OPTIMIZING GLUFOSINATE FOR WEED CONTROL IN AGRICULTURAL SYSTEMS

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DOCTOR OF PHILOSOPHY

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ABSTRACT

Weed management is an essential component of production agriculture. While many weed management methods exist today, chemical practices have proven to be the most efficient and are the most widely adopted methods. The objectives of this research were to: 1) maintain glufosinate weed control activity using a larger than recommended ultra-coarse spray droplet spectrum through utilizing commercially available adjuvants and 2) improve the activity of commercial glufosinate formulations in terms of increased weed control and shortened rainfast interval. Field trials were conducted to identify adjuvants that would maintain glufosinate weed control activity at an ultra coarse spray quality. Commercially available adjuvants representing acidic ammonium sulfate (AMS) replacements, deposition aids, and organosilicone surfactants were applied with a medium and ultra coarse spray quality. The negative impact of an ultra coarse spray quality on glufosinate activity was only observed when utilizing only AMS in the spray solution, and these impacts were dependent on the treated species. While there were individual additives that provided enhanced weed control of certain species, no specific adjuvant class improved Liberty 280 SL efficacy consistently throughout the tested species. To determine which adjuvants enhanced glufosinate weed control efficacy and rainfastness in a commercial formulation, trials were conducted with sublethal rates using a simplified glufosinate formulation (GFA 196 SL), which contained a lower adjuvant load. Candidates of three adjuvant classes, polymers, surfactants, and oils, were tested. The additives were evaluated for effect on efficacy in field trials, and their effect on uptake and rainfastness were evaluated in radiolabeled laboratory work, as well as in simulated rainfall environments in both the field and greenhouse. Overall, the polymer Kuraray provided the best enhancement of glufosinate activity for both efficacy and rainfast characteristics. Oils were the only class of adjuvant to consistently improve

glufosinate activity in these trials. The included oils provided the most consistent enhancement of glufosinate in the greenhouse rainfast trial by reducing the rainfast period by over 50% compared to GFA 196 SL alone and improving glufosinate uptake into common lambsquarters. Further research is needed to consider the feasibility of directly formulating these additives into a future glufosinate formulation.

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DEDICATION

To my Matka, she has always been there teaching, guiding, and loving me along my journey. Without her, this work would not be possible. For that reason, I dedicate this dissertation to her, Frances Kazmierczak. I love you more than you will ever know.

TABLE OF CONTENTS

LIST OF TABLES

Table | Page

LIST OF FIGURES

Figure | Page

LIST OF APPENDIX TABLES

INTRODUCTION

Weed management is an essential component of production agriculture. Methods of managing weeds can include biological, chemical, cultural, and mechanical practices. Herbicides have been widely adopted over the past 60 years (USDA-ERS 2014). The incorporation of herbicides for weed management has allowed for improvement of soil health including the reduction of soil erosion (VanGessel 2019). With the introduction of herbicide-tolerant crops, the use of non-selective chemistry in field crops became possible (USDA-ERS 2018). Glufosinate is a non-selective, contact herbicide that can be utilized for non-crop and directed use in perennial, plantation, and vegetable crops, and also in-crop use following the introduction of glufosinate-resistant crops.

Changing a herbicide formulation can either be related to improving herbicide efficacy or enhancing ease of use for the applicator. Improving the rainfastness of a herbicide formulation or reducing the chance of off-target movement are benefits to the applicator, the latter helping relax regulatory requirements such as spray buffers and increased regulations that are in place to protect endangered species. Label requirements identifying specific spray qualities or nozzle types can also satisfy regulations, but may not always consider how herbicide efficacy might be altered (Butts et al. 2018).

The main objective of this research was to optimize glufosinate for use in agricultural systems. Two separate approaches were utilized: 1) evaluate Liberty 280 SL herbicide with various adjuvant classes in a tank-mix including acidic ammonium sulfate replacements, deposition aids, and organosilicone additives at two different spray qualities (medium and ultra-coarse droplet sizes); 2) identify the best additive compared to the herbicide alone to include in a formulated product with glufosinate.

CHAPTER 1. LITERATURE REVIEW

Background on Glufosinate-Ammonium

The non-selective herbicide glufosinate, also called phosphinotricin [2-amino-4-(hydroxymethylphosphinyl)butanoic acid], belongs to the chemical class of glutamine synthetase inhibitors (WSSA 2014). It is a weak acid and highly water soluble (500 g L^{-1} at 25 °C) (Shaner 2014). Glufosinate is a racemic mixture of the L- and D- enantiomers with L-glufosinate being the active isomer (Ruhland et al 2004). It is used as a non-selective post-emergence herbicide to control a broad range of broadleaf and grass weeds in various cropping systems around the world. Beside its current use in herbicide resistant broad acre crops, in right of way situations or non-selective uses, it is regularly used as a “safe” herbicide treatment during susceptible growth stages in plantations and vegetables where high systemic movement of an active compound can cause significant crop damage. It has a high level of efficacy when used to control young and actively growing broadleaf weeds up to a growth stage of BBCH 30 (Hess et al. 1997). Although glufosinate is generally less efficacious on grass weeds, they are sufficiently controlled when exposed at smaller, susceptible growth stages. Glufosinate binds irreversibly the glutamine synthetase enzyme (EC 6.3.1.2), which catalyzes the incorporation of ammonium into glutamate, a key enzyme of nitrogen metabolism (Devine et al. 1993). The irreversible binding of glufosinate to glutamine synthetase inhibits the enzyme activity. Inhibition of glutamine synthetase in this plant pathway leads to decreased levels of the amino acid glutamate and an accumulation of ammonia in the thylakoid lumen in the plant cell, leading to an uncoupling of photophosphorylation. The accumulation of ammonia in the plant inhibits photosynthesis and destroys plant cells followed by a rapid accumulation of ammonia that is produced by the plant, with death as the final result (Vencill 2002). Beside the increased ammonia levels, the uncoupling of photophosphorylation causes the production of reactive oxygen species, lipid peroxidation, membrane destruction and finally plant cell death (WSSA 2014).

Glufosinate is a derivative of the tripeptide bialaphos (L-Alanyl-L-alanyl-phosphinothricin), a herbicidal compound naturally produced by the soil born actiniobacteria species of Streptomyces. Glufosinate is the herbicidally active part of the bialaphos molecule (phosphinothricin) (Wild and Ziegler 1989). Glufosinate is characterized as a contact herbicide with low ability to translocate in the plant. It is reported that the intrinsic species sensitivity level is related to the specific amount of glufosinate uptake and ability to translocate (Mersey et al. 1990). On most species, glufosinate is able to penetrate green leaf and stem tissue easily, especially when combined with an appropriate surfactant system. As a contact herbicide, it destroys all photosynthetic parts of the plant exposed to the herbicide spray solution. Perennial below ground plant parts, dormant buds or plant parts covered with bark are protected from glufosinate uptake and damage. This allows for the use of glufosinate for sucker control in orchards where the herbicide is applied to tree suckers, which die off, with no visible injury to the rest of the tree. Additionally, the above ground plant biomass that emerges from rhizomes will be controlled, while regrowth from underground storage organs is not inhibited, which is detrimental for control of perennial weeds such as *Sorghum halepense* or *Agropyron repens*.

Glufosinate symptomology in young weeds includes chlorosis of leaf tissue and plant wilting within days of application of the herbicide. The severity of symptom development depends on environmental conditions; activity increases with exposure in increased sunlight, humidity, and soil moisture (Shaner 2014). Glufosinate is active on green plant tissue and provides no soil residual activity as it is rapidly degraded by soil microorganisms (Takano and

Dayan 2020). This allows for short planting intervals into treated areas and makes it suitable for susceptible crops like vegetables to be planted or seeded soon after treatment.

Glufosinate-resistant crops are a result of the introduction of the phosphinothricin-N-acetyl-transferase (pat) gene or bar gene into sensitive crop species (Dekker and Duke 1995) from *Streptomyces viridochromogenes* Tii494 (Strauch et al. 1988; Wohlleben et al. 1988). The introduced gene encodes for proteins that detoxify the herbicide in the plant by a rapid acetylation of the glufosinate molecules. Due to the rapid acetylation, glufosinate is not able to inhibit glutamine synthetase and disturb photorespiration (Droge et al. 1992).

Optimal spray coverage is extremely important for contact herbicides to maximize the amount of surface area that comes into contact with the herbicide. Insufficient spray coverage might result in whole-plant survival, with cell death occurring only on parts of the plant which were exposed to the herbicide. Globally, several glufosinate formulations have been marketed since the initial introduction in 1983, with use patterns including non-selective use in perennial, plantation and vegetable crops, to in-crop use with the introduction of glufosinate-resistant crops (Anonymous 2019, Anonymous 2020a, Anonymous 2020b). Various formulations were introduced according to the different market needs, with concurrent variation in concentration of glufosinate and/or adjuvants (SL 060 (60 g a.e. / L glufosinate), SL 150 (150 g a.e. / L glufosinate), Basta, SL 200 (200 g a.e. / L glufosinate) and SL 280 (280 g a.e. / L glufosinate)) (Lorentz et al. 2020).

Weak acid herbicides can exist as the protonated acid species or deprotonated conjugate base species. The pKa of a weak acid is the dissociation constant which determines the relative proportion of an acid and its conjugate base at a given pH. When the pH of the solution is equal to the pKa, the herbicide is in a 1:1 ratio of ionized to non-ionized form (NIANR 2021). An increase of a weak-acid herbicide uptake into the leaf was reported when the pH of the carrier solution was below the pKa (Green and Hale 2005). Zollinger et. al (2013) reports that by lowering the spray solution pH to near 2.0 may prevent most glyphosate molecules from binding with antagonistic cations. Glufosinate shares a similar molecular structure to glyphosate and has three pKa values: <2, 2.9, and 9.8 (Shaner 2014). This may lead to speculation that carrier water properties may influence efficacy of glufosinate (Devkota and Johnson 2016).

Factors Influencing Herbicide Efficacy

Pesticide efficacy, especially herbicide weed control efficacy, is dependent on the chemical, the target species, the quality of application, the amount of active ingredient that reaches the target, and the environmental conditions at herbicide application. Application technology and the formulation of the chemistry are the main factors determining those aspects. Other key factors that can impact herbicide efficacy include the droplet size of the spray which determines the deposition and the coverage on the target, and the behavior of the spray solution when it hits the leaf surface. The chemistry of the herbicide determines the method of uptake into the plant, and the most appropriate formulation adjuvants and surfactants are typically chosen in order to aid the uptake, retention, rainfastness, spray drift, spray quality, mixability and stability for a given chemical. Spray quality has recently gained increased interest in order to reduce off target movement and environmental impact of each application while still maintaining effective weed control activity.

Spray Quality

Spray quality or droplet size spectrum is defined as the droplet size that a particular nozzle at a designated pressure and spray solution produces (PES 2012) and the categories range from extremely fine to ultra coarse (Figure 1.). The droplet size can be altered in many cases including; choice of nozzle tip type, nozzle flow rating, and adjusting spray pressure for a given nozzle by spray solution combination. Spray droplets are measured and given a value referred to as the volume median diameter (VMD) or the $DV_{0.5}$ value. This value refers to the midpoint droplet size where half of the spray volume is in droplets larger while the other half is in droplets smaller than the VMD (PES 2012).

Spray Quality*	Size of Droplets	VMD Range (Microns**)	Color Code	Retention on Difficult to Wet Leaves	Used for	Drift Potential
Extremely Fine	Small	<60	Purple	Excellent	Exceptions	High
Very Fine		61-105	Red	Excellent	Exceptions	
Fine		106-235	Orange	Very Good	Good Cover	
Medium		236-340	Yellow	Good	Most Products	
Coarse		341-403	Blue	Moderate	Systemic Herbicides	
Very Coarse		404-502	Green	Poor	Soil Herbicides	
Extremely Coarse		503-665	White	Very Poor	Liquid Fertilizer	
Ultra Coarse	Large	>665	Black	Very Poor	Liquid Fertilizer	Low

Figure 1.1. Droplet size classification by the American Society of Agricultural and Biological Engineers to measure and interrupt spray quality from tips. The color code column corresponds to the related spray quality (ASABE S572.1).

Spray quality is important from two different aspects: drift to non-target plants and herbicide efficacy. Smaller droplets increase the chance of drift to non-target organisms. This chance increases in the presence of wind, which can drastically increase the distance fine droplets can travel. Smaller droplets weigh less and are likely to float in wind currents because they are not able to overcome air resistance to allow settling (Wilson 2012). Herbicide efficacy is also affected by spray quality; certain herbicides work preferentially with a specific spray quality which generally is linked to the herbicide being primarily a contact or systemic herbicide. The “Pile Theory” developed by Dr. John Nalewaja, states that having a larger droplet at a given carrier volume for a translocated herbicide like glyphosate [N-(phosphonomethyl)glycine] will allow for a higher concentration in the droplet increasing the chance for more herbicide to be absorbed, along the concentration gradient, into plant (Ikley et al. 2021). Using larger droplets also satisfies concerns of drift; larger droplets will not move as far laterally as smaller droplets. In contrast, a contact herbicide generally requires good coverage which is achieved by having many smaller droplets (Prokop and Veverka 2003, McKinley et al. 1972), which may be more prone to drift onto non-target plants (Hanks 1995).

Currently in the pest management sciences, there is concern for potential regulation from the Environmental Protection Agency (EPA) to address issues with drift (USEPA 2021). The awareness to mitigate drift is a concern and could result in herbicide label language that would require manufactures to include spray quality recommendations that lessen the chance of spray drift, but potentially decrease the efficacy of the herbicide because of how it reaches the site of action. There has been research conducted that indicated a change in efficacy with certain herbicides by altering the spray quality (Downer et al. 1997). Butts et al. (2018) reports that a Medium droplet size is recommended for glufosinate applications, but applications being made when particle drift could be of concern the authors suggest increasing the droplet size. This increase of droplet size to Extremely Coarse could result in reduction of weed control. Efficacy of a herbicide and drift; reduction could be achieved by additional additives to either increase the activity of the herbicide or a deposition aid to facilitate the droplet reaching its intended destination.

In contrast to smaller droplets at risk for off-target movement, larger droplets may not be retained on the target due to droplet bounce or sliding and rolling off the leaf surface, depending on spray solution composition and type of leaf surface. Improving the chances of contact and adhesion could be increased with the use of deposition and retention aids (Stock and Briggs 2000).

Rainfastness

There are several physical, biological, and chemical factors that can influence the efficacy of a herbicide. While there are many dynamics that can impact activity, rain is the main environmental factor that can decrease the efficacy of a herbicide (Knoche 1994). Rainfastness is defined as the period after application that is required for a pesticide to have adequately dried or been absorbed by plant tissues to prevent wash-off due to rain. Several rainfall factors (amount, intensity, duration, and size of droplets) can adversely affect the performance of a herbicide application; directly washing the pesticide off the plant surface, diluting the product to a less efficacious concentration, moving the active ingredient, or removing the pesticide from the plant material (Wells and Fishel 2011). Mitigating the negative influence of rain on an application can be reduced by delaying the application until conditions are more favorable, utilizing a formulation that has a shorter rainfast interval or adding adjuvants to improve retention or absorption (Lorentz et al. 2020).

Adjuvants

Adjuvants are defined by the Weed Science Society of America as "any substance in an herbicide formulation or added to the spray tank to modify the herbicidal activity or application characteristics" (Hazen 2000). They have been further characterized as activator adjuvants and utility adjuvants.

Activator adjuvants are additives that directly enhance or increase herbicidal activity which can include herbicide absorption, droplet spread, improved rainfastness, and/or decreased phototransformation of the herbicide (Penner 2000). Utility adjuvants are classified as generally working on the properties of spray solution or spray mixture which either change the physical characteristics of the spray solution or allow for applications to be made in a broader range of conditions (McMullan 2000, Penner 2000). Hess and Foy (2000) further characterize specifically the action of surfactants into two categories: spray modifiers and activators. Spray modifier action of surfactants directly influences the characteristics of a water-based spray solution to improve the wetting, spreading and sticking on the plant surface. While activator action of surfactants is described by directly influencing herbicide absorption into the leaf.

Classification of an adjuvant into one particular classification can be difficult and typically is determined by the manufacturer. While adjuvants are placed in a specific category, they are not regulated by government agencies which require information regarding composition, etc. for submission of a Federal label. The Council of Producers and Distributors of Agrotechnology (CPDA) has a certification program that allows adjuvant manufactures to submit products to be certified by meeting certain standards, but these are just quality standards and not based on composition as defined by ASTM International (American Society for Testing and Materials) (Hazen 2000, CPDA 2019). This provides some accountability of the manufacture, but it still allows for products in the marketplace to not follow the same standards that are described by ASTM and leads to a lack of detailed information on the composition of adjuvants. Understanding the properties of an adjuvant can give insight to how the adjuvant can affect the spray solution to help end users determine the need to include the correct one for the desired outcome.

