic herbicide that can be enhanced by both surfactant and oil adjuvants. Variability in herbicide efficacy with the addition of adjuvants may be due to oil type, emulsifier type, ratio of oil to emulsifier, and rate used.

Since herbicide tank-mixing is getting more complex with the increasingly problematic rise of glyphosate-resistant weeds, additional research can identify adjuvants that can be used with these complex tank-mixes to increase the efficacy of multiple herbicides. Additionally, herbicide labels recommend rate ranges of multiple adjuvant options that can be paired with the herbicide. Often, these rates differ from publications created by land-grant universities. For example, the Laudis label (Anonymous 2007) recommends oil adjuvants be added to tembotrione at rates based on percent of total water volume while the North Dakota State University Weed Control Guide (Zollinger et al. 2017) recommends oil adjuvants be added to tembotrione at rates based on area covered. The intended research can help determine adjuvants to use in complex tank-mixes such as glyphosate plus dicamba or glyphosate plus tembotrione and the optimum oil adjuvant rates to increase efficacy.

CHAPTER 1. REVIEW OF LITERATURE

Adjuvants

Products have been used to increase pesticide activity in agriculture for hundreds of years. In the 18th and 19th centuries people applied additives such as pitch, resins, flour, molasses, sugar with lime, sulfur, copper, and arsenates to improve "sticking" and biological performance of these mixtures and increase pesticide activity (Green and Beestman 2007). Fundamentally, the goal of using adjuvants has stayed the same. Today, agricultural adjuvants for weed control are defined as "any substance added to an herbicide formulation or to a spray solution to modify herbicidal activity or application characteristics to improve herbicide performance" (Shaner 2014). There are two categories of adjuvants that are characterized according to their function: utility and activator adjuvants (Hazen 2000).

Utility adjuvants are tank-mixed in spray solution to improve the spray application process and work on the properties of the spray solution to improve compatibility, but do not directly influence herbicide efficacy (McMullan 2000). However, utility adjuvants can indirectly affect herbicide efficacy by reducing or minimizing any negative effects on the application. Utility adjuvants contain subcategories including compatibility agents, deposition agents, drift control agents, defoaming agents, water conditioning agents, acidifying agents, buffering agents, and colorants.

Activator adjuvants directly increase herbicide efficacy once a spray droplet has been deposited on the target surface. Activator adjuvants aid post-emergence herbicide efficacy by increasing spray retention on leaf surfaces and absorption into the plant through the leaf cuticle (Anderson 1984; Penner 2000). Increased retention is achieved by reducing the surface tension of the spray droplet to improve contact area while increased absorption is achieved by solubilizing the leaf cuticle (Penner 2000). Additionally, activator adjuvants can provide emulsifier action, decrease droplet drying, and modify spray deposition on plant foliage. Activator adjuvants contain subcategories including surfactants, oils, and fertilizers (Hazen 2000).

Each subcategory of activator adjuvant has a purpose and affects herbicide efficacy differently depending on the target plant species and herbicide selection (Zollinger 2000). Therefore, it is unlikely one activator adjuvant can be used universally with all herbicides, weed species, and environmental conditions. Results can vary when comparing specific adjuvants, even within subcategories such as surfactant or oil adjuvants (Zollinger 2014).

Surfactant Adjuvants

Surfactant adjuvants are the most commonly used subcategory of activator adjuvant for post-emergence herbicides (Miller and Westra 1996). There are many types of surfactant adjuvants used in agriculture including nonionic, cationic, anionic, or amphoteric that are used either alone or in combination (Behrens 1964). Nonionic surfactant (NIS) adjuvants are the most widely used, although the blending of NIS adjuvants with other types is becoming more popular. The two primary functions of all surfactant adjuvants are altering spreading and wetting on leaf surfaces and emulsifying and dispersing oil-soluble molecules in aqueous solution.

Surfactant adjuvants improve herbicide efficacy through altering wetting and spreading characteristics of droplets on leaf surfaces by reducing surface tension which allows a droplet to have a lower contact angle by flattening on a leaf surface (Hazen 2000). Surface tension is an inwardly directed force within an aqueous droplet that causes it to form a relatively spherical shape. A spherical droplet tends to prevent adhesion to a hydrophobic surface such as a leaf surface. Reduced surface tension and droplet contact angle results in better retention on the leaf surface. As surface tension and droplet contact angle decreases, spray droplet retention and absorption of herbicide active ingredient increases, which results in increased weed control (Bruns and Nalewaja 1998).

Surfactant adjuvants also emulsify and disperse oil-soluble molecules in aqueous solutions by reducing the surface tension between oil and aqueous phases (Manthey et al. 1989b). Certain surfactant concentrations need to be met to effectively emulsify oil molecules in aqueous solution. To effectively emulsify oil molecules in aqueous solution, surfactant concentration needs to reach the critical micelle concentration (CMC). The CMC is the point of surfactant concentration at which micelles form and all additional added surfactants go to micelles. Micelles are an aggregate of molecules in a colloidal solution. When surfactant concentration is above the CMC the solubility is exceeded in the aqueous phase and micelles are formed (Becher 1973). The formation of micelles aid in emulsifying oil herbicides or adjuvants into aqueous solution. Surfactant adjuvants are made of a lipophilic moiety and a hydrophilic moiety, which affects lipid and water solubility properties (Manthey et al. 1997). Surfactant adjuvants aggregate with the polar, hydrophilic moiety of the molecule oriented out-ward toward the aqueous solution and the non-polar, lipophilic moiety oriented in-ward toward the oil (Becher 1973).

The relationship between the hydrophilic moiety and lipophilic moiety of a surfactant adjuvant is expressed using hydrophilic-lipophilic balance (HLB). The HLB of a surfactant adjuvant is important for predicting droplet spread, surfactant adjuvant phytotoxicity (Manthey et al. 1996), and improved herbicide efficacy (Manthey et al. 1995). However, the HLB required for maximum enhancement of herbicide efficacy varies with herbicide and plant species. The HLB is given a numerical range from 1 to 20 (Hess and Foy 2000). Surfactant adjuvants with a high HLB range of 11 to 20 generally work best with hydrophilic herbicides while those with a low HLB range of 1 to 10 generally work best with lipophilic herbicides (Miller and Westra 1996; Hess and Foy 2000). Surfactant adjuvants with higher HLB values are speculated to aid hydrophilic herbicide absorption by increasing the hydration of the cuticle which increases rate of diffusion (Hess and Foy 2000). Likewise, surfactant adjuvants with lower HLB values are speculated to aid lipophilic herbicide absorption through the leaf cuticle by increasing the fluidity of the cuticular wax which increases rate of diffusion. Surfactant adjuvants with lower HLB values use a similar mechanism of action as oil adjuvants.

Oil Adjuvants

Oil adjuvants are a widely used subcategory of activator adjuvant for post-emergence herbicides. The two main types of oil adjuvants are POC and seed oil (SO) based adjuvants. POC and SO adjuvants have similar physical characteristics, but greatly differ in fatty acid composition, iodine number, and present usage (Robinson and Nelson 1975).

POC adjuvants are the oldest penetration products and are derived from paraffin crude oil (Manthey et al. 1989a). Original POC adjuvants were typically comprised of 98-99% paraffin oil and 1-2% surfactant. However, Wilson and Ilnicki (1968) reported increasing surfactant concentration to 15-20% in POC adjuvants resulted in equal performance at lower use rates. Oil adjuvants must contain surfactant to help emulsify and disperse oil-soluble molecules in aqueous solution to ensure even distribution of herbicides and oils in the spray droplet (Manthey et al. 1989b). Different surfactants may be required to help emulsify specific oils in aqueous solution depending upon the oil source and refinement (Miller and Westra 1996). PO adjuvants with a surfactant concentration of 15-20% are called POC adjuvants (ASTM

2016). POC, commonly referred to as crop oil concentrate adjuvants, are the most common type of petroleum-based oil adjuvants on the market today.

SO adjuvants were created as POC adjuvant substitutes (McMullan 1993) because they exhibit very low toxicity and are considered renewable resources (Robinson and Nelson 1975). In some instances, SO adjuvants were as effective as POC adjuvants. Robinson and Nelson (1975) reported SO adjuvant at 2.3 L ha^{-1} enhanced atrazine at 1.68 kg ha^{-1} similarly to POC adjuvant at 2.3 or 9.4 L ha^{-1} on multiple weeds. Likewise, trans-esterified oils derived from seed oils, commonly referred to as MSO adjuvants, have also been used as POC adjuvant substitutes. MSO adjuvants are produced by reacting fatty acids from corn, soybean, sunflower, or canola seed oils with an alcohol to form esters. Methyl or ethyl esters produced in this reaction are combined with surfactant adjuvants to form an esterified seed oil (Miller and Westra 1996). In many cases, MSO adjuvants increase herbicide activity on weeds more than POC, SO, and other adjuvants. Nalewaja et al. (1995) reported oil adjuvants enhanced nicosulfuron control of either yellow foxtail or large crabgrass control; however, methylated canola oil enhanced nicosulfuron the most, followed by canola-based SO, and POC.

All oil adjuvants are penetration agents that assist herbicide movement from the leaf surface through natural cuticular barriers to increase herbicide concentration in the plant (Hazen 2000). Oils soften or dissolve cuticular barriers allowing diffusion of herbicides to less lipophilic structures beneath (Manthey and Nalewaja 1992). MSO adjuvants increase post-emergence herbicide absorption more than POC adjuvants because they are more effective at dissolving the leaf cuticle (McMullan 1993). Nalewaja et al. (1986) reported ^{14}C-fluazifop and ^{14}C-sethoxydim absorption in oats increased with the addition of methylated sunflower oil by 39 and 35 percentage points, respectively, compared to the addition of POC which increased absorption by 33 and 20 percentage points, respectively. In field trials, Nalewaja et al. (1986) also reported oat and wheat control with fluazifop and sethoxydim increased with the addition of methylated sunflower oil by 25 and 24 percentage points, respectively, compared to the addition of POC which increased control 19 and 19 percentage points, respectively. The oil type, specific oil within a type, surfactant type, and amount of surfactant all influence the effectiveness of an oil adjuvant (Zollinger 2014).

High Surfactant Oil Concentrate Adjuvants

Hydrophilic and lipophilic herbicides are often tank-mixed. Hydrophilic herbicides rely on surfactants for optimum weed control while lipophilic herbicides require oil-type adjuvants for optimum weed control (Zollinger 2009). HSOC adjuvants were developed to increase weed efficacy with lipophilic herbicide without antagonizing hydrophilic herbicides in a tank-mix (Zollinger 2014). HSOC adjuvants are at least 50% oil, POC- or MSO-based, 25 to 50% surfactant, and usually applied at half the rate of a POC or MSO adjuvant (ASTM 2016). Wide variability has been observed among HSPOC adjuvants with many performing no different than common POC adjuvants. Conversely, HSMOC adjuvants typically improve weed control with both glyphosate and lipophilic herbicides more than HSPOC adjuvants (Zollinger 2014).

Glyphosate

The herbicidal activity of glyphosate was discovered by Dr. John Franz in 1970 and was first commercially registered for use in 1974 (Benbrook 2016). Glyphosate is a foliar-applied herbicide that rapidly translocates from treated foliage to metabolically active regions of roots, rhizomes, and apical meristems in plants (Franz 1985). Due to the non-selective activity of glyphosate, initial usage was limited to direct-target or burndown applications. However, genetically engineered glyphosate-resistant crops were introduced in 1996 which allowed glyphosate to be utilized as a broadcast, post-emergence herbicide to control a variety of weeds without harming the crops (Benbrook 2016). Glyphosate is currently the most widely used herbicide on the market and is used in a variety of applications including pre-plant, post-emergence, pre-harvest desiccation, and post-harvest applications. The use of glyphosate in crops has led to improved yields, increased conservation tillage systems, and higher-quality agricultural products (Gianessi and Sankula 2004).

The site of action of glyphosate is exclusive to the shikimic acid pathway that plants possess (Cole 1985). Glyphosate inhibits 5-enolpyruvylshikimate-3-phosphate synthase (EPSPS), which produces 5-enolpyruvylshikimate-3-phosphate (EPSP) from shikimate-3-phosphate and phosphoenolpyruvate in the shikimic acid pathway (Shaner 2014). The inhibition of EPSPS increases shikimate concentrations and prevents production of essential aromatic amino acids tryptophan, tyrosine, and phenylalanine.

