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WATER QUALITY, CARRIER VOLUME AND DROPLET SIZE EFFECTS ON HERBICIDE EFFICACY AND DRIFT POTENTIAL

by

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WATER QUALITY, CARRIER VOLUME AND DROPLET SIZE EFFECTS ON HERBICIDE EFFICACY AND DRIFT POTENTIAL

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University of Nebraska, 2022

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Herbicide performance is directly related to the amount of active ingredient that has been deposited on the plant. Hence, spray solution characteristics and application parameters are crucial in determining the efficacy of an herbicide application. To maximize the effectiveness of chemical control, methods to deliver full chemical dose must be utilized: allowing the active ingredient to be readily absorbed once added to the carrier and mitigating off-target movement and low herbicide doses. Water is the most frequently used carrier in herbicide applications. Chemical parameters, such as water hardness and pH, can have a critical role in herbicide performance. It is generally believed that weak acid herbicides, such as glyphosate and 2,4-D, have higher dissociation in higher carrier pH, which leads to decreased uptake into plants. Moreover, increased concentration of hard water cations may have antagonistic effect on weak acid herbicide applications. To overcome the negative effect of water quality on weak acid applications, addition of water conditioning adjuvants is recommended. Carrier volume and droplet size are crucial parameters in application technology that can also impact herbicide performance. Nozzles and their spray characteristics have gone under significant development in past decades to enhance spray potential under a wide range of conditions. Introduction of air inclusion nozzles provided the ability to create larger droplets at the same pressure and flow rate as conventional nozzles, resulting in less drift. Controlling off target movement

essentiality decreases the potential for herbicide resistance selection on weeds, as well as injury on sensitive crops. Hence, the objectives of this research were to investigate water quality, carrier volume and droplet size effects on herbicide efficacy and drift potential.

Dedication

For my family, friends, peers, and everyone who believed in me along the way.

"The course of events in life does not depend on us, or it depends very little, but the way in which we will handle these events depends to a large extent on us."

-Ivo Andric

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Table of Contents

CHAPTER 1

Literature review

Herbicide Use in Weed Control

Weed control is essential step in crop production systems. Weeds may reduce yields by competing with the crop for water, nutrient, and light resources. Growers across US are spending approximately 6.6 billion dollars on herbicides each year. To maximize the effectiveness of chemical control methods through increased flexibility in timing, available chemistries, safe over-the-top herbicide application, herbicide resistant (HR) crops were designed. These crops provide simple and flexible programs of weed control that rely on one or more herbicides to control broad spectrum of weeds without crop injury (Carpenter and Gianessi 1999). The first genetically tolerant crops were soybean and corn, as these are the largest crops grown in the US. Sulfonylurea tolerant soybeans were first introduced in 1993. In 1996, Roundup Ready soybeans became available, allowing to spray glyphosate over the top of growing soybeans, followed by Roundup Ready corn in 1998 (Johnson et al. 2009). In 2009, Liberty Link soybeans were launched for commercial purposes allowing glufosinate application over the top (Beckie et al. 2019). Recently, Enlist E3 soybeans became available, providing tolerance to three herbicides - 2,4-D choline, glyphosate and glufosinate. XtendFlex soybeans were introduced in 2021 to provide farmers more options for noxious weed control through tolerance to glufosinate, glyphosate, and dicamba. Overall, the introduction of HR crops had a positive effect on the environment by reducing soil erosion, the fuel use for tillage and the reduced use of herbicides with groundwater advisories (Vencill et al. 2012). However, with the increase in HR crops, the use of herbicides also increased, which led to weed control program becoming more complex as a consequence of weed resistance evolution (Duke 2018). Seventeen weed species have shown resistance to glyphosate, with thirteen of being found in glyphosate-resistant crops. The first economically important weed species that evolved resistance to glyphosate were Palmer amaranth (*Amaranthus palmeri* S. Watson) and waterhemp [*Amarathus tuberculatus* (Moq.) Sauer], which were found in 27 and 18 US states, respectively (Heap and Duke 2018). Weeds have evolved resistance to 21 out of the 31 known herbicide sites of action and to 164 different herbicides. HR weeds have been reported in 95 crops in 71 countries (HRAC, 2021). Common strategies for preventing the spread of HR weeds are herbicide applications only when necessary, rotation of herbicides with multiple sites of action, herbicide applications with multiple modes of action, crop rotation, and inclusion of non-chemical management practices. To minimize HR development, pesticide application must be optimized. It is known that off target movement can cause severe injury on sensitive vegetation and crops. Recurrent selection to low herbicide doses can gradually select for metabolism alleles present within the standing genetic variation of the population, which can progressively lead to herbicide resistance on weeds (Busi et al. 2013). Vieira et al. 2020 have found that herbicide drift towards field margins can select for biotypes with reduced herbicide sensitivity. Hence off target mitigation is critical component of weed management programs.

Water as a Primary Herbicide Solvent

Pesticides have been an integral part of US agriculture since its earliest days. Pesticides represent the main tool in food production, with an estimated of 20-40% in yield losses if their use was eliminated (Lykogianni et al. 2021). A total of 330 active ingredients among 25 herbicide modes of actions are currently being used in global agriculture (HRAC, 2021). Despite the widespread use of pesticides in crop protection in US, pests destroy 37% of all potential crops with 12% being attributed to weeds (Pimentel and Burgess 2014). It is estimated that in 2019 over 250,000 tons of herbicides have been used in the US, which is about 60% of total pesticide use (FAO, 2021).

Water is the most frequently used carrier in herbicide applications. Numerous parameters, classified as physical, chemical, and biological, have an impact on water quality. Chemical parameters, such as water hardness and pH, can have a critical role in herbicide performance (Green and Hale 2005). Since water used for pesticide applications is usually obtained from underground sources, water quality varies geographically. Most groundwater originates from percolating precipitation and is affected by the type of aquifer through which water passes. Percolating water is rich with carbon dioxide in soils with a significant fraction of organic matter due to microbial decomposition and root respiration. These processes eventually lead to reduced water pH. This water is also efficient in dissolving calcium carbonate in the soil and underlying limestone bedrock creating a solution that contains calcium and bicarbonate ions (Pentecost, 2005).

Water hardness is defined by the concentration of calcium and magnesium ions present and is expressed as calcium carbonate equivalent in parts per million. The limestone bedrock contributes to higher concentration of calcium and magnesium ions in underground water throughout midwestern United States (Devkota and Johnson, 2016a; IDNR 1980). Nebraska is one of the most groundwater-rich states in the United States. Approximately 88% of the state’s residents rely on groundwater as a drinking source and agricultural utilizations (Nebraska Groundwater Monitoring Report, 2020). Water containing calcium carbonate at concentrations below 60 mg L^{-1} is generally considered soft; 61–120 mg L^{-1} is moderately hard; 121–180 mg L^{-1} is hard; and more than 180 mg L^{-1} is very hard (USGS). The average water hardness for Nebraska is 204 mg L^{-1}, which is considered very hard. Since Nebraska has a strong farming community with agriculture ranking as the state's top producing industry, greater attention is needed on water quality. Nebraska has water high in calcium, which might negatively affect spray solution impact on herbicide efficacy due to hard water cations (Aliverdi et al. 2014, Butts et al. 2019, Devkota and Johnson 2016a).

It is generally believed that weak acid herbicides, such as glyphosate and 2,4-D, have higher dissociation in higher carrier pH, also called alkaline hydrolysis, which leads to decreased uptake into plants (Wang and Liu 2007). Non-dissociated herbicides are more readily absorbed than those that dissociate (Griffin, 2009). Carrier water pH also affects the solubility of herbicides (Roskamp et al. 2013b). Spray solution pH can be adjusted by adding buffering or acidifying agents. Buffering agents usually contain phosphate salt which maintain slightly acidic pH when added to alkaline water. Like pesticides, their labels should be followed closely.

Utility adjuvants are tank-mixed in the spray solution to improve the spray application process and modify the physical and chemical characteristics of the spray solution, and can indirectly impact herbicide efficacy (Hazen 2000, McMullan 2000). There are five primary utility adjuvant types: compatibility agents, deposition agents, drift control agents, defoaming agents, and water conditioning agents; and three secondary utility adjuvant types: acidifying agents, buffering agents, and colorants (McMullan 2000). Since carrier water quality is an important consideration for herbicide efficacy, addition of water conditioning agents, acidifying agents and/or buffers is a common practice in optimizing water quality. The addition of water conditioning adjuvants is recommended for weak acid application in hard water. One of the most used is ammonium sulfate (AMS). Ammonium ions build a complex with a weak acid herbicide and outcompete the antagonistic cations which leads to enhanced herbicide absorption and translocation. The sulfate anions bind with the antagonistic cations preventing the formation of hard water cation-herbicide complex which is less readily absorbed (Zollinger et al. 2016). The addition of AMS to a spray solution for overcoming the negative effects of hard water has previously been reported (Devkota et al. 2016, Patton et al. 2016, Schortgen and Patton 2020). AMS also increases foliar absorption and translocation of some herbicides (Maschhoff et al. 2000).

Carrier Water pH and Herbicide Efficacy

Water pH is amount of hydrogen ion (H^+) and hydroxide ion (OH^-) present in water. pH is measured on a logarithmic scale from 1 to 14, where 1 is most acidic, 7 is neutral, and 14 is most alkaline. As the acidity increases, the pH number decreases. With pH decreasing by one unit, H^+ concentration increases by a factor of 10.

The carrier water pH limits the solubility and controls ionic state of weak acid herbicides influencing their uptake and biological activity. Weak acid herbicides are molecules with a functional group, usually carboxylic acid, that gains or loses hydrogen ion depending on the pH of surrounding solution (Plant and Soil Sciences eLibrary). The pH at which the herbicide is present in 50:50 ration of ionized (hydrophilic) and non-ionized (lipophilic) forms is called pK_a. pK_a is the negative base-10 logarithm of the acid dissociation constant of a solution (Helmenstine 2020). When the herbicide is dissociated, it loses its full phytotoxicity. The amount of active herbicide in the solution is influences by the rate of dissociation of the herbicide and can be measured in the half-life of the herbicide. The half-life is amount of time needed for 50% of the herbicide to degrade to a non-active form. It is known that weak acid herbicides have shorter half-lives in alkaline pH solutions (Deer and Beard n.d.). When the pH of water is below the herbicide's pK_a, increasing pH can increase the solubility and activity of the herbicide. When the pH of water is above the herbicide's pK_a, weak acids become anionic which makes it harder for an herbicide to penetrate the lipophilic cuticle and negatively charged membrane and cell wall. Decreasing the pH below pK_a, causes anionic forms to transform to non-ionic and thus makes it easier to penetrate negatively charged barriers (Molin and Hirase 2004, Sobiech et al. 2020). When the herbicide is at low concentrations and solubility is not a limiting factor, uptake is greater at low pH. However, when the herbicide is at high concentration and solubility is limiting, then higher pH increases uptake (Green and Hale 2005). Weak acid herbicides are more lipophilic and more readily absorbed at a lower carrier pH (Hale, 1970). Glyphosate herbicides have pK_a values of 2.27, 5.58 and 10.25. Typically, glyphosate spray solutions in agriculture are nearest to 5.58.

