CHARACTERIZATION OF SURFACTANT QUALITY AND VALIDATION OF STANDARD WATER CONDITIONING TESTING

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The Supervisory Committee certifies that this ***disquisition*** complies with North Dakota State University's regulations and meets the accepted standards for the degree of

DOCTOR OF PHILOSOPHY

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ABSTRACT

Adjuvants are products added to pesticide applications to increase pest control. There are many different types of adjuvants designed to solve certain problems. Surfactants are a major class of agricultural adjuvant used to increase the efficacy of pesticides. Many companies use physical and chemical characteristics to market surfactants. However, producers do not understand these characteristics. Field efficacy data should be used to effectively market surfactants, but is somewhat limited. The objective of the first study was to evaluate if chemical and physical characteristics of agricultural surfactants can be used to predict field performance. Chemical and physical characteristics tested included HLB, dynamic surface tension, contact angle, and absorption through isolated cuticles. When individual characteristics were used as covariates with field efficacy data, no consistent results were observed. Therefore, physical and chemical characteristics cannot be used to accurately predict field performance of surfactants. In 2011, Zollinger et al. published a paper titled "A test method for evaluating water conditioning adjuvants" as a standardized test method. While this has been an effective test method, a comparison of salt type used has never been conducted. The objective of this research was to validate the standardized test method using three artificially mixed hard water samples with calcium chloride, calcium formate, and calcium nitrate. Field trials were conducted near Hillsboro, ND in 2016 and 2017. Glyphosate and mesotrione were applied at 342 and 70 g ai ha^{-1}, respectively. Three types of water conditioners were evaluated with glyphosate: diammonium sulfate (AMS), AMS replacement, and monocarbamide dihydrogen sulfate (AMADS). Herbicide antagonism was similar between the simulated hard water samples. Within each type of water conditioning adjuvant, antagonism was overcome similarly in all water types. The results of these studies validate the test method established by Zollinger et al. (2011).

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CHAPTER 1. CHARACTERIZATION OF SURFACTANT QUALITY

Abstract

Surfactants are a major class of agricultural adjuvant used to increase the efficacy of pesticides. Many companies use physical and chemical characteristics to market surfactants. However, producers do not understand these characteristics. Field efficacy data should be used to effectively market surfactants, but is somewhat limited. The objective of this study was to evaluate if chemical and physical characteristics of agricultural surfactants can be used to predict field performance. Chemical and physical characteristics tested included HLB, dynamic surface tension, contact angle, and absorption through isolated cuticles. Surfactant characteristics were used as covariates to compare against field trials. When individual characteristics were used as covariates with field efficacy data, no consistent results were observed. The plants leaf surface, surfactant, and herbicide all interact to create a dynamic system which is difficult to predict. Therefore, physical and chemical characteristics cannot be used to accurately predict field performance of surfactants. Surfactant manufacturers should conduct field trials and market products based on field performance data.

Introduction

Agriculture producers utilize adjuvants to enhance the performance of pesticides. Adjuvants are defined as any “material added to a tank mix to aid or modify the action of an agrichemical, or the physical characteristics of the mixture” (ASTM 2016). Adjuvants primarily aid the action of an agrichemical in one or more of three primary categories: spray retention, deposition on the leaf surface, and absorption into the plant (Zollinger et al. 2017). There are many different types of adjuvants available which fulfill different purposes. With so many options, grower confusion on adjuvant selection is very apparent (Zollinger 2000). Much of the confusion is due to the lack of efficacy information and regulation of new products in the market place. Therefore, reliable data for adjuvants is needed to reduce grower confusion.

Surfactants are a major class of agricultural adjuvants. Surfactants are defined as "material comprised of lipophilic and hydrophilic parts that when added to a liquid medium modifies the properties of the surface or interface by concentrating at the surface or interface" (ASTM 2016). In other words, surfactants are designed to aid the agrichemical by improving the interaction at the leaf surface. Surfactants are sometimes separated into various categories based on chemical families (Zollinger 2000), or separated into the function they serve (e.g. spreaders, stickers, emulsifying agents) (ASTM 2016). The specific activity of surfactants are determined by the combination of chemical and physical characteristics of the product.

A major chemical characteristic of surfactants that is widely used to predict the effect on herbicides is the hydrophilic-lipophilic balance (HLB) (Bruns and Nalewaja 1998; Hess and Foy 2000; Stock and Briggs 2000). The HLB is a measure of the interaction of the surfactant between the lipid and aqueous phases of the spray solution. The HLB is roughly calculated by using the percent weight of the hydrophilic moiety of the total molecule divided by 5 (Hess and Foy 2000). The traditional range of HLB values ranges from 1 to 20. Lipophilic surfactants will generally have an HLB below 8, while hydrophilic surfactants will be above 11. There is a relationship between the HLB of an optimal surfactant for a herbicide based on the octonol:water partition coefficient (K_{ow}). For example, a herbicide with a log K_{ow} (>0) will likely be optimized by using a surfactant with a low HLB. Conversely, Nalewaja et al. (1996) evaluated glyphosate absorption with surfactants with various HLB values. Glyphosate is highly water soluble and has a log K_{ow} of -2.9 (Shaner 2014) and absorption was optimized using a surfactant with an HLB of 17.2 (Nalewaja et al. 1996). While HLB can be a useful value to predict the interaction of surfactants with agrichemicals, it fails to take into account many other chemical factors that may affect efficacy (Stock and Briggs 2000). It is possible to have two surfactants that have very different moieties as a part of the structure and have the same HLB. For example, surfactants with longer ethoxylated chains generally interact favorably with hydrophilic herbicides (Hess and Foy 2000). However, the size of the lipophilic moiety will determine the calculated HLB value for the surfactant.

The addition of surfactants to a tank mix may also affect many physical properties of the spray solution, which in turn may affect efficacy. Dynamic surface tension, contact angle, viscosity, and physical deposition are all affected by surfactants (Stock and Briggs 2000). Dynamic surface tension measurements are useful to predict the leaf wetting and spray formation during application. During spray formation the surface tension of the solution is not at equilibrium; therefore, measurements of surface tension are made using timeframes that are relevant for the development of agricultural spray. The measured dynamic surface tension can be used to predict the spreading of the droplet on the leaf surface. However, in order to fully predict the spreading, the critical surface tension for a leaf surface must be known. The critical surface tension is the surface tension at which a contact angle of 0 is achieved. Since critical surface tension is not known in many cases, the measurement of dynamic surface tension is a relative measurement.

Surface tension also affects the development of the contact angle of the droplet on the leaf surface (Stock and Briggs 2000). Surfactants generally lower the contact angle of spray deposits (Xu et al. 2010). Lowering the contact angle increases the contact area of the leaf surface, which typically increases herbicide activity. By increasing the contact area, surfactants increase the "wettability" of the leaf surface. A leaf surface is considered wettable if the contact angle of water is below 90°. The wettability of a leaf is determined by leaf cuticle formation, roughness, and thickness. For example, lambsquarters (*Chenopodium album* L.) is considered a hard-to-wet species due to the crystalline wax on the leaf surface (De Rutter et al. 1990). Reducing the contact angle of the spray droplet aids in wetting the leaf surface of lambsquarters.