Glyphosate is a hydrophilic herbicide with a log K_{ow} of -2.77 to -3.22. The log K_{ow} is the octanol to water partition coefficient and indicates whether an herbicide is hydrophilic or lipophilic. Any herbicide with a log K_{ow} below 0 is considered hydrophilic while greater than 0 is considered lipophilic. Due to the hydrophilicity of glyphosate, surfactant adjuvants increase phytotoxicity (Singh and Singh 2005; Zollinger 2009). Conversely, POC and MSO adjuvants may antagonize glyphosate phytotoxicity (Nalewaja and Matysiak 1993; Zollinger 2014). Oil adjuvant antagonism has been speculated to be caused by nonpolar materials preventing glyphosate absorption by coating or blending with cuticular waxes which serves as a barrier to absorption of polar glyphosate (Nalewaja and Matysiak 1993).

Glyphosate efficacy is affected by many factors including type of surfactant adjuvant (Kirkwood 1993), application rate (Ambach and Ashford 1982), and quality of carrier water (Nalewaja and Matysiak 1993). Efficacy can also vary by weed species (Flint and Barrett 1989a; Flint and Barrett 1989b). Currently, there are 53 weed species resistant to glyphosate worldwide, including 17 in the United States (Heap 2021). Therefore, developments have been made to create cropping systems with multiple herbicide sites of action other than glyphosate (Behrens et al. 2007). Dicamba- and glyphosate-resistant soybean and cotton (*Gossypium hirsutum* L.) are two examples of multiple herbicide-resistant crops that have introduced a new herbicide site of action into these crops to help control glyphosate-resistant weeds.

Dicamba

The herbicidal activity of dicamba was discovered by Sidney B. Richter in 1958 and was first commercially registered for use in 1967 (Senseman et al. 2007). Dicamba was historically used for foliar-applied, broadleaf weed control before planting (Everitt and Keeling 2007) or in cereal crops such as corn, wheat, and barley. However, with new developments of glyphosate- and dicamba-resistant crops, dicamba can also be utilized post-emergence in soybean and cotton. The addition of dicamba tank-mixed with glyphosate provides another site of action to help control many broadleaf weed species that are resistant to glyphosate including Palmer amaranth, kochia, common ragweed, giant ragweed, waterhemp, and horseweed (Anonymous 1987).

The specific site of action of dicamba is unknown; however, the mode of action of dicamba is known to function as a synthetic auxin that mimics the natural plant hormone indole-3-acetic acid. Dicamba affects cell wall plasticity and nucleic acid metabolism in target weed species (Shaner 2014) which causes unregulated growth (Everitt and Keeling 2007). Visible symptoms of unregulated growth include epinasty, leaf cupping, strapped veins, and calloused leaves or stems (Grossmann 2010).

Dicamba is a hydrophilic herbicide with a log K_{ow} of -0.54. Although dicamba is a hydrophilic herbicide and commonly recommended to be used with surfactant adjuvants, oil adjuvants can also be utilized (Anonymous 1987) since both adjuvants can increase efficacy of dicamba depending on environment. Zollinger et al. (2010) reported 25% greater control of multiple indicator species when an MSO adjuvant was added to dicamba plus diflufenzopyr and ammonium sulfate compared to NIS adjuvant.

Tembotrione

Tembotrione is a common herbicide tank-mixed with glyphosate applied in corn. Hans-Peter Krause et al. created tembotrione in 2001 and it was first commercially sold in 2008. Tembotrione is primarily a post-emergence herbicide that controls numerous broadleaf and grass weed species, including many that are resistant to glyphosate such as Palmer amaranth, kochia, common ragweed, giant ragweed, common waterhemp, and goosegrass. (Anonymous 2007; Hinz et al. 2005).

The mode of action of tembotrione is a pigment inhibitor while the site of action of tembotrione is a *p*-hydroxyphenyl-pyruvatedioxygenase (HPPD) inhibitor (Lee et al. 1997). The HPPD enzyme aids in the formation of α-tocopherol and plastoquinone. α-tocopherol aids in the breakdown of radical singlet oxygen created by ultraviolet light while plastoquinone is an essential cofactor for phytoene desaturase, an enzyme used in the production of carotenoids. With the inhibition of yellow and orange carotenoids, chlorophyll is degraded by radical singlet oxygen. Therefore, inhibition of the HPPD enzyme will cause bleaching (whitening) symptoms of leaf tissue.

Tembotrione is a slightly lipophilic herbicide with a log K_{ow} of 0.08. The use of MSO adjuvant is recommended when tembotrione is applied (Anonymous 2007). The use of NIS or POC adjuvants may result in unacceptable or erratic weed control. However, alternative adjuvants such as HSOC adjuvants may be used with tembotrione to increase weed control. Zollinger and Reis (2007) reported on average all adjuvants enhanced tembotrione at 31 g ha^{-1} 14 days after treatment; however, HSOC adjuvants increased weed efficacy with tembotrione by 54 percentage points, followed by MSO adjuvants by 43 percentage points, POC adjuvants by 36 percentage points, and NIS adjuvants by 23 percentage points.

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CHAPTER 2. FIELD EXPERIMENTS TO EVALUATE EFFICACY OF MULTIPLE HIGH SURFACTANT OIL CONCENTRATES WITH GLYPHOSATE PLUS DICAMBA AND GLYPHOSATE PLUS TEMBOTRIONE

Introduction

Lipophilic herbicides are applied with glyphosate [N-(phosphonomethyl) glycine] to control glyphosate-tolerant or- resistant weeds and volunteer glyphosate-resistant crops. Tembotrione (2-[2-chloro-4-(methylsulfonyl)-3-[(2,2,2-trifluoroethoxy0 methyl] benzoyl]-1,3-cyclohexanedione), a lipophilic herbicide, is a selective herbicide that is optimized with the addition of oil adjuvants while glyphosate, a hydrophilic herbicide, is optimized with the addition of surfactants and may be antagonized by oil adjuvants. Dicamba (3,6-dichloro-2-methoxybenzoic acid) is a hydrophilic herbicide that can be enhanced by both surfactant and oil adjuvants. Variability in herbicide efficacy with the addition of adjuvants may be due to oil type, emulsifier type, ratio of oil and emulsifier, and rate used.

High surfactant oil concentrate (HSOC) adjuvants increase lipophilic herbicide efficacy without antagonizing hydrophilic herbicides, which enables them to satisfy the needs of each (Zollinger 2014). HSOC adjuvants are defined by the American Society for Testing and Materials (ASTM) (2016) as emulsifiable, oil-based products containing 25 to 50% surfactant and a minimum of 50% oil. HSOC adjuvants are either methylated seed oil based which are called high surfactant methylated oil concentrate (HSMOC) adjuvants or they are petroleum oil based which are called high surfactant petroleum oil concentrate (HSPOC) adjuvants. The surfactant portion of an HSOC is used to improve wetting and spreading characteristics on the leaf surface while also emulsifying and dispersing oil-soluble molecules in aqueous solution (Miller and Westra 1996). The oil portion of an HSOC is used as a penetration agent to assist herbicide movement from the leaf surface through the natural cuticular barriers to increase plant uptake (Hazen 2000). Thus, an HSOC adjuvant can increase both hydrophilic and lipophilic herbicide efficacy, but it depends on the properties of the oil, the properties of the surfactant, and the oil to surfactant ratio.

Few field research trials have been published on the addition of HSOC adjuvants. Therefore, research was conducted to screen multiple HSOC adjuvants to quantify their relative effectiveness with tank-mixtures of glyphosate plus dicamba or glyphosate plus tembotrione. The objective of this research was to compare the effects that different HSOC adjuvants have with herbicide tank-mixes on target assay species. This research can be used to assist herbicide applicators make more educated adjuvant selections to fit their complex herbicide tank-mixes.

Materials and Methods

Two field research trials were conducted in both 2015 and 2016 near Hillsboro, North Dakota to evaluate HSOC adjuvant responses when added to either glyphosate plus dicamba in one trial or glyphosate plus tembotrione in another trial. The experimental design for both trials was a randomized complete-block design (RCBD) with three replications. Plot dimensions were 3 by 12 m with four indicator species planted perpendicular to the spray path. Indicator species were grown to an approximate target application height of 30 cm. Treatments (Table 2.1) were applied to the center 2 m of each plot using a CO_2-pressurized backpack sprayer equipped with Turbo TeeJet 11001 nozzles, (TeeJet Spraying Systems. 1801 Business Park Dr. Springfield, IL 62703) delivering 80 L ha^{-1} at 276 kPa and a speed of 5 kph. Adjuvants were applied at full labeled rates, while herbicides (Table 2.2) were applied at sub-lethal rates to avoid 100% control and so treatment weed control differences could be observed.

Indicator species for the glyphosate plus dicamba trial included glyphosate-resistant soybean [*Glycine max* (L.)], grain amaranth [*Amaranthus hypochondriacus* (L.)], quinoa [*Chenopodium quinoa* (Willd.)], and glufosinate-resistant canola [*Brassica napus* (L)]. Indicator species for the glyphosate plus tembotrione trial included glyphosate-resistant soybean, grain amaranth, quinoa, and flax [*Linum usitatissimum* (L.)]. Glyphosate-resistant soybean was used to indicate dicamba and tembotrione efficacy with adjuvant additions. Flax and glufosinate-resistant canola were used to indicate glyphosate efficacy with adjuvant additions since tembotrione has poor control of flax and dicamba has poor control of canola. Amaranth and quinoa were used to mimic the properties of common *Amaranthus* and *Chenopodium* species, respectively, which are both controlled by glyphosate, dicamba, and tembotrione.

Indicator species were evaluated 14 and 28 days after application (DAA). Species control was visibly evaluated on a scale of 0 to 100% with 0% representing no control and 100% representing complete plant death. Average height of each species population was also measured. Height measurements were compared to the nontreated check and converted to percent of control. Data from the glyphosate plus dicamba trial and the glyphosate plus tembotrione trial were subjected to Proc GLM using Statistical Analysis System (SAS) version 9.4 (SAS Institute, Cary, NC) and mean separations were determined using Fisher's protected LSD test at α = 0.05 where appropriate. Linear contrasts were used to separate differences between HSMOC groups and HSPOC groups. Treatment was considered a fixed effect while time (year) was considered a random effect in a repeated measures analysis.

Table 2.1. Each trial included a tank-mix of glyphosate at 473 g ae ha^{-1} with either dicamba at 214 g ae ha^{-1} or tembotrione at 46 g ai ha^{-1} applied with standard NIS, MSO, and POC adjuvants and multiple HSMOC and HSPOC adjuvants. Treatments were applied near Hillsboro, ND in 2015 and 2016.

Treatment	Adjuvant rate
	--ml ha^{-1}--
Nontreated	------
Glyphosate	------
Glyphosate + NIS[a]	795
Glyphosate + MSO[b]	1170
Glyphosate + HSMOC (S)[c]	1170
Herbicide	------
Herbicide + NIS	795
Herbicide + MSO	1170
Herbicide + HSMOC (S)	1170
Glyphosate + herbicide	------
Glyphosate + herbicide + NIS	795
Glyphosate + herbicide +MSO	1170
Glyphosate + herbicide + HSMOC (S)	1170
Glyphosate + herbicide + HSMOC (1)[d]	1170
Glyphosate + herbicide + HSMOC (2)	1170
Glyphosate + herbicide + HSMOC (3)	1170
Glyphosate + herbicide + HSMOC (4)	1170
Glyphosate + herbicide + HSMOC (5)	1170
Glyphosate + herbicide + HSMOC (6)	1170
Glyphosate + herbicide + HSMOC (7)	1170
Glyphosate + herbicide + HSMOC (8)	199
Glyphosate + herbicide + HSMOC (9)	1170
Glyphosate + herbicide + HSMOC (10)	1170
Glyphosate + herbicide + HSMOC (11)	1170
Glyphosate + HSPOC (S)[e]	1170
Herbicide + HSPOC (S)	1170
Glyphosate + herbicide + POC[f]	1170
Glyphosate + herbicide + HSPOC (S)	1170
Glyphosate + herbicide + HSPOC (1)[g]	1170
Glyphosate + herbicide + HSPOC (2)	1170
Glyphosate + herbicide + HSPOC (3)	1170
Glyphosate + herbicide + HSPOC (4)	1170
Glyphosate + herbicide + HSPOC (5)	1170
Glyphosate + herbicide + HSPOC (6)	1170

[a] NIS = nonionic surfactant.
[b] MSO = methylated seed oil.
[c] HSMOC (S) = standard high surfactant methylated oil concentrate.
[d] HSMOC (1-11) = coded high surfactant methylated oil concentrate.
[e] HSPOC (S) = standard high surfactant petroleum oil concentrate.
[f] POC = petroleum oil concentrate.
[g] HSPOC (1-6) = coded high surfactant petroleum oil concentrate.