Many research efforts have evaluated biological responses to the hard water effect on herbicide efficacy, which are shown to be weed species dependent. Buhler and Burnside (1983) observed decrease in glyphosate phytotoxicity on oats (*Avena fatua* L.) when well and distilled water pH was adjusted to 7 and 9. However, glyphosate activity on sorghum (*Sorghum* spp.) decreased in alkaline solution, but the reaction was due to the time required to kill the plants rather than lack of phytotoxicity (Stahlman and Phillips 1979).

In assessing different water conditioning methods, Aliverdi et al. 2014 found that activity of glyphosate on jimsonweed (*Datura stramonium* L.) was increased in the presence of water conditioning methods in hard water. They were ranked based on their performance as follows: AMS (2.5-fold) > magnetized carrier (2.1-fold) ≥ citric acid (1.6-fold) ≥ ammonium nitrate (1.4-fold) > potassium phosphate (1.0-fold).

Acidification also increases 2,4-D activity allowing its neutral form to be solubilized into the oily surfactant micelles. When 2,4-D is inside the surfactant micelle, it also reduces odor or volatility issues and improves hard water and fertilizer compatibility (Green and Beestman 2007). Pavlovic et al. (2005) were looking into 2,4-D, clopyralid and picloram adsorption on hydrotalcite calcined at 500 C (HT500) at different pH levels. The data shows 23% in clopyralid adsorption when pH was decreased from 11 to 3, whereas 2,4-D and picloram had similar adsorption across all pH monitored.

Glufosinate efficacy was also studied when applied in acidic compared to alkaline carrier water. Devkota and Johnson (2016b) observed giant ragweed (*Ambrosia trifida* L.) and Palmer amaranth biomass reduction of at least 10 and 7%, respectively when glufosinate was applied in carrier water pH 4 compared with pH 9 under greenhouse conditions. They also observed a 10% increase in horseweed (*Conyza canadensis* L.) control when glufosinate was applied with carrier water pH 4 compared to pH 9 in a field study. Increased glufosinate uptake when the solution was acidified to pH 4 was also observed by Takano et al. (2020). Since glufosinate has pK_a values of 2, 2.6 and 9.8, greater protonation of the molecule increases with the acidity of the spray solution. Higher uptake rates at pH 4 suggests that glufosinate protonation could neutralize negative charges, making the molecule less hydrophilic and thus easier to cross lipophilic membrane (Takano et al. 2019).

Carrier Water Hardness and Herbicide Efficacy

Hard water contains dissolved minerals, with Ca and Mg being predominant (Patton et al. 2016). Increased concentration of hard water cations may be problematic when used as a carrier for weak acid herbicide applications.

Polyvalent cations in hard water can easily react with glyphosate. Glyphosate, as a weak acid herbicide, reacts as a chelating agent because of its amine, carboxylic and phosphonate groups. Chelation leads to decreased herbicide penetration into the plant cuticle (Bernards et al. 2005) or can cause precipitation of the herbicide from the solution (Thelen et al. 1995). Zollinger et al. 2010 showed that activity of several weak acid herbicides including glyphosate, aminopyralid, tembotrione, dicamba plus diflufenzopyr and glufosinate were reduced by Ca and Mg salts. Glyphosate activity was also reduced at Ca and Mg concentrations greater than 250 mg L^{-1} on broadleaf signalgrass [*Brachiaria platyphylla* (Griseb.) Nash], pitted morningglory (*Ipomoea hederacea* Jacq.), Palmer amaranth and yellow nutsedge (*Cyperus esculentus* L.) (Mueller et al. 2006). Nalewaja and Matysiak 1991 were looking into various acids and their ammonium salts antagonism with glyphosate where they found that citric acid and ammonium citrate overcame antagonism to glyphosate from sodium bicarbonate, calcium chloride, and ferric sulfate. Calcium chloride antagonism of glyphosate was not overcome by phosphoric acid and ammonium nitrate or chloride, but these salts overcame sodium bicarbonate. AMS was also found to prevent glyphosate crystal formation which can play a role in enhancement of herbicide uptake (Macisaac et al. 1991).

Interaction of polyvalent cations in hard water with 2,4-D carboxylic groups with essentially reduced herbicide efficacy was also observed by Schortgen and Patton (2020). Patton et al. (2016) found that Ca, Mg and Mn cations antagonized 2,4-D dimethylamine and reduced control of dandelion (*Taraxacum officinale* G.H. Heber ex Wiggers) and broadleaf plantain (*Plantago major* L.). Similar results were observed by Nalewaja et al. (1991) where antagonism occurred between 2,4-D and Ca salts, which resulted in reduced kochia (*Bassia scoparia* (L.) AJ Scott) control. Schortgen and Patton 2020 observed increased 2,4-D efficacy in hard water (600 ppm) on horseweed and dandelion when AMS was added to the solution. They also investigated different nitrogen sources in overcoming antagonism between hard water and 2,4-D. Results indicated that urea ammonium nitrate (UAN) and ammonium nitrate (AMN) in hard water (600 ppm and 1000 ppm), and urea in soft water produced the highest epinasty (≥63%) when mixed with 2,4-D. AMS caused intermediate epinasty compared to other nitrogen sources across water hardness levels, whereas potassium nitrate (KNO_3) and urea in hard water did not overcome 2,4-D – hard water antagonism (Schortgen and Patton 2021). 2,4-D in calcium solution without AMS had decreased herbicide efficacy on horseweed and redroot pigweed for 48% and 27%, respectively compared with 2,4-D alone in calcium solution (Roskamp et al. 2013a). Devkota and Johnson 2016a found that increasing water hardness from 0 to 1000 ppm giant ragweed control with 2,4-D choline was reduced at a greater rate in the absence of AMS (55%) compared to when AMS was added (24%) to the spray solution. They also found that addition of AMS enhanced 2,4-D efficacy on giant ragweed, horseweed and Palmer amaranth for 14-, 16- and 6%, respectively compared to 2,4-D alone (Devkota and Johnson 2019).

Since the molecule structure of glufosinate is similar to the one of glyphosate it is not odd to speculate that carrier water quality factors may influence glufosinate efficacy as well (Devkota and Johnson 2016b). Several research studies evaluated hard water antagonism on glufosinate efficacy, and the results show contrasting responses. Soltani et al. (2011) found that hard water did not have effect on glyphosate and glufosinate efficacy on common lambsquarters, redroot pigweed (*Amaranthus retroflexus* L.) and several annual grasses. However, glufosinate did affect control of velvetleaf in hard water. Devkota and Johnson (2016b) research showed that linearly increasing in water hardness by 1 mg L^{-1}, giant ragweed control reduces by 0.019% when treated with glufosinate. Reduced efficacy of glufosinate in 500 mg $L-^{1}$ hard water was also observed on velvetleaf by Pratt et al. (2003). Similar results were observed by (Zollinger et al. 2010) where glufosinate activity was reduced from 35% with no hard water to 27% with 500 mg L^{-1} hard water, and to 20% with 1000 mg L^{-1} hard water. Previous research has shown different results of AMS effect on glufosinate efficacy in hard water, and they are mostly species dependent. Addition of AMS to glufosinate increased the absorption of glufosinate in giant foxtail (*Setaria faberi* Herrm.) and sicklepod (*Cassia obtusifolia* L.), but not in common lambsquarters. Subsequently, AMS antagonized glufosinate efficacy on common lambsquarters (Pline et al. 1999). AMS (2% v $v-^{1}$) also increased velvetleaf control once it was added to glufosinate in hard water (500 ppm) for about 50% compared to glufosinate alone (Pratt et al. 2003). In the research done by Devkota and Johnson 2016b, addition of AMS was not significant for Palmer amaranth control, whereas control of giant ragweed was enhanced when AMS was added to glufosinate.

Carrier Volume and Droplet Size

Herbicide performance is directly related to the amount of active ingredient that has been deposited on the plant. Hence, spray solution characteristics and application parameters are crucial in determining the efficacy of a herbicide application (Creech et al. 2015). Carrier volume of post-emergent herbicides is one of the components of application technology that can impact herbicide performance (Knoche 1994). Spray technology has evolved toward faster moving spray equipment and lower carrier volumes to reduce fuel costs from transporting large quantities of water and the need to cover more area per tank-load (Etheridge et al. 1999). For example, herbicide programs that rely primarily on glyphosate for weed control often use carrier rates as low as 50 L ha^{-1} (Creech et al. 2015). Generally, across herbicides, efficacy decreases as carrier volume decreases. The reason for this is because reduced volume often results in decreased coverage of the targeted plant (Butts et al. 2018). Many herbicides other than glyphosate require higher carrier volume for maximized performance, thus this application practice often needs smaller orifice nozzles that consequently produce finer droplets prone to drift (van de Zande, 2003). Smaller droplet sizes and larger carrier volumes produce better weed control (Normie W. Buehring et al. 1973). In a survey conducted by Butts et al. 2021, applicators in Arkansas reported a range of 46.8 to 187.1 L ha^{-1} for carrier volumes used for systemic and contact herbicide application from ground spray equipment. Increase in average spray volume when switching from systemic to contact herbicides was also reported. This is common knowledge, since increase in spray volume produces greater number of droplets that are available for potential deposition and retention on weed surfaces (Knoche 1994).

Droplet size is another parameter in pesticide application technology that has impact on herbicide efficacy. Herbicide efficacy has been correlated with droplet size and spray volume in literature, but the relationship differs among herbicides and weed species. Smaller droplets tend to be more effective than larger droplets when spray volumes are held constant (Meyer et al. 2016). Smaller droplets are more important for retention on grasses than they are on broadleaves. The importance of adequate coverage, which is achieved with smaller droplets, has a more consistent effect on the efficacy of contact herbicides, such as glufosinate (Etheridge et al. 2001). Butts et al. 2018 observed maximized weed control with glufosinate at 310 µm and decreased efficacy as droplet size increased. Conversely, carrier volume did not impact weed control when glufosinate was applied at 47 L ha^{-1} and 187 L ha^{-1}. Decreased weed control was also observed by McKinlay et al. 1974 on common sunflower (*Helianthus annuus* L.) and wild oat when paraquat was sprayed with larger droplets. Conversely, droplet size is more forgiving on systemic herbicides. For example, glyphosate had greater absorption and translocation with larger droplets (Feng et al. 2017). Ferguson et al. 2018 did not find droplet size to be significant for glyphosate control on four winter annual grasses, so their recommendation is larger droplets for minimizing drift potential. Similarly, Legleiter et al. 2018 observed equivalent herbicide deposition, absorption, and efficacy on Palmer amaranth, waterhemp, giant ragweed, and horseweed when weeds were sprayed with air-induction nozzles, which are known to produce very coarse to ultra-coarse droplets compared to non-DRT nozzles, which produce smaller droplets.

Since herbicide performance is directly related to the amount of active ingredient deposited on the plant, we wanted to evaluate spray solution characteristics (water hardness and water pH) and application parameters (droplet size and carrier volume) influencing the herbicide fate. The objectives of this thesis were to evaluate: 1) water quality, carrier volume and droplet size effect on herbicide efficacy and 2) droplet size effect on drift potential.