Lastly, surfactants can affect the physical deposition of the agrichemical on the leaf surface (Stock and Briggs 2000). Surfactants may affect the solubilization of the agrichemical, which during the dry down of the droplet will affect the quality of the deposit. The deposit of active ingredient crystals on the leaf surface reduces herbicide efficacy greatly. In addition, adjuvants added to the spray solution affect the distribution of herbicide in the deposit (Xu et al. 2010). Not much is known about how surfactants affect the deposition of active ingredients on the leaf surface; however, it is clear that the deposit of active ingredients on the leaf surface is very important for absorption into the plant (Stock and Briggs 2000).

Many companies market the benefits of their surfactants using chemical and physical properties such as solubilization, retention, HLB, or surface tension (Zollinger 2000). However, producers do not understand or consider these properties; rather they typically choose adjuvants based on price and field performance. Field efficacy data for many surfactants is limited due to lack of field testing, distribution of the information, and proprietary information. Currently, few scientific papers are published relating the chemical and physical properties to field efficacy trials. The objective of this study was to evaluate if chemical and physical characteristics of agricultural surfactants can be used to predict field performance.

Materials and Methods

Herbicide Efficacy Trials

Surfactant effects on herbicide efficacy was evaluated in field indicator trials near Hillsboro, ND in 2016 and 2017. Indicator species were planted across the plot area to ensure uniform growth and distribution at the time of application (Zollinger et al. 2011). Indicator species included flax (*Linum usitatissimum* L.), amaranth (*Amaranthus cruentus* L.), quinoa (*Chenopodium quinoa* Willd.), and conventional soybean (*Glycine maxx* (L.) Merr.) for the glyphosate trial. Indicator species were amaranth, quinoa, tame buckwheat (*Fagopyrum exculentum* Moennch), and sunflower (*Helianthus annuus* L.) for the dicamba and glyphosate plus dicamba trials. All surfactants were applied in separate trials with glyphosate, dicamba,

Table 1.1. Treatments for herbicide efficacy trials to be applied in 2016 and 2017 near Hillsboro, ND. Herbicides included glyphosate at 315 g ae ha^{-1}, dicamba at 214 g ha^{-1}, and the combination of glyphosate and dicamba in separate trials. Adjuvants applied at recommended use rates based on equivalent surfactant load. Adjuvant rates were also used for absorption studies.

No.	Treatment	Adjuvant	Adjuvant rate
			% v v^{-1}
1	Untreated	----	----
2	Herbicide	----	----
3	Herbicide	ADJ1	0.10
4	Herbicide	ADJ1	0.25
5	Herbicide	ADJ2	0.10
6	Herbicide	ADJ2	0.25
7	Herbicide	ADJ3	0.10
8	Herbicide	ADJ3	0.25
9	Herbicide	ADJ4	0.10
10	Herbicide	ADJ4	0.25
11	Herbicide	ADJ5	0.10
12	Herbicide	ADJ5	0.25
13	Herbicide	ADJ6	0.25
14	Herbicide	ADJ6	1.50

and glyphosate plus dicamba (Table 1.1). Glyphosate (Touchdown HiTech, Syngenta Crop Protection LLC, PO Box 18300, Greendboro, NC, 27419) was applied at 315 g ae ha^{-1}, while dicamba (Clarity, BASF Corporation, 26 Davis Drive, Research Triangle Park, NC 27709) was applied at 214 g ae ha^{-1} alone, and in the tank mix trial. Adjuvants were applied at 0.10 and 0.25 % v v^{-1}, except ADJ6 which was applied at 0.25 and 1.50 % v v^{-1} which is equivalent surfactant load.

Applications were made to the center 2 m of 3 m by 12 m plots perpendicular to indicator species planting with a CO_2 pressurized backpack type sprayer delivering 80 L ha^{-1} at 138 kPa (Zollinger et al. 2011). Treatments were applied when amaranth and quinoa were 20 to 25 cm in height. Treatments were arranged as an RCBD with 3 replications. The average height of each indicator species was measured 14 and 28 days after treatment (DAT). Percent weed control was determined by comparing the height of each species to the untreated control. Years and reps were considered as random effects, while treatments were considered as a fixed effect. Analysis of variance was conducted using SAS 9.3 (SAS Institute, SAS Circle, Cary, NC) for each indicator species individually combined across years with results considered significant at $p \leq 0.05$, and separation of means calculated with an F-protected least significant difference test at $\alpha = 0.05$.

Dicamba Absorption

Surfactant effects on herbicide absorption was determined using isolated leaf cuticles from Pinova apple trees (*Malus pumila* var. *Pinova* Miller). The leaf cuticle was attached to a sampling column by applying a thin layer of wax to the column then placing a cap over the leaf cuticle. Dicamba was then be applied at 0.5 % v v^{-1} in 10 µL H_2O with each surfactant treatment to the leaf cuticle and allowed to dry. All surfactants were added at similar rates to the herbicide efficacy trials (Table 1.1). Treatments were arranged as a CRD with 10 samples and then replicated. The sample columns were then inverted and placed in sampling trays with a well with a drop of calcium nitrate tetrahydrate at 2.7 kg L^{-1} to maintain the relative humidity at approximately 56% on the adaxial side of the cuticle. The sampling column was filled with 1000 µL of an acceptor solution of diethylene glycol and distilled water mixed at 0.43 m m^{-1}. The sampling trays were placed in the high performance liquid chromatography (HPLC) machine (Agilent Technologies 1290 infinity, 5301 Stevens Creek Blvd, Santa Clara, CA 95051) for sampling.

Samples were taken by removing 10 µL of acceptor solution at 3, 12, 24, and 48 h after application using an auto sampler. The samples were injected into the HPLC machine and run through a Kinetex C18 reversed phase column (Phenomenex, 411 Madrid Avenue, Torrence, CA 90501). The column temperature was 40 C and sampling time set at 3 min per sample. The elution was isocratic using 80% eluent A (phosphoric acid and acetonitrile at 95/5 % v v^{-1}) and 20% eluent B (acetonitrile and phosphoric acid 95/5% v v^{-1}). Data from cuticles that broke during the sampling process were excluded from the analysis. The absorption of dicamba was

Table 1.2. Treatments for lab trials conducted in Frankfurt, Germany in 2015.

No.	Treatment	Dicamba rate	Adjuvant	Adjuvant rate
		% v v^{-1}		% v v^{-1}
1	Untreated	----	----	----
2	Dicamba	0.5	----	----
3	Dicamba	0.5	ADJ1	0.25
4	Dicamba	0.5	ADJ2	0.25
5	Dicamba	0.5	ADJ3	0.25
6	Dicamba	0.5	ADJ4	0.25
7	Dicamba	0.5	ADJ5	0.25
8	Dicamba	0.5	ADJ6	1.50

recorded as a percent of applied. Analysis of variance of the 48 h absorption data was conducted as a CRD with sampling with PROC ANOVA in SAS 9.3. All effects were considered as fixed. Results were considered significant at $p \leq 0.05$.