Table 2.2. Sources of commercial products used in field experiments

Common name	Brand name	Manufacturer	Mode of action	Rate
				g ha^{-1}
Dicamba	Clarity®	BASF Corp.[a]	Synthetic auxin	214
Glyphosate	Touchdown HiTech®	Syngenta Crop Protection, LLC[b]	EPSPS inhibitor	473
Tembotrione	Laudis®	Bayer CropScience LP[c]	HPPD Inhibitor	46

[a] 26 Davis Drive, Research Triangle Park, NC 27709.
[b] P.O. Box 18300, Greensboro, NC 27419-8300.
[c] 800 N. Lindbergh Blvd, St. Louis, MO 63167.

Results and Discussion

Glyphosate Plus Dicamba Trial

The addition of any HSOC adjuvant to glyphosate plus dicamba increased indicator species control (Figure 2.1). The average indicator species control across all HSOC adjuvants was 73%. Most treatments that included an HSMOC adjuvant achieved above average control while most treatments that included an HSPOC adjuvant achieved below average control.

When an HSMOC adjuvant was added to glyphosate plus dicamba, the average indicator species control was 74% (Figure 2.1). This was the same as what the addition of the standard HSMOC [HSMOC (S)] provided. The addition of HSMOC (6) to glyphosate plus dicamba provided the greatest control of indicator species at 80%, while the addition of HSMOC (8) provided the least control of indicator species at 70%. Few differences can be made within the HSMOC adjuvant group due to a difference of 10 percentage points between the greatest control and the least control and an LSD of 7%.

When an HSPOC adjuvant was added to glyphosate plus dicamba, the average indicator species control was 70% (Figure 2.1). This was the same as what the addition of HSPOC (4) provided. The addition of the standard HSPOC [HSPOC (S)] to glyphosate plus dicamba provided the greatest control of indicator species at 73% while the addition of HSPOC (2) and HSPOC (3) provided the least control of indicator species at 68%. There were no differences within the HSPOC group due to a difference of 5% between the most control and the least control and an LSD of 7%.

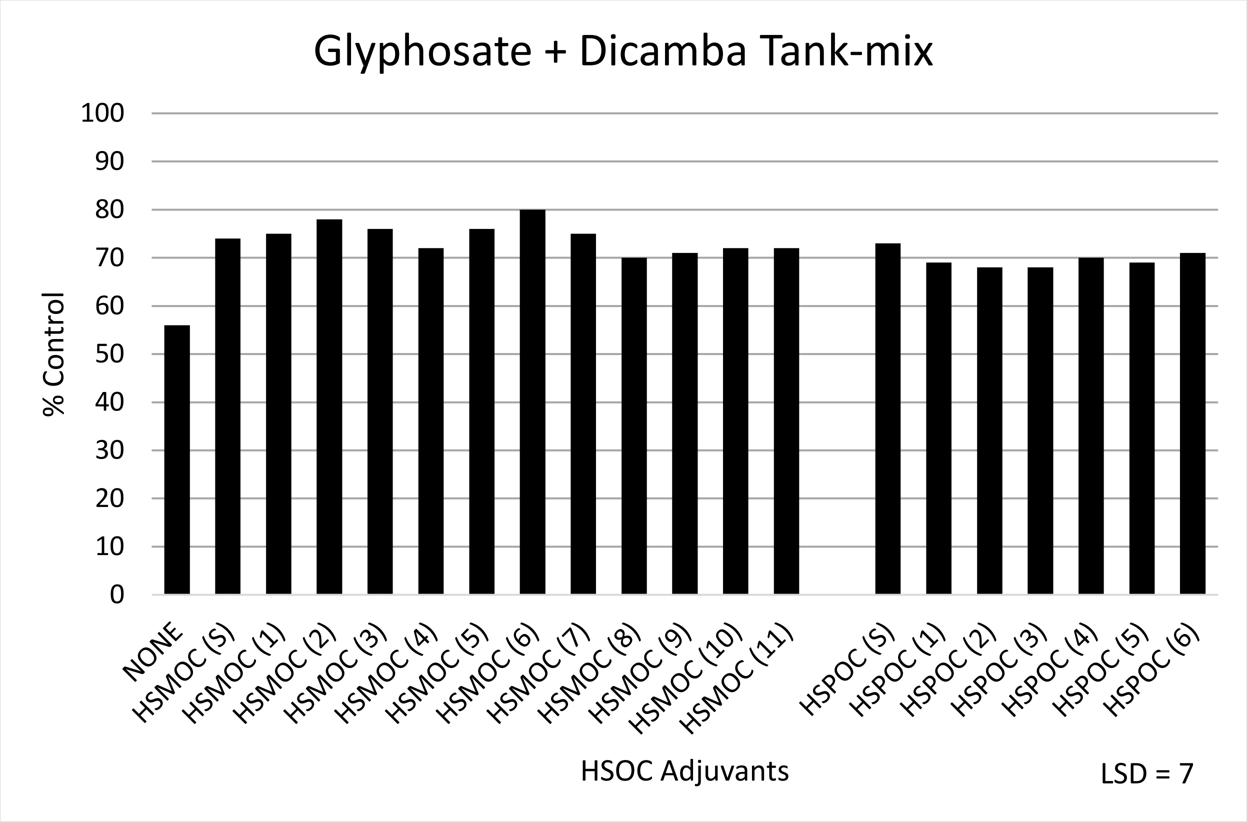

Figure 2.1. Average species control from glyphosate plus dicamba alone, with HSMOC adjuvants, and with HSPOC adjuvants in Hillsboro, ND in 2015 and 2016. NONE = no adjuvant, HSMOC (S) = standard HSMOC, HSMOC (1-11) = coded HSMOCs, HSPOC (S) = standard HSPOC, HSPOC (1-6) = coded HSPOCs.

Glyphosate Plus Tembotrione Trial

The addition of any HSOC adjuvant to glyphosate plus tembotrione increased indicator species control (Figure 2.2). The average indicator species control across all HSOC adjuvants was 60%. Most HSMOC adjuvants added to glyphosate plus tembotrione achieved above average control while most treatments with HSPOC adjuvants achieved below average control.

When HSMOC adjuvants were added to glyphosate plus tembotrione, the average indicator species control was 62% (Figure 2.2). The addition of HSMOC (6) provided the greatest control of indicator species at 69% while, the addition of HSMOC (4) and HSMOC (9) provided the least control of indicator species at 57%. Few differences can be made within the HSMOC adjuvant group due to a difference of 12 percentage points between the greatest indicator species control and the least control and an LSD of 8%.

When HSPOC adjuvants were added to glyphosate plus tembotrione, the average was 56% (Figure 2.2). The addition of the standard HSPOC [HSPOC (S)] provided the greatest control of indicator species at 61% while the addition of HSPOC (5) provided the least control of indicator species at 49%. Few differences can be made within the HSPOC adjuvant group due to a difference of 12 percentage points between the greatest indicator species control and the least control and an LSD of 8%.

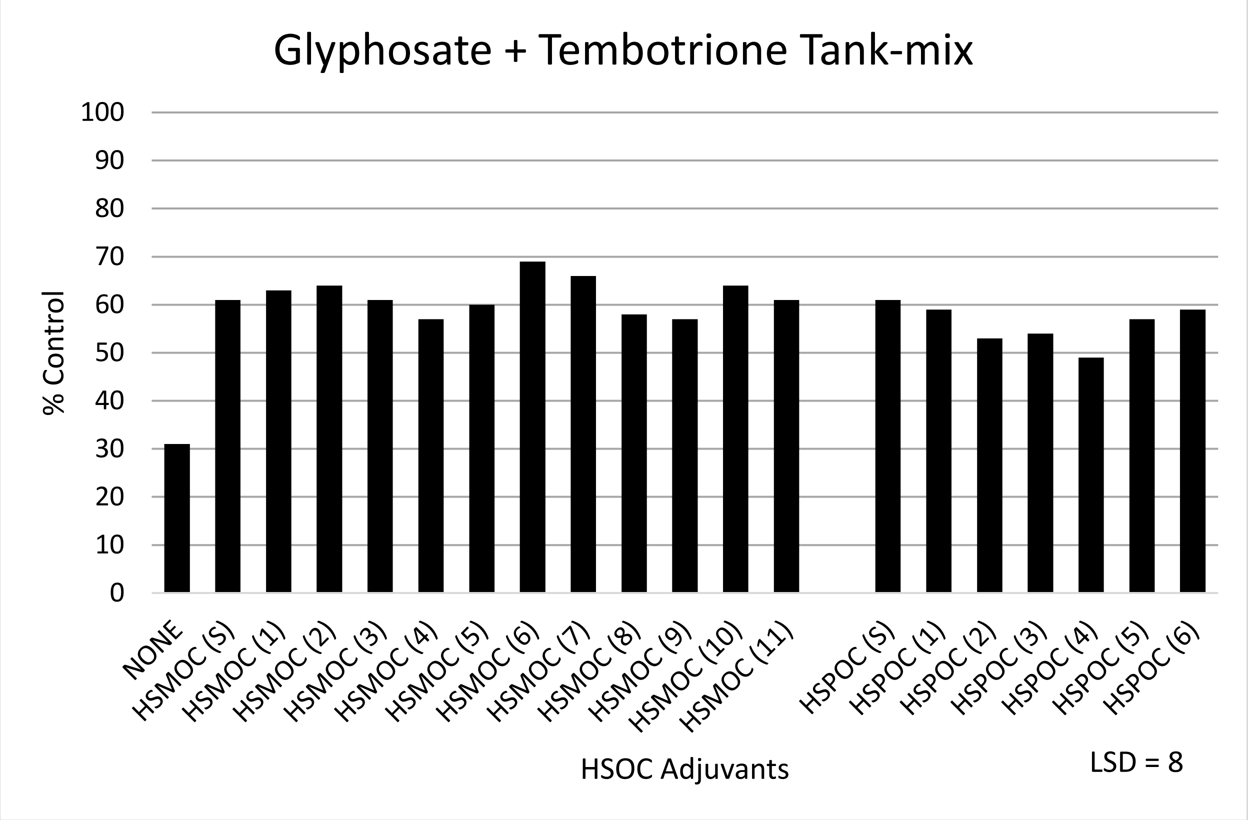

Figure 2.2. Average species control from glyphosate plus tembotrione alone, with HSMOC adjuvants, and with HSPOC adjuvants in Hillsboro, ND in 2015 and 2016. NONE = no adjuvant, HSMOC (S) = standard HSMOC, HSMOC (1-11) = coded HSMOCs, HSPOC (S) = standard HSPOC, HSPOC (1-6) = coded HSPOCs.

The addition of HSOC adjuvants to either glyphosate plus dicamba or glyphosate plus tembotrione increased indicator species control. There were few differences among all HSOC adjuvants and within HSMOC and HSPOC groups. In both trials, the addition of HSMOC adjuvants increased indicator species control more than HSPOC adjuvants. However, the performance of an HSOC varied depending on the herbicide tank-mix.

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CHAPTER 3. GREENHOUSE EXPERIMENTS TO EVALUATE EXPERIMENTAL HSMOC RATIOS WHEN ADDED TO GLYPHOSATE PLUS DICAMBA AND GLYPHOSATE PLUS TEMBOTRIONE

Introduction

The addition of high surfactant oil concentrate (HSOC) adjuvants have been shown to increase lipophilic herbicide efficacy without antagonizing hydrophilic herbicides (Zollinger 2014). HSOC adjuvants are defined by the American Society for Testing and Materials (ASTM) (2016) as emulsifiable, oil-based products containing 25 to 50% surfactant and a minimum of 50% oil. These adjuvants are either methylated seed oil-based (MSO) and referred to as high surfactant methylated oil concentrate (HSMOC) adjuvants or petroleum oil concentrate-based (POC) and referred to as high surfactant petroleum oil concentrate (HSPOC) adjuvants. The surfactant portion of an HSOC is used to improve wetting and spreading characteristics on the leaf surface in addition to emulsifying and dispersing oil-soluble molecules in aqueous solution (Miller and Westra 1996). The oil portion of an HSOC is used as a penetration agent to assist herbicide movement from the leaf surface through natural cuticular barriers to aid in herbicide absorption into the plant (Hazen 2000).

Many commercial HSOC adjuvants have different ratios of oil to surfactant due to the broad parameters set by ASTM. Therefore, the objective of this research was to evaluate multiple experimental methylated seed oil to surfactant ratios tank-mixed with glyphosate plus dicamba in one trial and glyphosate plus tembotrione in another trial to optimize herbicide efficacy. Results from these experiments should help to identify the optimum oil to surfactant ratio of HSOC adjuvants to increase herbicide efficacy on multiple indicator species.