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Chapter 2

Water Conditioners Effect on Glufosinate, Glyphosate and 2,4-D Efficacy

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Abstract

Water is the most frequently used carrier in herbicide applications. Water properties, such as hardness and pH, can impact herbicide performance. Water conditioners (WCs) are commonly used to counter these effects. Most current research has focused on evaluating the addition of ammonium sulfate (AMS) to weak acid herbicides. Hence, the objective of this study was to evaluate the efficacy of citric acid, phosphoric acid, and AMS used in tank-mixture with glufosinate, glyphosate and 2,4-D across a range of droplet sizes. A greenhouse study was conducted where herbicides were sprayed alone and in tank-mixture with WCs on waterhemp [*Amaranthus tuberculatus* (Moq.) Sauer], common lambsquarters (*Chenopodium album* L.) and green foxtail (*Setaria viridis* L. Beauv.), except for 2,4-D on green foxtail. Water properties were adjusted to 240 ppm (expressed as $CaCO_3$) hard water and 7 pH prior to adding herbicides and WCs. Non-venturi nozzles were used to deliver the treatments with 150, 450, 600 and 900 µm VMDs (volume median diameters). Treatments were applied using three-nozzle spray chamber at 140 L ha^{-1}. Application speed was adjusted for each nozzle type by pressure combination to deliver targeted VMD. At 21 days after treatment (DAT), above ground weed biomass

was harvested and dried to constant mass. Dry weight was converted to percentage of dry biomass reduction and compared to nontreated control. The results show that the addition of phosphoric acid across herbicides increased control for common lambsquarters compared to other tank-mixtures. Common lambsquarters biomass reduction increased for 17%, 10% and 22% when phosphoric acid was added to glufosinate, glyphosate and 2,4-D, respectively, compared to herbicides alone. AMS was significant only in 2,4-D tank-mixture where biomass reduction increased for 32% compared to 2,4-D alone. Droplet size was not significant across tank-mixtures in control of common lambsquarters. Addition of any WCs improved control for 2,4-D on waterhemp with biomass reduction increasing 17% compared to 2,4-D alone. Larger VMDs improved control for glyphosate across tank-mixtures compared to fine VMD, with biomass reduction decreasing from 75% to 65%, respectively. None of the glufosinate treatments were significant for common lambsquarters or waterhemp. There were no significant interactions for green foxtail control.

Introduction

Glyphosate, a non-selective, systemic, and postemergence herbicide, is one of the most widely used of all herbicides. It works by disrupting the shikimate pathway, resulting in the abruption of aromatic acid production via inhibition of the 5-enolpyruvylshikimate-3-phosphate synthase (EPSPS) (Heap and Duke 2018). Glyphosate was a highly successful herbicide prior to the introduction of glyphosate-resistant crops (GR), however this led to increased use which has in turn led to the evolution of weed resistance (Duke 2018). Inadequate herbicide applications, including improper rates, can enhance weed resistance evolution (Norsworthy et al. 2012). It is known, and typically recommended on the labels, that the use of AMS provides for better uptake and increased glyphosate performance, especially in hard water. Ammonium ions build a complex with a weak acid herbicide, such as glyphosate, outcompeting the antagonistic cations which leads to enhanced herbicide absorption and translocation. The sulfate anions bind with the antagonistic cations preventing the formation of hard water cation-herbicide complex which is less readily absorbed (Zollinger et al. 2016). Glyphosate reacts as a chelating agent because of its amine, carboxylic, and phosphonate groups. Chelation leads to decreased herbicide penetration into the plant cuticle (Bernards et al. 2005) or can cause precipitation of the herbicide from the solution (Thelen et al. 1995). Numerous studies observed reduced phytotoxicity in hard water (Nalewaja and Matysiak 1991, Bernards et al. 2005, Devkota and Johnson 2016a). Glyphosate is also prone to alkaline hydrolyses under high pH values. It is generally believed that weak acid herbicides, such as glyphosate and 2,4-D, have higher dissociation in higher carrier pH which leads to decreased uptake into plants (Wang and Liu 2007).

Glufosinate is a non-selective, broad-spectrum, postemergence herbicide used for grass and broadleaf weeds control in non-crop and agricultural systems (Takano et al. 2020). Glufosinate inhibits glutamine synthetase, which leads to ammonia accumulation, but the herbicidal activity of glufosinate is caused by a rapid light-dependent formation of reactive oxygen species (ROS) (Takano et al. 2019). Glufosinate is an alternative option for postemergence control for glyphosate-resistant weeds. It is also a safe tool in glufosinate-resistant crops for postemergence applications. As with glyphosate, decreased glufosinate phytotoxicity under unfavorable water conditions, such as high pH and hard water, was observed on several weed species (Buhler and Burnside 1983, Devkota and Johnson 2016b, Zollinger et al. 2010). AMS is the only recommended adjuvant in the USA to enhance glufosinate activity (Anonymous, 2019), though response varies by weed species. Addition of AMS to glufosinate increased the absorption of glufosinate in giant foxtail (*Setaria faberi* Herrm.) and sicklepod (*Cassia obtusifolia* L.), but not in common lambsquarters (Pline et al. 1999). While Devkota and Johnson 2016b did not observe increased control in Palmer amaranth (*Amaranthus palmeri* S. Wats) with the addition of AMS to glufosinate, control was enhanced on giant ragweed (*Ambrosia trifida* L.).

2,4-dichlorophenoxyacetic acid (2,4-D), also a weak acid herbicide, is selective and systemic and is generally applied as postemergence for control of broadleaf weeds and woody plants in crops, noncropland, pastures, rangelands, and turf (Peterson et al. 2016, Grossmann 2010). Being in the auxin family, 2,4-D mimics the plant growth hormone auxin (indole acetic acid), and when administered at effective doses causes uncontrolled and disorganized plant growth that leads to plant death (Song 2014). As a weak acid, when dissociated 2,4-D binds with cations present in hard water. Patton et al. 2016, observed enhanced 2,4-D activity on broadleaf plantain (*Plantago major* L.) and dandelion (*Taraxacum officinale* G.H. Weber ex Wiggers) when AMS was added to the spray solution in hard water. Horseweed (*Conyza canadensis* (L.) Cronq.) and dandelion had higher shoot and root weights when treated with 2,4-D in hard water compared to 2,4-D + AMS (Schortgen and Patton 2020). These effects were also confirmed by Roskamp et al. 2013 where the addition of AMS to 2,4-D in a hard water solution increased control of horseweed and redroot pigweed (*Amaranthus retroflexus* L.), by 48% and 27% respectively.

Knowing that herbicidal activity can be reduced by unfavorable water quality, the objective of this work was to evaluate the efficacy of citric acid, phosphoric acid, and AMS tank-mixtured with glufosinate, glyphosate and 2,4-D across a range of droplet sizes. The hypothesis were that: 1) water conditioning adjuvants will improve weed control compared to herbicides alone, and 2) droplet size will be significant for glufosinate, but not glyphosate and 2,4-D.

Materials and Methods

A greenhouse study was conducted during fall 2020 and winter 2021 at the Pesticide Application Technology (PAT) Laboratory in North Platte, NE. Waterhemp, common lambsquarters and green foxtail seeds were planted in 656 cm^3 cone containers (Heavyweight Deepot Cell, Stuewe & Sons, Tangent, OR) using growing medium (Pro-Mix BX General Purpose Growing Medium, Premier Tech Horticulture Ltd, Quakertown, PA). The greenhouse was maintained with day/night temperature at 30/20 C with lighting to provide 16-h photoperiod (Philips GreenPower LED Toplighting, Deep

Red/Blue). Treatments were applied as a three-way factorial of herbicide, adjuvant, and droplet size. Herbicides used were glufosinate (Liberty, 328 g ai ha^{-1}, Bayer CropScience, LP, Research Triangle Park, NC, USA), glyphosate (Roundup PowerMax, 328 g ae ha^{-1}, Monsanto Company, St. Louis, MO, USA) and 2,4-D (Enlist One, 400 g ae ha^{-1}, Dow AgroSciences, Indianapolis, IN, USA). Adjuvants used were AMS (Imperial AMS, 20 g L^{-1}, Rosen's Inc, Fairmont, MN, USA), Citric acid (0.2 v v^{-1}, Adjuvants Unlimited, Memphis, TN, USA), and Phosphoric acid (0.09 v v^{-1}, Adjuvants Unlimited). Distilled water was adjusted to pH 6.7 using Vaporgrip (Bayer CropScience) and water hardness to 240 mg L^{-1} by adding calcium chloride (Calcium Chloride Dihydrate, Fisher Scientific, Pittsburgh, PA) and magnesium sulfate (Magnesium Sulfate Heptahydrate, Fisher Scientific, Pittsburgh, PA) in a 3:1 ratio prior the addition of herbicides and adjuvants. Water hardness was measured with a water hardness test kit (Total Hardness Test Kit; HACH, Loveland, CO, USA), and pH with a pH meter (P200 Series Benchtop pH and pH/Conductivity Meter, Cole Parmer, Vernon Hills, IL, USA). Nozzle type, orifice, and application pressure required to create volume median dimeters (VMDs) of 150 µm, 400 µm, 650 µm, and 900 µm were determined using a Sympatec HELOS-VARIO/KR laser diffraction system equipped with R7 lens (Sympatec, Inc. Clausthal, Germany) in the wind tunnel at the PAT Lab. Creech et al. 2016 provide in-depth details regarding the test methods used for droplet size evaluations. The nozzles selected were non-venturi ComboJet spray tips (Wilger Inc, Lexington, TN, USA) which allowed for the full range of targeted VMDs to be achieved using nozzles of similar design eliminating confounding spray characteristics factors. Spray classifications were assigned according to ASABE S572.1 (ASABE, 2009). Treatments were applied on weeds using a three-nozzle spray chamber (Devries Manufacturing, Hollandale, MN, USA) that allowed for variable speed traversal of the boom over the weeds. The spraying speed, nozzle type and spray pressure combinations required to deliver the targeted VMDs at an application rate of 140 L/ha^{-1} were determined prior to herbicide applications (Table 1). Nozzles were spaced 50.8 cm apart at a boom height of 50.8 cm. Waterhemp, common lambsquarters and green foxtail were 22-, 18-, and 20 cm tall at the time of application, respectively. 2,4-D tank-mixtures were not applied on green foxtail due to natural tolerance.

Statistical Analyses

Studies were designed in a randomized complete block design with five replications and repeated twice over time. Nontreated controls were included for comparison. Control is defined by the reduction in weed biomass after treatment compared to nontreated controls with greater control indicated by larger reductions. At 21 DAT the above ground mass was harvested and dried to constant mass, after which dry weight was converted to percentage of dry biomass reduction compared to nontreated controls (Equation 1):

$$\mathrm{BR} = 100 * \frac{\mathrm{X} * 100}{\mathrm{Y}}$$

Where BR is biomass reduction (%), X is biomass (g) of individual experimental unit after being treated, and Y is the mean biomass (g) of nontreated controls.

Data were analyzed separately for each weed species using PROC GLIMMIX in SAS 9.4. There was no significant effect between two runs over time, therefore data were combined for the analyses. BR data were arcsine square root transformed and subjected to Analyses of Variance (ANOVA). Treatment means were separated using an adjusted Tukey test at $\alpha \leq 0.05$.

Results and Discussion

There were no significant interactions among water conditioners and droplet sizes. Only main effects were significant in control of common lambsquarters and waterhemp. The addition of WCs significantly affected control of common lambsquarters control for all herbicides. Waterhemp control was only significantly impacted by changes in VMD for glyphosate, and the use of WC for 2,4-D. There were no significant interactions in green foxtail control.