Contact Angle

Contact angle was measured using a Data Physics Contact Angle System OCA (Data Physics Instruments GmbH, Raiffeisenstrasse 34, D 70794 Filderstadt). Dicamba was applied at 0.5 % v v^{-1} with all surfactants in 5 µL of spray solution (Table 1.2) to a corn (*Zea mays* L.) leaf. The contact angle of the droplet was recorded for 3 min after application. Each treatment was repeated on a different corn leaf. The data are presented as the average contact angle across the 3 min application.

Dynamic Surface Tension and HLB

Dynamic surface tension and hydrophilic-lipophilic balance (HLB) are two characteristics commonly used to promote surfactant quality. Dynamic surface tension for each surfactant mixture with dicamba (Table 1.2) was measured using a Kruss Pocket Dyne (Krüss GmbH – Germany, Borsteler Chaussee 85, 22453 Hamburg, Germany) at 100 ms. The solution temperature was 25 C at the time of measurement. The HLB value for each surfactant was obtained from the primary manufacturer of each product.

Spray Deposition

The deposition of spray droplets containing dicamba with surfactants (Table 1.2) was captured using a scanning electron microscope. Treatments were applied in 0.3 µL droplets on cabbage leaves (*Brassica oleracea* L.) and allowed to dry for approximately 1 h. The leaves were then freeze dried using liquid nitrogen and then sputtered with gold. Samples were put into the scanning electron microscope and several images at various magnifications were taken. The scanning electron microscope was equipped with an ion detector which allowed the detection of certain ions. Since the dicamba molecule contains 2 chlorine atoms (Shaner 2014), the detector was set to image the distribution of chlorine in the spray droplet. The chlorine images were most helpful in evaluating the deposition quality of dicamba in the spray droplet. The images were used to view the relative quality of spray droplet deposition on the leaf surface.

Surfactant Characteristic Analysis

To assess surfactant quality, a covariate analysis was conducted to evaluate the effect of individual physical or chemical characteristics to predict field performance of each surfactant with dicamba. The dependent variable in the model was percent control of each indicator species at each evaluation date run individually. PROC MIXED was used with absorption means, contact angle, surface tension at 100 ms, and HLB used as covariates in the model. The type I method was used to calculate differences between treatments. Results were considered significant at $p \leq 0.05$.

Results and Discussion

Physical and Chemical Characteristics

The HLB for each surfactant was obtained from the primary manufacturers. The HLB values ranged from 10.4 to 16.0 (Table 1.3). Because the HLB values were near or above 11, they were all considered to be hydrophilic surfactants (Hess and Foy 2000). Both dicamba and glyphosate are hydrophilic and have log K_{OW} values of -0.5 and -2.9, respectively (Shaner 2014). Therefore, both active ingredients should be optimized by surfactants with HLB values above 11 (Hess and Foy 2000). For example, glyphosate could be optimized with ADJ4 with an HLB of 16, due to glyphosate being optimized with a surfactant with a HLB of 17.2 (Nalewaja et al. 1996).

Table 1.3. Physical and chemical properties of spray solutions with the different surfactants evaluated in the lab for this study.

Treatment	Adjuvant rate	HLB	Contact angle	Surface tension	Absorption
	% v v^{-1}		Degree	mN m^{-1}	%
Water	------	------	141.3	------	------
Dicamba	0.50	------	142.5	72.8	18.9
+ ADJ1	0.25	10.4	50.5	66.4	28.5
+ ADJ2	0.25	11.5	25.0	42.2	35.4
+ ADJ3	0.25	13.0	36.0	38.9	40.1
+ ADJ4	0.25	16.0	96.0	54.2	17.0
+ ADJ5	0.25	11.9	9.50	43.4	44.6
+ ADJ6	1.50	13.0	65.0	60.0	59.0

Contact angle of spray droplets was measured and was affected by surfactants (Table 1.3). The contact angle of water on a corn leaf averaged 141.3°. When dicamba at 0.5 % v v^{-1} was added to the spray solution, contact angle did not significantly change and was 142.5°. However, when surfactants were added, the contact angle was reduced to 96° or below. ADJ5 provided the lowest contact angle at 9.5°. The reduction of contact angle is related to the reduced surface tension of the droplet (Xu et al. 2010). A reduction of contact angle also results in a larger wetted area on the leaf surface. For example, on *Kalanchoe serrata* leaves, the addition of an NIS surfactant reduced the contact angle by 88.2°, which increased the wetted area of the leaf surface by 0.728 mm^2. Due to a larger wetted area, weed control generally increased. Therefore, ADJ5 would be predicted to perform the best, due to the lowest contact angle of 9.5° (Table 1.3).

Dynamic surface tension differed among the surfactant treatments. The surface tension for dicamba alone was 72.8 mN m^{-1} (Table 1.3). The addition of surfactants reduced the dynamic surface tension significantly. ADJ3 provided the lowest dynamic surface tension at 38.9 mN m^{-1}. Reduction of surface tension improved pesticide efficacy by increasing retention (De Rutter et al.

1990). Retention is improved by reducing bouncing of spray drops as they hit the leaf surface. The reduction of surface tension also improves wetting of leaves with crystalline epicuticular waxes, such as those of lambsquarters (Chenopodium album L.). Therefore, a surfactant which reduces surface tension would be predicted to provide the greatest field performance.

Dicamba absorption was measured across isolated apple cuticles. Dicamba alone absorption averaged 18.9% after 48h (Table 1.3). The addition of surfactants generally increased absorption. Numerically ADJ6 provided the highest level of absorption at 59%. However, the F-test of the treatments was non-significant with a *p*-value of 0.06. This was due to large variability within each individual treatment. For example, in one replicate, ADJ3 varied approximately 80% in absorption values. One reason for the large amount of variability observed may be due to the variability observed in cuticle formation even within a species (Fernandez et al. 2017). Isolated cuticles were used from individual leaves from Pinova apple trees. There is potentially large amounts of variability in each isolated cuticle which could account for the high variability. However, increased absorption through the cuticle would be predicted to increase field performance.