Materials and Methods

Two greenhouse research trials were conducted twice in 2017 to evaluate the effect experimental ratios of MSO to surfactant adjuvants have on two herbicide tank-mixes. Herbicide tank-mixes used in each trial were either glyphosate [N-(phosphonomethyl) glycine] plus dicamba (3,6-dichloro-2-methoxybenzoic acid) or glyphosate plus tembotrione (2-[2-chloro-4-(methylsulfonyl)-3-[(2,2,2-trifluoroethoxy0 methyl] benzoyl]-1,3-cyclohexanedione). Experimental ratios were formulated with the same individual raw oil and surfactant materials to keep ratios consistent. Experimental ratios of methylated seed oil to surfactant included 85:15, 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80, 10:90, and 0:100. A minimum of 15% surfactant was needed to effectively emulsify the methylated seed oil in water. Greenhouse trials were a completely random design (CRD) with four replications. Two indicator species were seeded separately into 10- by 15- by 5-cm pots that contained a peat-based soil media (Sunshine Mix #1, Sun Gro Horticulture 770 Silver Street Agawam, MA 01001). Indicator species were seeded to a depth of 1-cm. Emerged plants were thinned to four plants per pot after reaching a height of 5-cm. Greenhouse temperatures were maintained at 23° C. Natural daylight was supplemented with 450 µE $m^{-2}s^{-1}$ metal halide lamps set to a 16-h photoperiod. Species were watered to field capacity daily. Treatments (Table 3.1) were applied to 10-cm tall indicator species using a chamber sprayer (DeVries Manufacturing. Minneapolis, MN. Serial number SB8-095) equipped with a Turbo TeeJet 11001 nozzle tip (TeeJet Spraying Systems. 1801 Business Park Dr. Springfield, IL 62703), traveling 5.6 km h^{-1}, and delivering 80 L ha^{-1} at 276 kPa. Nozzle traveled 50-cm above plant canopy. Herbicides (Table 3.2) were applied to at sub-lethal rates to avoid 100% plant death so that treatment differences could be observed. Adjuvants (Table 3.3) were applied at full labeled rates. Amaranth [*Amaranthus hypochondriacus* (L.)] and quinoa [*Chenopodium quinoa* (Willd.)] were used as indicator species to mimic the properties of common *Amaranthus* and *Chenopodium* weed species which are both controlled by dicamba, glyphosate, and tembotrione.

Indicator species control was visually evaluated 14 and 28 days after application (DAA) on a scale of 0 to 100% with 0% representing no control and 100% representing complete plant death. Pots were rerandomized biweekly to minimize the effect of microenvironments. Plants were harvested at 28 DAA for dry weight biomass cutting stems at the soil surface, oven drying at 35° C for 72 hours, and weighing. However, data from biomass measurements may have been skewed due to high aphid pressure in the greenhouse. Therefore, visible indicator species control values will be relied upon for more representative data.

Data were subjected to Proc GLM ANOVA using Statistical Analysis System (SAS) version 9.4 (SAS Institute, Cary, NC) and mean separations were determined using Fisher’s protected LSD test at $\alpha = 0.05$ where appropriate. Data in each trial were combined across runs if mean square error values between runs were within a factor of ten. Treatment was considered a fixed effect and time (run) was considered a random effect in a repeated measures analysis.

Table 3.1. Experimental ratio comparison when added to the combination of glyphosate applied at 473 g ae ha^{-1} plus dicamba applied at 214 g ae ha^{-1} or glyphosate applied at 473 g ae ha^{-1} plus tembotrione applied at 46 g ai ha^{-1}. Greenhouse trials were conducted in 2017.

Treatment	Adjuvant rate
	--ml ha^{-1}--
Nontreated	------
Herbicide	------
Herbicide + NIS[a]	795
Herbicide + MSO[b]	1170
Herbicide + HSMOC[c]	1170
Herbicide + 85% MSO : 15% NIS	1170
Herbicide + 80% MSO : 20% NIS	1170
Herbicide + 70% MSO : 30% NIS	1170
Herbicide + 60% MSO : 40% NIS	1170
Herbicide + 50% MSO : 50% NIS	1170
Herbicide + 40% MSO : 60% NIS	1170
Herbicide + 30% MSO : 70% NIS	1170
Herbicide + 20% MSO : 80% NIS	1170
Herbicide + 10% MSO : 90% NIS	1170
Herbicide + 0% MSO : 100% NIS	1170

[a] NIS = nonionic surfactant.
[b] MSO = methylated seed oil.
[c] HSMOC = high surfactant methylated oil concentrate.

Table 3.2. Sources of commercial products used in greenhouse experiments.

Common name	Brand name	Manufacturer	Mode of action	Rate
				g ha^{-1}[d]
Dicamba	Clarity®	BASF Corp.[a]	Synthetic auxin	214
Glyphosate	Touchdown HiTech®	Syngenta Crop Protection, LLC[b]	EPSPS inhibitor	473
Tembotrione	Laudis®	Bayer CropScience LP[c]	HPPD Inhibitor	46

[a] 26 Davis Drive, Research Triangle Park, NC 27709.
[b] P.O. Box 18300, Greensboro, NC 27419-8300.
[c] 800 N. Lindbergh Blvd, St. Louis, MO 63167.
[d] Dicamba and glyphosate are g ae ha^{-1}; tembotrione is g ai ha^{-1}.

Table 3.3. Commercial products used in experiments.

Adjuvant Category	Brand name	Manufacturer
NIS[a]	Activator 90	Loveland Products Inc.[d]
HSMOC[b]	Destiny® HC	Winfield United[e]
MSO[c]	Super Spread® MSO	Wilbur-Ellis®[f]

[a] NIS = non-ionic surfactant.
[b] HSMOC = high surfactant methylated oil concentrate.
[c] MSO = methylated seed oil.
[d] P.O. Box 1286, Greeley, CO 80632-1286.
[e] P.O. Box 64589, St. Paul, MN 55164-0589.
[f] P.O. Box 16458, Fresno, CA 93755.

Results and Discussion

Glyphosate Plus Dicamba Trial

HSOC adjuvants are commonly used in complex tank-mixes that include hydrophilic and lipophilic pesticides because HSOC adjuvants include both oil and surfactant. However, each herbicide included in this trial (glyphosate and dicamba) was hydrophilic which means they may respond more positively to the addition of surfactants rather than oils. Dicamba labels recommend the addition of oil adjuvants to dicamba in certain times in the year or under certain growing conditions, so evaluation of oil adjuvants is warranted (Anonymous 1987).

Visible control of amaranth generally increased from the 14 to the 28 DAA evaluations (Table 3.4). There were few differences in amaranth control across all treatments indicating that the herbicide rate should have been reduced even further. The addition of any adjuvant to glyphosate plus dicamba did not increase amaranth control at either the 14 or the 28 DAA ratings. Since amaranth leaves do not have a thick cuticle or hairs to obstruct droplet deposition and spread, the tank-mix of glyphosate plus dicamba may not have needed an adjuvant to increase control.

In some instances, the addition of an adjuvant may have decreased the efficacy of glyphosate plus dicamba. For example, at 14 DAA glyphosate plus dicamba alone provided 94% control while the addition of the standard MSO provided 88% control (Table 3.4). By 28 DAA; however, there was no difference observed when the standard MSO was added to glyphosate plus dicamba compared to glyphosate plus dicamba alone. The standard MSO consisted of 85% oil and 15% surfactant which was comparable to the experimental 85:15 ratio also included in the experiment. Amaranth control was similar when either the standard MSO or the experimental 85:15 ratio was added to glyphosate plus dicamba. However, unlike the addition of the standard MSO, the addition of the experimental 85:15 ratio was statistically similar to glyphosate plus dicamba applied alone. The addition of the experimental 85:15 ratio resulted in 88% amaranth control while glyphosate plus dicamba lone resulted in 91% amaranth control.

Similar to the standard MSO, when the standard NIS was added to glyphosate plus dicamba, amaranth control decreased by 10 percentage points at 14 DAA and 9 percentage points at 28 DAA when compared to glyphosate and dicamba alone (Table 3.4). Conversely, the addition of the experimental 0:100 ratio provided equivalent control to glyphosate plus dicamba applied alone. A reason why the experimental 0:100 ratio did not decrease amaranth control while the standard NIS did may be due to two different factors. First, the chemical properties of the surfactant active ingredient used in each product may be different. Certain surfactant active ingredients are utilized for different purposes (Hess and Foy 2000). Some surfactant active ingredients are better at spreading and wetting while others are better at emulsifying oil in water or at increasing the biological activity of herbicides. The chemical properties of a surfactant depend on the active ingredients utilized and at what ratio they're included in the overall product. Second, the standard surfactant used in this experiment contained 90% surfactant and 10% inert ingredients while the experimental 0:100 ratio did not contain any inert ingredients. Since inert ingredients are not regulated by the EPA, much like adjuvants, manufacturers do not need to claim which inert ingredients are used in formulations. Therefore, potential herbicide antagonism may be due to an inert ingredient that was used in the standard NIS.

There were few differences between experimental HSMOC ratios (Table 3.4). Since the definition of an HSOC is an adjuvant that contains at least 50% oil and 25 to 50% surfactant (ASTM 2016), there were only three ratios in these treatments that fit that definition. The experimental 60:40 ratio provided 94% amaranth control at 14 DAA, followed by the experimental 50:50 ratio at 93%, and the experimental 70:30 ratio at 91% amaranth control. At 28 DAA there were few differences in control. The experimental 60:40 and 70:30 ratios both provided 99% amaranth control followed by the experimental 50:50 ratio at 97% control. The standard HSMOC provided 92 and 99% amaranth control at 14 and 28 DAA, respectively which was consistent with control provided by all experimental ratios. Ultimately, there was no difference in amaranth control between glyphosate plus dicamba applied alone or when any experimental MSO:NIS ratio was added at either 14 or 28 DAA. Therefore, there was no optimal ratio of MSO:NIS needed for glyphosate plus dicamba to control amaranth.

Visible quinoa control generally increased from 14 to 28 DAA (Table 3.4). The addition of any adjuvant increased quinoa control compared to glyphosate plus dicamba with no adjuvant. This is likely due to quinoa's crystalline globular bladder hairs on leaf surfaces that are hydrophobic which reduces droplet deposition and retention (Hess and Falk 1990). The addition of surfactants have been shown to increase deposition and retention of spray droplets on leaf surfaces (Riechers et al. 1995). Therefore, since all treatments contained adjuvants, they utilized some amount of surfactant, which resulted in increased quinoa control because droplet deposition and retention likely increased compared to glyphosate plus dicamba alone.

The addition of MSO adjuvants, such as the standard MSO and the experimental 85:15 ratio, increased quinoa control (Table 3.4). At 28 DAA glyphosate plus dicamba alone provided 63% quinoa control, but when the experimental 85:15 ratio was added to glyphosate plus dicamba, quinoa control increased by 31 percentage points. Likewise, at 28 DAA, the addition of the standard MSO to glyphosate and dicamba increased control of quinoa by the same amount (31 percentage points) when compared to the experimental 85:15 ratio. Even though only 15% of the composition of these adjuvants were surfactant, it was enough to help increase droplet deposition and retention on the leaf of quinoa. Likewise, the oil portion likely aided in herbicide penetration of the leaf cuticle for increased quinoa control.

The addition of surfactants to glyphosate plus dicamba also increased quinoa control (Table 3.4). Similar to the results for glyphosate plus dicamba applied to amaranth, the experimental 0:100 ratio provided similar control than the standard NIS. At 14 DAA the addition of the experimental 0:100 ratio increased quinoa control by 30 percentage points while the standard NIS increased quinoa control by 22 percentage points (compared to the no adjuvant check). Likewise, at 28 DAA the addition of the experimental 0:100 ratio increased quinoa control by 36 percentage points compared to 31 percentage points when the standard NIS was added.

The addition of any HSOC increased quinoa control compared to glyphosate plus dicamba alone (Table 3.4). The standard HSMOC used in this study is formulated as a 75% oil and 25% surfactant. Most HSOC adjuvants currently on the market such as Advatrol, Aggrestrol, Covrex, Penetrec, Succeed Ultra, Hot MES, High Load, Stake, Between, Exchange and others have a ratio of 60:40 (Young et al. 2016). However, some products such as Glacier EA, Hybrid, Destiny HC, or Superb HC contain ratios closer to 70:30 or 75:25. When added to glyphosate plus dicamba, the standard HSMOC provided 85% quinoa control at 28 DAA. At 28 DAA, the experimental ratios added to glyphosate plus dicamba that were closest to the standard HSMOC used in this trial were the 80:20 and 70:30 experimental ratios which provided 94 and 93% quinoa control, respectively. Additionally, the experimental 60:40 and 50:50 ratios in this trial provided 94% and 95% quinoa control, respectively. These were equal to the experimental 80:20 and 70:30 ratios used to compare against the standard HSMOC. Therefore, since all experimental

HSMOC results were similar, there was no optimal ratio of MSO:NIS when applied with glyphosate plus dicamba and applied to quinoa.