Herbicide-Resistant Crops

Herbicide-resistant (HR) crops have been widely adopted by growers (USDA ERS 2018) with glyphosate-resistant (GR) crops being more rapidly adopted than other weed management technologies (Duke and Powles 2008). This rapid adoption can be attributed to low weed management cost and ease of use. Glyphosate-resistant crops have provided growers the ability to use glyphosate in-crop and, subsequently, weed management has become easier, more efficient, and more cost effective (Green 2012). In some crops, GR sugarbeet (*Beta vulgaris* L.) in particular, weed control has become less labor intensive. Prior to GR sugarbeet, the micro-rate system developed by Dr. Alan Dexter was the primary method of chemical weed control in sugarbeet in addition to mechanical or hand labor (Dexter 1994). Although the micro-rate system was effective, it still required growers to make herbicide applications every 7 days, but reduced the amount of cultivation or hand labor that needed to occur. Until 2007, 9 years after release, fewer than 50% of the US corn acres were planted with HR corn (*Zea mays* L.) with many corn producers still utilizing atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine) in their weed management programs (Dill et al. 2008) due to a stable price for many traditional corn herbicides such as atrazine and decreased the reliance on glyphosate (Prince et al. 2012). In contrast, GR soybean (*Glycine max*) and cotton (*Gossypium hirsutum* L.) were planted on over 50% of the respective crop hectares within 4 years of release. United States (US) growers adopted GR soybean more rapidly than any other crop with over 90% of the hectares 10 years after release while growers in Argentina were planting 98% of their soybean crop to a GR cultivar only 5 years after commercialization (Green 2012).

Wide adoption of the GT technology has also provided certain challenges, mainly glyphosate resistance in weeds (Vencill et al. 2012). Many growers have adopted glyphosate as the only weed management tool in their management plan and now it "has become a victim of its own success" (Green 2012). The evolution of glyphosate resistance is a consequence of the intensive use of glyphosate as the sole weed management method, and this practice has increased the selection pressure for resistance on the weed community (Beckie 2011). In addition, reduced tillage systems have also increased the selection pressure and occurrence of glyphosate resistance as glyphosate is used prior to planting in the spring to control weeds before planting, in season, and pre or post harvest (Prince et al. 2012).

Glufosinate-resistant ((GFA-R) Liberty Link; BASF Corporation, Research Triangle Park, NC)) crops have not been adopted as rapidly as GR crops; there may be several reasons for the delay in adoption. Whitaker et al. (2011) suggest that the delay of suitable cultivars for a specified region that consistently perform well in official cultivar trials could be a reason for the deferred response as well as herbicide use perception. Glyphosate can be sprayed on larger weeds in contrast to glufosinate that needs to be sprayed on smaller weeds, providing the disadvantage of a less application flexibility to farmers. The restricted application flexibility combined with the higher price of the chemistry explains part of the disadvantage of the GFA-R system compared to the GR system. Ahmed and Holshouser (2012) suggested this difference as a positive attribute to the GFA-R cropping system; it may encourage a pre-emergence herbicide to be applied, which helps to diversify a weed management plan and will require glufosinate to be applied to smaller weeds. These suggestions will aid in a successful herbicide application and possibly decrease the chance of weed resistance developing. While a valid argument, commodity prices will typically influence a grower's decision on how much to spend on additional inputs.

Beside the widely used Roundup Ready (Bayer CropScience; St. Louis MO) and Liberty Link crop herbicide resistance systems, additional herbicide-resistance technologies have been developed, but not all have been currently introduced into the market. The most current marketed HR systems include dicamba and 2,4-D tolerance, allowing for applications of dicamba or 2,4-D in soybean and cotton. But other HR systems are widely available, such as 4-hydroxyphenyl-pyruvate-dioxygenase (HPPD) resistant soybean (tolerance to isoxaflutole (BASF Corporation, Research Triangle Park, NC))), acetolactate synthase (ALS) inhibitor resistant canola (*Brassica* *napus* L.) (imidazolinone chemistry, Clearfield-technology (BASF Corporation, Research Triangle Park, NC)), or SMART KWS which are ALS inhibitor resistant sugarbeets, which are tolerant to sulfonylurea herbicides (KWS; Bloomington, MN). The most recent HR development, which is not yet available to the market, is increased tolerance to protoporphyrinogen oxidase (PPO) inhibitors.

CHAPTER 2. ACIDIC AMMONIUM SULFATE REPLACEMENTS, DEPOSITION AIDS, AND ORGANOSILICONE FIELD TRIALS

Materials and Methods

Applying herbicides to be both efficacious for weed control and optimized for mitigating off-target movement may not always align. Data suggest that applying contact herbicides with droplet spectra less than 484 µm improved weed efficacy by improving the spray coverage with many small droplets (Prokop and Veverka 2003). The same application can also increase the occurrence of off-target movement to unintended plants (Dexter 1993). The aim of this research was to use three different classes of adjuvants to help better identify the best adjuvant while maintaining weed control of a contact herbicide applied at ultra coarse spray quality compared to medium spray quality.

Field experiments were established in 2013 at Hillsboro, North Dakota and 2014 at Hillsboro, North Dakota and Sabin, Minnesota. The experiments evaluated the impact of glufosinate mixed with different adjuvant classes at different spray qualities. Hillsboro is located at longitude -97.09, latitude 47.33 at an elevation of 282 m above sea level. The soil type at Hillsboro is a Gardena silt loam. Sabin is located at longitude -96.61, latitude 46.79 at an elevation of 281 m above sea level. The soil type at Sabin is a Wheatville silt loam.

Experiments were initiated in the spring of each year. Separate experiments were established to evaluate each adjuvant class: acidic ammonium sulfate replacements, deposition aids, and organosilicones. The experimental design was a randomized complete block with three replicates. Plant species were arranged in a block arrangement. 'Mancan' common buckwheat (*Fagopyrum esculentum* Moench), quinoa (*Chenopodium quinoa* Willd.), tame amaranth (*Amaranthus cruentus* L.), and 'York' flax (*Linum usitatissimum* L.) were planted in 1.5-m-wide strips using a Great Plains 3P600 drill with 19-cm row spacings at a planting depth of 1.25 cm. Buckwheat was planted at a rate of 50 kg ha^{-1}, quinoa was planted at 1.7 kg ha^{-1}, amaranth was planted at 1.7 kg ha^{-1} and flax was planted at 39 kg ha^{-1}. Indicator species were utilized to represent natural populations with various plant architectures and leaf types, but cultivated species were seeded rather than relying on natural weed infestations to insure a more uniform population to evaluate treatments. Common buckwheat was utilized to represent wild buckwheat (*Polygonum convolvulus*). Flax represented species that have a smaller leaf area to intercept droplets. Common lambsquarters (*Chenopodium album*) was represented by quinoa as a specie that has a waxy leaf surface, which is hard to wet. Tame amaranth was utilized to represent *Amaranthus* sp. including redroot pigweed (*Amaranthus retroflexus*) and waterhemp (*Amaranthus tuberculatus*). Crop species were not randomized within each replicate to prevent shading of the shorter crops by the taller crop plants.

Herbicide treatments consisted of glufosinate at 450 g ai ha^{-1} alone and with candidates from each adjuvant class (Table 2.1, 2.2, and 2.3) and were applied perpendicular to the species blocks. Plant height and density at application timing were 15-25 cm and 15-25 plants m^{-2} amaranth, 18-25 cm and 10-20 plants m^{-2} common buckwheat, 15-20 cm and 10-20 plants m^{-2} flax, and 25-30 cm and 15-20 plants m^{-2} quinoa, respectively. Herbicide and adjuvant combinations were applied at two spray qualities: medium and ultra coarse. The plot area was 3 by 12.2 m and included all planted species. Treatments were applied with an ATV-mounted, CO_2-pressurized sprayer boom at a speed of 6.44 km hr^{-1} containing four nozzles on 48.8-cm spacing with TeeJet (TeeJet Technologies, Springfield, Illinois) Turbo TeeJet 11002 (medium spray quality) or Turbo TeeJet Induction 11002 (ultra coarse spray quality) tips at 276 kPa to deliver 140 L ha^{-1} spray application volume to the center 2 m for the length of the plot.

Assessments included visual evaluations and biomass measurements. Evaluations were based on a visual scale with 0 being no visible injury and 100 being complete plant death. Visible injury was evaluated 14 and 28 d after application (DAA). Plants were harvested 28 DAA by clipping the plant at the soil surface, and fresh weight was recorded. Plant tissue was dried at 65° C for 7 d before dry weights of shoots were recorded. Biomass of flax and amaranth were collected from 1 m of one row. Quinoa and tame buckwheat were collected from 0.5- and 1-m2 quadrats, respectively.

Table 2.1. Acidic ammonium sulfate replacement product information for field trials applied at two spray qualities at Hillsboro, ND in 2013 and both Hillsboro, ND and Sabin, MN in 2014.

Treatment[a]	Rate	Chemical Name	Manufacturer
Untreated	-	-	-
Liberty®	450 g ai ha^{-1}		BASF[b]
+ AMADS	+ 0.5% v/v	Monocarbamide dihydrogen sulfide	N/A
+ Import®	+ 0.5% v/v	Monocarbamide dihydrogen sulfide, tallow amine ethoxylate, polyoxyethylene tridecyl ether phosphate	Precision Labs[c]
+ Hel-Fire®	+ 0.5% v/v	Animated phosphoric, carboxylic acids, sulphurated amides, deposition aids	Helena[d]
+ Brimstone®	+ 0.5% v/v	Monocarbamide dihydrogen sulfide and surfactants	Wilbur Ellis[e]

[a] All herbicide treatments contained glufosinate using the commercial product Liberty 280 SL. All herbicide treatments were applied at a medium and ultra coarse spray quality at an application volume of 140 L ha^{-1}.
[b] Research Triangle Park, NC
[c] Waukegan, IL
[d] Collierville, TN
[e] San Francisco, CA

Table 2.2. Deposition aid product information for field trials applied at two spray qualities at Hillsboro, ND in 2013 and both Hillsboro, ND and Sabin, MN in 2014.

Treatment[a]	Rate	Chemical Name	Manufacturer
Untreated	-	-	-
Liberty®	450 g ai ha^{-1}		BASF[b]
+ Placement®	+ 0.44 L/ha	Petroleum distillates, amine salts of fatty acids, aromatic acid	Winfield Solutions[c]
+ Interlock®	+ 0.37 L/ha	Modified vegetable oil and emulsifiers	Winfield Solutions
+ In-Place®	+ 0.29 L/ha	Amine salts of organic acids, aromatic acid, aromatic and petroleum distillate	Wilbur Ellis[d]

[a] All herbicide treatments contained glufosinate using the commercial product Liberty 280 SL and dry ammonium sulfate at 3363 g ha^{-1}. All herbicide treatments were applied at a medium and ultra coarse spray quality at an application volume of 140 L ha^{-1}.
[b] Research Triangle Park, NC
[c] St. Paul, MN
[d] San Francisco, CA

Data were analyzed using the Proc GLIMMIX procedures in SAS 9.4 (SAS Institute, Cary, NC) for analysis of variance, and treatment mean separation was performed using Tukey's comparison test at $P \leq 0.05$. Replicates and environment were random effects. Species and herbicide treatment were fixed effects. Data were combined across locations when error means squares over environments were homogeneous.

Table 2.3. Organosilicone product information for field trials applied at two spray qualities at Hillsboro, ND in 2013 and both Hillsboro, ND and Sabin, MN in 2014.

Treatment[a]	Rate	Chemical Name	Manufacturer
Untreated	-	-	-
Liberty®	450 g ai ha^{-1}		BASF[b]
+ Dyne-Amic®	+ 0.5% v/v	Proprietary blend of polyethoxlated dimethyl siloxanes, alkylaryl ethoxylates, and methylated seed oils	Helena[c]
+ Syltac®	+ 0.5% v/v	Ethylated seed oil, polyether-polymethylsiloxane-copolymer, and polyoxyalkylene fatty ester	Wilbur Ellis[d]
+ Airforce®	+ 0.5% v/v	Methylated seed oil, organosilicones, and nonionic surfactant	Precision Labs[e]

[a] All herbicide treatments contained glufosinate using the commercial product Liberty 280 SL and dry ammonium sulfate at 3363 g ha^{-1}. All herbicide treatments were applied at a medium and ultra coarse spray quality at an application volume of 140 L ha^{-1}.
[b] Research Triangle Park, NC
[c] Collierville, TN
[d] San Francisco, CA
[e] Waukegan, IL

Results

Increasing the droplet size spectra from medium to ultra coarse will reduce the potential for driftable fine droplets and help mitigate off-target movement. Likewise, increasing the droplet size and maintaining the applied solution volume per area also reduces the total number of droplets and the overall droplet coverage on plant surfaces. Coverage on plant surfaces can impact activity of non-systemic herbicidal actives, so the adjuvants tested are intended to improve weed control despite an application with ultra coarse droplets rather than medium droplets, which is normally preferred for contact herbicides such as glufosinate. The adjuvant classes that were chosen to be evaluated included: AMADS, deposition aids, and organosilicones.

- **AMADS** (1-aminomethanamide dihydrogen tetra oxosulfate) contains monocarbamide dihydrogen sulfide, which comprises sulfuric acid complexes with urea and will reduce spray water pH to approximately 2.0 (Zollinger et al. 2013). By lowering the spray solution, it has been reported that weak acid herbicides, like glufosinate, are more readily absorbed (Shea and Tupy 1984, Buhler and Burnside 1983).
- **Deposition aid** is defined as a material that improves the ability of a pesticide spray solution to reach the targeted surfaces (ASTM 1996). The effect of the pesticide reaching the target surface has two benefits, which include increased application efficacy and reduced off target movement (McMullan 2000).
- **Organosilicone** adjuvants enhance herbicide activity by reduced surface tension on the leaf surface in addition to an increase in leaf wetting, spreading, and cuticle penetration (Field and Bishop 1988, Roggenbuck et al. 1990).

Acidic Ammonium Sulfate Replacements (AMADS)

Treatments included the adjuvants AMADS, Import, Helfire and Brimstone in mixture with Liberty 280 SL and tested at a medium and ultra coarse spray quality, and did not contain an additional ammonia source in the spray solution as previously evaluated. To not mask the urea effects of the AMADS, an additional ammonia source was not added to the spray solution.

The addition of all tested adjuvants showed a trend for increased overall weed control of glufosinate on amaranth, common buckwheat, flax, and quinoa, and some adjuvant by species interactions did increase control of tested species. The adjuvant product Import showed overall the best improvement of weed control activity over all tested species and spray qualities, compared to Liberty 280 SL alone (Tables 2.4, 2.5, 2.6, and 2.7).

Table 2.4. Effect of acidic ammonium sulfate replacement products on glufosinate efficacy applied at two spray qualities on amaranth near Hillsboro, ND in 2013 and 2014.

Treatments[a]	Visible control								Amaranth biomass (28 DAA)							
	14 DAA[bc]				28 DAA				Fresh weight				Dry weight			
	Medium		Ultra coarse		Medium		Ultra coarse		Medium		Ultra coarse		Medium		Ultra coarse	
	----- % -----				----- % -----				----- kg/1 m of row -----				----- kg/1 m of row -----			
Untreated	0				0				1.04				0.18			
None[d]	26	c	30	c	25	b	27	ab	0.40	a	0.59	a	0.06	a	0.09	a
AMADS[e]	37	abc	46	abc	37	ab	47	ab	0.47	a	0.34	a	0.07	a	0.05	a
Import®	54	a	42	abc	45	ab	38	ab	0.48	a	0.51	a	0.07	a	0.08	a
Helfire®	32	bc	51	ab	30	ab	48	a	0.66	a	0.45	a	0.10	a	0.08	a
Brimstone®	38	abc	38	abc	31	ab	38	ab	0.77	a	0.40	a	0.13	a	0.06	a

[a] Treatments contained glufosinate at 450 g ai ha^{-1} and were applied using the commercial product Liberty 280 SL.
[b] DAA; days after application.
[c] Mean values separated with the use of Tukey's Honestly Significant Difference. Values followed by different letters within each evaluation parameter column are significantly different ($P \leq 0.05$).
[d] Glufosinate alone.
[e] AMADS = Monocarbamide dihydrogen sulfate.

Comparing the differences between spray qualities, treatments with adjuvants that were assessed at 14 and 28 DAA were not different for applications made to amaranth, buckwheat, flax and quinoa (Tables 2.4, 2.5, 2.6, and 2.7). For medium spray quality, the addition of Import increased control of amaranth at 14 DAA compared to glufosinate alone (Table 2.4). For ultra coarse spray quality, the addition of Helfire increased control of amaranth at 14 DAA compared to glufosinate alone. The only difference at 28 DAA was the addition of Helfire at ultra coarse spray quality provided better amaranth control than glufosinate alone at a medium spray quality.

Though there were not many differences among the treatments, there were some trends in the data that merit discussion (Table 2.4). The addition of the adjuvant products AMADS, Import, Helfire and Brimstone in mixture with glufosinate increased weed control of amaranth by 8 to 21% and reduced biomass by 13 to 42%, relative to glufosinate alone when utilizing an ultra-coarse spray quality. The addition of Import increased control of amaranth by 28% (medium) and 12% (ultra coarse) at 14 DAA compared to glufosinate alone. Comparing ultra coarse spray quality to medium spray quality within an individual adjuvant, the addition of

AMADS and Helfire improved efficacy, the addition of Import reduced efficacy, and there was no difference between medium and ultra coarse spray quality with Brimstone.

Despite some differences between treatments for visible control of amaranth, there were no differences among any treatments for plant biomass (Table 2.4). Though not different, treatments containing an additive compared to glufosinate alone had higher amaranth biomass from applications made with a medium spray quality compared to those from an ultra coarse, suggesting the ultra coarse spray quality could perform better than medium spray quality on plants in this genus under some circumstances.

The addition of an acidic ammonium sulfate replacement adjuvant did not improve the control of common buckwheat relative to glufosinate alone (Table 2.5). For the final evaluation, the numerical average of all additives suggested greater control than glufosinate alone within each spray quality, although greater relative improvements were observed by using the ultra coarse spray quality.

Table 2.5. Effect of acidic ammonium sulfate replacement products on glufosinate efficacy applied at two spray qualities on common buckwheat near Hillsboro, ND in 2013 and 2014.