Spray Deposition

The scanning electron microscope images confirmed that surfactant choice affected herbicide deposition on the leaf surface (Figures 1.1 A-F). Surfactants typically caused the herbicide to be deposited in a “coffee ring” shape (Xu et al. 2010). However, deposits that are more uniform in distribution typically provide higher levels of control. Based on the images, dicamba alone and ADJ1 provided the most ideal uniform distribution pattern of dicamba on the leaf surface of cabbage, which would predict increased field performance (Figures 1.1 A-F). Herbicide solubility was also affected by surfactants (Behrens 1964). If poorly solubilized in

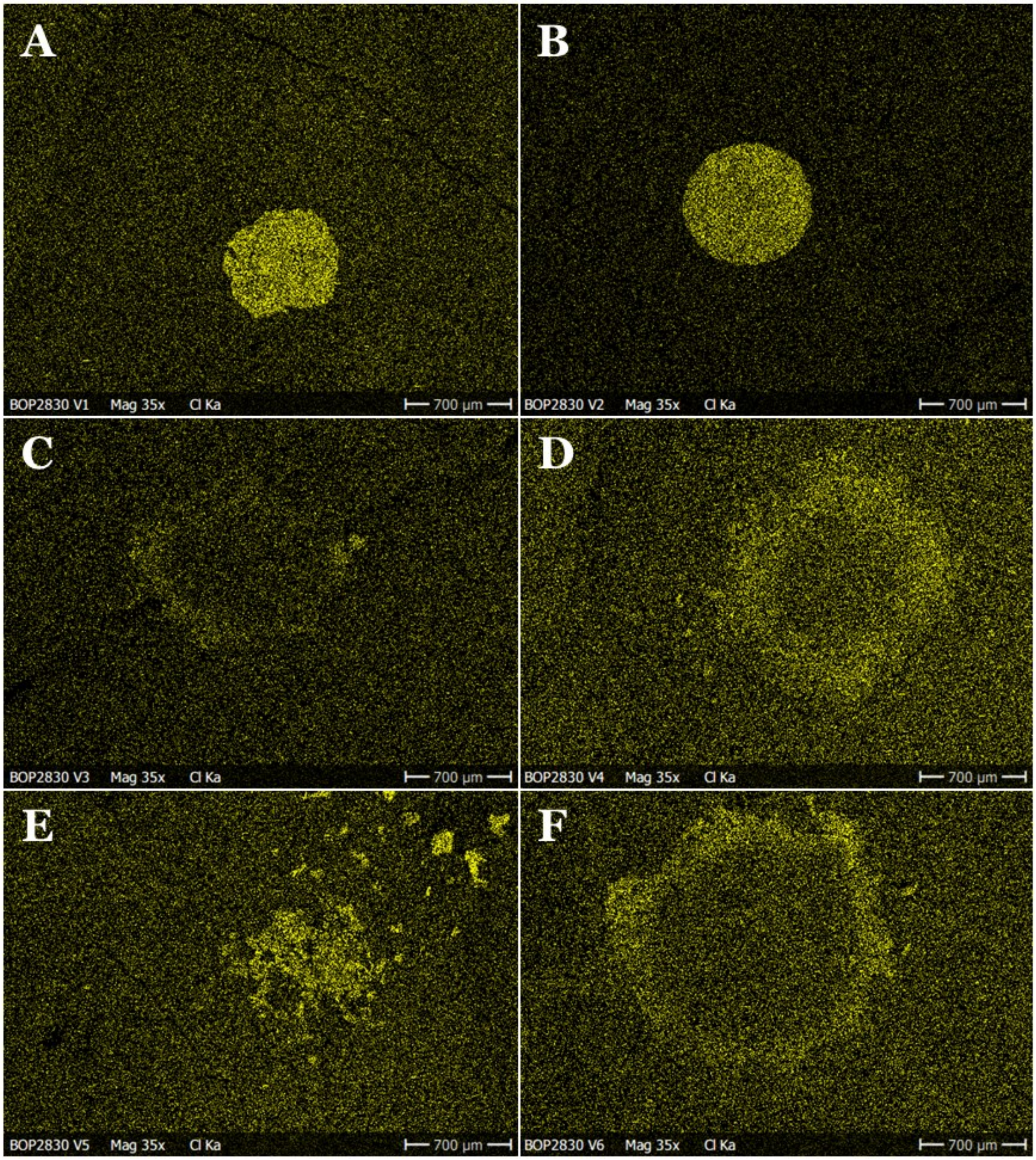

Figure 1.1. Scanning electron microscope images of dicamba applied on cabbage leaves at 0.5 v v^{-1} in 3 µL deposits as affected by surfactants. A- no adjuvant, B- ADJ1, C-ADJ2, D-ADJ3, E-ADJ4, F-ADJ5.

solution, herbicides will be deposited on the leaf surface as crystals (Hess and Foy 2000; Stock and Briggs 2000). Crystalline size and shape of herbicide deposits reduce efficacy due to reduced absorption. ADJ4 and ADJ5 have a larger crystalline deposit structure compared to other surfactants (Figures 1.1 E-F). Comparatively, the crystal size of no adjuvant and ADJ1 indicate are smaller and more ideal (Figures 1.1 A-B). The poor quality deposit of ADJ 4 and ADJ5 would indicate poor field performance while dicamba alone and ADJ1 would indicate increased field performance.

Herbicide Efficacy Trials

Glyphosate efficacy was affected by surfactants mixed in the spray solution (Table 1.4). Control was increased with the addition of surfactants to glyphosate on all indicator species.

Table 1.4. Effect of surfactants on glyphosate at 315 g ae ha^{-1} efficacy on flax, amaranth, quinoa, and conventional soybean near Hillsboro, ND in 2016 and 2017.

Treatment	Adjuvant rate	Flax		Amaranth		Quinoa		Conv soybean	
		14	28	14	28	14	28	14	28
	% v v^{-1}	%							
Glyphosate	------	27	7	46	40	15	12	16	8
+ ADJ1	0.10	67	68	48	38	26	31	23	12
+ ADJ1	0.25	67	73	49	43	48	42	43	17
+ ADJ2	0.10	52	42	43	35	38	30	28	10
+ ADJ2	0.25	40	20	41	39	46	33	43	22
+ ADJ3	0.10	73	80	47	40	68	50	39	18
+ ADJ3	0.25	73	73	57	45	73	66	55	33
+ ADJ4	0.10	90	90	50	43	66	62	52	28
+ ADJ4	0.25	90	95	50	44	75	65	65	41
+ ADJ5	0.10	83	87	50	41	76	65	51	28
+ ADJ5	0.25	77	70	53	42	78	68	58	33
+ ADJ6	0.25	43	27	53	43	29	20	26	17
+ ADJ6	1.50	75	67	65	49	68	59	68	45
LSD (α=0.05)		12	11	7	5	10	7	8	5

Glyphosate alone averaged only 17 % control across all indicator species. The performance of each surfactant varied on each indicator species. For example, ADJ4 at 0.25 % v v^{-1} provided the best control on flax and soybean, while ADJ6 at 1.5 % v v^{-1} provided the highest control of amaranth, and ADJ5 at 0.25 % v v^{-1} provided the highest control of quinoa. Surfactants have long been shown to increase glyphosate efficacy. For example, glyphosate absorption was increased 78% with the addition of surfactants (Leaper and Holloway 2000). Glyphosate activity was also influenced by the type of surfactant used similar to the results of this study.

Dicamba provided 43 % average control of indicator species (Table 1.5). The addition of surfactants increased control of dicamba in all indicator species. However, the range of increased control observed was less than the range observed for glyphosate. For example, control ranged

Table 1.5. Effect of surfactants on dicamba at 214 g ai ha^{-1} efficacy on amaranth, quinoa, tame buckwheat, and sunflower near Hillsboro, ND in 2016 and 2017.