Table 3.4. Control of amaranth and quinoa with glyphosate applied at 473 g ae ha^{-1} plus dicamba applied at 214 g ae ha^{-1} with multiple experimental ratios. Greenhouse trials were conducted in 2017.

	Amaranth			Quinoa		
Treatments	14 DAA[a,b]	28 DAA	Biomass[c]	14 DAA	28 DAA	Biomass
	----------- % -----------		---- kg ----	---------- % ----------		---- kg ----
Untreated check	0	0	13.20	0	0	8.79
Glyphosate + dicamba	94 a	99 A	1.02 a	58 d	63 d	3.60 a
+ NIS[d]	84 c	90 B	1.30 a	80 abc	94 ab	2.10 bc
+ MSO[e]	88 bc	96 A	1.27 a	80 abc	93 b	1.95 bc
+ HSMOC[f]	92 ab	99 A	1.23 a	70 c	85 c	2.59 b
+ 85% MSO : 15% NIS	91 ab	99 A	1.34 a	79 abc	94 b	2.19 bc
+ 80% MSO : 20% NIS	91 ab	98 A	1.38 a	84 ab	94 ab	1.73 cd
+ 70% MSO : 30% NIS	91 ab	99 a	1.28 a	83 ab	93 b	1.53 cd
+ 60% MSO : 40% NIS	94 a	99 a	1.02 a	85 ab	94 ab	1.94 bc
+ 50% MSO : 50% NIS	93 ab	97 a	1.14 a	80 abc	95 ab	1.65 cd
+ 40% MSO : 60% NIS	94 a	99 a	1.30 a	81 ab	91 b	2.00 bc
+ 30% MSO : 70% NIS	94 a	99 a	1.29 a	82 ab	94 ab	1.71 cd
+ 20% MSO : 80% NIS	94 a	95 a	1.21 a	76 bc	91 b	2.21 bc
+ 10% MSO : 90% NIS	93 ab	98 a	1.30 a	84 ab	94 b	1.58 cd
+ 0% MSO : 100% NIS	93 ab	99 a	1.15 a	88 a	99 a	1.06 d
LSD (α=0.05)	5	5	0.37	11	5	0.84

[a] Values followed by the same letter within a column are not different according to Fisher’s protected LSD at alpha=0.05.
[b] DAA = days after application.
[c] Compared to non-treated control.
[d] NIS = nonionic surfactant.
[e] MSO = methylated seed oil.
[f] HSMOC = high surfactant methylated oil concentrate.

Glyphosate Plus Tembotrione Trial

Glyphosate is hydrophilic, which means surfactants are often recommended to increase efficacy (Anonymous 1987) whereas tembotrione is lipophilic and oil adjuvants are often recommended to increase efficacy (Anonymous 2007). Therefore, glyphosate plus tembotrione is a tank-mix that is commonly paired with an HSOC adjuvant due to the surfactant portion enhancing glyphosate activity and oil portion enhancing tembotrione activity.

Amaranth control increased from 14 to 28 DAA for all treatments (Table 3.5). Any treatment including an adjuvant with glyphosate plus tembotrione increased amaranth control compared to the no adjuvant check. At 28 DAA, glyphosate plus tembotrione alone provided 39% amaranth control while the addition of any adjuvant increased control by at least 54 percentage points. However, there was no difference among any of the treatments that included an adjuvant at either 14 or 28 DAA. These results highlight why adjuvants, in general, are often added to herbicide tank-mixes to increase weed control.

The standard MSO, formulated as a blend of 85% oil and 15% surfactant, provided 89 and 93% amaranth control when added to glyphosate plus tembotrione at 14 and 28 DAA, respectively (Table 3.5). The experimental 85:15 ratio treatment provided similar control with 92 and 96% control at 14 and 28 DAA, respectively.

Similar to the results with MSO, the addition of surfactants also increased efficacy over glyphosate plus tembotrione applied alone (Table 3.5). Even though data suggest that oils, such as the standard MSO or the 85:15 experimental ratio, enhanced tembotrione activity to increase amaranth control, surfactants can also increase glyphosate activity to help control amaranth. The addition of the standard NIS increased amaranth control by 58 and 46 percentage points at 14 and 28 DAA, respectively, while the addition of the experimental 0:100 ratio increased glyphosate plus tembotrione activity by 62 and 60 percentage points at 14 and 28 DAA, respectively.

All experimental HSMOC ratios increased amaranth control when added to glyphosate plus tembotrione, compared to the no adjuvant treatment (Table 3.5). When the standard HSMOC, a 75% oil and 25% surfactant, was added to glyphosate plus tembotrione, amaranth control increased from 32 to 90% at 14 DAA and from 39 to 95% at 28 DAA. Likewise, when the experimental HSMOC ratios 70:30, 60:40, or 50:50 were added to glyphosate plus tembotrione, amaranth control increased to 95, 94, and 92% respecively, at 14 DAA and to 99, 98, and 97%, respectively, at 28 DAA. Therefore, all HSOC ratios tank-mixed with glyphosate plus tembotrione provided equal amaranth control so there was no “optimal” experimental HSMOC ratio observed.

Visible control of quinoa mostly increased from 14 to 28 DAA (Table 3.5). Control with glyphosate plus tembotrione alone decreased from 16% at 14 DAA to 10% at 28 DAA. After 14 DAA, regrowth of quinoa in this treatment started to occur. However, no regrowth was observed with any glyphosate plus tembotrione treatments that contained an adjuvant. Similar to amaranth, there were no differences among any treatments that contained an adjuvant by 28 DAA. There was also no difference between the standard MSO and the experimental 85:15 ratio. Each oil increased quinoa control by over 45 percentage points at 14 DAA and by over 80 percentage points by 28 DAA when added to glyphosate plus tembotrione. Even though there was only 15% surfactant in each of these adjuvants, it was enough to overcome the waxy crystalline material that reduces spray droplet retention on quinoa leaves. Likewise, the oil portion likely aided in penetration of the leaf cuticle for increased quinoa control.

Treatments including surfactants alone with glyphosate plus tembotrione provided similar control to the treatments where an oil was included (Table 3.5). At 14 DAA, the addition of the standard surfactant provided 58% control while the addition of the standard MSO provided 62% control. By 28 DAA, quinoa control increased in both treatments to 89% and 92%, respectively. Likewise, the experimental 85:15 ratio was similar to the experimental 0:100 ratio when added to glyphosate plus tembotrione at 28 DAA.

There were differences between the HSMOC ratios at 14 DAA (Table 3.5). When the experimental 70:30 ratio was added to glyphosate plus tembotrione, quinoa control was 68% which was better than the experimental ratio 60:40 at 60% control. However, the addition of the experimental 50:50 ratio to glyphosate plus tembotrione provided 62% quinoa control which was not different than either the 70:30 or 60:40 experimental ratios. By 28 DAA there were no differences among HSOC experimental ratios. The addition of the experimental 70:30, 50:50, and 60:40 ratios to glyphosate plus tembotrione provided 93, 91, and 91% quinoa control, respectively. Therefore, there was no optimal ratio of MSO:NIS that enhanced glyphosate plus tembotrione control of quinoa more than others.

Table 3.5. Control of amaranth and quinoa with glyphosate applied at 473 g ai ha^{-1} plus tembotrione applied at 46 g ai ha^{-1} with multiple experimental ratios. Greenhouse trials were conducted in 2017.

	Amaranth			Quinoa		
Treatments	14 DAA[ab]	28 DAA	Biomass[c]	14 DAA	28 DAA	Biomass
	---------- % ----------		---- kg ----	---------- % ----------		---- kg ----
Untreated check	0	0		0	0	
Glyphosate + tembotrione	32 b	39 b	4.78 a	16 f	10 b	8.12 a
+ NIS[d]	90 a	95 a	1.86 bc	58 cde	89 a	1.67 bc
+ MSO[e]	89 a	93 a	2.82 b	62 abcde	92 a	1.72 b
+ HSMOC[f]	90 a	95 a	2.36 bc	66 ab	91 a	1.73 b
+ 85% MSO : 15% NIS	92 a	96 a	2.24 bc	63 abcd	93 a	1.66 bc
+ 80% MSO : 20% NIS	94 a	98 a	1.66 c	63 abcd	91 a	1.70 b
+ 70% MSO : 30% NIS	95 a	99 a	1.51 c	68 a	93 a	1.57 bc
+ 60% MSO : 40% NIS	94 a	98 a	1.59 c	60 bcde	91 a	1.47 bc
+ 50% MSO : 50% NIS	92 a	97 a	1.71 c	62 abcde	91 a	1.75 b
+ 40% MSO : 60% NIS	93 a	98 a	1.66 c	59 cde	90 a	1.55 bc
+ 30% MSO : 70% NIS	94 a	99 a	1.77 bc	64 abc	92 a	1.62 bc
+ 20% MSO : 80% NIS	95 a	99 a	1.56 c	57 de	89 a	1.46 bc
+ 10% MSO : 90% NIS	94 a	99 a	1.61 c	66 ab	91 a	1.49 bc
+ 0% MSO : 100% NIS	94 a	99 a	1.61 c	56 e	90 a	1.38 c
LSD (α=0.05)	10	12	1.07	7	4	0.32

[a] Values followed by the same letter within a column are not different according to Fisher's protected LSD at alpha=0.05.
[b] DAA = days after application.
[c] Compared to non-treated control.
[d] NIS = nonionic surfactant.
[e] MSO = methylated seed oil.
[f] HSMOC = high surfactant methylated oil concentrate.

Conclusions

Even though there were few differences among treatments in both greenhouse experiments, some overall conclusions can be discussed. The addition of any adjuvant to glyphosate plus tembotrione increased both amaranth and quinoa control by 28 DAA (Table 3.5). Tembotrione may have benefitted more from the addition of adjuvants than glyphosate. For example, oil adjuvants are often known to antagonize glyphosate (Nalewaja and Matysiak 1993; Zollinger 2014). Despite this, amaranth and quinoa control increased when oil adjuvants were added to glyphosate plus tembotrione. By 28 DAA there were no differences among any of the treatments that included adjuvants when applied to either amaranth or quinoa. This means there was no optimal experimental ratio of oil to surfactant when added to glyphosate plus tembotrione.

In the glyphosate plus dicamba trial, visible amaranth control did not increase with the addition of any adjuvant at either the 14 or the 28 DAA evaluations (Table 3.4). There was also no difference in amaranth control when any experimental HSMOC ratio was added to glyphosate plus dicamba. In contrast to amaranth, quinoa control did increase with the addition of any adjuvant to glyphosate plus dicamba at both the 14 and 28 DAA evaluations. However, the addition of any experimental HSMOC to glyphosate plus dicamba provided similar enhancement. Therefore, there was no optimal experimental HSMOC ratio.

Even though there was no optimal experimental HSMOC ratio found in either trial, two of the ratios that were always among the highest amaranth and quinoa control values were the experimental 60:40 and 70:30 ratios. This is important because most of the commercial HSMOC adjuvants currently on the market contain either 60:40 or 70:30 ratios. However, the standard HSMOC in these trials was a commercial HSMOC adjuvant with a 75:25 ratio. The standard HSMOC provided control values similar to other ratios except for when it was mixed with glyphosate plus dicamba and applied to quinoa. The addition of the standard HSMOC provided less quinoa control than any other adjuvant when added to glyphosate plus dicamba. This may be due to the smaller amount of surfactant in the standard HSMOC.

These trials support the comments made by Zollinger (2000) which said, “each plant species can react differently for each herbicide, environment, and adjuvant due to plant morphology, variation in leaf surfaces, composition, and quality of cuticular substances which all influence absorption and contribute to variability in plant response to herbicides.” He went on to say, “Likewise, each herbicide also reacts differently for each plant, environment, and adjuvant.” An example of how environment affects cuticle formation of plants was observed by Sherrick et al. (1986) when field bindweed (*Convolvulus arvensis* L.) was grown under environments of high light intensity and low humidity (HLLH) or low light intensity and high humidity (LLHH). They found that field bindweed grown in a HLLH environment had almost 3 times thicker cuticular wax than field bindweed grown in a LLHH environment. This resulted in 12% less glyphosate absorbed into the plant grown in the HLLH environment versus the LLHH environment. This was also in agreement with Bandurska et al. (2013) and Manetas et al. (1997) that reported that UV radiation in open field conditions lead to higher lignin deposition in cell walls, an increased cuticle thickness, and a lower rate of transpiration compared to greenhouse plants.