	Visible control								Common buckwheat biomass (28 DAA)							
Treatments[a]	14 DAA[bc]				28 DAA				Fresh weight				Dry weight			
	Medium		Ultra coarse		Medium		Ultra coarse		Medium		Ultra coarse		Medium		Ultra coarse	
	----- % -----				----- % -----				----- kg/1 m^{-2} -----				----- kg/1 m^{-2} -----			
Untreated	0				0				0.59				0.13			
None[d]	67	a	67	a	73	a	64	a	0.16	a	0.56	a	0.02	a	0.09	a
AMADS[e]	73	a	76	a	75	a	78	a	0.15	a	0.22	a	0.02	a	0.04	a
Import®	83	a	73	a	83	a	72	a	0.14	a	0.30	a	0.02	a	0.05	a
Helfire®	68	a	63	a	76	a	72	a	0.29	a	0.27	a	0.05	a	0.05	a
Brimstone®	78	a	75	a	74	a	70	a	0.32	a	0.24	a	0.05	a	0.04	a

[a] Treatments contained glufosinate at 450 g ai ha^{-1} and were applied using the commercial product Liberty 280 SL.
[b] DAA; days after application.
[c] Mean values separated with the use of Tukey's Honestly Significant Difference. Values followed by different letters within each evaluation parameter column are significantly different ($P \leq 0.05$).
[d] Glufosinate alone.
[e] AMADS = Monocarbamide dihydrogen sulfate.

Within the ultra-coarse spray quality, fresh weight biomass was reduced by < 47% with glufosinate + an acidic ammonium sulfate adjuvant, compared to glufosinate alone. Helfire and Brimstone treatments had greater biomass measurements of common buckwheat by 45 and 55%, respectively, compared to glufosinate alone. Ultimately, no differences were observed by adding any adjuvant to either spray quality. This could be partially explained by the fact the glufosinate by itself is an efficacious herbicide on vining plants like wild buckwheat or morningglory species, and acidic ammonium sulfate replacement adjuvants do not influence this base level of weed control (Anonymous 2020).

For flax control, all additives improved the efficacy of glufosinate at 14 DAA with a medium spray quality. Within the ultra coarse spray quality, flax control was increased greater than 15% with the addition of an acidic ammonium sulfate replacement adjuvant at 14 DAA (Table 2.6). The addition of Import and Helfire at an ultra coarse spray quality resulted in a 20% increase of flax control at 14 DAA compared to glufosinate alone (68%).

Table 2.6. Effect of acidic ammonium sulfate replacement products on glufosinate efficacy applied at two spray qualities on flax near Hillsboro, ND in 2013 and 2014.

	Visible control				Flax biomass (28 DAA)			
Treatments[a]	14 DAA[bc]		28 DAA		Fresh weight		Dry weight	
	Medium	Ultra coarse	Medium	Ultra coarse	Medium	Ultra coarse	Medium	Ultra coarse
	----- % -----		----- % -----		----- kg/1 m of row -----		----- kg/1 m of row -----	
Untreated	0		0		0.09		0.03	
None[d]	64 c	68 bc	64 b	64 b	0.05 a	0.06 a	0.01 a	0.02 a
AMADS[e]	92 a	87 ab	87 a	83 ab	0.05 a	0.08 a	0.01 a	0.02 a
Import®	92 a	88 a	90 a	79 ab	0.04 a	0.05 a	0.01 a	0.01 a
Helfire®	86 ab	88 a	82 ab	83 ab	0.04 a	0.07 a	0.01 a	0.01 a
Brimstone®	86 ab	83 ab	80 ab	78 ab	0.09 a	0.08 a	0.03 a	0.02 a

[a] Treatments contained glufosinate at 450 g ai ha^{-1} and were applied using the commercial product Liberty 280 SL.
[b] DAA; days after application.
[c] Mean values separated with the use of Tukey's Honestly Significant Difference. Values followed by different letters within each evaluation parameter column are significantly different ($P \leq 0.05$).
[d] Glufosinate alone.
[e] AMADS = Monocarbamide dihydrogen sulfate.

At 28 DAA, most acidic ammonium sulfate replacement adjuvants improved flax control more than 20 and 18% compared to glufosinate alone within medium and ultra coarse spray quality, respectively. AMADS and Import, within a medium spray quality, increased flax control compared to glufosinate alone at 28 DAA by greater than 23%. There were no differences observed within biomass measurements with the addition of an acidic ammonium sulfate replacement adjuvant or either spray quality.

When comparing treatments containing acidic ammonium sulfate replacement adjuvants to glufosinate alone for quinoa control, there were no differences between spray qualities across assessment timings and adjuvants (Table 2.7). However, numerically all acidic ammonium sulfate replacement adjuvants increased quinoa control relative to glufosinate alone within each respective spray quality. Import in mixture with glufosinate provided the least amount of quinoa control (30%) of all the acidic ammonium sulfate replacement adjuvants tested with an ultra coarse spray quality, while only reducing quinoa fresh weight biomass by 40% compared to the untreated.

Table 2.7. Effect of acidic ammonium sulfate replacement products on glufosinate efficacy applied at two spray qualities on quinoa near Hillsboro, ND in 2013.

Treatments[a]	Visible control								Quinoa biomass (28 DAA)							
	14 DAA[bc]				28 DAA				Fresh weight				Dry weight			
	Medium		Ultra coarse		Medium		Ultra coarse		Medium		Ultra coarse		Medium		Ultra coarse	
	----- % -----				----- % -----				----- kg/0.5 m^{-2} -----				----- kg/0.5^{-2} -----			
Untreated	0				0				1.02				0.24			
None[d]	35	ab	25	b	30	ab	32	ab	0.52	a	0.54	a	0.09	a	0.10	a
AMADS[e]	40	ab	52	ab	42	a	52	a	0.38	a	0.42	a	0.07	a	0.08	a
Import®	62	a	30	ab	70	a	35	ab	0.31	a	0.60	a	0.06	a	0.12	a
Helfire®	38	ab	38	ab	45	a	38	ab	0.37	a	0.43	a	0.07	a	0.08	a
Brimstone®	40	ab	47	ab	42	a	38	ab	0.41	a	0.48	a	0.07	a	0.09	a

[a] Treatments contained glufosinate at 450 g ai ha^{-1} and were applied using the commercial product Liberty 280 SL.
[b] DAA; days after application.
[c] Mean values separated with the use of Tukey's Honestly Significant Difference. Values followed by different letters within each evaluation parameter column are significantly different ($P \leq 0.05$).
[d] Glufosinate alone.
[e] AMADS = Monocarbamide dihydrogen sulfate.

Treatments containing an acidic ammonium sulfate replacement adjuvant tended to reduce biomass measurements compared to glufosinate alone within a respective spray quality, with the exception of Import with an ultra coarse spray quality. In addition, when comparing within a treatment across spray qualities, biomass tended to be greater for ultra coarse compared to medium. This suggests when utilizing a larger droplet spectrum for an application of glufosinate, there may be a disadvantage to include an acidic ammonium sulfate replacement for control of Chenopodium species compared to the herbicide alone.

Deposition Aids

Placement, Interlock, and In-Place are adjuvants that are classified as deposition aids. They were all included in mixture with glufosinate and applied at a medium spray quality and compared to an application using an ultra coarse spray quality. All treatments contained ammonium sulfate in the spray solution. The addition of a deposition aid generally reduced weed control for all species numerically, but also statistically in certain treatments (Tables 2.8, 2.9, 2.10, and 2.11).

At 28 DAA, both Interlock and In-Place reduced the visible control of amaranth compared to glufosinate alone within the ultra coarse spray quality (Table 2.8). In-Place also reduced control of amaranth compared to glufosinate alone within the medium spray quality. Though not different, Interlock and Placement reduced amaranth control by 16 and 17%, respectively, compared to glufosinate alone within the medium spray quality. These results indicate that this class of adjuvant should not be added to glufosinate when applied at the preferred medium or ultra coarse spray quality if amaranth is the target species.

Assessing the combination of glufosinate with deposition aids for control of amaranth at both observation timings (14 and 28 DAA), most additives reduced glufosinate efficacy on amaranth compared to glufosinate alone (Table 2.8). Only Placement at an ultra coarse spray quality was able to improve weed control activity compared to glufosinate. In addition, Placement was the only deposition aid to improve efficacy from medium to ultra coarse spray quality at 14 and 28 DAA (6 and 5%, respectively). Biomass measurements showed a similar trend with GFA alone at both spray qualities and Placement with ultra coarse droplet spectra resulting in the lowest biomass weights.

Table 2.8. Effect of deposition aid products on glufosinate efficacy applied at two spray qualities on amaranth near Hillsboro, ND in 2013 and 2014 and Sabin, MN in 2014.

Treatments[a]	Visible control								Amaranth biomass (28 DAA)							
	14 DAA[bc]				28 DAA				Fresh weight				Dry weight			
	Medium		Ultra coarse		Medium		Ultra coarse		Medium		Ultra coarse		Medium		Ultra coarse	
	----- % -----				----- % -----				----- kg/1 m of row -----				----- kg/1 m of row -----			
Untreated	0				0				0.65				0.12			
None[d]	71	a	58	abc	81	a	67	ab	0.18	a	0.23	a	0.03	a	0.04	a
Placement®	61	abc	67	ab	66	abc	71	a	0.30	a	0.23	a	0.05	a	0.04	a
Interlock®	65	ab	47	c	65	abcd	44	d	0.24	a	0.32	a	0.05	a	0.05	a
In-Place®	53	bc	48	c	47	bcd	45	cd	0.26	a	0.35	a	0.05	a	0.06	a

[a] Treatments contained glufosinate at 450 g ai ha^{-1} and were applied using the commercial product Liberty 280 SL SL and dry ammonium sulfate at 3363 g ha^{-1}.
[b] DAA; days after application.
[c] Mean values separated with the use of Tukey's Honestly Significant Difference. Values followed by different letters within each evaluation parameter column are significantly different ($P \leq 0.05$).
[d] Glufosinate alone.

None of the included deposition aids improved common buckwheat control compared to glufosinate alone within each spray quality, nor were differences observed at 14 and 28 DAA (Table 2.9) In general, a reduction of common buckwheat control was noted when comparing the ultra coarse to the medium spray quality. In a comparison of the three deposition aids, common buckwheat control was most reduced by using Interlock and In-Place, compared to a lower reduction using Placement within each spray quality and each assessment timing. The same effects were observed for fresh and dry weight measurements where Placement showed the least negative effect on glufosinate weed control efficacy. Results with the deposition aids on common buckwheat were similar to the ammonium replacement adjuvants. Both categories of adjuvants did not influence glufosinate control of common buckwheat. These data suggest that adjuvants do not need to be included for control of common buckwheat or species with similar composition to common buckwheat, but that their addition to the spray tank also does not compromise control of these species.

Table 2.9. Effect of deposition aid products on glufosinate efficacy applied at two spray qualities on common buckwheat near Hillsboro, ND in 2013 and 2014.

Treatments[a]	Visible control								Common buckwheat biomass (28 DAA)							
	14 DAA[bc]				28 DAA				Fresh weight				Dry weight			
	Medium		Ultra coarse		Medium		Ultra coarse		Medium		Ultra coarse		Medium		Ultra coarse	
	----- % -----				----- % -----				----- kg/1 m^{-2} -----				----- kg/1 m^{-2} -----			
Untreated	0				0				0.60				0.13			
None[d]	88	a	86	a	88	a	83	a	0.05	b	0.06	ab	0.02	b	0.03	ab
Placement®	88	a	83	a	86	a	78	a	0.08	ab	0.13	ab	0.03	ab	0.04	ab
Interlock®	82	a	81	a	80	a	75	a	0.12	ab	0.21	a	0.04	ab	0.05	a
In-Place®	82	a	81	a	78	a	73	a	0.13	ab	0.21	ab	0.04	ab	0.05	ab

[a] Treatments contained glufosinate at 450 g ai ha^{-1} and were applied using the commercial product Liberty 280 SL SL and dry ammonium sulfate at 3363 g ha^{-1}.
[b] DAA; days after application.
[c] Mean values separated with the use of Tukey's Honestly Significant Difference. Values followed by different letters within each evaluation parameter column are significantly different ($P \leq 0.05$).
[d] Glufosinate alone.

At 14 DAA there were few differences in visible control ratings between all treatments. The addition of Interlock (56%) and In-Place (56%) to glufosinate at an ultra coarse spray quality decreased control of flax compared to glufosinate alone at a medium spray quality (80%) (Table 2.10). While those two adjuvants did not decrease control of flax within the medium spray quality, their addition to the tank did result in 12 and 7% reductions in visible control compared to glufosinate alone. These data indicate that Interlock and In-Place are not good adjuvants to include with glufosinate when the target species is flax or a weed species with similar composition to flax.

Similar to the observations in amaranth, the addition of a deposition aid compared to the glufosinate treatment reduced control of flax (Table 2.10). The exception was the product Placement applied at an ultra coarse spray quality maintained (14 DAA) or improved numerical control values of flax (28 DAA). In addition, Placement was the only additive where flax control was improved when applied with an ultra coarse compared to a medium spray quality. Biomass measurements were not different, while there were slight numerical trends with all additives maintaining or increasing biomass measurements relative to glufosinate alone, which would suggest these products are not suitable tank-mix partners for glufosinate when control of flax and species similar in composition to flax are the target species.

Table 2.10. Effect of deposition aid products on glufosinate efficacy applied at two spray qualities on flax near Hillsboro, ND in 2013 and 2014 and Sabin, MN in 2014.

	Visible control								Flax biomass (28 DAA)							
Treatments[a]	14 DAA[bc]				28 DAA				Fresh weight				Dry weight			
	Medium		Ultra coarse		Medium		Ultra coarse		Medium		Ultra coarse		Medium		Ultra coarse	
	----- % -----				----- % -----				----- kg/1 m of row -----				----- kg/1 m of row -----			
Untreated	0				0				0.09				0.02			
None[d]	80	a	76	a	86	a	83	a	0.03	a	0.03	a	0.01	a	0.01	a
Placement®	69	ab	76	a	74	a	89	a	0.03	a	0.03	a	0.01	a	0.01	a
Interlock®	68	ab	56	b	69	a	58	a	0.04	a	0.06	a	0.01	a	0.01	a
In-Place®	73	a	56	b	73	a	58	a	0.03	a	0.05	a	0.01	a	0.01	a

[a] Treatments contained glufosinate at 450 g ai ha^{-1} and were applied using the commercial product Liberty 280 SL SL and dry ammonium sulfate at 3363 g ha^{-1}.
b DAA; days after application.
[c] Mean values separated with the use of Tukey's Honestly Significant Difference. Values followed by different letters within each evaluation parameter column are significantly different ($P \leq 0.05$).
[d] Glufosinate alone.

The deposition aids showed no statistical significance when comparing across spray qualities nor any beneficial effect on quinoa control when mixed with glufosinate within a spray quality (Table 2.11). Only at 14 DAA, the deposition aid product Placement numerically increased quinoa control at an ultra coarse spray quality, which was not observed at the 28 DAA assessment. Similar to the previous species, quinoa control was reduced using Interlock and In-

Place at both visual assessment timings. In-Place at the medium spray quality reduced quinoa control at 14 and 28 DAA compared to glufosinate alone within the same spray quality. The same tendency was observed for biomass measurements, with exception that there were no significant differences in dry biomass.

Table 2.11. Effect of deposition aid products on glufosinate efficacy applied at two spray qualities on quinoa near Hillsboro, ND in 2013 and 2014.

Treatments[a]	Visible control								Quinoa biomass (28 DAA)							
	14 DAA[bc]				28 DAA				Fresh weight				Dry weight			
	Medium		Ultra coarse		Medium		Ultra coarse		Medium		Ultra coarse		Medium		Ultra coarse	
	----- % -----				----- % -----				----- kg/0.5 m^{-2} -----				----- kg/0.5 m^{-2} -----			
Untreated	0				0				0.88				0.17			
None[d]	76	a	61	abc	81	a	65	ab	0.14	b	0.21	ab	0.03	a	0.05	a
Placement®	63	abc	67	ab	66	ab	64	ab	0.25	ab	0.26	ab	0.05	a	0.06	a
Interlock®	61	abc	57	abc	61	ab	50	b	0.25	ab	0.29	ab	0.05	a	0.06	a
In-Place®	52	bc	42	c	50	b	43	b	0.21	ab	0.32	a	0.04	a	0.06	a

[a] Treatments contained glufosinate at 450 g ai ha^{-1} and were applied using the commercial product Liberty 280 SL SL and dry ammonium sulfate at 3363 g ha^{-1}.
[b] DAA; days after application.
[c] Mean values separated with the use of Tukey's Honestly Significant Difference. Values followed by different letters within each evaluation parameter column are significantly different ($P \leq 0.05$).
[d] Glufosinate alone.

Organosilicones

Organosilicone surfactants reduce the surface tension of water droplets. Because of this characteristic, they can lead to better droplet spread across surfaces. The organosilicone adjuvants Dyne-Amic, Syltac, and Airforce were tested to determine if the addition of a droplet spreading adjuvant in mixture with glufosinate would improve coverage on the leaf surface and with it the overall weed control while using larger droplet sizes compared to a medium spectrum. The medium spray quality provides a greater overall coverage of the leaf surface compared to the ultra coarse spray at equal spray volumes (Knoche 1994).

In general, the organosilicone adjuvants did not enhance the activity of glufosinate, but there were trends with numerical differences observed. Similarly, improved control of all species with the inclusion of an organosilicone adjuvant was not observed when comparing the activity between the medium and ultra coarse spray quality. However, improved weed control at the ultra coarse spray quality compared to glufosinate alone was observed in some species-organosilicone combinations, underlining the importance of uniform plant surface coverage when using contact herbicides (Tables 2.12, 2.13, 2.14, and 2.15).