Treatment	Adjuvant rate	Amaranth		Quinoa		Tame buckwheat		Sunflower	
		14	28	14	28	14	28	14	28
	% v v^{-1}	%							
Dicamba	------	41	40	38	40	50	41	37	50
+ ADJ1	0.10	49	39	56	58	54	43	35	50
+ ADJ1	0.25	48	40	60	63	52	43	37	52
+ ADJ2	0.10	46	36	63	66	55	45	34	49
+ ADJ2	0.25	57	42	63	68	54	44	30	49
+ ADJ3	0.10	57	44	60	64	48	39	38	52
+ ADJ3	0.25	45	39	63	72	56	45	38	53
+ ADJ4	0.10	45	34	63	64	55	46	37	55
+ ADJ4	0.25	57	38	61	68	56	44	36	53
+ ADJ5	0.10	52	38	62	71	60	48	35	51
+ ADJ5	0.25	48	39	61	74	58	49	38	55
+ ADJ6	0.25	52	38	55	63	58	49	36	53
+ ADJ6	1.50	54	40	64	71	54	48	38	55
LSD (α=0.05)		7	5	4	4	5	5	3	NS

34 % control on quinoa with dicamba and surfactants compared to 56 % with glyphosate. This indicates that surfactants are not as important for dicamba. Similar to glyphosate, indicator species control varied by surfactant with dicamba with ADJ3 at 0.1 % v v^{-1}, ADJ5 at 0.25 % v v^{-1}, ADJ5 & 6 at 0.25 % v v^{-1} providing the highest level of control of amaranth, quinoa, and tame buckwheat, respectively.

When glyphosate and dicamba were mixed, control averaged 63 % across all indicator species (Table 1.6). The addition of surfactants generally increased control of glyphosate plus dicamba. Similar to the other field trials, control of each indicator species varied by surfactant. Amaranth control 28 DAT was greatest with ADJ1 at 0.1 % v v^{-1}, quinoa control was highest

Table 1.6. Effects of surfactants on glyphosate at 315 g ae ha^{-1} and dicamba at 214 g ai ha^{-1} on amaranth, quinoa, tame buckwheat, and sunflower near Hillsboro, ND in 2016 and 2017.

Treatment	Adjuvant rate	Amaranth		Quinoa		Tame buckwheat		Sunflower	
		14	28	14	28	14	28	14	28
	% v v^{-1}	%							
Glyphosate									
+ Dicamba	------	66	52	57	56	77	74	64	71
+ ADJ1	0.10	73	63	81	73	71	77	58	60
+ ADJ1	0.25	68	56	82	76	71	75	68	70
+ ADJ2	0.10	63	53	82	81	80	79	61	70
+ ADJ2	0.25	63	48	86	79	82	78	60	75
+ ADJ3	0.10	63	43	79	75	76	76	58	63
+ ADJ3	0.25	68	48	86	81	80	78	64	74
+ ADJ4	0.10	59	43	76	79	80	78	63	73
+ ADJ4	0.25	58	45	81	78	82	80	73	78
+ ADJ5	0.10	68	49	83	78	85	79	69	74
+ ADJ5	0.25	69	50	88	80	88	81	72	78
+ ADJ6	0.25	73	48	53	63	77	76	73	74
+ ADJ6	1.50	73	52	81	79	85	83	80	79
LSD (α=0.05)		6	6	5	5	5	4	9	8

with ADJ2 at 0.1 % v v^{-1}, ADJ5 at 0.25 % v v^{-1} increased wild buckwheat control the most, and sunflower control was highest with ADJ6 1.5% v v^{-1}.

Surfactant Characteristic Analysis

The main objective of this study was to evaluate if chemical and physical characteristics of agricultural surfactants can be used to predict field performance. When individual chemical and physical characteristics were used as covariates to predict field performance, no relationship could be established. *P*-values for individual tests ranged from 0.1 to 0.9, indicating no relationship between the covariates and control of indicator species. Control of each indicator species varied by surfactant regardless of herbicide choice (Tables 1.4-1.6). For example, ADJ5 had the lowest contact angle of 9.5° which might be predicted to be the most ideal. ADJ5 provided the highest control in many species, but not for all species. ADJ6 provided the highest level of dicamba absorption in isolated apple cuticles, however ADJ3 and ADJ5 provided higher control of indicator species in the field. There was no consistency between the predictions of individual chemical and physical characteristics and the field performance. ADJ5 was the most common surfactant providing the highest level of control in the herbicide efficacy trials. The individual characteristics of ADJ5 would predict an average level of control, however field performance may be due to a combination of individual components interacting in the field.

Herbicide efficacy is affected by many factors (Taylor 2011). Factors such as dynamic surface tension, contact angle, droplet velocity, surfactant type, and concentration can affect spray retention, which can in turn affect herbicide efficacy. In this study, the surfactants varied in surface tension, contact angle, and HLB which would affect the herbicides differently. Herbicides have different characteristics such as vapor pressure, K_{ow}, solubility, and formulation type which can influence the interaction with plant species (Zollinger 2000). In this study, glyphosate and dicamba were used to evaluate the effect of surfactants. The two herbicides vary in characteristics such as K_{ow}, solubility, and mode of action (Shaner 2014). Due to the differences in herbicides, the surfactants used to optimize the herbicides would vary. DeRutter et al. (1990) identified leaf surface characteristics as a major factor of herbicide activity. Factors such as cuticle thickness, composition, crystalline wax structures, and hairs have all contributed to herbicide activity. The indicator species evaluated here vary greatly in leaf structure. For example, amaranth has a thick shiny waxy cuticle compared to the crystalline wax cuticle of quinoa. Flax has small linear leaves compared to large leaves of tame buckwheat. These differences in leaf characteristics would affect the field performance of each adjuvant. Additionally factors such as plant density and canopy structure can affect herbicide efficacy (Taylor 2011). It may be possible to observe individual components to predict how an adjuvant may perform in a laboratory setting; however, the field performance of surfactants has so many variables that accurate predictions cannot be made (Stock and Briggs 2000). Due to the complexity of field performance, surfactants should be marketed and promoted based on field performance studies instead of individual chemical and physical characteristics.

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CHAPTER 2. VALIDATION OF STANDARD WATER CONDITIONING TESTING

Abstract

In 2011, Zollinger et al. published a paper titled "A test method for evaluating water conditioning adjuvants" as a standardized test method. Artificial hard water is mixed to 1000 mg L^{-1} of calcium chloride and magnesium chloride. Water conditioning agents are mixed with herbicides and evaluated for the ability to overcome the antagonistic effects of cations in the water. While this is an effective test method, a comparison of salt type used has never been conducted. The objective of this research was to validate the standardized test method using 3 artificially mixed hard water samples mixed to 500 mg L^{-1} Ca using calcium chloride, calcium formate, and calcium nitrate. Field trials were conducted near Hillsboro, ND in 2016 and 2017. In separate studies, glyphosate and mesotrione were applied at 342 and 70 g ai ha^{-1}, respectively. Three types of water conditioners were evaluated with glyphosate: diammonium sulfate (AMS), AMS replacement, and monocarbamide dihydrogen sulfate (AMADS). AMADS was not included in the mesotrione study. Indicator species included flax (*Linum usitatissimum* L.), amaranth (*Amaranthus cruentus* L.), sunflower (*Helianthus annuus* L.), and conventional corn (*Zea mays* L.) for the glyphosate study. Amaranth, foxtail millet (*Setaria italica* (L.) P. Beauvois), quinoa (*Chenopodium quinoa* Willd.), and sunflower were indicator species for the mesotrione study. Herbicide antagonism was similar between the simulated hard water samples. Within each type of water conditioning adjuvant, antagonism was overcome similarly in all water types. The results of these studies validate the test method established by Zollinger et al. (2011).