Common lambsquarters. The use of phosphoric acid significantly increased control for glufosinate (38% to 51%), glyphosate (58% to 68%), and 2,4-D (34% to 56%), compared to each herbicide alone (Table 1). AMS provided significant increase in control when added to 2,4-D, compared to 2,4-D alone (34% to 66%). Citric acid, while not providing any significant increases in control compared to herbicides alone, did provide an equal level of control as when phosphoric acid was added to glyphosate. These results correspond to those reported by Pline et al. 1999, who found that the addition of AMS did not improve glufosinate absorption and translocation, likely due to weed sensitivity observed under greenhouse conditions and AMS antagonistic effects on glufosinate. While, Soltani et al. 2011 did not observe differences in control of common lambsquarters from glyphosate applications with and without AMS at 353 mg L^{-1} hardness, improved control was seen when AMS was added to glufosinate at 1799 mg L^{-1} hardness (Soltani et al. 2011) showing that the degree of water hardness also plays a role. However, increase in control was observed in dandelion, horseweed and broadleaf plantain with the addition of AMS to 2,4-D (Patton et al. 2016, Schortgen and Patton 2020).

Droplet size did not significantly impact control of common lambsquarters with any of the tank-mixtures. Results from previous research on the relationship between droplet size and biological activity of herbicides are contradictory. Sikkema et al. 2008 observed no difference in glyphosate (systemic) and fomesafen (contact) control of common lambsquarters with changes in spray droplet size. Etheridge et al. 2001 also found that glyphosate efficacy was not impacted across a large range of droplet sizes. While Creech et al. 2016 found that finer sprays provide better control of common lambsquarters from 2,4-D (200 g ha^{-1}), the multiple formulations and rates used somewhat confound the results.

Waterhemp. None of the WCs provided significant improvement to control from either the glyphosate or glufosinate treatments (Table 1). Soltani et al. 2011 found similar results on control of velvetleaf, redroot pigweed, common lambsquarters, and annual grasses (*Setaria* spp.) from glyphosate applications being the same with and without AMS. In contrast, Mueller et al. 2006 observed reduced effectiveness from glyphosate applications made in 500 mg L^{-1} hard water. Differences in hard water (240 to 500 mg L^{-1}) between the studies may explain why glyphosate treatments were not significant. Previous research has confirmed that effect of hard water on herbicide efficacy is weed species and hard water level dependent (Devkota and Johnson 2019, Soltani et al. 2011). All three WCs significantly improved control from 2,4-D treatments, with 89-, 86- and 84% control with AMS, phosphoric acid, and citric acid tank-mixed with 2,4-D, respectively as compared to 69% for 2,4-D alone. Roskamp et al. 2013 observed similar results on horseweed and redroot pigweed, where 2,4-D + AMS in hard water gave 48% and 27% higher control, respectively, than 2,4-D alone.

Droplet size effects on control were only significant for glyphosate treatments, with the finest spray (150 µm VMD) providing 10% less control than the other spray treatments (Table 2). Butts et al. 2019 found similar results where 90% of Palmer amaranth and common lambsquarters weed control was achieved when treated with dicamba + glyphosate 570- (Extremely Coarse) and 900 µm (Ultra Coarse) VMD spray. While suggested that coarser droplets may result in higher adhesion on the horizontal leaf surfaces (D. B. Smith et al. 2000), that was not the case here likely due to waxy cuticle and possible droplet bounce off leaf surfaces due to lack of droplet retention surfactants.

Conclusions

The current research demonstrates that carrier water pH and hardness, and use of WCs are critical considerations for optimizing glufosinate, glyphosate and 2,4-D efficacy on common lambsquarters. Glufosinate and glyphosate efficacy increased with the addition of phosphoric acid. Phosphoric acid, as a water conditioner, manages pH and hardness by shifting the pH to acidic and binding with the hard water cations. AMS improved 2,4-D efficacy, which resulted in greater common lambsquarters control. Droplet size was only significant for glyphosate treatments on waterhemp, where larger VMDs provided higher control. Since droplet size was not significant in most cases, applicators should utilize nozzles that produce larger VMDs to effectively reduce particle drift from future glufosinate, glyphosate and 2,4-D applications.

List of Tables

Table 1. Nozzle, spray pressure, and boom traverse speed combinations required to achieve the targeted Volume Median Diameters (VMDs) for herbicide tank-mixture applications at 140 L ha^{-1}.

Spray Solutions[a]	Volume Median Diameter (µm)	Nozzle[b]	Application Pressure (kPa)	Application Speed (km h^{-1})
Glufosinate	150 (F)[c]	ER110015	434	4.5
	400 (C)	MR11005	276	11.9
	650 (EC)	DR11010	200	20.3
	900 (UC)	UR11010	172	18.9
Glu + AMS	150	ER110015	441	4.5
	400	MR11004	234	8.8
	650	DR11010	262	23.3
	900	UR11010	207	20.7
Glu + Citric acid	150	ER110015	455	4.6
	400	MR11004	262	9.3
	650	DR11010	214	21.0
	900	UR11010	207	20.8
Glu + Phosphoric acid	150	ER110015	469	4.5
	400	MR11004	207	8.4
	650	DR11010	214	21.0
	900	UR11010	207	20.8
Glyphosate	150	ER110015	469	4.7
	400	MR11005	379	14.0
	650	DR11008	207	16.6
	900	UR11010	207	20.7
Gly + AMS	150	ER110015	469	4.5
	400	MR11005	414	14.6
	650	DR11008	241	17.9
	900	UR11010	262	23.4
Gly + Citric acid	150	ER110015	469	4.5
	400	MR11005	414	14.6
	650	DR11008	228	17.4
	900	UR11010	241	22.2
Gly + Phosphoric acid	150	ER110015	469	4.5
	400	MR11005	414	14.6

	650	DR11008	228	17.4
	900	UR11010	248	22.7
2,4-D	150	ER11015	552	5.1
	400	MR11004	386	11.3
	650	DR11008	290	19.6
	900	UR11010	221	22.6
2,4-D + AMS	150	ER11015	552	5.0
	400	MR11005	303	12.4
	650	DR11008	290	19.6
	900	UR11010	248	22.7
2,4-D + Citric acid	150	ER11015	552	5.0
	400	MR11004	310	10.0
	650	DR11008	290	19.6
	900	UR11010	255	22.9
2,4-D + Phosphoric acid	150	ER11015	552	5.0
	400	MR11004	276	9.6
	650	DR11008	234	17.7
	900	UR11010	221	21.3

[a] Glu – glufosinate, Gly – glyphosate

[b] Flat fan, non-venturi nozzles (Wilger Inc, Lexington, TN, USA)

[c] Spray classifications determined according to ASABE S572.1. F – Fine, C – Coarse, EC – Extremely Coarse, UC – Ultra Coarse

Table 2. Common lambsquarters and waterhemp biomass reduction for glufosinate, glyphosate and 2,4-D tank-mixtures.

	Common lambsquarters	Waterhemp
Water conditioners	Herbicides	
	Glufosinate	
	%	
None	38 B	ns*
AMS	33 B	ns
Citric acid	35 B	ns
Phosphoric acid	51 A	ns
p value	0.0002	0.5014
	Glyphosate	
None	58 B	ns
AMS	57 B	ns
Citric acid	61 AB	ns
Phosphoric acid	68 A	ns
p value	0.0195	0.3314
	2,4-D	
None	34 C	69 C
AMS	66 A	89 AB
Citric acid	38 C	84 B
Phosphoric acid	56 B	86 AB
p value	<0.0001	<0.0001

*No significant differences were detected using Tukey's adjustment test at the 0.05 significance level. Means followed by the same letter within a column are not

Table 3. Waterhemp biomass reduction across droplet sizes for glufosinate, glyphosate, and 2,4-D tank-mixtures.

Droplet size[1]	Glufosinate	Glyphosate		2,4-D
	———————	—————%	———————	———————
150	ns*	65	B	ns
450	ns	76	A	ns
600	ns	75	A	ns
900	ns	75	A	ns

*No significant differences were detected using Tukey's adjustment test at the 0.05 significance level. Means followed by the same letter within a column are not statistically different.

[1] Droplet size expressed as volume median diameter (μm).

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Chapter 3

Spray Carrier Volume and Droplet Size Effect on Glufosinate, Glyphosate and 2,4-D Efficacy Across a Range of pH and Water Hardness Levels

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Abstract

Proper herbicide application is critical to ensure products achieve their full potential for weed control. Droplet size and carrier volume play crucial role in herbicide coverage and efficacy. The concern for off target movement has led to the movement towards nozzles that produce larger droplets. It has been recommended to utilize spray volumes at the higher ends of recommended range to ensure greater coverage and improvement of consistency of weed control. The objective of this study is to investigate influence of spray carrier volume and droplet size on glufosinate, glyphosate and 2,4-D efficacy under several water quality conditions. Application parameters investigated in this study were carrier volume at 47 and 187 L ha^{-1}, and droplet size at 150 and 900 µm, expressed as volume median diameters (VMDs). Water properties were adjusted to 0, 500, 1000 and 1500 ppm, expressed as $CaCO_3$, and 5, 7 and 9 pH prior to the addition of herbicides. The hypotheses of this study were: 1) lower carrier volume will improve herbicide efficacy for high water hardness levels; 2) larger droplets will improve efficacy when lower carrier volume is utilized; 3) smaller droplets will improve efficacy when higher carrier

volume is utilized; 4) herbicide efficacy will be improved when applied in soft and acidic water.

Introduction

Generally, herbicide efficacy is directly related to the amount of active ingredient that has reached the target (Creech et al. 2015). Thus, spray solution characteristics and application parameters need to be optimized for the efficient herbicide applications. Spray carrier volume and droplet size are crucial parameters that can impact herbicide performance (Knoche 1994). It is a common understanding that contact herbicides require greater coverage, thus utilization of higher carrier volumes and/or smaller droplet sizes, whereas systemic herbicides are less affected by lower carrier volumes and/or bigger droplet sizes which lead to decrease in coverage. However, with the utilization of high spray volumes and smaller droplet sizes, comes greater risk for off-target movement. Additionally, low spray volumes are preferred due to saving in time required to fill sprayer tanks and to travel to and from fields (Moraes et al. 2021) as well as to reducing fuel costs from transporting large quantities of water and needing to cover more area per tank-load (Etheridge et al. 1999). Moreover, herbicides are more concentrated in lower carrier volumes, thus there is less hard water cations (HWC) to be bound with the active ingredient (Ramsdale et al. 2003). This phenomenon of HWC-herbicide complex formation is well known for weak acid (WA) herbicides, such as glyphosate, glufosinate and 2,4-D. Hard water contains dissolved minerals, with Ca^{2+} and Mg^{2+} being predominant (Patton et al. 2016). Increased concentration of HWC may be problematic when used as a carrier for WA herbicide applications. Once any of the aforementioned herbicides are added to hard water, the positively charged ions in water bind with the negatively charged herbicide, and thus form a complex which is not readily absorbed (Zollinger et al. 2016).