Table 2.12. Effect of organosilicone products on glufosinate efficacy applied at two spray qualities on amaranth near Hillsboro, ND in 2013 and 2014 and Sabin, MN in 2014.

Treatments[a]	Visible control								Amaranth biomass (28 DAA)							
	14 DAA[bc]				28 DAA				Fresh weight				Dry weight			
	Medium		Ultra coarse		Medium		Ultra coarse		Medium		Ultra coarse		Medium		Ultra coarse	
	----- % -----				----- % -----				----- kg/1 m of row -----				----- kg/1 m of row -----			
Untreated	0				0				0.72				0.15			
None[d]	71	a	51	b	58	ab	39	b	0.40	a	0.36	a	0.07	a	0.06	a
Dyne-Amic®	66	ab	57	ab	66	a	57	ab	0.34	a	0.34	a	0.05	a	0.05	a
Syltac®	62	ab	54	ab	60	ab	46	ab	0.31	a	0.37	a	0.06	a	0.06	a
Airforce®	56	ab	53	ab	50	ab	62	ab	0.39	a	0.40	a	0.06	a	0.07	a

[a] Treatments contained glufosinate at 450 g ai ha^{-1} and were applied using the commercial product Liberty 280 SL SL and dry ammonium sulfate at 3363 g ha^{-1}.
[b] DAA; days after application.
[c] Mean values separated with the use of Tukey's Honestly Significant Difference. Values followed by different letters within each evaluation parameter column are significantly different ($P \leq 0.05$).
[d] Glufosinate alone.

There were few differences observed when utilizing organosilicone adjuvants applied to amaranth. The only difference at 14 DAA was glufosinate alone at the medium spray quality provided better control than glufosinate alone at the ultra coarse spray quality (Table 2.12). Amaranth control with glufosinate, alone and in mixture with organosilicone adjuvants was reduced when compared within an adjuvant from a medium to an ultra coarse spray quality. However, while a reduction of weed control due to the addition of organosilicone could not be proven, there were trends with numerical differences. Amaranth control was reduced due to the addition of organosilicones for all three tested adjuvants at the medium spray quality at the 14 DAA rating; the results were less consistent at the 28 DAA visual assessment of amaranth control. At 28 DAA, the addition of Dyne-Amic at a medium spray quality provided better control than glufosinate applied by itself at the ultra coarse quality. Also, the adjuvants Dyne-Amic and Syltac improved or maintained amaranth control slightly at the medium spray quality at the 28 DAA rating. Whereas all three adjuvants improved the amaranth control when using a ultra coarse spray quality at the 14 and 28 DAA visual assessment compared to glufosinate itself sprayed without an organosilicone adjuvant.

Within medium spray quality, the addition of an organosilicone generally decreased efficacy relative to glufosinate alone (Table 2.12). In contrast, with an ultra coarse spray quality, efficacy was improved by adding an organosilicone product. These results indicate that the functioning activity of this class of adjuvant (i.e. spreading of droplets on a surface) does not influence the activity of glufosinate on amaranth and similar species. However, there are some trends in the data that are worth discussing, particularly with treatments applied at the ultra coarse spray quality. The addition of an organosilicone tended to improve amaranth control with an ultra coarse spray quality compared to glufosinate by itself which may indicate the candidates tested improved the droplet spread for better coverage of the leaf surface which translated into improved amaranth control. Despite some of the trends observed in the visual assessments, there were no differences in biomass across all adjuvants and spray qualities.

For common buckwheat control, no differences between the medium and ultra coarse spray quality were observed (Table 2.13). In fact, no differences were observed among any of the treatments or spray qualities. There was very little variation in visual evaluations at 28 DAA with ratings ranging from 70 to 74%. Biomass measurements for treatments that contained an organosilicone adjuvant trended higher compared with glufosinate alone for both spray qualities with the exception of Airforce which trended lower than glufosinate alone for ultra coarse fresh weight and medium dry weight.

Table 2.13. Effect of organosilicone products on glufosinate efficacy applied at two spray qualities on common buckwheat near Hillsboro, ND in 2013 and 2014.

Treatments[a]	Visible control								Common buckwheat biomass (28 DAA)							
	14 DAA[bc]				28 DAA				Fresh weight				Dry weight			
	Medium		Ultra coarse		Medium		Ultra coarse		Medium		Ultra coarse		Medium		Ultra coarse	
	----- % -----				----- % -----				----- kg/1 m^{-2} -----				----- kg/1 m^{-2} -----			
Untreated	0				0				1.04				0.22			
None[d]	68	a	68	a	71	a	73	a	0.22	a	0.23	a	0.04	a	0.03	a
Dyne-Amic®	65	a	76	a	70	a	74	a	0.28	a	0.38	a	0.05	a	0.06	a
Syltac®	70	a	66	a	70	a	71	a	0.26	a	0.24	a	0.05	a	0.05	a
Airforce®	74	a	68	a	73	a	71	a	0.23	a	0.20	a	0.03	a	0.05	a

[a] Treatments contained glufosinate at 450 g ai ha^{-1} and were applied using the commercial product Liberty 280 SL SL and dry ammonium sulfate at 3363 g ha^{-1}.
[b] DAA; days after application.
[c] Mean values separated with the use of Tukey's Honestly Significant Difference. Values followed by different letters within each evaluation parameter column are significantly different ($P \leq 0.05$).
[d] Glufosinate alone.

At 14 DAA, glufosinate applied alone in a medium spray quality provided the greatest control of flax, with all other treatments providing less control (Table 2.14). Though not different, Dyne-Amic and Airforce provided a 17% reduction at a medium spray quality by 28 DAA, and Syltac provided a 20% reduction at an ultra coarse spray quality compared to glufosinate by itself at a medium quality. All other treatments provided reduced flax control compared to glufosinate alone at a medium quality.

Contrary to the visible control of amaranth, common buckwheat and quinoa, the organosilicone adjuvants were not able to maintain the glufosinate activity at an ultra coarse spray quality compared to the medium spray quality for flax control (Table 2.14). In addition, the reduction of control using an ultra coarse spray quality compared to a medium was most reduced in flax compared to the other included species. Glufosinate alone with medium spray quality provided the greatest flax control at 14 and 28 DAA (81 and 83%), in addition to the least amount of biomass compared to all treatments. The addition of an organosilicone tended to reduce efficacy and increase biomass measurements compared to glufosinate alone over both spray qualities with the exception of Syltac at the 28 DAA visual evaluation. This would suggest on a species like flax, which has many small leaves, that reducing the droplet surface tension with the addition of an organosilicone adjuvant may increase the potential for run off before the droplet can adhere to the leaf surface.

Table 2.14. Effect of organosilicone products on glufosinate efficacy applied at two spray qualities on flax near Hillsboro, ND in 2013 and 2014 and Sabin, MN in 2014.

	Visible control								Flax biomass (28 DAA)							
Treatments[a]	14 DAA[bc]				28 DAA				Fresh weight				Dry weight			
	Medium		Ultra coarse		Medium		Ultra coarse		Medium		Ultra coarse		Medium		Ultra coarse	
	----- % -----				----- % -----				----- kg/1 m of row -----				----- kg/1 m of row -----			
Untreated	0				0				0.07				0.02			
None[d]	81	a	59	b	83	a	57	b	0.03	b	0.05	ab	0.00	a	0.01	a
Dyne-Amic®	58	b	48	b	66	ab	56	b	0.04	ab	0.05	ab	0.01	a	0.01	a
Syltac®	56	b	52	b	58	b	63	ab	0.05	ab	0.05	ab	0.03	a	0.02	a
Airforce®	57	b	45	b	66	ab	50	b	0.05	ab	0.07	a	0.01	a	0.02	a

[a] Treatments contained glufosinate at 450 g ai ha^{-1} and were applied using the commercial product Liberty 280 SL SL and dry ammonium sulfate at 3363 g ha^{-1}.
[b] DAA; days after application.
[c] Mean values separated with the use of Tukey's Honestly Significant Difference. Values followed by different letters within each evaluation parameter column are significantly different ($P \leq 0.05$).
[d] Glufosinate alone.

Assessing the influence of organosilicone adjuvants with glufosinate on quinoa control revealed no differences across treatments (Table 2.15). Within the medium spray quality, mixing an organosilicone with glufosinate resulted in a trend of reduced quinoa control compared to glufosinate alone. For the ultra coarse spray quality, the addition of Dyne-Amic and Airforce with glufosinate resulted in the trend of maintained or improved efficacy at both visual evaluations compared to the herbicide alone. Similar to common buckwheat biomass measurements, weights from Dyne-Amic and Syltac treatments trended higher than glufosinate alone, while Airforce provided the greatest reduction of both fresh and dry weight biomass compared to the herbicide alone. Overall the data indicated the addition of an organosilicone adjuvant did not improve control beyond glufosinate alone for quinoa and similar species. It suggested that the adjuvants contained in Liberty 280 SL provide sufficient surfactant to promote droplet spread on the leaf surface for plants in this genus.

Table 2.15. Effect of organosilicone products on glufosinate efficacy applied at two spray qualities on quinoa near Hillsboro, ND in 2013 and 2014.

Treatments[a]	Visible control				Quinoa biomass (28 DAA)			
	14 DAA[bc]		28 DAA		Fresh weight		Dry weight	
	Medium	Ultra coarse	Medium	Ultra coarse	Medium	Ultra coarse	Medium	Ultra coarse
	----- % -----		----- % -----		----- kg/0.5 m^{-2} -----		----- kg/0.5 m^{-2} -----	
Untreated	0		0		0.95		0.23	
None[d]	60 a	50 a	63 a	53 a	0.35 a	0.36 a	0.07 a	0.08 a
Dyne-Amic®	55 a	63 a	58 a	62 a	0.36 a	0.36 a	0.09 a	0.07 a
Syltac®	53 a	50 a	57 a	52 a	0.45 a	0.33 a	0.10 a	0.07 a
Airforce®	53 a	53 a	52 a	53 a	0.31 a	0.27 a	0.06 a	0.06 a

[a] Treatments contained glufosinate at 450 g ai ha^{-1} and were applied using the commercial product Liberty 280 SL SL and dry ammonium sulfate at 3363 g ha^{-1}.
[b] DAA; days after application.
[c] Mean values separated with the use of Tukey's Honestly Significant Difference. Values followed by different letters within each evaluation parameter column are significantly different ($P \leq 0.05$).
[d] Glufosinate alone.

CHAPTER 3. GLUFOSINATE FORMULATION DEVELOPMENT

Materials and Methods

Herbicide performance can be improved by many factors including the use of adjuvants, either as a tank mixture or included in the herbicide formulation. The aim of this research was to develop an improved glufosinate formulation with new additives compared to the current formulations commercially available (Table 3.1).

Table 3.1. Product information for glufosinate formulation development in field, laboratory, and greenhouse trials conducted in Germany and United States during 2016 and 2017.

Trade name	Reference name	Chemical name	Manufacturer[a]
Genapol LRO Paste	Genapol or SLES	C_{12}/C_{14} fatty alcohol diethylene glycol ether sulfate sodium, used as a 70% wt.-% solution in water	Clariant
Dowanol PM		1-Methoxy-propan-2-ol	Dow
Silcolapse 482		Polydimethylsiloxane defoamer with silica gel	Bluestar Silicones
Polymer			
Atplus FA	Atplus	N/A	Croda
Sokalan CP5	Sokalan	Copolymer of methacrylic acid and acrylic acid	BASF
Kuraray Poval 4-88	Kuraray	Polyvinyl alcohol	Kuraray
Reax 88 A	Reax	Lignosulfonic acid, sodium salt, sulfomethylated	DKSH
Ultrazin Na	Ultrazin	Purified sodium lignosulphonate	Borregaard
Surfactant			
Agnique PG 8105G (APG)	APG	C_8-C_{10} Alkyl polyglycosides	BASF
Synergen GA	Synergen	C_8-C_{10} alkylglucamides	Clariant
Ammonyx M	Ammonyx	Myristamine Oxide	Stepan
Empigen BS/H50	Empigen	Cocamidopropyl betaine	Huntsman
Empicol SDD/O	Empicol	Disodium Laureth-3 Sulfosuccinate	Huntsman
Oil			
Salacos 99	Salacos	Isononyl isononanoate	Nisshin Oillio
DEHA	DEHA	Bis(2-ethylhexyl)adipat	Lanxess
Disflamoll TOF	Disflamoll	Tri-(2-ethylhexyl)-phosphate	Lanxess

[a] Clariant - Muttenz, Switzerland; Dow – Midland, MI; Bluestar Silicones – Lyon, France; Croda – Snaith, United Kingdom; BASF – Ludwigshafen, Germany; Kuraray – Tokyo, Japan; DKSH – Zurich, Switzerland; Borregaard – Sarpsborg, Norway; Stepan – Northfield, IL; Huntsman – The Woodlands, TX; Nisshin Oillio – Tokyo, Japan; Lamxess – Cologne, Germany.

GFA 196 SL Formulation Development

A test formulation of glufosinate was created to screen the new additive candidates (Table 3.2). The test formulation was based on the Basta 200 SL formulation that contained a reduced (25%) Genapol load which will be referred to as GFA 196 SL.

Table 3.2. Formulation components and composition of GFA 196 SL and Basta 200 SL. GFA 196 SL was developed with a reduced Genapol load based off the Basta 200 SL formulation to better separate tested additives in field, laboratory and greenhouse trials conducted in Germany and United States during 2016 and 2017.[a]

Component	GFA 196 SL	Basta 200 SL
	Amount in wt.-%	
Glufosinate-ammonium (GFA)	18	18
Genapol LRO Paste	22.5	30
Dowanol PM	10	10
Silcolapse 482	0.25	0.25
Water	add to 100	add to 100

[a] Lorentz et al. 2020

Glufosinate Formulation Field Trials

Field experiments were established spring of 2017 in Sabin, Minnesota. The experiments evaluated the impact of different adjuvant additives with glufosinate on crop phytotoxcity and weed efficacy. Sabin is located at longitude -96.61, latitude 46.79 at an elevation of 281 m above sea level. The soil type at Sabin is a Wheatville silt loam.

The experimental design was a randomized complete block with three replicates. Species were arranged in a block arrangement. Two rows each of 'G84J92-3011A' Liberty-Link corn (*Zea mays* L.), 'L05-11N' Liberty-Link soybean (*Glycine max* L.), 'L525' Liberty-Link canola (*Brassica napus* L.), wild oat (*Avena fatua* L.), Italian ryegrass (*Lolium perenne* L. ssp. multiflorum (Lam.) Husnot.), kochia (*Bassia scoparia* L. Schrad.), and common lambsquarters (*Chenopodium album* L.) were planted in 30.5-cm-wide strips using a Great Plains 3P600 drill with 19-cm row spacings at a planting depth of 1.25 cm. Crop and weed species were not randomized within each replicate to prevent shading of the shorter species by the taller plant species. Plant height and density (per 1 m of row) at application timing was 30-45 cm and 8-10 plants m^{-2} corn, 15-20 cm and 15-20 plants m^{-2} soybean, 38-50 cm and 20-25 plants m^{-2} canola, 18-25 cm and 15-20 plants m^{-2} common lambsquarters, 18-22 cm and 12-20 plants m^{-2} Italian ryegrass, 26-30 cm and 10-15 plants m^{-2} kochia, and 40-45 cm and 15-20 plants m^{-2} wild oat.

Herbicide treatments were applied perpendicular to the blocks with the plant species. The plot area was 3 by 12.2 m and included all planted species. Treatments included Liberty 280 SL and Basta 200 SL as formulated standards and GFA 196 SL alone or with each additive: Atplus, Sokalan, Kuraray, Reax, Ultrazin, APG, Synergen, Ammonyx, Empigen, Empicol, Salacos, DEHA, and Disflamoll. Herbicides were applied at 350 g ai glufosinate ha^{-1} and adjuvants at 10% v/v ratio to GFA 196 SL (Table 3.1, 3.2). Adjuvants were prepared as a 10% stock solution for easier handling and were stored over a 24 h timeframe to improve adjuvant mixing in respective stock solutions. Applications were made with a backpack CO_2-pressurized sprayer hand boom containing four nozzles on 48.8 cm spacing with 11002 flatfan nozzle tips to deliver 187 L ha^{-1} application spray volume with 276 kPa of pressure at a speed of 4.0 km hr^{-1} to the center 2 m for the length of the plot. Data were analyzed using the PROC GLIMMIX procedures in SAS 9.4 (SAS Institute 2012) for analysis of variance, and treatment mean separation was performed using Tukey's comparison test at $P \leq 0.05$. Replicates were random effects. Species and herbicide treatment were fixed effects.

Radiolabeled Glufosinate Laboratory Experiments

Laboratory experiments were conducted to measure the amount of uptake of glufosinate in common lambsquarters (*Chenopodium album*). Common lambsquarters was chosen due to its importance as a weed species with a leaf surface that is difficult to wet. Plants were grown in the greenhouse from seed and transplanted as single plants into 4.5-cm Jiffy fertile pot (Jiffy Group; Zwijndrecht, The Netherlands) with a peat:loam 1:1 soil mixture and were cultivated at a photoperiod of 16 h light, 22°C/8 h dark, 14°C under natural light supplemented with a light intensity of 220 µE m^{-2} s^{-1} (Phillips Son-T AGRO). Watering and fertilization with 0.4% Wuxal Super (Precision Laboratories Waukegan, IL 60085) solution was applied when needed.