Introduction

Calcium, iron, and magnesium are ions typically found in hard water which can greatly reduce the efficacy of herbicides such as glyphosate (Subramaniam and Hoggard 1988). For example, glyphosate efficacy was reduced from 60 to 23 % control when applied with calcium nitrate at 0.5% w v^{-1} (Woznica et al 2003). Weed control of other herbicide active ingredients can also be reduced by cations in the water (Roskamp et al 2013). For example, horseweed control was reduced over 10 % when 2,4-D was applied in water with calcium, magnesium, manganese, and zinc compared to distilled water. The basis for the reduced efficacy was due to binding of calcium and other various cations to the anionic form of weak acid herbicides (Thelen et al 1995). In the case of glyphosate, calcium will bind with the carboxyl and phosphonate functional groups of the herbicide, which reduces absorption. The amount of antagonism will vary with various salt combinations found in water (Nalewaja and Matysiak 1991). The general trend for cation antagonism was iron > calcium ≥ magnesium > sodium > potassium.

The source of calcium used in testing can result in different levels of antagonism at similar cation concentrations (Nalewaja and Matysiak 1991). For example, the percent fresh weight reduction of wheat treated with glyphosate ranged from 0 to 45 % depending on the source of calcium used. Since many sources of calcium can be used to mix hard water samples, evaluation of various calcium sources must be completed. For example, calcium chloride and calcium nitrate had similar antagonistic effects on glyphosate compared to calcium carbonate and calcium sulfate which antagonized glyphosate less.

Many farmers use water pumped from wells as the spray carrier so antagonism from cations can be a major concern. In order to overcome antagonism from cations in the spray carrier, water conditioning adjuvants such as diammonium sulfate (AMS) are added to the spray tank to overcome antagonism (Zollinger et al 2016). AMS overcomes cation antagonism through two reactions. First, the ammonium ion will outcompete other cations, such as calcium, for the binding to glyphosate. Ammonium bound to glyphosate generally also increases absorption. Second the sulfate anion will bind to the cations in the water. The addition of AMS overcame the antagonistic effect of calcium and increased absorption of glyphosate in sunflower (Thelen et al 1995). The use of AMS is very common for glyphosate applications; however, there are other types of water conditioning adjuvants available. For example, acids can be used to overcome hard water antagonism (Zollinger et al 2013). Acids are used to lower the spray solution pH to below the pKa of the herbicide. Below the pKa the herbicide is more likely to be in the parent acid (neutral) form and not available to bind with cations in solution. Additionally, new types of water conditioners are created each year in order to address new herbicide technology requirements. Continued research is needed to evaluate different forms of water conditioning adjuvants in light of new herbicide technology requirements.

In order to accurately evaluate water conditioning adjuvants across the United States, Zollinger et al. (2011) proposed a standard test method. The method uses distilled water mixed with calcium chloride and magnesium chloride to simulate natural hard water. This method is enacted by mixing calcium chloride and magnesium chloride to equal 1000 mg L^{-1}. Water conditioning agents are mixed with herbicides and evaluated for the ability to overcome the antagonistic effects of cations in the water. A total of six researchers conducted experiments in geographically distinct regions of the United States and evaluated similar results. Differences in the water conditioning adjuvants could be discerned. This indicated the effectiveness of the test method for discerning which adjuvants function as water conditioners. However, this test method does not compare the various calcium containing salts that can be used to mix hard water.

Additionally, this test method has been evaluated with glyphosate efficacy, but has not been applied to other herbicides that may be antagonized by cations. The objective of this study was to evaluate the effect of several calcium containing salts on water conditioner performance. In addition to glyphosate, mesotrione will also be evaluated in a separate trial to evaluate the effectiveness of the current standard test method.

Materials and Methods

Water conditioning trials were conducted similarly to the standard water conditioning protocol laid out by Zollinger et al (2011). Glyphosate (Touchdown HiTech, Syngenta Crop Protection LLC, PO Box 18300, Greendboro, NC, 27419) at 342 g ae ha^{-1} and mesotrione (Callisto, Syngenta Crop Protection LLC, PO Box 18300, Greendboro, NC, 27419) at 70 g ha^{-1} was applied mixed in four water types in separate trials (Table 2.1). Herbicide rates are approximately half field-use rates and chosen to accentuate adjuvant treatment differences (Zollinger et al 2011). All treatments were applied with NIS (Chemsurf 90, United Suppliers Inc, 30473 260th St. Eldora, IA 50627) at 0.25 % v v^{-1}. Glyphosate was applied with diammonium sulfate (AMS), an AMS replacement water conditioner (Request, Helena Chemical Company, 225 Schilling Blvd, Collierville, TN 38017), or monocarbamide dihydrogen sulfate (AMADS) (Brimstone, Wilbur-Ellis Company LLC, PO Box 16458, Fresno, CA 93755) in each of the four water types. Mesotrione was applied with AMS or AMS replacement in each of the water types. The mixing order was the herbicide added to water, followed by the NIS, followed by the water conditioner.

Water conditioner efficacy was evaluated in field indicator trials near Hillsboro, ND in 2016 and 2017. Indicator species were planted across the plot area to ensure uniform growth and distribution at the time of application (Zollinger et al 2011). Hard water was mixed so that the calcium concentration was 500 mg L^{-1} in 7.6 L distilled water based on the salt molecular weight for comparison using three different calcium sources: calcium chloride (CaCl), calcium formate (CaFo), and calcium nitrate ($CaNO_3$) (Table 2.2). Therefore the salts were added in different

Table 2.1. Treatments for water conditioning trials applied in 2016 and 2017 near Hillsboro, ND. Herbicides included glyphosate at 342 g ae ha^{-1} and mesotrione at 70 g ha^{-1} in separate trials. The mesotrione trial did not include the AMADS treatments.