General concern for off-target movement has shifted to utilization of larger droplets. However, as droplet diameter increases, the volume of solution contained within the droplet increases (Butts et al. 2018). It takes eight times as much liquid to apply a given number of 200 µm droplet size as it does to apply an equal number of 100 µm droplets (McKinlay et al. 1974). This, again, can have a negative impact on potential HWC-herbicide complex formation. Conversely to the theory of contact herbicides needing higher coverage for better weed control, Butts et al. 2018 observed equal to better weed control when glufosinate was applied at 47 L ha^{-1} compared to 187 L ha^{-1} across a wide range of droplet sizes. Their hypothesis was that more concentrated droplets at 47 L ha^{-1} carrier volume were able to overcome antagonistic HWC, resulting in greater weed control. Low spray volumes were found efficacious for enhanced glyphosate efficacy as well, due to higher concentration of glyphosate in the spray deposit (Ramsdale et al. 2003). Another characteristic of a spray solution that can have an impact on a WA herbicide performance is carrier pH. When pH of the solution is below the WA herbicide's pKa, herbicide turns into a unionized form and as such can easily penetrate through lipophilic cuticle but has decreased solubility. However, if pH is above herbicide's pKa value, WA turns anionic and has decreased uptake but increased solubility. The benefit of high pH will be greatest at low spray volumes when solubility is limiting, and the benefit of low pH will be greatest at high spray volumes when solubility is not limiting (Green and Hale 2005a). Knowing the concepts behind the water quality parameters aforementioned, the objectives of this study were to investigate the effect of 1) four hard water levels; 2) three pH levels; 3) two droplet size classifications and 4) two carrier volumes on glufosinate, glyphosate and 2,4-D efficacy. The hypothesis for this study were: 1) lower carrier volume will improve herbicide efficacy for high water hardness levels; 2) larger droplets will improve efficacy when lower carrier volume is utilized; 3) smaller droplets will improve efficacy when higher carrier volume is utilized; 4) herbicide efficacy will be improved when applied in soft and acidic water.

Materials and Methods

A greenhouse study was conducted during Fall 2021 and Winter 2022 at the Pesticide Application Technology (PAT) Laboratory in North Platte, NE. Waterhemp (*Amaranthus tuberculatus* (Moq.) Sauer), common lambsquarters (*Chenopodium album* L.) and green foxtail (*Setaria viridis* L. Beauv.) seeds were planted in 656 cm^3 cone containers (Heavyweight Deepot Cell, Stuewe & Sons, Tangent, OR) using growing medium (Pro-Mix BX General Purpose Growing Medium, Premier Tech Horticulture Ltd, Quakertown, PA). The greenhouse was maintained with day/night temperature at 30/20 C with lighting to provide 16-h photoperiod (Philips GreenPower LED Toplighting, Deep Red/Blue). Spray application treatment experimental design was a four-way factorial with main effects being carrier volume (CV), droplet size (DS), water hardness (WH) and water pH (WpH). Herbicides used were glufosinate (Liberty, 219 g a.i. ha^{-1}, Bayer CropScience, LP, Research Triangle Park, NC, USA), glyphosate (Roundup PowerMax, 219 g ae ha^{-1}, Monsanto Company, St. Louis, MO, USA) and 2,4-D (Enlist One, 400 g ae ha^{-1}, Dow AgroSciences, Indianapolis, IN, USA). Carrier water hardness was maintained at 0, 500, 1000 and 1500 ppm by adding calcium chloride (Calcium Chloride Dihydrate, Fisher Scientific, Pittsburgh, PA) and magnesium sulfate (Magnesium Sulfate Heptahydrate, Fisher Scientific, Pittsburgh, PA) in a 3:1 ratio. WpH was maintained at 5, 7 and 9 using organic pH buffers. Potassium hydrogen phthalate salt (Acros Organic, Geel, Belgium); potassium phosphate monobasic salt (VWR International, Radnor, PA); and tris salt (Tris hydroxymethyl, aminomethane, Acros) were dissolved in distilled water to create 5, 7 and 9 pH, respectively. WH was measured with a water hardness test kit (Total Hardness Test Kit; HACH, Loveland, CO, USA), and pH was measured with a pH meter (P200 Series Benchtop pH and pH/Conductivity Meter, Cole Parmer, Vernon Hills, IL, USA) prior to the addition of herbicides. Nozzle type, orifice, and application pressure combinations required to create volume median dimeters (VMDs) of 150 µm and 900 µm were determined using a Sympatec HELOS-VARIO/KR laser diffraction system equipped with an R7 lens which allows for measurements up to 3500 µm (Sympatec, Inc. Clausthal, Germany). All DS testing was completed in the PAT Lab wind tunnel following procedures outline by Creech et al. 2016. The nozzles used were non-venturi ComboJet spray tips (Wilger Inc, Lexington, TN, USA). The similarity in design ensured elimination of confounding spray characteristics factors. Additionally, these nozzles are compatible with the pulse width modulation system (PWM) at the duty cycles necessary to achieve the larger VMD at the lower carrier volume due to limitations in the speed of the equipment used for herbicide applications. In-depth principle behind the PWM system is covered by Butts et al. 2019. Spray classifications were assigned according to ASABE S572.1 (ASABE, 2009). Prior to application, VMDs were recorded for each tank-mix by testing various orifice sizes and pressures to get the desired VMD. Treatments were applied on weeds using a three-nozzle spray chamber (Devries Manufacturing, Hollandale, MN, USA) at 47 and 187 L ha^{-1}, with the nozzle traverse speed adjusted for each nozzle type by pressure combination to deliver targeted droplet size and carrier volume. Nozzles were 50.8 cm spaced, with a boom height of 50.8 cm from the target. In addition, a nontreated control was included for comparison. Waterhemp, common lambsquarters and green foxtail were 22-, 18-, and 20 cm tall at the time of application, respectively. 2,4-D tank-mixtures were not applied on green foxtail due to natural tolerance.

Studies were designed in a randomized complete block design with five replications and repeated over time. Nontreated controls were included for comparison. Control is defined by the reduction in weed biomass after treatment compared to nontreated controls with greater control indicated by larger reductions. At 21 DAT the above ground mass was harvested and dried to constant mass, after which dry weight was converted to percentage of dry biomass reduction compared to nontreated controls (Equation 1):

$$\mathrm{BR} = 100 * \frac{\mathrm{X} * 100}{\mathrm{Y}}$$

Where BR is biomass reduction (%), X is biomass (g) of individual experimental unit after being treated, and Y is the mean biomass (g) of nontreated controls.

Data were analyzed separately for each weed species using PROC GLIMMIX in SAS 9.4. There was no significant effect between two runs over time, therefore data were combined for the analyses. Percentage of dry biomass reduction data were arcsine square root transformed and subjected to ANOVA. Treatment means were separated using an adjusted Tukey test at $P \leq 0.05$.

Results and Discussion

Glufosinate. Two-way interactions (CV x DS, CV x WH) were found significant for glufosinate treatments in common lambsquarters ($P = 0.0007$, $P < .0001$) and green foxtail ($P = 0.0057$, $P = 0.0012$) control. However, only main effects – CV ($P < .0001$), DS ($P < .0001$) and WH ($P < .0003$) were significant in waterhemp control.

Results have shown 10% increase in common lambsquarters control for plants treated with 150 µm VMD, compared to 900 µm VMD applied at 187 L ha^{-1} (Table 1). However, glufosinate applied at 47 L ha^{-1} overcame the droplet size effect. Evident difference between the VMDs at 187 L ha^{-1} can be attributed to ricochet or shatter of larger droplets after contact with the leaf surface. Also, waxes on the leaf surface increase the contact angle due to their hydrophobic character (D. B. Smith et al. 2000). Similarly, 150 µm VMD increased waterhemp control by 9% compared to 900 µm VMD across glufosinate treatments. Glufosinate is considered a contact herbicide because of its fast activity and limited translocation in plants (Takano et al. 2020). Ferguson et al. 2018 observed reduced droplet size density by half for the nozzles producing Ultra Coarse droplet size compared to the Coarse droplet producing nozzles. The reduction in spray coverage and droplet density can be crucial for the efficacy of contact herbicides. In contrary, coarser VMD increased green foxtail control by 20 and 10% at 47 and 187 L ha^{-1}, respectively.

Polyvalent cations in hard water can easily react with weak acid herbicides. It was observed that WH was not significant in glufosinate applications at 47 L ha^{-1} in common lambsquarters and green foxtail control. Moreover, no difference was observed when glufosinate was applied at 187 L ha^{-1} in soft water compared to 47 L ha^{-1} in 1000- and 1500 mg L^{-1} hard water. Waterhemp control decreased by 6-13% across all hard water levels compared to soft water for glufosinate treatments (Table 2). However, 500 mg L^{-1} was not statistically different from soft water. Similar results were recorded by Devkota and Johnson 2016 who observed reduction in Palmer amaranth control by 13% when WH increased from 0 to 1000 mg L^{-1}. Zollinger et al. 2010 observed that activity of several weak acid herbicides including glyphosate, aminopyralid, tembotrione, dicamba plus diflufenzopyr, and glufosinate were reduced by Ca and Mg salts. Ca^{2+} and Mg^{2+} in water bind with the negatively charged herbicide, and as such the molecule is not readily absorbed (Bernards et al. 2005) or can cause precipitation of the herbicide from the solution (Thelen et al. 1995), which can result in reduced weed control. Results have shown that glufosinate applied at 47 L ha^{-1} increased control by 23% compared to the applications at 187 L ha^{-1}. Similar results were reported by Butts et al. 2018 who found equal to greater weed control with glufosinate applications at 47 compared to 187 L ha^{-1} across a wide range of droplet sizes. It is generally known that contact herbicides require greater coverage, thus higher carrier volumes. It is possible that more concentrated droplets within 47 L ha^{-1} carrier volume were able to overcome the negative effect of water quality, resulting in greater weed control.

Glyphosate. CV, DS and WH were also significant in glyphosate treatments as either main effects or two-way interactions across weed species tested.

CV x DS were significant in common lambsquarters ($P = 0.0019$) and green foxtail ($P < .0001$) control. For both species, 47 L ha^{-1} overcame the droplet size effect (Table 3). However, glyphosate applied at 187 L ha^{-1} with 150 μm VMD increased control for common lambsquarters by 13%. As with glufosinate, green foxtail control increased with 900 μm VMD applied at 187 L ha^{-1}. Waterhemp biomass reduction also increased with 150 μm VMD across CVs by 7% ($P = 0.0008$). The weed control is usually equivalent with the amount of herbicide deposited onto the plant (Creech et al. 2015). Legleiter et al. 2018 found decreased deposition density with increasing droplet size at a fixed carrier volume. The effect of droplet size and spray coverage on target plants for foliar herbicide efficacy largely depends on the type of herbicide. Systemic herbicides are less effected by decrease in coverage due to decreasing the carrier volume or using the nozzles that produce larger droplets.

Glyphosate is the most researched herbicide in hard water antagonism (Bernards et al. 2005). Its efficacy is reduced because it forms a complex with cations in water, and as such has reduced absorption and translocation throughout the plant (Thelen et al. 1995). Common lambsquarters control decreased for 10-, 14-, and 18 % when applied in 500-, 1000-, and 1500 mg L^{-1} hard water, respectively compared to the glyphosate applications in soft water ($P < .0001$). CV x WH ($P < .0001$) was significant in green foxtail and waterhemp control. For both species, 187 L ha^{-1} applied in soft water was not significantly different than 47 L ha^{-1} application across all WH levels. It is not surprising that one of the components of glyphosate applications that increased its adoption among applicators was that plant response and subsequent control often increased as carrier volume decreased, whereas the performance of other herbicides generally decreases as carrier volume decreases (Knoche 1994). This is a benefit to the applicator because the amount of water and time required for an application is reduced and more area is sprayed with each tank load.