At BBCH 14-16, plants were selected for further testing to be homogenous across treatments and test time points. Treatments included 200 µl GFA SL196 + ^{14}C labeled GFA + 160 µl adjuvant which included either Sokalan, Kuraray, Reax, Ultrazin, APG, Synergen, Ammonyx, Empigen, Empicol, Salacos, DEHA, or Disflamoll. All adjuvants were used at a 10 % w/v diluted stock solution (Table 3.1, 3.2). To determine the proportional amount of glufosinate in the different partitions, ^{14}C-labeled glufosinate was used to trace glufosinate and mixed with the test samples. In the first experiment run, 4000 Bq ^{14}C-labeled glufosinate were added, while 3000 Bq ^{14}C-labeled glufosinate were used in the second run. An aliquot of each mixture was measured in the scintillation counter.

Each of the test mixtures were applied to 12 plants per experiment, with two runs completed for each treatment for a total of 24 plants. Applications of 20 droplets of 0.5 µl were made with a micro-applicator to the youngest fully expanded leaf for a total of 10 µl solution per plant. Plants were kept in the fume hood for 16 h after application in dry, low light conditions at 23°C. Treated leaves were excised from the plant and rinsed for 20 seconds in 1 ml of distilled water on a Vortex. Leaves were then transferred to a 1.5 ml Eppendorf centrifuge tube containing 90% acetonitrile solution and rinsed for an additional 20 sec. The intention was to determine the water-soluble amount of glufosinate on the leaf surface, which is prone to be washed off by a rain event. The acetonitrile wash was used to remove all glufosinate left on the leaf surface. After the rinse process was completed, leaves were then destroyed with a ball mill (Retsch MM200) in an Eppendorf tube containing 1 ml of water and 5 mm stainless steel beads at 30 hz for 60 sec. Aliquots of water and acectonitrile solutions (500 µl each) and of the destroyed leaf material (250 µl) were then mixed with 20 ml scintillation liquid (Roth; Eco Plus) and measured in a scintillation counter (Packard 2000CA TriCarb Liquid Scintilation Counter).

The rest of the plant was combusted and released $^{14}CO_2$ was trapped in scintillation liquid and contained ^{14}C was measured in decays per minute in a scintillation counter.

All values were normalized to the reference treatment GFA 196 SL which was included into each subsample set. For the leaf rinsate, values greater than 1.0 indicated more ^{14}C-glufosinate was rinsed off the leaf surface compared to GFA 196 SL alone, while values below 1.0 indicated less. Data were analyzed using the PROC GLIMMIX procedures in SAS 9.4 (SAS Institute 2012) for analysis of variance, and treatment mean separation was performed using Tukey's comparison test at $P \leq 0.05$. Replicates and environment were random effects. Additive treatments were fixed effects. Data were combined when error means squares over environments were homogeneous.

Rainfast Greenhouse Trials

A greenhouse experiment was established to evaluate the influence on rainfastness of additives with GFA 196 SL. Experimental design was a randomized complete block with six replicates and repeated two times. Common lambsquarters was established from seed in 7-cm diameter Jiffy fertile pot (Jiffy Group; Zwijndrecht, The Netherlands) filled with a peat:loam 1:1 soil mixture; herbicide applications were made at BBCH growth stage 17 to 19. GFA 196 SL and additive compounds were applied at 400 g ai ha^{-1} and 10% w/w, respectively. Additives tested included Atplus, Sokalan, Kuraray, Reax, Ultrazin, APG, Synergen, Ammonyx, Empigen, Empicol, Salacos, DEHA, and Disflamoll. Applications were made with a linear track sprayer (Bayer CropScience, Frankfurt) at 3.22 kph utilizing a 8002 flat fan nozzle tip and 410 kPa to deliver a spray application volume of 300 L ha^{-1}. For each herbicide treatment, there were six sets of plants with four replicates within each set. One set did not receive irrigation while each of the remaining sets received irrigation at 0.5, 2, 4, 8, 24 h after herbicide application (one set per time period). Rainfall amount of 5.5 mm was simulated with 8005 flat fan nozzles and 150 kPa of pressure with a linear track sprayer to each set of plants.

Visual evaluations were recorded 14 DAT on a percentage scale with 0 being no visible injury and 100 being complete plant death. Common lambsquarters weed control at the different rain simulation time points was used to determine differences in the rainfastness of the additives (additive * rain simulation timing) in a sigmoidal dose response model. The estimates for the inflection point and its slope were calculated using a two-parameter log-logistic model using the drc package in R software (R Foundation for Statistical Computing, Vienna, Austria).

$$y = 1/(1 + exp\ (b\ (log\ x - log\ e)))$$

The displayed two-parameter model is derived from the commonly used four-parameter log logistic model where y represents efficacy (% above untreated), b is the slope at the inflection point, and e is the inflection point (time to 50% control) (Ritz et al. 2015).

Rainfast Field Trials

A field experiment was established in 2017 at Sabin, Minnesota to evaluate selected additive compounds to be tested in the field to determine rainfastness improvement. Sabin is located at longitude -97.09, latitude 47.33 at an elevation of 281 m above sea level. The soil type at Sabin is a Wheatville silt loam. The experimental design was a randomized complete block with two replicates.

Treatments included GFA 196 SL at 350 g ai ha^{-1} with adjuvants mixed at 3 and 5% v/v ratio to GFA 196 SL with selected candidates (Kuraray, Salacos, Empicol, and DEHA) from the greenhouse trials, and treatments were applied with and without irrigation to ‘Glenn’ spring wheat (*Triticum aestivum* L.) at BBCH stage 23. Applications were made with a handheld backpack sprayer outfitted with 110015 even flat fan nozzles delivering 140 L ha^{-1} spray volume.

Irrigation occurred 1 h after herbicide application containing 20 L m^{-2} of water on half of the plots by a lateral irrigation unit moving in the same direction as the herbicide application was made.

Fourteen days after application, visual evaluations were recorded as a percentage control with 0 being no visible injury and 100 being dead. Data were analyzed using the PROC GLIMMIX procedures in SAS 9.4 (SAS Institute 2012) for analysis of variance, and treatment mean separation was performed using Tukey's comparison test at $P \leq 0.05$. Replicates were random effects and herbicide treatments were fixed effects.

Results

Improvement of the current glufosinate formulations is necessary to increase the application efficacy under less favorable or more challenging environmental conditions. Furthermore, formulation improvements can be made to increase absorption in order to reduce the length of time between application and rainfall necessary for adequate weed control and to reduce the amount of active ingredient applied. To accomplish this, three adjuvant classes were chosen to be evaluated: polymers, surfactants and oils (Table 3.1).

- **Polymers** are large carbon molecules that aid in reducing surface tension of water and improve the ability of the spray deposit to adhere to the leaf surface (Pacanoski 2015).
- **Surfactants** primary function is to increase droplet retention by plant foliage through reducing the dynamic surface tension of the spray solution (Kirkwood 1993). The activator action of surfactants also influences herbicide absorption into the leaf by the surfactant, increasing herbicide solubility, which thereby increase herbicide mobility through the cuticle (Hess and Foy 2000).

- **Oils** can enhance herbicide uptake by increasing the retention time of the spray solution on the leaf surface (Pacanoski 2015). Oils also have the ability to partly solubilize cuticular waxes on the leave surface and aid leaf penetration (McWhorter and Barrentine 1988).

The current commercial formulations containing glufosinate-ammonium, such as Basta 200 SL or Liberty 280 SL, are considered optimized formulations, and improvements to these formulations are difficult to detect. To allow for an easier differentiation, a sub-optimized formulation was developed with less of the main formulation surfactant, sodium-lauryl ether sulfate (SLES). This GFA 196 SL formulation had a reduced SLES load of 25% compared to Basta 200 SL and was used to evaluate the additives (Table 3.2).

All candidate additives were evaluated individually in mixture with the reference formulation GFA 196 SL. All applications were made at a rate lower than the recommended dose rate to help separate treatments. Additionally, some additives were chosen to be tested in combination in separate experiments (data not shown).

The objectives of this research were to:

1.) Determine which of the included additives improve the rainfast characteristics of the tested mixture compared to GFA 196 SL as a weaker representative formulation

2.) Identify additives that enhance the weed control activity of GFA 196 SL.

Glufosinate Formulation Field Trials

Three glufosinate reference formulations were included as standards: Basta 200 SL, Liberty 280 SL, and GFA 196 SL. Basta 200 SL is a glufosinate formulation marketed for non-selective use in a wide range of crops (Anonymous 2020a). In the US, Liberty 280 SL is labeled for use in Liberty Link cropping systems and for burndown applications prior to emergence of 7 crops (Anonymous 2020b). GFA 196 SL was a formulation developed to be similar to Basta 200 SL, but with 20% less SLES adjuvant. This reduced load formulation was developed to encourage greater differences among the additives tested in the field and greenhouse and make the formulation more vulnerable to environmental influences.

Comparing the reference glufosinate formulations under environmental conditions favorable for optimal weed control, Basta 200 SL provided the greatest weed control while Liberty 280 SL provided the least overall weed control across all weed species at 21 DAA (Tables 3.3, 3.4, and 3.5). Within a species, GFA 196 SL and Basta 200 SL provided similar control of common lambsquarters and kochia, while Italian ryegrass and wild oat control was similar for treatments containing GFA 196 SL and Liberty 280 SL. Crop phytotoxicity data was recorded and no injury was observed for any of the treatments (data not shown).

The addition of polymers Atplus, Sokalan, Kuraray, Reax and Ultrazin in mixture with GFA 196 SL provided variable results across the species tested (Table 3.3). Overall weed control across the tested mixtures was greater among the dicot species versus monocot, with Italian ryegrass being the more difficult to control monocot compared to wild oat. The SL196 formulation in mixture with Kuraray provided the greatest control across all species at a level of control similar to the Basta 200 SL formulation or exceeding it in terms of control of Italian ryegrass. Reax in mixture provided the least control across all species, even reducing control of common lambsquarters and wild oats compared to GFA 196 SL alone.

All mixtures of the SL196 with polymers provided a similar common lambsquarters control comparable with Basta at a level between 50 and 78 % weed control, except of the mixture with Reax (30% control) (Table 3.3). Liberty 280 SL provided less weed control of common lambsquarters at 21 DAA than Basta 200 SL or most polymer mixtures. All treatments resulted in low control of Italian ryegrass. The mixture including Kuraray provided the greatest control of Italian ryegrass compared to the standard 196 SL and improved efficacy by 38% compared to Basta 200 SL. Atplus and Ultrazin, in mixture with GFA 196 SL, improved Italian ryegrass control compared to the GFA 196 SL without additives and provided similar control to Basta 200 SL at 18 and 20% weed control, respectively. The visual evaluations for kochia control across all GFA196 SL + polymer treatments generally provided a similar level of control to Basta 200 SL, while kochia control was reduced to 33% when GFA 196 SL was mixed with Reax compared to GFA 196 SL (60%).

Table 3.3. Effect of polymer additives on glufosinate efficacy on common lambsquarters, Italian ryegrass, kochia, and wild oat near Sabin, MN in 2017.[a]

	Visible control (21 DAA[c])							
Treatment[b]	CHEAL		LOLMU		KCHSC		AVEFA	
	% control							
Liberty 280 SL	35	bc[d]	0	d	40	b	33	bc
Basta 200 SL	78	a	20	b	85	a	70	a
GFA 196 SL	66	ab	0	d	60	ab	58	b
GFA 196 SL+ Atplus	77	a	18	bc	73	a	22	c
GFA 196 SL + Sokalan	50	abc	7	cd	70	a	30	c
GFA 196 SL + Kuraray	78	a	58	a	72	a	62	a
GFA 196 SL + Reax	30	c	0	d	33	b	20	c
GFA 196 SL + Ultrazin	68	ab	20	b	72	a	22	c

[a] Abbreviations: CHEAL, common lambsquarters; LOLMU, Italian ryegrass; KCHSC, kochia; AVEFA, wild oat.
[b] Treatments contained glufosinate at 350 g ai ha^{-1}. Additives were included at 10% v/v ratio to GFA 196 SL.
[c] DAA; days after application.
[d] Mean values separated with the use of Tukey's Honestly Significant Difference. Values followed by different letters within column are significantly different ($P \leq 0.05$).

Basta and the mixture of Kuraray with SL196 provided the greatest control of wild oat with 70 and 62% visible control, respectively (Table 3.3). The addition of polymers Atplus, Sokalan, Reax, and Ultrazin reduced wild oat control by 28-38% compared to GFA 196 SL alone.

Several surfactants were tested in mixture with GFA 196 SL, which included APG, Synergen, Ammonyx, Empigen, and Empicol (Table 3.4). None of the mixtures with the included surfactants improved control of common lambsquarters, kochia, or wild oat greater than GFA 196 SL alone.

Table 3.4. Effect of surfactants additives on glufosinate efficacy on common lambsquarters, Italian ryegrass, kochia, and wild oat near Sabin, MN in 2017.[a]

Treatment[b]	Visible control (21 DAA[c])							
	CHEAL		LOLMU		KCHSC		AVEFA	
	--------------------------------- % control ---------------------------------							
Liberty 280 SL	35	bc[d]	0	b	40	bc	33	bc
Basta 200 SL	78	a	20	a	85	a	70	a
GFA 196 SL	66	ab	0	b	60	ab	44	b
GFA 196 SL+ Agnique	23	c	3	b	32	bc	7	d
GFA 196 SL + Synergen	47	abc	0	b	53	b	25	c
GFA 196 SL + Ammonyx	28	c	20	a	20	c	22	cd
GFA 196 SL + Empigen	67	ab	20	a	60	ab	43	b
GFA 196 SL + Empicol	45	abc	0	b	37	bc	20	cd

[a] Abbreviations: CHEAL, common lambsquarters; LOLMU, Italian ryegrass; KCHSC, kochia; AVEFA, wild oat.
[b] Treatments contained glufosinate at 350 g ai ha^{-1}. Additives were included at 10% v/v ratio to GFA 196 SL.
[c] DAA; days after application.
[d] Mean values separated with the use of Tukey's Honestly Significant Difference. Values followed by different letters within column are significantly different ($P \leq 0.05$).

Assessing the influence of surfactants on common lambsquarters control, only the addition of Empigen resulted in a similar level of control compared to 196 SL with no additional surfactant (Table 3.4). Synergen and Empicol provided numerically reduced visible weed control compared to the no surfactant reference, while the mixtures with APG and Ammonyx strongly reduced the control ($P<0.05$). While maintaining similar levels of common lambsquarters control, it is important to note that Synergen and Empicol did reduce efficacy of GFA 196 SL alone by 19 and 21%, respectively. The APG and Ammonyx surfactants proved to be the worst additives to GFA 196 SL, providing only 23 and 28% control of common lambsquarters, respectively. Similar to observations from the polymer evaluations, the addition of a surfactant provided very little enhancement of GFA 196 SL for Italian ryegrass control. Two surfactants, Ammonyx and Empigen, improved Italian ryegrass control from 0 to 20% when compared to GFA 196 SL alone, providing control similar to Basta 200 SL. Empigen maintained a similar level of kochia control (60%) to Basta 200 SL and GFA 196 SL. APG, Synergen, and Empicol provided comparable control to that of GFA 196 SL alone, but control was lower with those surfactants compared to Basta 200 SL. The addition of Ammonyx only provided 20% kochia control, making it the worst product combination for control of that weed. The addition of a surfactant with GFA 196 SL did not improve wild oat control, and actually reduced wild oat control in many cases. One additive, Empigen, maintained a similar level of wild oat control to that of GFA 196 SL. While APG, Synergen, Ammonyx, and Empicol reduced GFA 196 SL efficacy on wild oat control between 19 and 37%. Basta 200 SL provided the greatest control of wild oat at 70%.

Salacos, DEHA, and Disflamoll were the oils selected to be tested in combinations with GFA 196 SL (Table 3.5). Salacos provided similar or greater control when compared to GFA 196 SL alone for all species with exception of wild oat, to which it provided 12% less control than GFA 196 SL alone. Wild oat control was reduced with the addition of Disflamoll and DEHA by 9 and 17%, respectively, when compared to GFA 196 SL. All oils increased the control of Italian ryegrass compared to GFA 196 SL alone, and provided similar control to that of Basta 200 SL.

Salacos, DEHA, and Disflamoll in mixture with GFA 196 SL provided similar control of common lambsquarters compared to Basta 200 SL and GFA 196 SL, but DEHA and Disflamoll (57 and 57%, respectively) did reduce efficacy by 11% in comparison to the herbicide itself (68%) (Table 2.5). For Italian ryegrass control, there were no differences observed between

Salacos, DEHA, Disflamoll and Basta 200 SL (20-22%). GFA 196 SL and Liberty 280 SL provided no control of Italian ryegrass at 21 DAA.

Table 3.5. Effect of oil additives on glufosinate efficacy on common lambsquarters, Italian ryegrass, kochia, and wild oat near Sabin, MN in 2017.[a]

	Visible control (21 DAA[c])							
Treatment[b]	CHEAL		LOLMU		KCHSC		AVEFA	
	% control							
Liberty 280 SL	35	b[d]	0	b	40	b	33	bc
Basta 200 SL	78	a	20	a	85	a	70	a
GFA 196 SL	68	a	0	b	60	ab	44	b
GFA 196 SL+ Salacos	67	a	20	a	80	a	32	c
GFA 196 SL + DEHA	57	ab	20	a	50	b	27	c
GFA 196 SL + Disflamoll	57	ab	22	a	63	ab	35	bc

[a] Abbreviations: CHEAL, common lambsquarters; LOLMU, Italian ryegrass; KCHSC, kochia; AVEFA, wild oat..
[b] Treatments contained glufosinate at 350 g ai ha^{-1}. Additives were included at 10% v/v ratio to GFA 196 SL.
[c] DAA; days after application.
[d] Mean values separated with the use of Tukey's Honestly Significant Difference. Values followed by different letters within column are significantly different ($P \leq 0.05$).