No.	Treatment	Water conditioner	Water conditioner rate	Water type[b]
1	Untreated	None	----------	
2	Herbicide + NIS[a]	None	----------	Distilled
3	Herbicide + NIS	AMS	3.8 kg 379 L^{-1}	Distilled
4	Herbicide + NIS	AMS Replacement	0.5 % v v^{-1}	Distilled
5	Herbicide + NIS	AMADS	0.5 % v v^{-1}	Distilled
6	Herbicide + NIS	None	----------	CaCl Water
7	Herbicide + NIS	None	----------	CaFo Water
8	Herbicide + NIS	None	----------	$CaNO_3$ Water
9	Herbicide + NIS	AMS	3.8 kg 379 L^{-1}	CaCl Water
10	Herbicide + NIS	AMS	3.8 kg 379 L^{-1}	CaFo Water
11	Herbicide + NIS	AMS	3.8 kg 379 L^{-1}	$CaNO_3$ Water
12	Herbicide + NIS	AMS Replacement	0.5 % v v^{-1}	CaCl Water
13	Herbicide + NIS	AMS Replacement	0.5 % v v^{-1}	CaFo Water
14	Herbicide + NIS	AMS Replacement	0.5 % v v^{-1}	$CaNO_3$ Water
15	Herbicide + NIS	AMADS	0.5 % v v^{-1}	CaCl Water
16	Herbicide + NIS	AMADS	0.5 % v v^{-1}	CaFo Water
17	Herbicide + NIS	AMADS	0.5 % v v^{-1}	$CaNO_3$ Water

[a]NIS= Chemsurf 90

[b]Water Source - all water sources have approximately a concentration of 500 mg L^{-1} calcium. CaCl = calcium chloride, CaFo = calcium formate, $CaNO_3$ = calcium nitrate.

amounts to achieve the desired calcium concentration (Table 2.2). Indicator species included flax (*Linum usitatissimum* L.), amaranth (*Amaranthus cruentus* L.), sunflower (*Helianthus annuus* L.), and conventional corn (*Zea mays* L.) for the glyphosate study. Amaranth, foxtail millet (*Setaria italica* (L.) P. Beauvois), quinoa (*Chenopodium quinoa* Willd.), and sunflower were the indicator species for the mesotrione study. Indicator species were chosen due to sensitivity to the active ingredients and response to hard water antagonism.

Table 2.2. Characteristics of mixed hard water samples used in both glyphosate and mesotrione trials. Water samples were mixed so that calcium concentration was 500 mg L^{-1} based on molecular weights (MW).

Water Type	Salt Form	MW	Salt Added in 7.6 L water	Ca	pH
			g	mg L^{-1}	
CaCl	$CaCl_2$ 2 H_2O	147.01	13.91	494	6.59
$CaNO_3$	$Ca(NO_3)_2$ 4 H_2O	236.15	22.28	452	6.61
CaFo	$Ca(O_2CH)_2$	130.11	12.28	420	7.09

Applications were made to the center 2 m of 3 m by 12 m plots perpendicular to indicator species planting with a CO_2-pressurized backpack type sprayer delivering 80 L ha^{-1} at 138 kPa using TT11001 nozzles (Turbo TeeJet 11001 nozzle, TeeJet Technologies, 200 W North Ave, Glendale Heights, IL 60139) (Zollinger et al. 2011). Treatments were applied when amaranth were approximately 20 to 25 cm in height. Treatments were arranged as an RCBD with 3 replications. The average height of each indicator species was measured 14 and 28 days after treatment (DAT) using a meter stick. The average was calculated by measuring the variable heights within each species and calculating the average height. Percent weed control was determined by comparing the height of each species to the untreated control. Analysis of variance was conducted for each indicator species individually with results considered significant at $p \leq 0.05$, and separation of means calculated with an F-protected least significant difference test using SAS 9.3 (SAS Institute, SAS Circle, Cary, NC).

Results and Discussion

Calcium salt type did not affect glyphosate control with any of the water conditioner types (Figure 2.1 A-D). Within water conditioner type the control of the indicator species was similar in all water types. For example, amaranth control with AMS averaged 48% control in all water types 28 DAT (Figure 2.1B). Similarly, no difference within each water conditioner type in all water types was observed in all indicator species. The antagonism of each salt was also similar with no water conditioner present. For example, sunflower control averaged 39% with calcium chloride, calcium formate, and calcium nitrate in distilled water (Figure 2.1C). All indicator species also displayed similar antagonism between the different water types (Figure 2.1A-D). Although the calcium source has varied antagonism of glyphosate in previous studies, calcium chloride and calcium nitrate antagonized glyphosate similarly (Nalewaja and Matysiak 1991). The addition of calcium formate to the present study indicates that source of calcium may not be a major factor in the evaluation of water conditioning adjuvants with glyphosate in field trials.

Salt type and water conditioner had little effect on mesotrione control (Figure 2.2A-D). Amaranth control averaged 39% 28 DAT in all water types with no water conditioner (Figure 2.2A). Similarly, AMS and AMS replacement water conditioners affected quinoa control very little in all water types averaging 91% control 28 DAT (Figure 2.2C). One surprising result is the apparent lack of antagonism observed in this study. Devkota et al (2016) observed a linear decrease in mesotrione control of three different weeds with increasing calcium concentration in the spray solution. At a similar water hardness to this study, mesotrione control was reduced