The controlled environment in which indicator species were grown in our research may explain why there were limited differences among treatments in both trials. The indicator species grown in the greenhouse were provided with routine water, nutrient supplementation, and kept at a constant temperature for the duration of an experiment. Additionally, indicator species grown in the greenhouse were not subject to outside stresses such as high light intensity, wind, pathogens, temperature extremes, moisture extremes, and other factors. Therefore, the indicator species could devote less energy into building thicker cuticular waxy barriers, or other physiological changes for stress mitigation. Therefore, like Sherrick (1986) observed, there may have been an increase in herbicide absorption in these studies because of a thinner cuticular barrier which led to increased indicator species control. With an increase in herbicide absorption, there was less need for adjuvants to be added especially with glyphosate and dicamba.

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CHAPTER 4. FIELD EXPERIMENTS TO EVALUATE OIL ADJUVANT RATES APPLIED BY AREA OR PERCENT VOLUME WITH DICAMBA AND TEMBOTRIONE

Introduction

Tembotrione (2-[2-chloro-4-(methylsulfonyl)-3-[(2,2,2-trifluoroethoxy0 methyl] benzoyl]-1,3-cyclohexanedione) and dicamba (3,6-dichloro-2-methoxybenzoic acid) are common post-emergence tank-mix partners with glyphosate applications to control many glyphosate-resistant weeds. Tembotrione is a lipophilic herbicide that is generally recommended to be paired with an oil adjuvant because oil adjuvants increase weed control with lipophilic herbicides more than surfactants (Zollinger and Reis (2007). Conversely, dicamba can be paired with surfactants or oil adjuvants because it is slightly hydrophilic. Oil adjuvants can be added to dicamba at certain times of the growing season (Anonymous 1987). Often these times are early in the season or late in the season when weeds are harder to control due to adverse weather conditions.

Oil adjuvants are used to penetrate the leaf cuticle and to increase the solubility of lipophilic herbicides. Oil adjuvant rates can be calculated on a percent volume of the spray tank (% v v^{-1}) or according to area covered (L ha^{-1}). Area-based rates directly correlate to number of hectares covered. Depending on oil type, common area-based rates are 2340 ml ha^{-1} for petroleum oil concentrate (POC) adjuvants, 1755 ml ha^{-1} for (methylated seed oil) MSO adjuvants, and 1170 ml ha^{-1} for high surfactant oil concentrate (HSOC) adjuvants. Most herbicide labels recommend oil adjuvants be applied on a percent volume-based rate system which directly correlates an oil adjuvant rate to the spray volume. The most common rates applied are 0.5 or 1% v v^{-1}. Oil adjuvants at 1% v v^{-1} in a total water volume of 160 L ha^{-1} are equivalent to 1590 ml ha^{-1}, or nearly the rate recommended by NDSU of 1755 ml ha^{-1} for MSO adjuvants, but less than the POC rate of 2340 ml ha^{-1} (Zollinger 2014). However, as total water volume decreases from 160 L ha^{-1} to 80 L ha^{-1} the equivalent area-based rate is 795 ml ha^{-1}, which is below the rate recommended by NDSU for any oil adjuvant. The objective of this research was to evaluate whether oil adjuvants should be applied with pesticides based on area or percent volume of total spray solution applied.

Materials and Methods

Two field research trials were conducted in both 2016 and 2017 near Hillsboro, North Dakota to evaluate either dicamba or tembotrione efficacy with multiple oils at varying rates of oil adjuvants and water volumes. The experimental design for both trials was a RCBD with three replications. Treatments were organized in a 4x4x2 factorial arrangement of oil adjuvant types, oil adjuvant rates, and water volumes. Treatments (Table 4.1) were applied to the center 2 m of each plot using a CO_2-pressurized backpack sprayer equipped with Turbo TeeJet 11001 nozzles (TeeJet Spraying Systems. 1801 Business Park Dr. Springfield, IL 62703) delivering 80 L ha^{-1} or 11002 nozzles delivering 160 L ha^{-1} at 276 kPa at a speed of 5 kph. Herbicides (Table 4.2) were applied at sub-lethal rates to avoid 100% plant death so that treatment differences could be observed. Adjuvants (Table 4.3) were applied at full labeled rates.

Indicator species were planted perpendicular to treatment application direction in 1.5-meter-wide strips using a Great Plains 3P600 drill with 19-cm row spacings at a planting depth of 1.25 cm. Indicator species for the dicamba trial included amaranth [*Amaranthus hypochondriacus* (L.)], quinoa [*Chenopodium quinoa* (Willd.)], sunflower [*Helianthus annuus* (L.)], and buckwheat [*Fagopyrum esculentum* (Moench)]. Amaranth was planted at a rate of 1.7 kg ha^{-1}, quinoa was planted at 1.7 kg ha^{-1}, sunflower was planted at 5.5 kg ha^{-1}, and buckwheat was planted at 50 kg ha^{-1}. Indicator species for the tembotrione trial included amaranth, quinoa, sunflower, and foxtail millet [*Setaria italic* (L.)]. Amaranth, quinoa, and sunflower were planted as previously described while foxtail millet was planted at a rate of 40 kg ha^{-1}. Amaranth, quinoa, buckwheat, sunflower, and foxtail millet were used as indicator species to mimic the properties of common *Amaranthus*, *Chenopodium*, *Fagopyrum*, *Helianthus*, and *Setaria* species, respectively.

Indicator species control were visibly evaluated 14 and 28 days after application (DAA) on a scale of 0 to 100% with 0% representing no control and 100% representing complete plant death. Average height of each species population was measured. Height measurements were compared to the nontreated check and converted to percent of control before analysis.

Data were subjected to Proc GLM ANOVA using Statistical Analysis System (SAS) version 9.4 (SAS Institute, Cary, NC) and mean separations were determined using Fisher's protected Least Significant Difference (LSD) test at $\alpha = 0.05$, where appropriate. Adjuvant, rate, and water volume treatment variables were considered fixed effects while time was considered a random effect in a repeated measures analysis.

Table 4.1. Dicamba at 214 g ae ha^{-1} or tembotrione at 46 g ai ha^{-1} applied with multiple rates of HSMOC, HSPOC, MSO, and POC adjuvants at two spray volumes. Treatments were applied near Hillsboro, ND in 2016 and 2017.

Treatment	Spray volume	Oil volume rate	Oil area rate
	L ha^{-1}	% v v^{-1}	--ml ha^{-1}--
Nontreated	80	------	------
Herbicide	80	------	------
Herbicide + HSMOC[a]	80	0.50%	398
Herbicide + HSMOC	80	1%	795
Herbicide + HSMOC	80	2%	1590
Herbicide + HSMOC	80	3%	2385
Herbicide + HSPOC[b]	80	0.50%	398
Herbicide + HSPOC	80	1%	795
Herbicide + HSPOC	80	2%	1590
Herbicide + HSPOC	80	3%	2385
Herbicide + MSO[c]	80	0.50%	398
Herbicide + MSO	80	1%	795
Herbicide + MSO	80	2%	1590
Herbicide + MSO	80	3%	2385
Herbicide + POC[d]	80	0.50%	398
Herbicide + POC	80	1%	795
Herbicide + POC	80	2%	1590
Herbicide + POC	80	3%	2385
Herbicide	160	------	------
Herbicide + HSMOC	160	0.25%	398
Herbicide + HSMOC	160	0.50%	795
Herbicide + HSMOC	160	1%	1590
Herbicide + HSMOC	160	1.50%	2385
Herbicide + HSPOC	160	0.25%	398
Herbicide + HSPOC	160	0.50%	795
Herbicide + HSPOC	160	1%	1590
Herbicide + HSPOC	160	1.50%	2385
Herbicide + MSO	160	0.25%	398
Herbicide + MSO	160	0.50%	795
Herbicide + MSO	160	1%	1590
Herbicide + MSO	160	1.50%	2385
Herbicide + POC	160	0.25%	398
Herbicide + POC	160	0.50%	795
Herbicide + POC	160	1%	1590
Herbicide + POC	160	1.50%	2385

[a] HSMOC = high surfactant methylated oil concentrate.

[b] HSPOC = high surfactant petroleum oil concentrate.

[c] MSO = methylated seed oil.

[d] POC = petroleum oil concentrate.

Table 4.2. Sources of commercial products used in field experiments.

Common name	Brand name	Manufacturer	Mode of action	Rate
				g ha^{-1} [c]
Dicamba	Clarity®	BASF[a]	Synthetic auxin	214
Tembotrione	Laudis®	Bayer CropScience LP[b]	HPPD Inhibitor	46

[a] 26 Davis Drive, Research Triangle Park, NC 27709.
[b] 800 N. Lindbergh Blvd, St. Louis, MO 63167.
[c] Dicamba and glyphosate are g ae ha^{-1}; tembotrione is g ai ha^{-1}.

Table 4.3. Commercial products used in experiments.

Adjuvant category	Brand name	Manufacturer
HSMOC[a]	Destiny® HC	Winfield United[e]
HSPOC[b]	Superb® HC	Winfield United
MSO[c]	Super Spread® MSO	Wilbur-Ellis®[f]
POC[d]	Herbimax®	Loveland Products Inc.[g]

[a] HSMOC = high surfactant methylated oil concentrate.
[b] HSPOC = high surfactant petroleum oil concentrate.
[c] MSO = methylated seed oil.
[d] POC = petroleum oil concentrate.
[e] P.O. Box 64589, St. Paul, MN 55164-0589.
[f] P.O. Box 16458, Fresno, CA 93755.
[g] P.O. Box 1286, Greeley, CO 80632-1286.

Results and Discussion

Oil Adjuvant Rates with Dicamba Trial

Oil type had no effect on amaranth ($p=0.60$ at 14 DAA) ($p=0.95$ at 28 DAA), quinoa ($p=0.96$ at 14 DAA) ($p=0.78$ at 28 DAA), buckwheat ($p=0.97$ at 14 DAA) ($p=0.52$ at 28 DAA), or sunflower ($p=0.52$ at 14 DAA) ($p=0.14$ at 28 DAA) control when oil adjuvants were added to dicamba. Therefore, data were pooled across oil types and interactions between oil rates and total water volume were analyzed. Amaranth, quinoa, and sunflower control mostly increased from 14 to 28 DAA indicating consistent herbicide activity (Table 4.4). Amaranth and sunflower control did not increase with the addition of any oil adjuvant at any rate compared to the no adjuvant check (data not shown). However, with the addition of any oil adjuvant at any rate to dicamba, quinoa control increased at both 14 and 28 days after application compared to the no-adjuvant check. Since all treatments containing oils utilize some amount of surfactant, quinoa control increased because droplet deposition and retention likely increased compared to dicamba alone. This increased deposition is likely due oil overcoming quinoa's crystalline substance on leaf surfaces that is hydrophobic which reduces droplet deposition and retention (Hess and Falk 1990). The addition of adjuvants increases deposition and retention of spray droplets on leaf surfaces (Riechers et al. 1995).

In general, there were few differences in the control of indicator species when any oil adjuvants were added to dicamba (Table 4.4). When oil adjuvants were added to dicamba, amaranth control ranged from 34 to 40% at 28 DAA which was considerably less than quinoa and sunflower control which ranged from 66 to 74% and 54 to 60% at 28 DAA, respectively. There were no differences between oil rate and total water volume across all oil types for amaranth, quinoa, and sunflower at 14 and 28 DAA. Therefore, control was similar whether oil adjuvants were applied based on percent volume or area. This may be attributed to dicamba being very active in most broadleaf plants. Surfactants are often recommended to enhance dicamba (Anonymous 1987) since dicamba is slightly hydrophilic. Oil adjuvants may be added in place of surfactants at certain times of the growing season (Anonymous 1987) when weeds develop thicker leaf cuticles and are not actively growing after being exposed to prolonged periods of extreme weather conditions. Using oils in these situations increases efficacy because they can slow the drying of a spray droplet on the leaf surface while solubilizing the leaf cuticle to help dicamba penetrate the leaf cuticle faster (Manthey and Nalewaja 1992). However, at the time these trials took place there was adequate growing conditions that led to unstressed, actively growing indicator species. For example, in 2016 and 2017 the average temperatures from time of planting to treatment applications (6 weeks) was 18.9- and 17.2- °C with total rain accumulation of 11.4- and 7.6-cm, respectively. For the four weeks after applications in both 2016 and 2017, average temperatures were 21.1 and 20.5 degrees Celsius with total rain accumulation of 10.2 and 5.1 centimeters, respectively.