All treatments, with the exception of Basta 200 SL (70%), controlled wild oat less than 45% (Table 3.5). None of the tested oils were able to improve GFA 196 SL control of wild oat. The addition of Disflamoll maintained similar efficacy to GFA 196 SL, but wild oat control was still reduced by 9%. Salacos and DEHA provided the least amount of control and less than that of GFA 196 SL alone (32 and 27%, respectively), but control for those products was similar to the wild oat control by Liberty 280 SL.

Radiolabeled Glufosinate Laboratory Experiments

The treated leaf and the rest of the plant material were analyzed for ^{14}C-glufosinate and values greater than 1.0 indicate more radio-labeled compound present compared to GFA 196 SL that would indicate greater uptake of the herbicide (Table 3.6). Not all additives from the greenhouse and field were included in the lab evaluations.

To measure the uptake of GFA formulated as SL196 and mixed with different additives, three polymers were selected to test with ^{14}C-glufosinate as a tracer relative to GFA 196 SL

(Table 3.6). In the repeated test series the mixture with Sokalan contained the lowest amounts of ^{14}C-GFA compared to the ^{14}C in the GFA 196 SL alone for both the water and acetonitrile rinsates (1.02 and 0.71, respectively). Of the polymers, the mixture with Kuraray had the greatest amount of ^{14}C detected with a value of at 1.11 from the water wash solution, while Reax had the most at 1.30 measured from the acetonitrile wash. Kuraray was the only polymer that showed an increased ^{14}C-GFA uptake compared to the 196 SL reference, while Sokalan and Reax measured 0.66 and 0.58, respectively, relative to the standard.

Table 3.6. Uptake of ^{14}C-GFA in different partitions of common lambsquarters plants. Experiment performed in laboratory, comparing different adjuvants in mixture with radiolabeled GFA and GFA formulated as 196 SL. Measurements included radiolabeled glufosinate in the water soluble fraction, the acetonitrile soluble fraction and uptake measured by leaf and remaining plant material.[a]

Treatment	Water rinsate		Acetonitrile rinsate		Leaf + plant[b]	
GFA 196 SL	1.00		1.00		1.00	
Sokalan	1.02	abc[c]	0.71	b	0.66	a
Kuraray	1.11	a	1.21	a	1.10	a
Reax	1.04	abc	1.30	a	0.58	a
APG	1.03	abc	1.02	ab	0.83	a
Synergen	1.05	ab	0.94	ab	1.22	a
Ammonyx	1.06	ab	1.10	ab	1.15	a
Empigen	0.92	bc	0.90	ab	0.98	a
Empicol	0.92	bc	0.65	b	0.96	a
Salacos	0.87	c	0.92	ab	1.01	a
DEHA	0.94	abc	0.92	ab	1.22	a
Disflamoll	0.98	abc	1.26	a	1.06	a
Liberty 280 SL	1.03	abc	1.40	a	0.84	a

[a] Data was normalized to the average GFA SL 196 samples across all sample times.
[b] Ground leaf liquid and whole plant combusted material.
[c] Mean values separated with the use of Tukey's Honestly Significant Difference. Values followed by different letters within column are significantly different ($P \leq 0.05$).

APG, Synergen, Ammonyx, Empigen, and Empicol were evaluated as representatives for the surfactants and had similar amounts of ^{14}C-glufosinate detected within the respective washes (Table 3.6). Empigen and Empicol had the lowest values of radio-labeled material detected for both washes (less than 0.92). For the water wash, Synergen values were greater than 1.0 (1.05), while the values fell below 1.0 for the acetonitrile wash (0.94). Providing the least enhancement of ^{14}C-GFA uptake compared to GFA 196 SL alone was APG and Ammonyx which had values greater than 1.0 for both wash values. Synergen and Ammonyx measured greater ^{14}C-uptake from the leaf and combusted plant material relative to GFA 196 alone, with APG, Empigen, and Empicol measuring below 1.0 (0.83, 0.98, and 0.96).

Of the three classes, the oils provided the greatest overall improvement of glufosinate uptake. Salacos, DEHA, and Disflamoll all provided similar values within the respective measurements, with Salacos providing the greatest enhancement across all measurements compared to DEHA and Disflamoll (Table 3.6). Within the water wash, Salacos (0.87), DEHA (0.94), and Disflamoll values were below 1.0, similar to acetonitrile with the exception of Disflamoll that rated at 1.26. All the oils measured the greatest amount of ^{14}C-glufosinate within the leaf and combusted material compared to GFA 196 SL alone (1.01-1.22).

Rainfast Greenhouse Trials

Greenhouse trials were established to determine if the tested additives could reduce the time period needed between herbicide application and rainfall to ensure full herbicidal activity (Table 3.7). To obtain a reliable comparison for the rainfast period, heavy rainfall was simulated in the spray chamber after herbicide application. GFA 196 SL alone and in mixtures was applied to common lambsquarters with set simulated rain intervals at 0.5, 2, 4, 8, and 24 h following the herbicide application to compare with plants not irrigated. A time course was developed to allow for a log-logistic regression analysis and determination of the time interval between herbicide application and first rain event point to achieve 50% control of the tested plants by interpolation of the results of each time point.

Overall, the additives provided mixed results (Table 3.7). The polymers tested in mixture with GFA 196 SL were Atplus, Sokalan, Kuraray, Reax, and Ultrazin, respectively. Kuraray was the only polymer that reduced the time to achieve rainfastness compared to GFA 196 SL, indicated by the parameter e (rain-free hours to result in 50% visual control) by more than 4 h. Sokalan provided a similar rainfast interval relative to GFA 196 SL. Atplus and Reax mixtures increased the time interval required to achieve rainfastness by an additional 2 h compared to GFA 196 SL alone. The addition of Ultrazin caused a doubling of the time to achieve rainfastness compared to the herbicide alone.

Table 3.7. Log-logistic model parameters estimates, standard errors, and time to 50% control of common lambsquarters as influenced by additive*time of rain simulation after herbicide treatment combination tested in the greenhouse rain simulation trial.

Treatment[a]	Estimate of log-logistic model parameters[b]	
	b	*e*
		---------- h ----------
GFA 196 SL	-1.45 ± 0.26	5.19 ± 0.65
Atplus	-1.32 ± 0.24	7.10 ± 0.99
Sokalan	-1.18 ± 0.20	5.31 ± 0.77
Kuraray	-0.71 ± 0.12	1.15 ± 0.30
Reax	-3.58 ± 1.29	7.45 ± 0.54
Ultrazin	-3.71 ± 1.45	10.29 ± 1.07
APG	-1.22 ± 0.25	3.66 ± 0.56
Synergen	-2.44 ± 0.56	5.38 ± 0.48
Ammonyx	-1.56 ± 0.34	8.45 ± 1.10
Empigen	-1.12 ± 0.22	5.15 ± 0.80
Empicol	-0.87 ± 0.13	2.08 ± 0.39
Salacos	-1.13 ± 0.19	1.81 ± 0.30
DEHA	-1.23 ± 0.21	2.12 ± 0.32
Disflamoll	-0.64 ± 0.10	2.28 ± 0.55

[a] Treatments contained glufosinate at 400 g ai ha^{-1} in mixture with the respective additives and were applied using the modified formulation GFA SL196.
[b] *c* parameter (lower limit) fixed to 0%; *b* parameter corresponds to slope at the inflection point; *d* parameter corresponds to the upper limit fixed to 100%; *e* parameter corresponds to the inflection point of the log-logistic function and the hours required to reach 50% visual control.

Few surfactants reduced the length of time needed to reach 50% visual control compared to GFA 196 SL alone (Table 3.7). The APG and Empicol surfactants in mixture with GFA SL 196 improved the rainfast interval by 1.5 and 3.1 h, respectively. Synergen and Empigen provided a similar rainfast interval comparable to the herbicide alone, while the length of time needed increased by more than 3 hours when mixed with Ammonyx.

Oil adjuvants when mixed with GFA 196 SL provided the greatest reduction in time by more than 3 hours compared to GFA 196 SL alone (Table 3.7). Overall, the oil mixtures provided the most consistent response for the amount of time (h) needed to reach 50% visual control (1.81, 2.12, and 2.28).

Rainfastness Field Trials

In the field trial to assess rainfastness of the included mixtures, spring wheat was used as model subject to allow for a more uniform plant stand and for higher flexibility in terms of application timing to prevent irregular growth stages (Table 3.8). Additionally, grasses were expected to be more prone to wash off than most dicot weeds in general due to the more erect orientation of leaves. A lateral irrigation unit was used to simulate rain 1 h after herbicide application.

Table 3.8. Effect of additives on glufosinate efficacy following rain simulation with lateral irrigation unit on spring wheat near Sabin, MN in 2017.

Treatment[a]	No rain		Rain		% reduction of control due to simulated rain
	-----------------------------% control		-----------------------------		
GFA 196 SL	28	b[b]	0	d	-100
Kuraray	48	a	29	b	-40
Empicol + Salacos	40	a	25	b	-37
DEHA	48	a	10	c	-79

[a] Treatments contained glufosinate at 350 g ai ha^{-1} and were applied using the modified formulation GFA SL196.
[b] Mean values separated with the use of Tukey’s Honestly Significant Difference. Values followed by different letters within column are significantly different ($P \leq 0.05$).

The mixtures of GFA 196 SL and Kuraray, Empicol + Salacos, and DEHA improved spring wheat control compared to GFA 196 SL alone for both rain simulation and no rain (control) (Table 3.8). When irrigation was utilized, the mixtures containing Kuraray and Empicol + Salacos maintained the highest level of efficacy, 29 and 25% respectively. The mixture with DEHA provided the least enhancement of GFA 196 SL with only 10% control, but still greater than the herbicide alone (0%). In the absence of rain simulation, Kuraray, Empicol + Salacos, and DEHA provided a similar level of control (40-48%) and improved GFA 196 SL control of wheat by more than 12%. Under both conditions, the mixture with Kuraray maintained the greatest numeric wheat control. GFA 196 SL in mixture with Kuraray increased wheat control by 20% without rain simulation and even greater under irrigation conditions by 29%. When comparing GFA 196 SL alone without rain to GFA 196 SL + Kuraray under rain simulation, the Kuraray mixture maintained the same level of wheat control.

CHAPTER 4. DISCUSSION

The testing of agricultural adjuvants requires consideration of specialized testing methods. Differences can be small enough that if the herbicide rate is too high, or if the wrong species, trial design, or assessment parameter is selected, any differences that could potentially be observed will be diminished. Testing environment can influence several parameters that can affect the outcome of the research. Field conditions can provide a natural environment that allows species to grow often more vigorous compared to greenhouse conditions. In a greenhouse, the plants may be easier to kill with herbicides since they are not exposed to the environmental stresses of the outdoor climate, the environmental conditions are fixed and can be kept constant. Several benefits exist for conducting research in a controlled environment and are especially of interest to reduce unwanted, influencing factors and variations. Decreasing the risk of environmental impact on the outcome of the research, factors such as excessive moisture or drought, extreme temperature changes, etc., could negatively influence the research results by not providing typical environmental conditions. Further, the ability to work in a fixed environment allows for more control of outside influences including unintended natural weed populations, disease, insects, or wildlife. However, the lack of stress to plants from certain environmental factors, such as UV radiation or large variability in temperature and humidity, can reduce the transferability of greenhouse results to field conditions. Of particular importance are the cuticle thickness and epicuticular waxes of plants that are often heavily influenced by environmental stresses and are key factors to consider when testing adjuvants for herbicides which are intended to provide guidance for field application. For example, UV radiation in open field conditions leads to higher lignin deposition in cell walls, an increased cuticle thickness and a lower rate of transpiration compared to greenhouse plants (Bandurska et al. 2013; Manetas et al. 1997).

While there were portions of the testing model that could be improved, there were benefits to the way the research was organized. Conducting the trials in a field setting allowed for species to develop in a natural environment versus artificial conditions like the greenhouse that can change the way a plant develops. In addition, applications were made with field grade equipment that allowed for circumstances that are closer to how these products are typically applied and subject to the environmental conditions at application.

There are many changes to the testing method utilized in this work that could be considered for future research. For some of the species, specifically flax, a larger biomass sample could have been collected which may have provided greater treatment differences and allowed for statistical significance within an adjuvant class. While resources may be a limiting factor, a fixed greenhouse environment may have allowed for more treatment differentiation when considering evaluating products in a given adjuvant class that may have very similar characteristics.

Acidic Ammonium Sulfate Replacements, Deposition Aids, and Organosilicone Field Trials

Acidic Ammonium Sulfate Replacements (AMADS)

The trials adding the acidic ammonium sulfate replacement adjuvant class in mixture with glufosinate had mixed results. Adding the adjuvants into spray solution caused a trend for increased weed control, but statistical differences ($p \leq 0.05$) were only detected for the product Import applied to quinoa, flax and amaranth, mainly at 14 DAA and using a medium spray quality. AMADS only improved control of flax at a medium spray quality. Generally speaking, the addition of an acidic ammonium sulfate replacement adjuvant improved glufosinate efficacy within a spray quality, but not always when comparing within a treatment between spray qualities (medium spray quality to ultra coarse). It appeared to be dependent on the acidic ammonium sulfate replacement adjuvant product and species, e.g. AMADS treatments improved amaranth control when comparing a medium spray quality to ultra coarse, while the same comparison resulted in a reduction of quinoa control. A comparison of glufosinate alone applied with a medium spray quality to treatments that include an acidic ammonium sulfate replacement adjuvant at an ultra coarse spray quality show a similar result. These results met the objective of this research; to maintain or enhance the same activity of glufosinate at an ultra coarse spray quality to the same efficacy level when applied at the preferred medium spray quality which provides improved coverage.

One trend observed over all species was improvement of glufosinate with addition of Import and medium spray quality. Although a detailed list of ingredients is not available, the label lists tallow amine ethoxylate as a functioning agent. While detected in all species, the greatest improvements were observed in amaranth, common buckwheat and quinoa. The additional surfactant could have allowed for better glufosinate absorption by helping to solubilize the leaf cuticle and could also have improved spray coverage on the leaf surface.

Deposition Aids

Overall, the addition of a deposition aid did not improve glufosinate efficacy for the species tested. This was also true when comparing between spray qualities within a treatment with the exception of Placement. Amaranth and flax control increased from a medium spray quality to the ultra coarse spray when Placement was included in mixture with glufosinate. Similarly, within an ultra coarse spray quality, amaranth and flax control improved with the addition of Placement compared to the herbicide alone. Interlock and In-Place tended to reduce control of Liberty 280 SL across all species tested. The least amount of variation across all treatments was observed with common buckwheat across all treatments and spray qualities (81-88%) The concern with utilizing a larger droplet on a species that generally has a smooth, waxy leaf surface like common buckwheat, is that there is a potential for a larger droplet to be displaced and not remain on the leaf. This could indicate that Liberty 280 SL formulation contains compounds to help maintain droplet adhesion even with larger droplets on a waxy leaf surface, yet provides enough droplet spread for adequate coverage. It also suggests that although Interlock and In-Place are within the same adjuvant class, there are specific components contained in the Placement formulation which provide enhancement to Liberty 280 SL for the control of amaranth and flax, but to identify the specific ingredients would be challenging due to the proprietary nature of the formulation.

Organosilicones

In general, the organosilicone adjuvants tested did not enhance glufosinate performance regardless of spray quality with a few exceptions. Dyne-Amic improved efficacy at the larger spray droplet spectrum. Similar to observations made from the deposition aid trials, there were slight numerical differences within the common buckwheat data. Again, this could be attributed to the smooth, waxy nature of the common buckwheat leaf surface. In addition to the characteristic of the leaf surface, Liberty 280 SL seemingly contains adjuvants built into the formulation that reduce surface tension to provide enough droplet spreading since the ultra coarse spray quality control ratings and biomass measurements did not differ greatly from the medium spray quality observations (Chachalis et al. 2001).

Overall, the data does not suggest AMADS, deposition aids, or organosilicone adjuvants provide strong enhancement of glufosinate within each class tested with some exceptions. This research only evaluated a selected group of products within each adjuvant class. Further research could include a broader view within each group to determine if there are other candidates that may provide improved functionality of glufosinate. A deeper understanding of the primary functioning agents of each adjuvant could provide insight to what components may be providing enhancement of glufosinate and could help determine which candidates might be a better mixture partner with glufosinate.

Adjuvant manufactures are not required to disclose components and concentrations included in an adjuvant formulation comparable to pesticide manufactures. This makes it difficult to identify what component of the adjuvant formulation is acting as the functioning agent and also could explain why adjuvants within the same class can produce very different results when tested with the same herbicide active ingredient. Further transparency would also provide the end user with information regarding the adjuvant composition so the end user would not strictly rely on the adjuvant manufacturer characterization since there is no formal regulating body for adjuvants. Currently there is a voluntary program within the manufacture sector through the Council of Producers and Distributors of Agrotechnology which provides methodology for a certification process. The seventeen criteria required for certification consist of a set of standards from ASTM International and also includes requirements of the EPA, U.S. Department of Transportation, and U.S. Occupational Safety and Health Administration (CPDA 2019). The issue is that not all adjuvant manufactures submit their products to be certified and vetted for quality assurances.