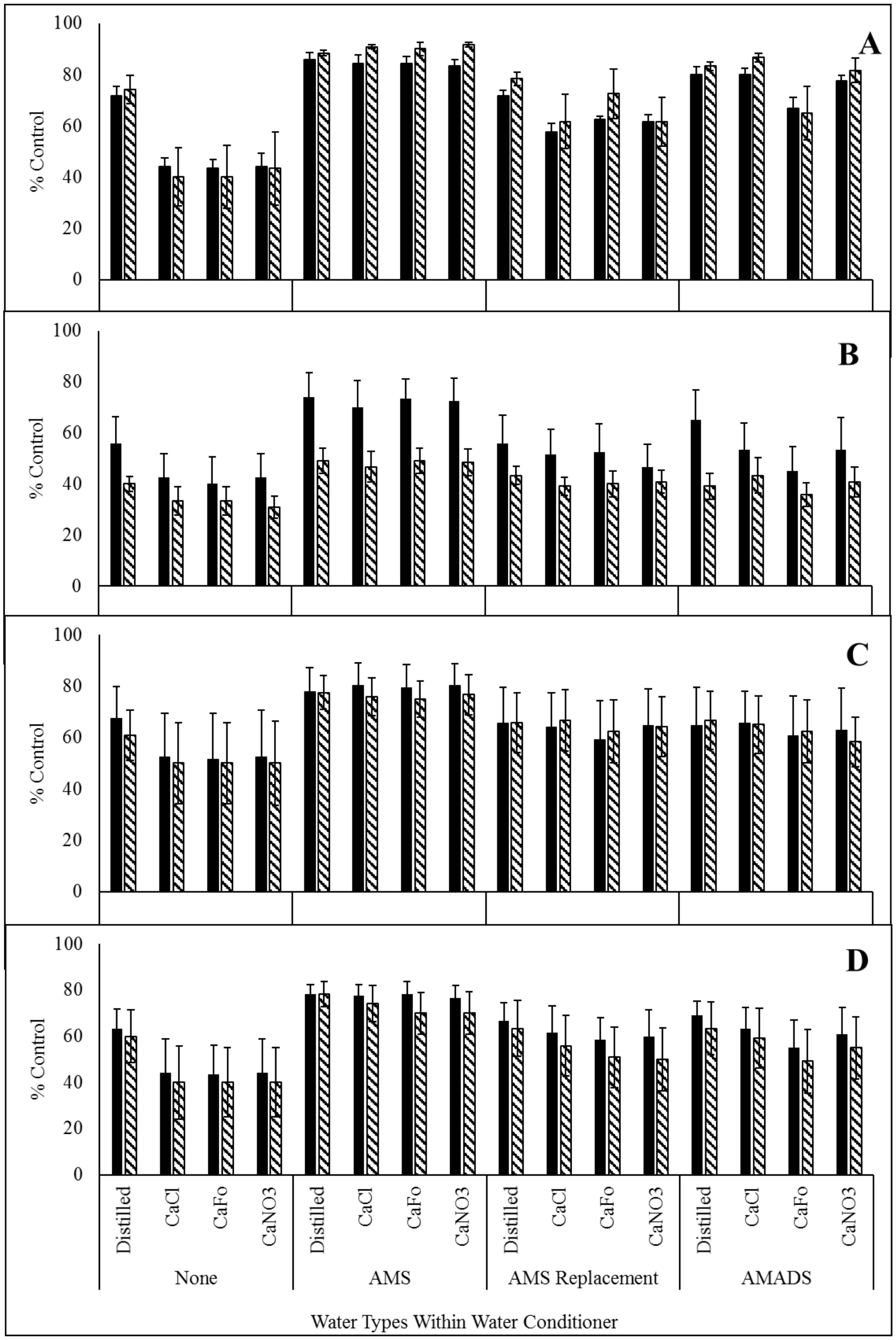

Figure 2.1. Indicator species control using glyphosate for different water types (calcium chloride = CaCl, calcium formate = CaFo, calcium nitrate = CaNO3) within different water conditioners for amaranth (A), foxtail millet (B), quinoa (C), and sunflower (D) near Hillsboro, ND in 2016 and 2017. Black bars = 14 DAT rating and striped bars = 28 DAT rating.

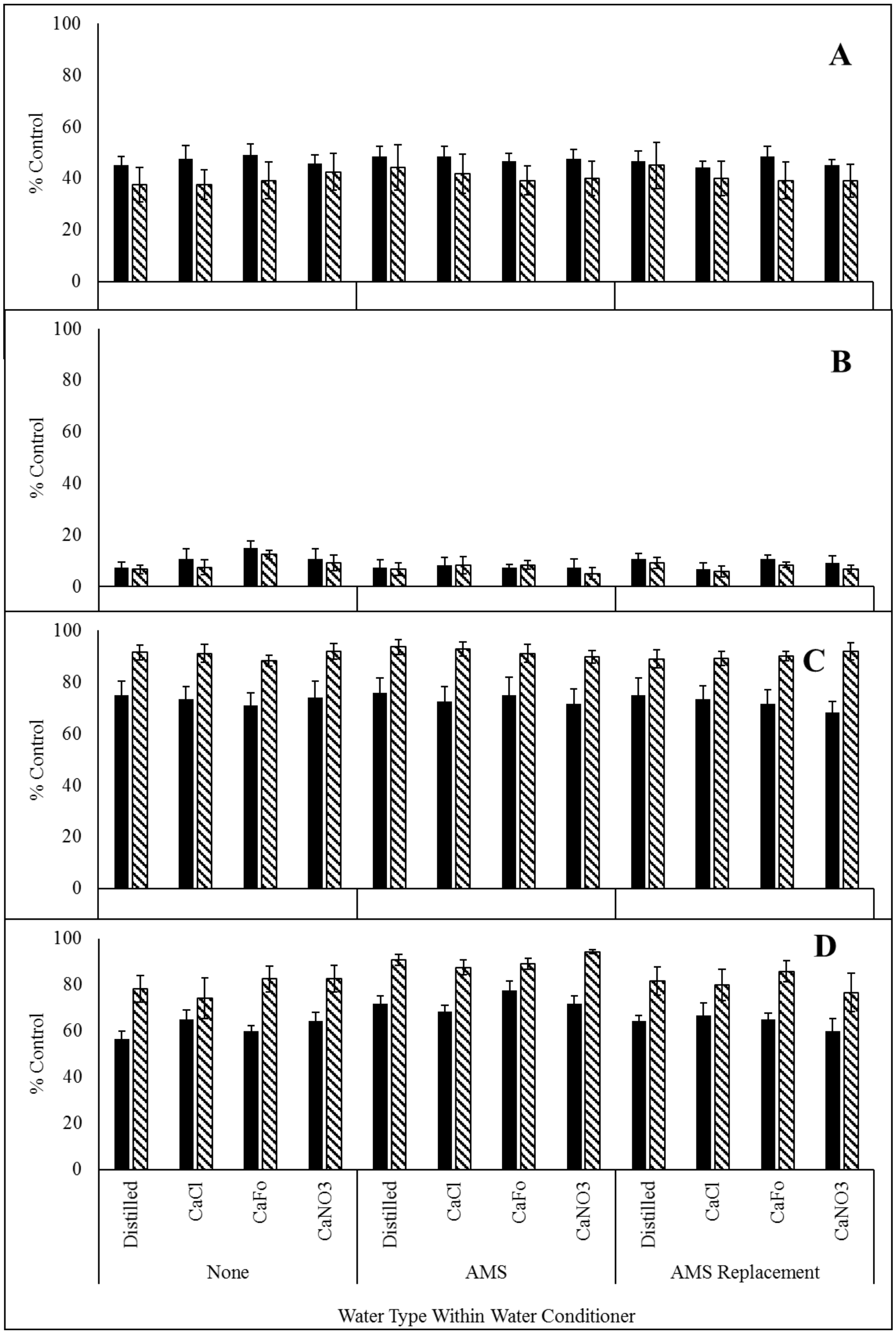

Figure 2.2. Indicator species control using mesotrione for different water types (calcium chloride = CaCl, calcium formate = CaFo, calcium nitrate = CaNO3) within different water conditioners for amaranth (A), foxtail millet (B), quinoa (C), and sunflower (D) near Hillsboro, ND in 2016 and 2017. Black bars = 14 DAT rating and striped bars = 28 DAT rating.

approximately 10 to 15% across the three weed species. In this study, there was no antagonism of mesotrione control of any indicator species compared to distilled water alone (Figure 2.2A-D).

Any standardized test method must be robust to detect differences between treatments. Similar to Zollinger et al (2011) differences among water conditioner types were able to be evaluated in this study. When averaged across all indicator species, control ranged from 60 to 75% control using glyphosate based on water conditioner (Figure 2.1). Similarly, control of weeds had a range from 30 to 60% control in past studies (Zollinger et al 2011). The test method is robust enough to separate water conditioner performance in overcoming antagonistic cation effects in the spray solution.

The test method set forth by Zollinger et al. (2011) had the objective of setting up a standard test method for evaluating adjuvants as water conditioners. The test method was deemed appropriate for evaluating adjuvants as water conditioners. This study had the objective of evaluating the standard test method to see if the calcium salt used to simulate hard water affected the results. All water conditioner types responded similarly in all water types with both glyphosate and mesotrione. Differences in water conditioner performance was able to be detected within all water types. Herbicide antagonism was similar with different calcium sources used. Therefore, the test method set forth by Zollinger et al (2011) is a suitable test method for the evaluation of water conditioning adjuvants.

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