2,4-D. WpH was not found to be significant in weed control except for 2,4-D treatments. Three-way interaction between CV, WpH and WH ($P = 0.0155$) and CV x DS was significant in common lambsquarters control, whereas CV x WpH x WH x DS ($P = 0.0187$) was significant in waterhemp control.

As with abovementioned herbicides, 47 L ha^{-1} treatments provided equal common lambsquarters control. Moreover, 187 L ha^{-1} applications in soft water, and 500 mg L^{-1} in

5 pH carrier were not statistically different than 47 L ha^{-1} treatments (Table 4). It was also observed that 2,4-D efficacy on common lambsquarters decreases with increasing the carrier volume and droplet size (Table 5). Similarly, waterhemp control was not different across 47 L ha^{-1} treatments, except for the 47 L ha^{-1} application in 1500 mg L^{-1}, 9 pH applied with 900 µm VMD. Applications at 187 L ha^{-1} in soft water, as well as 500 mg L^{-1} were not different than low carrier volume applications (Table 6). It was previously reported that 2,4-D as a weak acid herbicide, when dissociated, can bind with cations present in hard water (Devkota and Johnson 2016b, Patton et al. 2016, Schortgen and Patton 2020). When dissociated, weak acid acts as chelating agent, forming a herbicide-hard water cations complex which decreases herbicide absorption and translocation (Bernards et al. 2005). There are less free cations in lower carrier volumes, thus more herbicide to penetrate and translocate throughout the plant. The carrier water pH limits the solubility and controls ionic state of weak acid herbicides influencing their uptake and biological activity. When the herbicide is at low concentrations and solubility is not a limiting factor, uptake is greater at low pH. However, when the herbicide is at high concentration and solubility is limiting, then higher pH increases uptake (Green and Hale 2005b). 2,4-D is highly water soluble in water, and in this research was applied at a third of a recommended labeled rate. This can explain greater weed control at low WpH.

Conclusions

Spray applications are complex processes beginning in the spray tank even before pesticides are added to the tank. Having the right pesticide, nozzle, environmental conditions at the time of spraying, weed growth stage, etc. is crucial in the application process. However, if the first piece of the puzzle is overlooked, and that is quality of the water being in the tank, the pest management success might be compromised. This research confirms that weak acid herbicides, such as glufosinate, glyphosate and 2,4-D, have reduced activity on weed control in hard water. It has been shown that low carrier volumes can mask the effect of water quality. To address the disadvantage arising from utilizing low carrier volumes which are usually achieved by using smaller orifice nozzles, thus higher drift potential, future research should be focused on optimizing water quality. Low carrier volumes can be detrimental in herbicide applications that require greater coverage. One way of overcoming the negative effect of water quality is addition of water conditioning adjuvants.

List of Tables

Table 1. Common lambsquarters and green foxtail biomass reduction as a result of carrier volume x droplet size and carrier volume x water hardness interactions across glufosinate treatments.

Droplet size[1] (µm)	Carrier volume (L ha^{-1})							
	Common lambsquarters				Green foxtail			
	47		187		47		187	
	%							
150	55	A	34	B	57	B	33	D
900	58	A	25	C	77	A	43	C
Water hardness (mg L^{-1})								
0	60	A	47	B	74	A	56	C
500	58	A	34	C	67	AB	34	D
1000	56	AB	20	D	65	ABC	32	D
1500	53	AB	16	D	59	BC	29	D

Means followed by the same letter for carrier volume x droplet size and carrier volume x water hardness interactions by weed species are not different ($\alpha \leq 0.05$).

[1] Droplet size expressed as volume median diameter.

Table 2. Waterhemp biomass reduction influenced by carrier volume, droplet size and water hardness across glufosinate treatments.

Variables	Biomass reduction	
	———%———	
Carrier volume (L ha^{-1})		
47	84	A
187	61	B
Droplet size[1] (µm)		
150	77	A
900	68	B
Water hardness (mg L^{-1})		
0	79	A
500	74	AB
1000	70	B
1500	67	B

Means followed by the same letter for carrier volume, droplet size and water hardness are not different ($\alpha \leq 0.05$).

[1] Droplet size expressed as volume median diameter.

Table 3. Common lambsquarters, waterhemp and green foxtail biomass reduction impacted by carrier volume, droplet size and water hardness across glyphosate treatments.

Droplet size	Carrier volume (L ha^{-1})					
	Common lambsquarters[2]		Waterhemp[3]		Green foxtail	
	%					
	47	187	47	187	47	187
150	67 A	41 B	76 A		97 A	75 C
900	71 A	28 C	69 B		97 A	84 B
Water hardness (mg L^{-1})						
0	62 A		89 A	81 A	97 A	96 A
500	52 B		86 A	61 B	97 A	88 B
1000	44 B		83 A	53 BC	97 A	71 C
1500	48 B		79 A	48 C	97 A	63 D

Means followed by the same letter for carrier volume x droplet size and carrier volume x water hardness interactions, as well as carrier volume and droplet size only by weed species are not different ($\alpha \leq 0.05$).

[1] Droplet size expressed as volume median diameter (µm).

[2] Carrier volume x water hardness not significant (P = 0.5928). Results presented are pulled across carrier volume.

[3] Carrier volume x droplet size not significant (P = 0.1412). Results presented are pulled across carrier volume.

Table 4. Common lambsquarters biomass reduction affected by carrier volume x water pH x water hardness size interaction across 2,4-D treatments.

Water hardness (mg L^{-1})	Carrier volume (L ha^{-1})					
	47			187		
	Water pH					
	5	7	9	5	7	9
	%					
0	75 AB	73 AB	72 AB	65 AB	62 ABC	59 BCD
500	75 AB	75 AB	77 A	71 AB	49 CDE	45 EDF
1000	74 AB	71 AB	73 AB	40 EF	40 EF	34 EF
1500	71 AB	72 AB	72 AB	33 EF	39 EF	31 EF

Means followed by the same letter for carrier volume x water pH x water hardness interaction are not different ($\alpha \leq 0.05$).

Table 5. Common lambsquarters biomass reduction influenced by carrier volume x droplet size interaction across 2,4-D treatments.

Droplet size[1] (µm)	Carrier volume (L ha^{-1})	
	47	187
	%	
150	76 A	59 C
900	70 A	36 D

Means followed by the same letter for carrier volume x droplet size interaction are not different ($\alpha \leq 0.05$).

[1] Droplet size expressed as volume median diameter.

Table 6. Waterhemp biomass reduction influenced by carrier volume x water pH x water hardness and droplet size interaction across 2,4-D treatments.

Water hardness (mg L^{-1})	Carrier volume (L ha^{-1})					
	47					
	Droplet size[1] (µm)					
	150			900		
	Water pH					
	5	7	9	5	7	9
	%					
0	86 A	84 AB	83 AB	82 AB	77 ABC	88 A
500	81 ABC	78 ABC	85 A	85 A	70 A-E	67 A-F
1000	74 A-D	77 ABC	79 ABC	67 A-F	62 A-H	78 ABC
1500	70 A-E	68 A-F	64 A-G	59 A-I	65 A-G	51 C-J
	187					
0	79 ABC	85 A	89 A	79 ABC	87 A	82 AB
500	59 A-I	54 B-I	44 D-J	51 C-J	60 A-H	62 A-H
1000	29 IJ	53 B-I	38 F-J	34 HIJ	44 D-J	28 IJ
1500	37 G-J	45 D-J	38 F-J	22 J	36 G-J	40 F-J

Means followed by the same letter for carrier volume x water pH x water hardness x droplet size interaction are not different ($\alpha \leq 0.05$).

[1] Droplet size expressed as volume median diameter.

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Chapter 4

Comparison of Spray Drift Models Estimated by AGDISP with Field Applications Using Air Inclusion Nozzles

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Abstract

Droplet size distribution (DSD) is a crucial factor affecting off-target movement. There are several models developed to estimate drift, including AGDISP (Agricultural Dispersal) used by the US EPA. AGDISP estimates downwind spray deposition using a number of parameters including nozzle type, DSD, and meteorological conditions. The objective of this study was to compare empirical spray drift data collected from a field study with data modelled by AGDISP for air inclusion nozzles. Field applications were made at 276 kPa and 2.4 m s^{-1} travel speed using a 40 nozzle-boom sprayer with 0.76 m nozzle spacing to deliver 140 L ha^{-1}. The nozzles used were AIXR11004, GA11004, TDXL11004, TTI11004 and ER11004 with five replications per nozzle. Mylar cards were used as drift collectors, positioned from 0.5 m to 80 m downwind from the nozzles. Spray solution was composed of water with a pyrene-tetra-sulfonic acid tetra-sodium salt (PTSA) fluorescent tracer. The tracer was washed off the collectors with a pre-mixture of water and 91% isopropyl alcohol (9:1) and quantified using fluorimetry. Air temperature, relative humidity, wind speed, and wind directions were recorded during the applications.

DSD of the nozzles was measured using laser diffraction system and the data were imported in the AGDISP model, as well as the meteorological conditions during field applications. The AGDISP model underestimated downwind deposition when compared to the empirical field data for nozzles tested, with the exception for ER nozzle where the deposition was overpredicted at 10-80m downwind. With differences being observed between field and estimated data, the same ranking of the nozzles was detected where ER11004 produced greatest spray drift followed by GA11004, AIXR11004, TDXL11004 and TTI11004, respectively. Future ground model development focused on nozzle type to get accurate downwind deposition for air inclusion nozzles is necessary if the models are going to be used to determine buffers or other regulatory decisions beyond bridging studies to empirical data.

Introduction

Spray drift is a part of the pesticide application deflected away from the target and lost as either droplets or vapors (Matthew et al. 2014). Spray drift management is crucial to reduce the risks of environmental contamination, exposure of susceptible species, and crop yield reductions resulting from injury (Vieira et al. 2018). The largest focus for spray drift reduction practices has been placed on increasing spray droplet size implementing different technologies (Sousa Alves et al. 2020). The US EPA (Environmental Protection Agency) has developed a Drift Reduction Technology program to encourage the use of spray technologies scientifically verified for reducing pesticide drift. Technologies included are use of spray shields, drift reducing nozzles and drift reducing adjuvants. All three technologies are related to the droplets being sprayed by minimizing spray exposure to the wind and allowing for finer droplets to optimize spray coverage (Wolf et al. 1993, Canella Vieira et al. 2022); increasing the droplet size with the air induction and pre-orifice nozzle technology (Etheridge et al. 1999, Sikkema et al. 2008, Butts et al. 2019), and increasing the droplet size by improving the sheet breakup mechanism and increasing the viscosity of the spray with the addition of drift reducing adjuvants (Creech et al. 2018).

It was identified that nozzle design has the greatest influence over droplet size (Creech et al. 2015). Nozzles and their spray characteristics have gone under significant development in past decades to enhance spray ability under a wide range of conditions. Pesticide application technology changed with the introduction of air inclusion nozzles (AI) in mid 1990s. Farmers were able to use nozzles that created larger droplets at the same pressure and flow rate as conventional nozzles, resulting in less drift (Post, 2019).