The first set of research focused on the use of commercialized adjuvants available on the market to maintain or potentially enhance the activity of glufosinate at an ultra coarse spray quality and the results were mixed. The next step was to evaluate glufosinate alone and in combination with potential adjuvant component candidates to be included in a formulated glufosinate product.

Glufosinate Formulation Development

Formulation Field Trials

The results from adding a polymer, surfactant, or oil with GFA 196 SL provided, as expected, mixed results depending on the additive and species. Overall, all treatments provided greater dicot (common lambsquarters and kochia) control when compared to monocot species (Italian ryegrass and wild oat); these results could be expected as glufosinate is considered to be more effective on annual broadleaf species than on grasses (Corbett et al. 2004; Culpepper et al. 2000; Steckel et al. 1997) and provides poor control when applications of glufosinate are made to grasses at a more advanced growth stage (Gardner et al. 2006). However, the advanced growth stage, combined with reduced herbicide rates increased the overall variation among treatments, but also allowed for better separation of single treatments. Of the three glufosinate reference treatments, Basta 200 SL provided the greatest control while Liberty 280 SL provided the least across all species tested.

Overall, most polymers improved GFA 196 SL activity compared to the herbicide alone with few exceptions depending on species and polymer. Control of wild oat was generally reduced when a polymer was included in mixture with GFA 196 SL, with the lone exception of Kuraray which improved efficacy by 4%. Future evaluations should not include Reax as it provided no improvement of GFA 196 SL compared to the herbicide alone for all species and reduced control by more than 36% across all species. Kuraray was the only polymer that increased control of all the tested species and could be considered as a suitable candidate to be included in formulation with glufosinate. When compared to commercialized formulations, the mixture of Kuraray with GFA 196 SL also provided comparable control of tested species to that of Basta 200 SL. The greater benefit of including a polymer may be better observed in a different testing model, such as rainfast trial simulation or by testing across more environments. Stock and Briggs (2000) suggested that the inclusion of an additive to improve the wetting or spreading abilities of a spray droplet to achieve greater coverage, does not always equate to greater uptake or efficacy which was observed with some of the polymers tested.

The addition of a surfactant generally did not improve the activity of GFA 196 SL. Weed control tended to be reduced when a surfactant was added, thus causing a negative effect with all surfactants with the exception of Empigen. Treatments that contained Empigen did not necessarily improve GFA 196 SL activity, but maintained control to the same level of the GFA 196 SL alone for all species except Italian ryegrass. GFA 196 SL activity with Empigen improved control of Italian ryegrass to a similar level as Basta 200 SL which could allow it to be considered for further evaluation with glufosinate. These data underline the importance of SLES being the surfactant of choice for the commercial glufosinate formulations (Albrecht et al. 1996).

In general, the oil candidates tested in mixture with GFA 196 SL provided a more consistent response enhancement compared to the other two classes of additives evaluated. GFA 196 SL with the addition of Salacos, DEHA, or Disflamoll maintained or improved GFA 196 SL activity across all tested species and control was similar to Basta 200 SL, except for control of wild oat. Again, these data support the known weaknesses of glufosinate on monocots, but is important for the northern geographies where wild oat is a problematic weed species.

Radiolabeled Glufosinate Laboratory Work

Four measurements were utilized to determine the amount of ^{14}C-glufosinate that was on the leaf surface, in the leaf cuticle, and taken up by the plant. The first water wash was intended to simulate a typical rain event that could occur in the field environment. After further consideration, the rinsing technique may have been more aggressive than needed for the intended outcome. The second wash, using an acetonitrile solution, was intended to rinse the remaining ^{14}C-glufosinate off the leaf surface which might have been bound to the wax layer or protected by a polymer layer. Leaf material values give an estimation of movement into the leaf cuticle, while the combusted plant material represents how much radiolabeled material was present beyond the treated leaf.

All polymers had values greater than 1.0 for the water and acetonitrile wash, with the exception of Sokalan from the acetonitrile wash. This means that more ^{14}C-glufosinate was rinsed off compared to GFA 196 SL. This would suggest that in an intense rain event, the tested polymers may not provide any additional rainfall protection if making a comparison of the current testing method to an environmental situation. Generally, this may be considered a negative effect, but the effect may have been enhanced given the dry lab environment under the exhaust hood where the plants were kept until sample collection. The results could be expected since there was little humidity to keep the droplet hydrated underneath the polymer coating, and this reduced the opportunity for additional glufosinate uptake. Typically, polymers are utilized to help preserve the spray droplet from the environment or aid in better droplet adhesion by providing a protective layer on the leaf surface. This was also observed during the application of the droplets on the leaf surface where, especially the samples containing Kuraray, droplet deposits had a gel-like appearance right after application which still dried off quickly. In a field environment, there may be enough humidity to help keep the droplet hydrated and potentially allow for more active ingredient to enter the plant. Stock and Briggs (2000) presented this consideration of adjuvants for optimizing herbicide delivery versus improving penetration enhancers whether tank-mixed or into a formulation. While an additive may improve the rainfastness of a given herbicide, this may not always result in improved efficacy in the absence of a rain event.

The surfactants provided mixed results depending on the surfactant tested. Mixtures with APG, Synergen, and Ammonyx had the greatest amount of radiolabeled material measured from the two washes performed relative to GFA 196 SL, while Empigen and Empicol had the least amount detected. Similar results were determined from the leaf and combusted plant material for additives that had a higher amount of ^{14}C-glufosinate measured from the washes, where there was also greater amount detected in the plant material with the exception of APG. While these compounds had more radiolabeled glufosinate found in the rinsate, these compounds also provided greater uptake into the plant. In contrast, Empigen and Empicol had some of the lowest values for the detected radioactivity in the washes and plant material values. This suggests that while Empigen and Empicol may behave more as a spray activator, which refers to the spreading and sticking characteristics of a surfactant; it may not provide the activator action that influences herbicide absorption into the leaf which some surfactants can provide as suggested by Hess and Foy (2000). Also, the low relative air humidity might be responsible for the lower uptake measurements found for Empigen, especially compared to the previous results found for weed control in the field trials, where Empigen provided similar weed control to 196 SL alone. Further, the data suggests APG, Synergen, and Ammonyx may provide more benefits as an activator surfactant, rather than spray activator characteristics. Empicol appeared to exhibit characteristics of both of the previously mentioned actions providing the lowest wash amounts and values near 1.0 for leaf and combusted material.

The results from the oils tested delivered the most consistent picture for all four parameters measured. The consistency was not only visible within the radioactive uptake trial under dry lab conditions but also in the field trials for weed control efficacy and rainfastness. Measurements of Sacosol, DEHA, and Disflamoll provided the lowest amounts of radiolabeled material collected from the water and acetonitrile washes with the exception of Disflamoll and the acetonitrile wash. Likewise, the oil additives also provided the greatest amount of ^{14}C-glufosinate in the leaf and combusted plant material. This suggested that the oils, having the least amount of material in the washes and more measured in the collected plant material, encourage uptake into the plant. This could be particularly important for a plant such as common lambsquarters that has a very distinct epicuticular wax layer that could be dissolved through the use of oil adjuvants to reduce the cuticle barrier and improve herbicide penetration into the plant.

Rainfast Greenhouse Trial

Unfavorable weather conditions at and after pesticide application are the biggest threat to achieve good efficacy, and these conditions are difficult to forecast and overcome. For example, a rain event shortly after pesticide application can wash the pesticide off of plant surfaces and lead to reduced efficacy or even lead to a complete failure. Reducing the period of time for a herbicide to be considered rainfast is therefore very important for a successful pesticide application and to reduce environmental impact due to wash off.

Several compounds from three additive classes, polymers, surfactants, and oils, were tested to determine if improvements could be made to the current commercial glufosinate formulations. The Liberty 280 SL and Basta 200 SL label states a time interval between application and first rain event for rainfastness of about 4 h and 6 h, respectively. However, the standard rain event in terms of strength, length of rain event, droplet size or amount is difficult to determine and further environmental influences as well as plant physiological conditions have an important additional impact on the rainfastness of a product. Any temporal number describing a time period between herbicide application and rain will only reflect a time interval for specific conditions tested during the label registration process, and provides a relative comparison among formulations. Therefore, in the presented case, the test under equal conditions allows for a fair and equal comparison of the additives and their influence on the rainfastness of glufosinate.

There were several additives identified with potential to reduce the period of time between application and rain event compared to the GFA 196 SL standard formulation. However, several of the included additives had a null or negative impact on the rainfastness interval of the GFA 196 SL formulation, indicating the importance of a specific optimization for each active ingredient and targeted formulation. The short time between application and rain event coupled with aggressive rain simulation provided challenging conditions by which the data that were collected show the potential of the additives tested even more.

First, sodium-lauryl ether sulfate (SLES) has been identified early on as key surfactant for glufosinate-ammonium and is widely used as a standard additive in the current commercial glufosinate formulations. A glufosinate formulation with a reduced load of SLES has been utilized in this research to improve differentiation of treatments. Initial weed control efficacy trials showed the negative impact of the 20% reduced amount of SLES in the standard test formulation GFA 196 SL and its higher vulnerability to environmental influences compared to the commercial Basta 200 SL formulation, which has the full load of SLES.

The GFA 196 SL formulation coupled with the humid conditions in the greenhouse lengthened the time needed for the droplet to dry compared to less humid conditions. The aggressive simulated rain event provided for plenty of large droplets hitting plant surfaces at a high velocity that should have increased wash off and may produce a more robust data set that highlighted the weaknesses of the included additives. Similar to results from the field rainfast trial, Kuraray provided the greatest benefit to glufosinate by reducing the rainfast interval to achieve 50% common lambsquarters control by more than 4 h compared to the herbicide alone. All oils tested also provided a significant reduction in time needed for 50% visual control to be reached compared to GFA 196 SL alone, which allows for quicker protection of the GFA 196 SL application towards wash off caused by rain.

Hunsche (2006) suggests two possible explanations: (1) enhancement of the attachment of a chemical deposit on the leaf surface to reduce susceptibility of removal, and (2) direct protection of the deposit by a water repellent layer. To accurately speculate the mechanism for the additives tested would require further testing, but visual observations made while conducting the RA lab work indicate a gel-like structure that formed over droplets that contained Kuraray. This could indicate either of the scenarios Hunsche suggested to be true. It was also described that Kuraray coagulates quickly in the presence of salts, especially sulfate, sodium and ammonium ions, which are key ingredients of the SLES-based glufosinate ammonium formulations, and will form a gel (Anonymous 2021). While Kuraray was easy to mix into the spray solution, with low ion concentrations due to the high water volume, it may start to coagulate on the leaf surface when the droplets starts to evaporate and ion concentrations within the droplets increase. This further supports observations from the lab trials with gel-like droplets, and may also explain the results from both the field and greenhouse rainfast trials. By forming this gel structure in the drying droplet, a layer of protection was provided to prevent detachment and wash off, but also acted as a humectant to retain moisture in the droplet on the leaf surface, allowing for improved glufosinate uptake into the plant.

The surprising effect of Kuraray on the droplet and the potential influence of the salt concentration in the spray solution underlines the need of a specific optimization for single herbicide formulations and shows the difficulty to provide generalized statements on the broad benefits of specific adjuvants across several different active ingredients or formulations. This is best demonstrated by the glufosinate response to the various polymers tested. While all were classified as polymers, they did not all provide the same level of weed control when included with glufosinate.

Regarding the oils, McWhorter and Barrentine (1988) speculated that the addition of selected oils in herbicidal solutions can aid in dissolving epicuticular waxes on the leaf surface that may aid in better herbicide uptake and absorption in the plant by removing barriers of entry. Another consideration was described by Tavernier et al. (2017); the waxes can be solubilized and may form a different type of wax crystal when they recrystallize. This effect supports the suggestion of McWhorter and Barrentine (1988) that oils included into the spray droplet can solubilize epicuticular waxes and may lead to a recrystallization within the drying spray droplet. Another consideration is the coffee ring effect described by Yunker et al. (2011) or Poulichet et al. (2020) which along the droplet edge, leaves the inner portion of the droplet with a lower concentration/coverage of epicuticular waxes and opens the epicuticular wax layer, allowing the herbicide to more readily penetrate the leaf cuticle. Furthermore, an altered crystal wax structure, when solubilized waxes form new crystals, as described by Tavernier et al. (2017) may also be true for epicuticular waxes solubilized in oil-containing surfactants. Those new crystals might also help the herbicide to penetrate the leaf cuticle or may help to retain the spray solution on the leaf surface better than the structure of the natural epicuticular wax layer optimized to prevent entry into the leaf and losses due to evaporation from the leaf.

Rainfast Field Trial

All compounds improved control of wheat under both rain simulation and no rain. Under both situations, Kuraray in mixture with GFA 196 SL provided the highest level of control. While previous field research evaluating the efficacy of single compounds indicated similar results, where Kuraray provided similar levels of weed control to GFA 196 SL, the improvement of wheat control under rain conditions (0 to 29%) should be noted. Kuraray, a polymer, may allow for more of the droplet to adhere on the leaf surface and be available for uptake for a greater period of time to improve absorption potential during less favorable environmental conditions. Likewise, the combination of Empicol (surfactant) and Salacos (oil) in mixture with GFA 196 SL may have improved uptake by the oil aiding in the solubilization of the waxy leaf surface as suggested by McWhorter and Barrentine (1988) allowing for more herbicide to enter the plant prior to the rain event by the surfactant providing a protective layer (Hess and Foy 2000). DEHA (oil) improved GFA 196 SL activity slightly (10%) over the herbicide alone, but lack of time after application perhaps did not allow for the oil to solubilize the epicuticular waxes enough to aid with increased uptake of the active ingredient by providing an easier entry into the plant through the cuticle.

CHAPTER 5. CONCLUSION

The overall goal of this research was to improve the current glufosinate formulations available for use in agricultural systems (i.e. Liberty 280 SL and Basta 200 SL). The first approach was to use commercially available additives to improve or maintain weed control activity even when the application was made with an ultra coarse droplet spectrum. This was in an effort to reduce drift to non target species, as increased droplet size for herbicide spray applications gain regulatory interest as a way to reduce the overall environmental impact.

AMADS, deposition aids, and organosilicone based additives were assessed in their behavior when mixed with Liberty 280 SL. While the positive influence of the addition of ammonium sulfate to the glufosinate spray solution was obvious, the addition of the specific additives provided mixed results in such a spray application, and a clear advantage of using such mixtures to control a typical weed spectrum under field conditions were not detected.

A challenge with these commercial adjuvants is the unknown composition of those products, which increases the difficulty to choose comparable formulations for research purposes. Furthermore, the unknown composition makes the use for the farmer even more troublesome. While the products might be classified in the same adjuvant class, the composition could deviate significantly. A clear statement of the active principle functioning agents within a product would increase the confidence for the customer. It would also allow for more specific use of the appropriate formulation and reduce the application of chemicals that do not provide a benefit to the application. Such unnecessary contamination of ecosystems should be avoided to prevent increased critical view on pesticide use and application.

In a second approach to improve the activity of glufosinate, single pure additives known for their adjuvant abilities, belonging to the polymer, surfactant and oil classes of adjuvants were evaluated as candidates to be formulated with glufosinate. While we observed in the previous section the difficulties to identify the clear influence of the composition of commercial adjuvants, these additives were chosen to identify candidates within each category that had the potential to positively influence glufosinate activity and rainfastness. These additives were tested for their influence on weed control. The influence on rainfastness and effect on uptake were evaluated using radiolabeled Glufosinate to describe the benefits of each of the included additives.

Understanding that each component of a formulation can influence the properties of the entire mixture, all trials were designed using a base commercial formulation of glufosinate with a reduced load of the surfactant sodium-lauryl ether sulfate (SLES). One of the key factors to achieve rainfastness of a herbicide is to increase uptake of the herbicidal active ingredient into the plant. It was hypothesized that the addition of a different surfactant, other than SLES, would allow for glufosinate to penetrate the leaf cuticle faster than the current commercial formulations. The results did not support this hypothesis and none of the added surfactants were able to compensate for the lower SLES concentration in the test formulation. This indicates that SLES is already an optimized surfactant for glufosinate. Polymers were considered for their potential to form a protective layer on the spray droplet, but all polymers failed to increase rainfastness of glufosinate, with exception of Kuraray. This highlights the importance of rigorous screening of new additives, as even additives within the same class can show a strong, null or even a negative impact on the herbicide mixture tested. One of the unexpected results of the present work was the effect of the oils included in the project. While the polymer Kuraray provided the most convincing results in the rainfastness trials, the oils also demonstrated a consistent activity when mixed with GFA 196 SL. Of the oils tested, Salacos and DEHA would be of interest for further evaluation as they provided good activity in the rainfastness evaluations and helped improve activity of glufosinate weed control. However, all the research described in the present document regarding glufosinate formulation development describe only the screening results for possible candidates to be included into a final product. This work does not take into account the actual formulation work and the challenges associated with that development. Further research is necessary to determine the suitability of the identified candidates for a commercial formulation and to further understand the interaction on the leaf surface and plant cuticle compared to the glufosinate – SLES based spray solutions. The presented results provide an example how established formulations can be improved by changing or adding components in a formulation. It also demonstrates the difficulties when using products with unknown composition.