In contrast to amaranth, quinoa, and sunflower, buckwheat control was higher at 14 DAA compared to 28 DAA (Table 4.4). At 14 DAA buckwheat control increased with the addition of any oil adjuvant at any rate to dicamba compared to the no adjuvant control (data not shown). However, by 28 DAA there was no difference in buckwheat control whether an oil adjuvant was added to dicamba or not. When oil adjuvants were added to dicamba, buckwheat control ranged from 59 to 62% at 14 DAA but by 28 DAA ranged from 40 to 46%. Regrowth occurred from 14 to 28 DAA which would indicate that dicamba is less active within buckwheat compared to other species that were tested. This is contrary to what was expected since dicamba is very active and provides excellent (90-99%) control of plants in the *Polygonaceae* family (Anonymous 1987). Likewise, Chang and Vanden Born (1971) reported rapid translocation of ^{14}C-dicamba to meristematic tissue, in the shoot apex and in leaf axials within three- to four-leaf tartary buckwheat (*Fagopyrum tataricum*). ^{14}C-dicamba activity in the shoot and young tissue continued for at least 20 days while metabolism was very slow. However, weed control ratings found in the North Dakota Weed Control Guide and results from Chang and Vanden Born (1971) are based on dicamba applied to smaller weeds, whereas buckwheat height in this trial at the time of application was approximately 61 cm tall. Therefore, buckwheat control, comparatively, may be less than what was found in the North Dakota Weed Control Guide and by Chang and Vanden Born (1971) due to plant size. At 14 DAA there was an interaction between oil rate and total water volume across all oil types; however, there was very little separation between individual treatments. When adjuvant treatments with dicamba were applied based on area, the only difference observed was with rates of 398 ml ha^{-1} (Table 4.4). When oils were added to dicamba at 398 ml ha^{-1} buckwheat control decreased from 61 to 59% as total water volume increased from 80 L ha^{-1} to 160 L ha^{-1}. As oil rates increased to 795-, 1590-, or 2385-ml ha^{-1}, there was no difference in buckwheat control whether treatments were sprayed at 80 L or 160 L ha^{-1} total water volume. However, there were also no differences within treatments sprayed at 0.5 or 1% v v^{-1}. For example, when oils were added to dicamba at 0.5% v v^{-1}, buckwheat control was 61% when applied with 80 L ha^{-1} total water volume and 60% when applied with 160 L ha^{-1} total water volume. Likewise, when oils were added at 1% v v^{-1} buckwheat control was 61% regardless of total water volume applied. Since there were very few differences among treatments, it was difficult to tell if oils applied based on area or percent volume were more effective.

Since there were very few differences among treatments, there was no definitive answer to whether dicamba should be applied with oils based on area or percent volume. Dicamba is a herbicide that, if applied with an adjuvant at all, is normally applied with a surfactant because of its hydrophilic properties. Dicamba usually doesn’t get tank-mixed with oil adjuvants unless weeds are hardened off due to drought stress, high temperatures, or other environmental factors. However, growing conditions were adequate as previously described. Therefore, oils may not have had any effect on dicamba efficacy in this trial.

Table 4.4. Effects of dicamba at 214 g ae ha^{-1} applied with multiple rates of oil adjuvants at two spray volumes on amaranth, quinoa, sunflower, and buckwheat near Hillsboro, ND in 2016 and 2017.

Treatments	Oil volume rate	Spray volume	Oil area rate	Amaranth 14 DAA[ab]	Amaranth 28 DAA	Quinoa 14 DAA	Quinoa 28 DAA	Sunflower 14 DAA	Sunflower 28 DAA	Buckwheat 14 DAA	Buckwheat 28 DAA
	% v v^{-1}	L Ha^{-1}	ml Ha^{-1}				------------------------------------ %[a] ------------------------------------				
+ Oils	3%	80	2385	35	39	73	74	45	59	62 a	46
+ Oils	1.50%	160	2385	35	37	70	74	47	60	61 ab	46
+ Oils	2%	80	1590	37	40	73	72	42	60	60 bc	43
+ Oils	1%	160	1590	36	36	68	73	45	59	61 ab	46
+ Oils	1%	80	795	31	36	73	71	43	54	61 ab	44
+ Oils	0.50%	160	795	32	34	68	68	45	56	60 bc	43
+ Oils	0.50%	80	398	35	38	71	66	43	56	61 ab	44
+ Oils	0.25%	160	398	35	36	65	68	42	55	59 c	40
LSD (α=0.05)				NS	NS	NS	NS	NS	NS	1	NS

[a] Mean values separated using Fisher's protected LSD. Values followed by different letters within column are significantly different ($P \leq 0.05$).
[b] DAA = days after application.

Oil Adjuvant Rates with Tembotrione Trial

Oil type had no effect on amaranth (p=0.34 at 14 DAA) (p=0.15 at 28 DAA), foxtail millet (p=0.87 at 14 DAA) (p=0.78 at 28 DAA), quinoa (p=0.16 at 14 DAA) (p=0.34 at 28 DAA), or sunflower (p=0.55 at 14 DAA) (p=0.71 at 28 DAA) control when oil adjuvants were added to tembotrione. Therefore, data were pooled across oil type and interactions between oil rate and total water volume were analyzed. The addition of oil adjuvants at most rates to tembotrione increased all species control compared to the no-oil check (data not shown). Trends indicated that there was a linear relationship between tembotrione and oil concentration applied across all species even though no differences were observed in amaranth (Table 4.5). As rate of oil increased from 0.25 to 3% v v^{-1}, so did tembotrione efficacy on these species. Control was generally greater at 14 DAA compared to 28 DAA for amaranth, sunflower, and foxtail millet. By 28 DAA regrowth of amaranth, sunflower, and foxtail millet were observed. However, quinoa control was fairly consistent from 14 to 28 DAA.

Amaranth control ranged from 20 to 63% at 14 DAA and 10 to 43% at 28 DAA (Table 4.5). However, there were no differences between oil rate and total water volume across all oil types at either 14 or 28 DAA for amaranth control. Therefore, control was similar whether oil adjuvants were applied based on percent volume or area.

Similar to amaranth, there were no differences between oil rate and total water volume across all oil types for foxtail millet at 14 DAA (Table 4.5). Foxtail millet control ranged from 7 to 50% at 14 DAA. By

28 DAA, foxtail control ranged from 6 to 23%. There were differences between oil rate and total water volume across all oil types at 28 DAA, even though regrowth had occurred by 28 DAA. There was a difference with treatments with area-based rates of 1590 or 2385 ml ha^{-1} when total water volume changed from 80 to 160 L ha^{-1}. For example, when oils were added to tembotrione at 2385 ml ha^{-1}, foxtail millet control decreased from 23 to 18% when total water volume changed from 80 to 160 L ha^{-1}. Likewise, when 1590 ml ha^{-1} area-based rate was added to tembotrione, foxtail millet control decreased from 18 to 14% when total water volume changed from 80 to 160 L ha^{-1}. However, once area-based rates of 398 or 795 ml ha^{-1} were used, there were no differences whether treatments were applied with 80 or 160 L ha^{-1} total water volume. The same trend was observed when rates based on percent volume were used. Foxtail millet control decreased when oil rates were added to tembotrione at 1% v v^{-1} and total water volume changed from 80 to 160 L ha^{-1}. However, at lower oil rates of 0.5% v v^{-1}, there was no difference whether treatments were sprayed at 80 or 160 L ha^{-1} total water volume. Even though differences were observed between treatments, neither area-based rates nor percent volume-based rates were consistent enough to determine whether one was more desirable to use over the other. Control generally increased in response to oil concentration. Treatments with higher oil rates generally increased foxtail millet control more than treatments with lower oil adjuvant rates.

There were differences in sunflower control between oil rate and total water volume across all oil types at the 14 DAA evaluation, but not at the 28 DAA evaluation (Table 4.5). At 14 DAA, sunflower control increased as oil rate increased from 0.25 to 3% v v^{-1}. Sunflower control ranged from 43% at the lowest rate (0.25% v v^{-1}) to 88% at the highest rate (3% v v^{-1}). As oil rates increased above 1.5% v v^{-1} there was no difference between treatments. As rates decreased below 1.5% v v^{-1}, sunflower control decreased as well. For example, when oil adjuvants were added to tembotrione at 1.5%, 1%, 0.5%, and 0.25% v v^{-1} sunflower control decreased to 73%, 59%, and 43%, respectively. Additionally, sunflower control fluctuated when area-based rates were applied, and total water volume changed from 80 to 160 L ha^{-1}. When oil adjuvants at 795 ml ha^{-1} were added to tembotrione with a total water volume at 80 L ha^{-1}, sunflower control was 73% but when 795 ml ha^{-1} was applied with a total water volume at 160 L ha^{-1}, sunflower control decreased to 59%. Likewise, sunflower control decreased from 59 to 43% when 398 ml ha^{-1} was applied with total water volumes at 80 and 160 L ha^{-1}, respectively. When area-based rates were applied at 2385- or 1590-ml ha^{-1}, there were no differences in sunflower control whether applied at either 80 or 160 L ha^{-1} total water volumes. This may be because tembotrione was optimized at the highest area-based rates regardless of total water volume applied.

Treatments with oil adjuvants based on percent volume stayed consistent regardless of water volume applied. For example, treatments applied at 0.5% v v^{-1} provided 59% sunflower control regardless of total water volume applied (Table 4.5). Likewise, when treatments were applied at 1% v v^{-1}, sunflower control stayed consistent at 78 and 73% with total water volumes at 160 and 80 L ha^{-1}, respectively.

In this experiment, tembotrione applied with oil adjuvant rates based on area and applied with 80 L ha^{-1} total water volume provided better sunflower control than area-based rates applied with a total water volume at 160 L ha^{-1} (Table 4.5). This agrees with Zollinger et al. (2013) that reported when total water volume decreased from 234 to 80 L ha^{-1}, species control with tembotrione plus methylated seed oil at 1.8 L ha^{-1} increased from 42 to 69%. This may be because, like glyphosate, tembotrione is a systemic herbicide that may not need high water volumes for optimal control. In another study conducted by (Zollinger et al. 2013), total water volume contributed to indicator species control with saflufenacil. Treatments with a total water volume at 160 L ha^{-1} consistently provided better control than treatments with a total water volume of 80 L ha^{-1}. This is because saflufenacil is a contact herbicide and may rely on higher total water volume for better coverage (Anonymous 2009). This is supported by the Sharpen® label, which states “use higher spray volumes such as 15 to 20 gallons of water per acre to increase spray coverage and optimize activity” (Anonymous 2009).

Like sunflower, quinoa control ranged from 21% at the lowest rate (0.25% v v^{-1}) to 84% at the highest rate (3% v v^{-1}) 14 DAA (Table 4.5). By 28 DAA, quinoa control ranged from 28 to 88%. There were differences between oil rate and total water volume across all oil types at 14 DAA, but not at 28 DAA when applied to quinoa. Quinoa control fluctuated when area-based rates were applied, and total water volume changed from 80 to 160 L ha^{-1}. For example, when oils at 795 ml ha^{-1} were added to tembotrione with total water volume at 80 L ha^{-1}, quinoa control was 66% but when 795 ml ha^{-1} was applied at 160 L ha^{-1} total water volume, quinoa control decreased to 42% control. Likewise, quinoa control decreased from 80 to 69% when 1590 ml ha^{-1} was applied with total water volumes at 80 and 160 L ha^{-1}, respectively. Similar results occurred when 398- and 2385-ml ha^{-1} rates were applied with water volumes at 80 and 160 L ha^{-1}. However, oil treatments applied based on percent volume stayed consistent regardless of water volume applied. For example, treatments applied at 0.5% v v^{-1} provided similar control with 43 and 42% at 80 and 160 L ha^{-1} total water volume, respectively. Likewise, when treatments were applied at 1% v v^{-1}, quinoa control stayed consistent at 69 and 66% with total water volumes at 160 and 80 L ha^{-1}, respectively.