This has been accomplished by adding a pre-orifice to the nozzle tip assembly ahead of the conventional discharge orifice. This technology reduces liquid velocity and pressure at the exit orifice, thus creating larger droplets (R. C. Derksen et al. 1999). Another nozzle design for creating larger droplets incorporates a hole on the size of the nozzle. These nozzles are designed with the venturi effect to draw in air (Butler Ellis at al., 2002) to be mixed with the solution in a low-pressure region inside the nozzle (Post, 2019). Drift related research has been conducted by many university, industry, and government entities. Performing large-scale spray drift trials in the field is a challenging endeavor, subject to the environmental conditions that cannot be controlled, but important for risk assessment. During 1990s a big effort was made to generate pesticide spray drift data for a variety of nozzles as part of the Spray Drift Task Force (SDTF) (Hewitt et al. 2002). This database was developed to improve the data for regulatory decision-making and provide a basis for the evaluation of risk mitigation strategies. The US EPA requires numerous studies for the registration of pesticide active ingredients. Some of those studies are for setting a no-spray buffer distance protective of downwind off-field nontarget plants (Moore et al. 2022), or approving a tank-mix partner for restricted use growth regulator herbicides (EPA 2022). Even though models being used today for risk assessment are practical and made to be conservative, the data they are built on – application nozzles and equipment – is now considered outdated. One of the models, Agricultural Dispersal (AGDISP), uses the deposition curves collected by SDTF for drift estimation. As computers are used in the guidance and application systems of modern equipment into decision making, it is important that users understand the limitations these models might have.

The objectives of this research were to collect empirical data on drift potential for AI nozzles and compare with AGDISP data.

Materials and Methods

The experiment was conducted at the West Central Water Resources Field Laboratory in Brule, NE, and at the Pesticide Application Technology Laboratory (PAT Lab) located at the West Central Research and Extension Center, North Platte, NE, both of the University of Nebraska – Lincoln.

Field Study

The trial was conducted in summer of 2020 in a corn stalk fields in Brule, NE to evaluate downwind deposition for AI nozzles. The trial was designed in a randomized complete block design with five nozzle treatments each being replicated eight times. Nozzles used were AIXR11004 (Air induction extended range flat fan, Teejet® Technologies Spraying Systems, Glendale Heights, IL), GA11004 (Guardian Air, Pentair Hypro, Waterfords, WI), TDXL11004 (TurboDrop XL, Greenleaf Technologies, Covington, LA) and TTI11004 (Turbo Teejet Induction, Teejet Technologies Spraying Systems). ER11004 (Combo-Jet non-venturi spray tip, Wilger Inc., Lexington, TN) served as a baseline for comparing drift reduction. The applications were made with John Deere 4830 (John Deere, Moline, IL) sprayer equipped with 40 nozzles spaced 0.76 m apart, and 0.6 m boom height. Sprayed solution consisted of water and pyrene-tetra-sulfonic acid tetra-sodium salt (PTSA) fluorescent tracer at 5 g L^{-1} to deliver 140 L ha^{-1} at 276 kPa and 2.4 m s^{-1}. Each spray line was 160 m long, with a spray swath of 33 m. During applications, meteorological conditions (wind speed, wind direction, air temperature, and relative humidity) were collected at 1-min intervals using a HOBO RX3000 Weather Station

(Onset Computer Co., Bourne, MA, USA). The sensors were positioned at 2 m above the ground level. The wind speed and direction data were collected using 2D WindSonic anemometers (Gill Instruments, Lymington, UK). Data from the anemometer were used to determine which applications fall under the ISSO 22866 guidelines (ISO, 2005), that is wind direction being within 30° perpendicular to the spray swaths and wind speed approximately 3.1 - 4.5 m s^{-1}. The environmental data were also used for AGDISP modeling.

Sampling

Mylar cards (Grafix Plastics, Cleveland, OH) were used to collect downwind deposition at 0.5, 1, 2, 3, 4, 6, 8, 10, 15, 20, 40 and 80 m. Collectors were positioned at 0.18 m height in three lines spaced 3 m perpendicular to the spray line (Figure 1). Three minutes after applications, Mylar cards were placed in plastic ziplock bags and stored in dark containers to avoid PTSA degradation. The collectors were washed off with premixed distilled water and 91% isopropyl alcohol (9:1). After PTSA dye was suspended in the wash solution, pipette was used to extract 5 ml into cuvettes. PTSA recovery was measured at the PAT Lab with Flame-S spectrofluorometer (Ocean Insight, Orlando, FL).

AGDISP Inputs

AGDISP (v9.0) was used to model the spray drift. The estimation of downwind deposition is dependent on several parameters including equipment configurations, droplet size distribution (DSD), environmental conditions, and spray material properties. Default values for the parameters not listed were not changed in the model.

DSDs for the same nozzles used in the field study were conducted at the PAT lab wind tunnel facility. DSD was evaluated using a laser diffraction system (HELOS/VARIO KR, Sympatec Inc., Clausthal, Germany). The system was equipped with R7 lens that detects droplets in a range from 9 to 3500 µm. Creech et al. 2016 explains in-depth laser configuration. Nozzles were positioned 0.3 m from the laser beam to ensure full break-up of the spray sheet. Nozzles were calibrated to deliver 0.03 L s^{-1} at 276 kPa. With nozzles attached to the actuator and traversed vertically at a constant speed of 0.2 m s^{-1}, the entire spray plume was able to cross the laser beam. Applications were performed at the constant wind speed of 6.7 m s^{-1}. Each treatment was replicated three times. Parameters of interest were Dv10, Dv50, Dv90 - the droplet diameters at which 10, 50 and 90% of the spray volume is contained in droplets of lesser diameter, respectively, driftable fines (DF) - volume percentage of droplets in size less than 141 µm, and relative span (RS) (ASABE Standards, 2016). Relative span measures the uniformity of the DSD, calculated using the Equation 1:

$$RS = \frac{(D_{V90} - D_{v10})}{D_{v50}} \qquad [1]$$

Where:

RS = relative span (dimensionless)

Dv90 = volumetric diameter of droplets in which 90% of the total spray volume is contained in droplets of lesser diameter (µm)

Dv50 = volumetric diameter of droplets in which 50% of the total spray volume is contained in droplets of lesser diameter (µm)

Dv10 = volumetric diameter of droplets in which 10% of the total spray volume is contained in droplets of lesser diameter (µm).

DSD data was imported into AGDISP using User-defined, Import option in the model (Table 1). Wind speed, wind direction, relative humidity and temperature monitored during applications were also implemented in the model (Table 2). Using the measured droplet size data for the nozzles tested in the field and meteorological conditions recorded for each application, AGDISP was used to predict the resulting downwind deposition.

Statistical Analysis

Normality of residuals and homogeneity of variance of data were analysed by Kolmogorov-Smirnov and Levene's tests, respectively, using SPSS Statistical Software, version 20 (SPSS Inc., Chicago, IL, USA). When the assumptions were significant at $\alpha = 0.01$, data were transformed by $(x + 0.5)^{0.5}$. Data were subjected to analysis of variance (ANOVA) using Sisvar Statistical Software, version 5.6 (Ferreira, 2011), considering a split plot design, being nozzle type as main plot and distance as subplot. Nozzles were compared to each other within each distance by Tukey's multiple comparison test, whereas regression analysis was performed for the distances, both at $\alpha = 0.05$. Regressions were adjusted using R Software, version 3.2.3 (R Foundation for Statistical Computing, Vienna, AUT) and data were fitted to the three-parameter log-logistic model of the *drc* package at 95% confidence interval according to the Equation 2 (Ritz et al., 2015):

$$y = d / (1 + \exp(b/\log(x+e))) \qquad [2]$$

in which y is the spray deposition ($\eta\text{L cm}^{-2}$), b is the slope at the inflection point, d is upper limit ($\eta\text{L cm}^{-2}$), e [(inflection point (m)] represents 50% y relative to d, and x is the downwind distance (m). This was the top model based on log likelihood of the function *mselect* in the *drc* package.

Results and Discussion

Droplet size classification

Droplet size distribution values – Dv10, Dv50, Dv90, DF, and RS for ER, GA, AIXR, TDXL, and TTI nozzles are reported in Table 3. Droplet size classifications were established in accordance with the reference nozzles (ASABE S572.3). In further text, each nozzle will be referred to the droplet size classification they fall under. That is, ER – F (fine) spray, GA – C (coarse) spray, AIXR – VC (very coarse) spray, TDXL – VC (very coarse) spray, and TTI – EC (extremely coarse) spray. DSD parameters – Dv10, Dv50 and Dv90 – were significantly different for the nozzles tested (α=0.05).

Field Study

Meteorological conditions during the applications met the recommendations of the ISSO 22866 standard (ISO, 2005), which indicates that the temperature must be between 5 and 35 °C, with a wind direction of 90°±30° relative to the spray line. Treatment replications that were outside of the wind direction recommendation were not included in statistical analysis. A wide range of wind speeds was measured during applications to allow for an evaluation of AGDISP's sensitivity to wind speed.

It was generally observed that as droplet size increases, downwind deposition decreases (Figure 2). Non-AI nozzle producing F spray had the greatest downwind deposition across all distances. AI nozzles producing C-UC spray had similar downwind deposition beyond 4 m from the treated area, even though producing a range of 441 to 774 μm for Dv50, and a range of 0.3 to 3.1 % DF. The highest and lowest percentages of applied were 25.6 for F spray at 2 m and 0.01 for VC and EC spray at 80 m. These results were expected due to differences in droplet size distributions between the sprays. It was previously recorded that spray drift is largely influenced by droplet size, with larger Dv50 resulting in less drift (Ellis et al. 2002, Bueno et al. 2017, Vieira et al. 2018).

At 2 m downwind, non-AI nozzle producing F spray had 3.1-, 6.7-, 8.1- and 8.5 x drift than GA (C), AIXR (VC), TDXL (VC), and TTI (EC) nozzle, respectively. Even though GA and TTI produce coarse sprays, there was 10-fold difference in collected drift. This can be attributed to the differences in nozzle design. Moreover, it was recorded in the wind tunnel that GA and TTI produce 3.1 and 0.3 % droplets smaller than 141 μm, respectively. Droplets smaller than 141 μm were used as a parameter for the nozzle drift potential. As GA nozzle has a greater drift potential, more downwind deposition was collected compared to TTI. At 10 m downwind less than 1 % of applied was collected for AI nozzles producing C-EC spray. For the same distance F spray had at least three times more drift collected.

Similar results were observed by Bueno et al. 2017. XR nozzle (F) had the highest drift percentage in the area closest to the spray line (2.5 m). In contrast, lowest percentage of drift was recorded for TTI nozzle (VC), up to 7.5 meters. For distances greater than 10 m, drift from all nozzles (XR, TT, AIXR, and TTI) decreased (Bueno et al. 2017). It was observed that most PTSA dye recovered up to 2 m was for ER (F), TTI (UC), GA (VC), TDXL (EC), and AIXR (VC), respectively. Larger droplets are expected to fall out of the airstream sooner than smaller droplets (Derksen et al. 2007), which results in reduced downwind deposition. This was also confirmed by Perine et al. 2021 who observed downwind deposition of thiamethoxam at 3.8 m from 0.517 to 1.65 g a.i. ha^{-1} for XR11003 nozzles (F), compared to 0.068 to 0.569 g a.i. ha^{-1} for AIXR11002 nozzles

(VC). In a similar study, Brain et al. 2017 observed no atrazine injury on lettuce and cucumber at 1.5 and 4.6 m, respectively using TTI11004 nozzle.