LITERATURE CITED

[ASABE] American Society of Agricultural and Biological Engineers. (2009). Spray nozzle classification by droplet spectra. Standard 572.1. American Society of Agricultural and Biological Engineers, St. Joseph, MI

ASTM (1996). Terminology relating to agricultural tank mix adjuvants. In Annual Book of ASTM Standards. Biological Effects and Environmental Fate; Biotechnology, Pesticides; ASTM: Philadelphia, PA 11.05:966–967

Ahmed A, Holshouser DL (2012) Controlling glyphosate-resistant palmer amaranth in soybean with glufosinate-based and conventional herbicide programs. Crop Man. 11(1)

Albrecht K, Kocur J, Langelueddeke P (1996) Liquid herbicidal formulations of glufosinate. US5491125A

Anonymous (2019) Finale herbicide product label. BASF Corporation Publication. Research Triangle Park, NC

Anonymous (2020a) Basta Non-Selective herbicide product label. BASF Australia Ltd. Southbank, Victoria, Australia

Anonymous (2020b) Liberty 280 SL herbicide product label. BASF Corporation Publication. Research Triangle Park, NC

Anonymous (2021) Basic Physical Properties of PVOH Resin. Kuraray Europe Hattersheim Germany

Bandurska H, Niedziela J, Chadzinikolau T (2013) Separate and combined responses to water deficit and UV-B radiation. Plant Sci. 213:98-105

Beckie HJ (2011) Herbicide-resistant weed management: focus on glyphosate. Pest Man. Sci. 67:1037-1048

Buhler DD, Burnside OC (1983) Effect of water quality, carrier volume, and acid on glyphosate toxicity. Weed Sci. 31:163-169

Butts TR, Samples CA, Franca LX, Dodds DM, Reynolds DB, Adams JW, Zollinger RK, Howatt KA, Fritz BK, Hoffmann WC, Kruger GR (2018) Spray droplet size and carrier volume effect on dicamba and glufosinate efficacy. Pest Man. Sci. 74(9):2020-2029

Chachalis D, Reddy KN, Elmore CD, Steele ML (2001) Herbicide efficacy, leaf structure, and spray droplet contact angle among Ipomoea species and smallflower morningglory. Weed Sci. 49:628-634

Corbett JL, Askew SD, Thomas WE, Wilcut JW (2004) Weed efficacy evaluations for bromoxynil, glufosinate, glyphosate, pyrithiobac, and sulfosate. Weed Technol 18:443–453

[CPDA] Council of Producers and Distributors of Agrotechnology (2019) https://cpda.com/adjuvant-certification-about/ Accessed: 13 Nov 2019

Culpepper AS, York AC, Jennings KM, Batts RB (2000) Weed management in glufosinate- and glyphosate-resistant soybean (Glycine max). Weed Technol 14:77–88

Dekker J, Duke SO (1995) Herbicide-Resistant Field Crops. Adv Agron 54:69-116

Devine M, Duke SO, Fedtke C (1993) Physiology of Herbicide Action. Prentice Hall, Englewood Cliffs, NJ

Devkota P, Johnson WG (2016) Glufosinate efficacy as influenced by carrier water pH, hardness, foliar fertilizer, and ammonium sulfate. Weed Technol 30:848–859

Dexter A (1994) History of Sugarbeet (Beta vulgaris) Herbicide Rate Reduction in North Dakota and Minnesota. Weed Technol 8:334-337

Dexter A (1993) Herbicide spray drift. NDSU Extension Service EXT A-657, Fargo ND

Dill GM, Cajacob CA, Padgette SR (2008) Glyphosate-resistant crops: adoption, use and future considerations. Pest Man. Sci. 64:326-331

Downer RA, Ebert TA, Thompson RS, Hall FR (1997) Herbicide spray distribution, quality and efficacy interactions: conflicts in requirements. Aspects of Applied Biol. 48:79-89

Droge W, Broer I, Puhler A (1992) Transgenic plants containing the phosphinothricin-N-acetyltransferase gene metabolize the herbicide L-phosphinothricin (glufosinate) differently from untransformed plants. Planta 187:142-151

Duke SO, Powles SB (2008) Glyphosate: a once-in-a-century herbicide. Pest Man. Sci. 64:319-325

Field RJ, Bishop NC (1988) Promotion of stomatal infiltration of glyphosate by an organosilicone surfactant reduces the critical rainfall perio. Pestic. Sci. 24:55-62

Gardner AP, York AC, Jordan DL, Monks DW (2006) Management of Annual Grasses and Amaranthus spp. in Glufosinate-resistant Cotton. J of Cotton Sci. 10:328-338

Green JM (2012) The benefits of herbicide-resistant crops. Pest Man. Sci. 68:1323-1331

Green JM, Hale T (2005) Increasing the biological activity of weak acid herbicides by increasing and decreasing the pH of the spray mixture. J ASTM Int 2:62-71

Hanks J (1995) Effect of Drift Retardant Adjuvants on Spray Droplet Size of Water and Paraffinic Oil Applied at Ultralow Volume. Weed Technol 9:380-384

Hazen JT (2000) Adjuvants: Terminology, Classification, and Chemistry. Weed Technol 14:773-784

Hess FD, Foy CL (2000) Interaction of surfactants with plant cuticles. Weed Technol 14:807-813

Hess M, Barralis G, Bleiholder H, Buhr L, Eggers TH, Hack H, Stauss R (1997) Use of the extended BBCH-scale – general for the description of the growth stages of mono- and dicotyledonous weed species. Weed Research 37:433-441

Hunsche M (2006) Rainfastness of selected agrochemicals as affected by leaf surface characteristics and environmental factors. Cuvillier Verlag, Göttingen, Germany

Ikley J, Christoffers M, Dalley C, Endres G, Gramig G, Howatt K, Jenks B, Keene C, Ostlie M, Peters T, Robinson A, Thostenson A, Valenti HH (2021) North Dakota Weed Control Guide. North Dakota State Univ Ext Serv Publ W-253-21, Fargo, ND

Kirkwood RC. (1993) Use and mode of action of adjuvants for herbicides: a review of some current work. Pestic. Sci. 38:93-102

Knoche M. (1994) Effect of droplet size and carrier volume on performance of foliage-applied herbicides. Crop prot. 13(3):163-178

Lorentz L, Deckwer R, Sachau S, Bickers U, Telscher M, Kazmierczak A (2020) Herbicide Compositions with Improved Properties. International Publication Number WO 2020/025394 A1

Manetas Y, Petropoulou Y, Stamatakis K, Nikolopoulos D, Levizou E, Psaras G, Karabourniotis (1997) Beneficial effects of enhanced UV-B radiation under field conditions: improvement of needle water relations and survival capacity of Pinus pinea L. seedlings during the dry Mediterranean summer. Plant Eco. 128:101-108

McKinley KS, Brandt SA, Morse P, Ashford R (1972) Droplet size and phytotoxicity of herbicides. Weed Sci 20:450–452

McMullan P (2000) Utility Adjuvants. Weed Technol 14:792-797

McWhorter CG, Barrentine WL (1988) Spread of Paraffinic Oil on Leaf Surfaces of Johnsongrass (Sorghum halepense). Weed Sci. 36:111-117

Mersey BG, Hall JC, Anderson DM, Swanton CJ (1990) Factors affecting the herbicidal activity of glufosinate ammonium: Absorption, translocation, and metabolism in barley and green foxtail. Pestic. Biochem. Physiol. 37:90-98

[NIANR] Nebraska Institure of Agriculture and Natural Resources. (2021) Herbicide Characteristics Important for Phloem Movement. https://passel2.unl.edu/view/lesson/c5acc4095d02/8 Accessed: April 12, 2021

Pacanoski Z (2015) Herbicides and Adjuvants; Herbicides, Physiology of Action, and Safety. IntechOpen, DOI: 10.5772/60842

Penner D (2000) Activator Adjuvants. Weed Technol 14:785-791.

[PES] Pesticide Environmental Stewardship (2012) Understanding Droplet Size. https://pesticidestewardship.org/pesticide-drift/understanding-droplet-size/ Accessed: February 25, 2021

Poulichet V, Morel M, Rudiuk S, Baigl D (2020) Liquid-liquid coffee-ring effect. J of Colloid and Interface Science 573:370-375

Prince JM., Shaw DR, Givens WA, Owen MDK, Weller SC, Young BG, Wilson RG, Jordan DL (2012). Benchmark Study: I. Introduction, Weed Population, and Management Trends from the Benchmark Survey 2010. Weed Technol. 26:525–530

Prokop M, Veverka K (2003) Influence of droplet spectra on the efficiency of contact and systemic herbicides. Plant Soil Env. 49: 75-80

Ritz C, Baty F, Streibig J, Gerhard D (2015) Dose-Response Analysis Using R. PLoS ONE 10(12): e0146021. doi:10.1371/journal.pone.0146021

Roggenbuck FC, Rowe L, Penner D, Petroff LG, Burrow RF (1990) Increasing postemergence herbicide efficacy and rainfastness with silicone adjuvants. Weed Technol 4:576–580

Ruhland M, Engelhardt G, Pawlizki K (2004) Distribution and metabolism of D/L-, L- and D-glufosinate in transgenic, glufosinate-tolerant crops of maize (Zea mays L ssp mays) and oilseed rape (Brassica napus L var napus). Pest Manag Sci 60:691–696

Shaner DL, ed (2014) Herbicide Handbook, 10th ed. Weed Science Society of America, Lawrence, KS

Shea PJ, Tupy ER (1984) Reversal of cation-induced reduction in glyphosate activity with EDTA. Weed Sci. 32:802-806

Strauch, E., Wohlleben, W., Piihler, A. (1988) Cloning of the phosphinothricin-N-acetyl-transferase gene from *Streptomyces viridochromogenes* Tfi 494 and its expression in *Streptomyees lividans* and *Eseherichia coli*. Gene 63:65-74

Steckel GJ, Wax LM, Simmons FW, Phillips WH, II (1997) Glufosinate efficacy on annual weeds is influenced by rate and growth stage. Weed Technol 11:484–488

Stock D, Briggs G (2000) Physiochemical properties of adjuvants: values and applications. Weed Technol 14:298-806

Takano HK, Dayan FE (2020) Glufosinate-ammonium: a review of the current state of knowledge. Pest Manag Sci. 76:3911-3925

Tavernier I, Doan CD, Van de Walle D, Danthine S, Rimaux T, Dewettinck (2017) Sequential crystallization of high and low melting waxes to improve oil structuring in wax-based oleogels. The Royal Sco. Of Chem. 7:12113:12125

TeeJet Technologies (2021) Drop Size Classification. Spraying Systems Co., Wheaton, IL

[USDA-ERS] United States Department of Agriculture Economic Research Service (2014) Pesticide composition and use has changed over past five decades. https://www.ers.usda.gov/data-products/chart-gallery/gallery/chart-detail/?chartId=77462. Accessed: February 20, 2020

[USDA-ERS] United States Department of Agriculture Economic Research Service (2018) Trends in the Adoption of Genetically Engineered Corn, Cotton, and Soybeans. https://www.ers.usda.gov/amber-waves/2018/december/trends-in-the-adoption-of-genetically-engineered-corn-cotton-and-soybeans/ Accessed: November 13, 2019

[USEPA] United States Environmental Protection Agency (2021) Reducing Pesticide Drift. https://www.epa.gov/reducing-pesticide-drift Accessed: April 18, 2021

VanGessel M, ed (2019) A Practical Guide for Integrated Weed Management in Mid-Atlantic Grain Crops. University of Delaware, Newark, DE

Vencill WK, ed (2002) Herbicide Handbook, 8th ed. Weed Science Society of America, Lawrence, KS

Vencill WK, Nichols RL, Webster TM, Soteres JK, Mallory-Smith C, Burgos NR, Johnson WG, McClelland MR (2012) Herbicide Resistance: Toward an Understanding of Resistance Development and the Impact of Herbicide-Resistant Crops. Weed Sci. 60:2-30

[WSSA] Weed Science Society of America (2014) Summary of Herbicide Mechanism of Action According to the Herbicide Resistance Action Committee (HRAC) and Weed Science Society of America (WSSA) Classification. https://wssa.net/wp-content/uploads/HerbicideMOAClassification.pdf. Accessed: February 20, 2020

[WSSA] Weed Science Society of America (2021) WSSA Glossary. https://wssa.net/wssa/wssa-glossary/#C19 Accessed: April 18, 2021

Wells B, Fishel FM (2011) Rainfastness of Pesticides. Univ of Florida Institute of Food and Agricultural Sciences Ext Serv Publ PI238

Whitaker JR, York AC, Jordan DL, Culpepper AS (2011) Weed management with glyphosate- and glufosinate-based systems in PHY 485 WRF cotton. Weed Technol. 25:183–191

Wild A, Ziegler C (1989) The effect of bialaphos on ammonium assimilation and photosynthesis. I. Effect on the enzymes of ammonium-assimilation. Z. Naturforsch. 44e, 97-102

Wilson J (2012) Understanding Droplet Size. http://pesticidestewardship.org/drift/Pages/UnderstandingDropletSize.aspx. Accessed: September 20, 2019

Wohlleben, W., Arnold, W., Broer, I., Hillemann, D., Strauch, E., Pfihler, A. (1988) Nucleotide sequence of the phosphinothricin-*N*-acetyl-transferase gene from *Streptomyces viridochromogenes* Tfi494 and its expression in *Nicotiana tabacum*. Gene 70:25-37

Yunker PJ, Still T, Lohr MA, Yodh AG (2011) Suppression of the coffee-ring effect by shape-dependent capillary interactions. Nature 476:308–311

Zollinger RK, Howatt K, Bernards ML, Peterson DE, Young BG (2013) Efficacy of acidic ammonium sulfate replacement adjuvants. ASTM STP 1558:183-195

APPENDIX. SUPPLEMENTARY TABLES

Table A.1. Effect of glufosinate efficacy without ammonium sulfate applied on amaranth, common buckwheat, flax, and quinoa at two spray qualities near Hillsboro, ND in 2013 and 2014.

		Visible control						Biomass (28 DAA)					
Species	Treatment	14 DAA[a]			28 DAA			Fresh weight			Dry weight		
		Medium	Ultra coarse	Δ	Medium	Ultra coarse	Δ	Medium	Ultra coarse	Δ	Medium	Ultra coarse	Δ
		------- % -------			------- % -------			------- kg -------			------- kg -------		
Amaranth	*UTC*		0			0			1.04			0.18	
	Liberty[b]	26	30	4	25	27	2	0.40	0.59	0.19	0.06	0.09	0.03
Common buckwheat	*UTC*		0			0			0.59			0.13	
	Liberty	67	67	0	73	64	- 9	0.16	0.56	0.4	0.02	0.09	0.07
Flax	*UTC*		0			0			0.09			0.03	
	Liberty	64	68	4	64	64	0	0.05	0.06	0.01	0.01	0.02	0.01
Quinoa	*UTC*		0			0			1.02			0.24	
	Liberty	35	25	- 10	30	32	2	0.52	0.54	0.02	0.09	0.10	0.01

[a] DAA; days after application.
[b] Treatments contained glufosinate at 450 g ai ha^{-1} and were applied using the commercial product Liberty 280 SL.

Table A.2. Effect of ammonium sulfate on glufosinate efficacy applied on amaranth, common buckwheat, flax, and quinoa at two spray qualities near Hillsboro, ND in 2013 and 2014 and Sabin, MN in 2014.

		Visible control						Biomass (28 DAA)					
Species	Treatment	14 DAA[a]			28 DAA			Fresh weight			Dry weight		
		Medium	Ultra coarse	Δ	Medium	Ultra coarse	Δ	Medium	Ultra coarse	Δ	Medium	Ultra coarse	Δ
		------- % -------			------- % -------			------- kg -------			------- kg -------		
Amaranth	*UTC*		0			0			0.65			0.12	
	Liberty[b]	71	58	-13	81	67	-14	0.18	0.23	0.05	0.06	0.09	0.03
Common buckwheat	*UTC*		0			0			0.60			0.13	
	Liberty	88	86	-2	88	83	- 5	0.05	0.06	0.01	0.02	0.03	0.01
Flax	*UTC*		0			0			0.09			0.03	
	Liberty	80	76	-4	86	83	-3	0.03	0.03	0.00	0.01	0.01	0.00
Quinoa	*UTC*		0			0			0.88			0.17	
	Liberty	76	61	- 15	81	65	-16	0.14	0.21	0.07	0.03	0.05	0.02

[a] DAA; days after application.
[b] Treatments contained glufosinate at 450 g ai ha^{-1} and were applied using the commercial product Liberty 280 SL. Treatments included dry ammonium sulfate at 3363 g/ha.

Table A.3. Effect of ammonium sulfate on glufosinate efficacy applied on amaranth, common buckwheat, flax, and quinoa at two spray qualities near Hillsboro, ND in 2013 and 2014 and Sabin, MN in 2014.

		Visible control						Biomass (28 DAA)					
Species	Treatment	14 DAA[a]			28 DAA			Fresh weight			Dry weight		
		Medium	Ultra coarse	Δ	Medium	Ultra coarse	Δ	Medium	Ultra coarse	Δ	Medium	Ultra coarse	Δ
		------- % -------			------- % -------			------- kg -------			------- kg -------		
Amaranth	*UTC*		0			0			0.72			0.15	
	Liberty[b]	71	51	-20	58	39	-19	0.40	0.36	-0.04	0.07	0.06	-0.01
Common buckwheat	*UTC*		0			0			1.04			0.13	
	Liberty	68	68	0	71	73	2	0.22	0.23	0.01	0.04	0.03	-0.01
Flax	*UTC*		0			0			0.09			0.03	
	Liberty	81	59	-23	83	57	-26	0.03	0.05	0.02	0.00	0.01	0.01
Quinoa	*UTC*		0			0			0.95			0.23	
	Liberty	60	50	- 10	65	53	-12	0.35	0.36	0.01	0.07	0.08	0.01

[a] DAA; days after application.
[a] Treatments contained glufosinate at 450 g ai ha^{-1} and were applied using the commercial product Liberty 280 SL. Treatments included dry ammonium sulfate at 3363 g/ha.