Similar results were observed by Zollinger et al. (2008). They applied tembotrione with multiple rates of methylated seed oil at multiple total water volumes. As oil rate with tembotrione increased, species control increased. Rates based on percent volume were more consistent than area-based rates as total water volume changed from 80 to 160 L ha^{-1}. Additionally, as previously described with sunflower control in this study and by Zollinger et al. (2013), Zollinger et al. (2008) also reported an increase in species control with tembotrione as water volume decreased. This was hypothesized by Zollinger et al. (2008) to be due to the "pile theory" which describes highly concentrated spray droplets with low water volume provide a better retention of spray droplets, a better deposit in the droplet giving a more effective interface between the active ingredient and the leaf surface, all resulting in more absorption of the active ingredient and greater weed control. Quinoa control treatments in this trial with area-based rates applied with 80 L ha^{-1} total water volume tended to have better quinoa control than area-based rates applied at 160 L ha^{-1} total water volume (Table 4.5). However, there was no statistical difference between treatments applied at 80 or 160 L ha^{-1} total water volume (P=0.22).

There were no differences in amaranth or foxtail millet control observed that could determine whether oil adjuvants should be applied with tembotrione based on area or percent volume (Table 4.5). However, sunflower and quinoa data suggest that applying tembotrione with oil rates based on percent volume provided more consistent control than rates based on area. This is contrary to research on saflufenacil conducted by Zollinger et al. (2013). They reported that oil adjuvant rates based on area optimized saflufenacil while rates based on percent volume fluctuated based on total water volume applied. They found that 1% v v^{-1} at 80 L ha^{-1} total water volume resulted in 57% species control while 1% v v^{-1} at 160 L ha^{-1} total water volume resulted in 67% control. However, saflufenacil is a contact herbicide with a log Kow of 2.57 while tembotrione is a systemic herbicide with a log Kow of 0.081. The differences between these two active ingredients, including both their lipophilicity and their movement within plants, may explain the differences seen between this study and the results observed by Zollinger et al. (2013).

Table 4.5. Effects of tembotrione at 46 g ai ha^{-1} applied with multiple rates of oil adjuvants at two spray volumes on amaranth, quinoa, sunflower, and foxtail millet near Hillsboro, ND in 2016 and 2017.

Treatments		Oil volume rate	Spray volume	Oil area rate	Amaranth		Quinoa			Sunflower			Foxtail millet		
					14 DAA[a,b]	28 DAA	14 DAA		28 DAA	14 DAA		28 DAA	14 DAA	28 DAA	
		% v v^{-1}	L Ha^{-1}	ml Ha^{-1}											
+	Oils	3%	80	2385	57	36	84	a	88	88	a	75	50	23	a
+	Oils	1.50%	160	2385	63	43	77	b	77	88	a	72	42	18	b
+	Oils	2%	80	1590	50	30	80	b	81	85	ab	75	41	18	b
+	Oils	1%	160	1590	54	36	69	c	66	78	bc	68	28	14	c
+	Oils	1%	80	795	33	17	66	c	58	73	c	63	19	10	d
+	Oils	0.50%	160	795	35	18	42	d	43	59	d	54	15	9	de
+	Oils	0.50%	80	398	21	10	43	d	31	59	d	48	11	7	de
+	Oils	0.25%	160	398	20	10	21	e	28	43	e	37	7	6	e
LSD (α=0.05)					NS	NS	3		NS	9		NS	NS	3	

[a] Mean values separated using Fisher's protected LSD. Values followed by different letters within column are significantly different (P ≤ 0.05).
[b] DAA = days after application.

Conclusions

Dicamba efficacy increased with the addition of oil adjuvants in quinoa at 14 and 28 DAA and in buckwheat at 14 DAA (data not shown). Dicamba efficacy did not increase with the addition of any oil at any rate when applied to amaranth or sunflower when compared to dicamba applied alone (data not shown). There was an interaction between oil rate and total water volume pooled across all oil types for buckwheat at 14 DAA (Table 4.4). However, there was very little separation between treatments. Neither area- nor percent volume-based oil adjuvant rates provided consistent buckwheat control when total water volume fluctuated from 80 to 160 L ha^{-1}. There was no difference in which method of calculating oil rate was used.

Tembotrione efficacy increased in all indicator species with the addition of oil adjuvants at most rates (data not shown). Trends indicated that there was a linear relationship between tembotrione and oil concentration applied across all species as well (Table 4.5). As rate of oil increased from 0.25 to 3% v v^{-1}, so did tembotrione efficacy. The Laudis® label recommends oil adjuvants be added to tembotrione at 1% v v^{-1} (Anonymous 2007). Data indicates that rates higher than 1% v v^{-1} provided higher foxtail millet control at 28 DAA, sunflower control at 14 DAA, and quinoa control at 14 DAA. This suggests that the optimal rate of oil to enhance tembotrione efficacy is greater than labelled oil rates. However, increased efficacy on tested species control may also mean increased crop phytotoxicity response, and the recommendation of using higher oil rates does not take into account potential increased crop response from the addition of oil rates higher than 1% v v^{-1}.

There was an interaction between oil rate and total water volume pooled across all oil types for foxtail millet at 28 DAA, sunflower at 14 DAA, and quinoa at 14 DAA (Table 4.5). Foxtail millet control increased as oil rate added to tembotrione increased. However, there was no consistency in foxtail millet control when oils were applied at either area-based or percent volume-based rates. Therefore, it didn't matter whether oil adjuvant rates were based on percent volume or area. Sunflower and quinoa control fluctuated when oil adjuvant rates were based on area and total water volume changed from 80 to 160 L ha^{-1} whereas when oil adjuvant rates were based off percent volume, sunflower control stayed consistent regardless of total water volume. However, Zollinger et al. (2013) found that saflufenacil applied with oil adjuvant rates based on percent volume fluctuated based on total water volume applied. The difference between tembotrione efficacy being more consistent with percent volume-based oil rates in this trial and saflufenacil benefitting from area-based oil rates in trials conducted by Zollinger et al. (2013) could be attributed to differences in chemical properties of each herbicide. Saflufenacil is a contact herbicide belonging to the pyrimidinedione chemical class, while tembotrione is a systemic herbicide belonging to the triketone chemical class. Area-based oil adjuvant rates may be more beneficial for contact, more strongly lipophilic herbicides while percent volume-based oil adjuvant rates may be more beneficial for systemic, slightly lipophilic herbicides.

The same concept could be applied to differences observed between low and high application water volumes. Zollinger et al. (2013) observed saflufenacil benefitted from high total water volumes because contact herbicides benefit from better coverage while sunflower and quinoa control increased in this trial when tembotrione was applied at lower water volumes because systemic herbicides benefit from higher droplet concentration on the leaf surface. However, total water volume has shown variable responses with herbicide efficacy. Etheridge et al. (2001) and Ramsdale and Messersmith (2001b) showed little efficacy reduction when total water volume decreased across multiple contact herbicides. Conversely, Meyer et al. (2016) observed a decrease in dicamba efficacy as total water volume decreased. Therefore, total water volume should be tailored for specific herbicides and weed species.

Since the total water volumes used with contact and systemic herbicides need to be tailored to specific herbicides and weeds, the same concept may need to be applied to oil adjuvant rates based on area or percent volume. These trials do not definitively answer whether all contact, lipophilic herbicides benefit from area-based oil adjuvant rates or all systemic, lipophilic herbicides benefit from percent-volume based oil adjuvant rates. Therefore, more research needs to be conducted to answer this specific question.

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CHAPTER 5. CONCLUSIONS

Extent of indicator species control in these trials depended on many different factors. For example, control changed depending on which herbicide was used, which indicator species tank-mixes were applied to, what adjuvant was added to the tank-mix, what rate of adjuvant was used, the environment indicator species were grown in, and the height of the indicator species the tank-mixes were applied to. This supports comments made by Zollinger (2000): “each plant species can react differently for each herbicide, environment, and adjuvant due to plant morphology, variation in leaf surfaces, composition, and quality of cuticular substances which all influence absorption and contribute to variability in plant response to herbicides.”

In the early 2000’s, high surfactant oil concentrate (HSOC) adjuvants were recognized by the American Society for Testing Materials (ASTM) as a new category of oil adjuvants containing a minimum of 50% oil with 25 to 50% emulsifier surfactant. Trials were conducted to evaluate multiple HSOC adjuvants when added to either glyphosate plus dicamba or glyphosate plus tembotrione. There are two sub-categories of HSOC adjuvants: high surfactant methylated oil concentrates (HSMOC) and high surfactant petroleum oil concentrates (HSPOC) adjuvants. The use of any HSOC adjuvant, whether HSMOC or HSPOC, increased the efficacy of both glyphosate plus dicamba and glyphosate plus tembotrione across indicator species. Linear contrasts were used to deduce whether there were any differences between HSMOC and HSPOC adjuvant subcategories. On average, the addition of HSMOC adjuvants to either glyphosate plus dicamba or glyphosate plus tembotrione increased indicator species more than the addition of HSPOC adjuvants. There were very few differences observed within HSOC sub-categories with either glyphosate plus dicamba or glyphosate plus tembotrione.

Most HSOC adjuvants currently on the market contain a ratio of 60% oil to 40% surfactant (Young et al. 2016). However, some products contain ratios closer to 70% oil to 30% surfactant or 75% oil to 25% surfactant. Greenhouse trials were conducted to evaluate which HSOC ratio increased the efficacy of either glyphosate plus dicamba or glyphosate plus tembotrione. Experimental oil:surfactant ratios ranged from 0:100 to 88:15. However, the only experimental ratios considered “true HSOC ratios” according to ASTM (2016) guidelines were 50:50, 60:40, 70:30, and 80:20. When any of the experimental HSOC ratios were added to glyphosate plus dicamba, amaranth control did not increase at either 14 or 28 days after application (DAA). Quinoa control at 14 and 28 DAA did increase with the addition of any experimental HSOC ratio. However, there was no difference in quinoa control between any experimental HSOC ratios at either 14 or 28 DAA. When any experimental HSOC ratio was added to glyphosate plus tembotrione, amaranth control increased. However, there was no differences between any experimental HSOC ratios when added to glyphosate plus tembotrione and applied to amaranth. The only difference observed between experimental ratios was observed at the 14 DAA ratings, where the 70:30 experimental HSOC ratio provided more quinoa control than the 60:40 experimental HSOC ratio when added to glyphosate plus tembotrione. However, by 28 DAA there were no differences in quinoa control between any of the experimental HSOC ratios. Results from these trials indicate that the addition of any experimental ratio to either glyphosate plus dicamba or glyphosate plus tembotrione increased quinoa control. The addition of any experimental HSOC ratio to glyphosate plus tembotrione increased both amaranth and quinoa control. However, by the final 28 DAA rating, control of all species was the same for all experimental HSOC ratios was added to either glyphosate plus dicamba or glyphosate plus tembotrione.

Oil adjuvant rates can be calculated based on area covered or by the volume of carrier water (percent volume). The NDSU weed guide recommends oil adjuvants be calculated based off area while many herbicide labels recommend oil adjuvants be calculated based off percent volume (Zollinger 2014). Research was conducted to determine which method of calculating oil rates is more preferable. The addition of oil adjuvants at any rate to dicamba did not increase amaranth or sunflower control at either 14 or 28 DAA. Additionally, there was no difference between any oil rates whether applied based on a percent volume or area. Quinoa control increased with the addition of oil adjuvants at both 14 and 28 DAA when compared to dicamba applied alone. However, there was no difference in quinoa control between any oil adjuvant rates when added to dicamba. Buckwheat control with dicamba also increased with the addition of oil adjuvants. Both area- and percent volume-based rates resulted in similar buckwheat control regardless of total water volume applied at, indicating neither method of calculation is more preferable than the other.

Tembotrione efficacy increased across all indicator species when oil adjuvants were added at any rate. There were no differences between oil rates when added to tembotrione to control amaranth. At 14

DAA there was no differences between oil rates when added to tembotrione to control foxtail millet. However, at 28 DAA results indicated that increasing oil rate increased control of foxtail millet. However, neither the area-based nor the percent volume-based rates were consistent when water volumes changed from 80 to 160 L ha^{-1} total water volume, indicating foxtail millet control could not consistently be improved by one method of calculation over the other. For quinoa and sunflower, control in each species fluctuated when oil was added to tembotrione with rates based on area and water volume changed from 80 to 160 L ha^{-1} total water volume. Conversely, when percent volume-based rates were used, both quinoa and sunflower control stayed consistent regardless of total water volume. Additionally, there tended to be increased quinoa and sunflower control when treatments were applied at 80 L ha^{-1} rather than 160 L ha^{-1}. Quinoa and sunflower control indicates that using the percent volume based oil rate method of calculation for tembotrione was more preferable than using the area-based oil rate method.

Overall, this research has provided clarity on the utility oil adjuvants to optimize dicamba and tembotrione efficacy on several broadleaf species. This research helped elucidate the utility of HSOC adjuvants, the optimal rates of oil to surfactant for composition of HSOC adjuvants, and the rate of oil needed for optimal efficacy of dicamba and tembotrione.

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