Meteorological conditions recorded during applications varied from 2.4 to 4.9 m s^{-1}, 19.8 to 33.9 °C, and 37.6 to 91.2 % for wind speed, temperature, and relative humidity, respectively. It was observed that wind speed had the greatest influence on downwind deposition (Arvidsson et al. 2011, Nuyttens et al. 2005). Nozzle producing F spray was most sensitive to increase in the wind speed, whereas nozzle producing EC spray had least difference in wind speed change (Figure 3). Similar results were observed by Sousa Alves et al. 2017 who found exponential increase in downwind deposition for XR , TT and AIXR nozzles, while the increase in deposition for TTI (UC) was linear.

AGDISP modeling

As expected, nozzles ranked by their Dv50 values from lowest to highest was with ER nozzle, followed by GA, AIXR, TDXL and TTI at 247, 441, 517, 580, and 774 µm, respectively (Table 3). The order of magnitude for pct<141 was the opposite – 17.8, 3.1, 1.8, 1.1 and 0.3 % for ER, GA, AIXR, TDXL and TTI nozzle, respectively. However, pct<141 was not statistically different for AIXR and TDXL, and TDXL and TTI nozzles (P=0.05). According to the reference nozzles (ASABE S572.3), ER, GA, AIXR, TDXL and TTI were defined as F, C, VC, VC, and EC spray, respectively. The DSD results corroborate with the downwind depositions measured in the field study where most drift was collected for F spray, followed by C, VC and EC spray. Highest and lowest RS was recorded for ER and TTI nozzle, respectively. RS is a reflection of how tight the droplet sizes are around the median value and can be thought of as the amount of control over the atomization process that an operator has for a particular combination of application conditions (W. C. Hoffmann et al. 2008). High RS indicates decreased droplet size uniformity, and low RS indicates reduced range of droplet sizes and tight droplet size spectrum (Meyer et al. 2015).

To support these data, previous research have found similar results. Vieira et al. 2020 found that TDXL11004 produced larger Dv50 of 544 µm compared to AIXR11004 nozzle which produced Dv50 of 464 µm. These results were also confirmed by Butts et al. 2016 who observed that application of water with a TDXL11004 nozzle had greater Dv50 and less driftable fines than AIXR11004 at 276 kPa. Vieira et al. 2018 also reported greater drift potential for ER nozzle across solutions compared to TTI nozzle, with pct<150 of 22.6% and 0.6%, respectively. Similar results were observed by Dorr et al. 2013 who found greater drift potential for standard flat fan nozzle (XR) compared to air inclusion nozzles (AI and TTI). Sousa Alves et al. 2017 observed highest and lowest potential risks of drift by standard flat fan (XR) and air induction (TTI) nozzles, respectively, for dicamba and dicamba plus glyphosate solutions. The XR nozzle produced droplets that were on average four times smaller than the TTI nozzle. Ferguson et al. 2016 found up to 82% decrease in spray drift potential between Fine and Coarse categories.

Complete droplet size distributions measured in the wind tunnel were imported into AGDISP for each nozzle. That is, percentage of droplets less than a particular bin measuring the size of the droplet (Table 1). Other configurations are selected as follows: nozzle type – flat fan for ER, and air injected for GA, AIXR, TDXL and TTI nozzle; boom pressure set to 40 psi; 0.6 m release height; 1 spray line. For the application technique 40 nozzles 0.76 m apart were set with a swath width of 33 m. Meteorology data (wind speed, wind direction, temperature, relative humidity) recorded during the applications were altered for each spray. That is, for five nozzles and eight replications, there was 40 configurations that were ran in AGDISP. Spray material was set to 140 l ha^{-1} to replicate the field application. Surface was adjusted to 0.03. Default swath offset was set to 0 under the advanced settings.

AGDISP results show the same general trend as the one observed in the field. That is, ER nozzle producing F spray had the highest downwind deposition, followed by nozzles producing C, VC, and EC spray, respectively (Figure 3). It was observed that VC and EC spray had 0 downwind deposition above 20 m downwind. Even though the fraction of applied recorded at 10 m for these nozzles was low ($<e^{-9}$), it is possible that detection limit was reached for farther distances. It was recorded that AGDISP estimations underpredict the downwind deposition in all cases, except for ER nozzle at distances greater than 10 m where the deposition was overpredicted. At 2 m downwind deposition was underpredicted by 2-, 15-, 23-, and 167-fold for F, C, VC and EC spray, respectively. At 10 m downwind deposition was overpredicted for F spray by 1-fold, and overprediction increased with increasing the distance. This was previously reported by Connell et al. 2012. Previous literature on aerial (W. C. Hoffmann et al. 2007) and ground spray (M. E. Teske et al. 2009) estimations showed that model underpredicts the downwind deposition in near-field locations and overpredicts in far-field locations. Similar results were found by Woodward et al. 2008 who found that AGDISP overestimated the deposition for flat fan XR nozzles by 10-fold for 10-20m downwind. However, the literature is limited with the information on AI nozzles tested in the model. It was previously reported that the model underpredicts vertical fluxes for AI nozzles,

which could be a result of different properties, such as the droplet being less dense, and differing evaporation and breakup characteristics. Moreover, it is assumed that larger droplets beyond the cutoff size determined by the algorithm would impact the ground and foliage and would be removed before evaporation made them small enough to drift (M. E. Teske et al. 2009). Bird et al. 2002 found largest disagreement between model predictions and field measurements for the solid stream nozzle that produces VC spray on a helicopter.

More information is needed on AI nozzles producing large droplets. Updating the ASABE reference curves in the model might be the first step. This will allow for the coarser sprays to be estimated with more certainty. Nozzles producing EC sprays are highly used nowadays, especially for the products with extreme precautions for off-target movement. An additional dataset for nozzle properties is needed to improve the existing model. Tested in this study were four different AI nozzles producing C to EC sprays. Nozzle design, and that is the mechanism of drawing air in and air-liquid ratio, that essentially has the impact on the droplet density can influence the droplet velocity. More replications are needed under similar weather conditions and application parameters and configurations to provide representative sample.

Conclusions

Field study corroborates the droplet size generated in the wind tunnel for the nozzles tested - ER nozzle producing F spray (DF=17.8%) had the highest downwind deposition collected, followed by GA with C spray (DF=3.1%), AIXR with VC spray (DF=1.8), TDXL with VC spray (DF=1.1) and TTI with EC spray (DF=0.3%), respectively. The same trend was observed with AGDISP estimations. However, the total downwind deposition was underpredicted by AGDISP for the nozzles tested. AGDISP overpredicted the deposition for ER nozzle at 10-80m. Future ground model development focused on nozzle type to get accurate downwind deposition for air inclusion nozzles is necessary if the models are going to be used to determine buffers or other regulatory decisions beyond bridging studies to empirical data.

List of Tables

Table 1. Droplet size distribution use in AGDISP measured with laser diffraction system.

DS diameter	Nozzle*				
	ER	GA	AIXR	TDXL	TTI
µm	%				
18	0.0	0.0	0.0	0.0	0.0
22	0.0	0.0	0.0	0.0	0.0
26	0.0	0.0	0.0	0.0	0.0
30	0.1	0.0	0.0	0.0	0.0
36	0.4	0.0	0.0	0.0	0.0
44	0.8	0.0	0.0	0.0	0.0
52	1.3	0.0	0.0	0.0	0.0
62	2.2	0.1	0.0	0.0	0.0
74	3.7	0.2	0.1	0.0	0.0
86	5.5	0.5	0.2	0.1	0.0
100	8.1	0.8	0.5	0.3	0.0
120	12.5	1.5	1.0	0.6	0.2
150	20.3	2.9	2.0	1.3	0.4
180	29.1	4.9	3.6	2.4	0.8
210	38.5	7.5	5.6	3.8	1.4
250	51.1	11.9	9.0	6.2	2.5
300	65.7	18.9	14.6	10.2	4.4
360	79.8	29.5	23.2	16.5	7.5
410	89.5	41.5	33.5	24.3	11.6
500	96.4	57.9	48.6	36.3	18.5
600	99.3	76.4	67.1	52.5	28.9
720	100.0	91.6	85.2	71.7	43.2
860	100.0	98.8	96.5	89.3	61.2
1020	100.0	100.0	99.9	99.8	81.2
1220	100.0	100.0	100.0	100.0	99.9
1460	100.0	100.0	100.0	100.0	100.0
1740	100.0	100.0	100.0	100.0	100.0
2060	100.0	100.0	100.0	100.0	100.0
2460	100.0	100.0	100.0	100.0	100.0
2940	100.0	100.0	100.0	100.0	100.0
3500	100.0	100.0	100.0	100.0	100.0

*All nozzles are 11004

Table 2. Average temperature, relative humidity and wind speed recorded during applications.

Replication	Nozzle*	Temperature	Relative humidity	Wind speed
		°C	%	m s^{-1}
1	ER	19.8	90.9	2.7
1	GA	21.6	85.2	3.5
1	AIXR	21.0	87.8	3.4
1	TDXL	22.5	82.4	3.2
1	TTI	22.2	83.4	2.8
2	ER	23.5	79.4	3.8
2	GA	26.0	71.9	4.5
2	AIXR	26.7	69.1	3.8
2	TDXL	24.7	76.0	3.8
2	TTI	25.1	73.5	4.4
3	ER	28.4	62.2	3.8
3	GA	29.4	61.3	3.0
3	AIXR	27.8	66.1	3.8
3	TDXL	28.1	62.1	3.1
3	TTI	28.2	62.3	3.3
4	ER	31.6	39.1	4.8
4	GA	31.3	37.6	4.8
4	AIXR	31.7	38.9	4.7
4	TDXL	31.1	38.6	4.9
4	TTI	31.2	38.8	4.1
5	ER	31.1	38.7	4.5
5	GA	32.0	39.4	3.4
5	AIXR	31.3	41.3	4.9
5	TDXL	32.2	38.9	3.9
5	TTI	31.6	39.8	4.5
6	ER	32.4	38.9	4.5
6	GA	31.7	39.2	4.4
6	AIXR	31.9	40.1	4.1
6	TDXL	31.9	39.1	4.4
6	TTI	31.8	43.0	3.7
7	ER	31.6	42.7	2.4
7	GA	31.5	45.5	3.5
7	AIXR	30.7	45.4	2.5
7	TDXL	30.8	44.3	2.6
7	TTI	32.0	42.0	2.8
8	ER	32.9	36.7	5.9
8	GA	33.4	36.8	4.2

8	AIXR	33.8	36.8	2.2
8	TDXL	32.2	41.4	2.7
8	TTI	33.1	36.2	2.7

*All nozzles are 11004

Table 3. Droplet size distribution parameters and classifications for ER11004, GA11004, AIXR11004, TDXL11004, and TTI11004 at 276 kPa.

Nozzle	Dv10[1]	Dv50	Dv90	DF[2]	Relative span[3]	Droplet size classification[4]
	———	μm	———	%	-	
ER	109 E	247 E	423 E	17.8 A	1.3 A	F
GA	219 D	441 D	685 D	3.1 B	1.1 BC	C
AIXR	258 C	517 C	812 C	1.8 C	1.1 B	VC
TDXL	291 B	580 B	886 B	1.1 CD	1.0 C	VC
TTI	393 A	774 A	1118 A	0.3 D	0.9 D	EC

[1] Dv10, Dv50, Dv90 parameters represent the droplet size such that 10, 50, and 90% of the spray volume is contained of droplets of lesser diameter, respectively

[2] Driftable fines represent percent of spray volume that contains droplets less than 141 μm

[3] Relative span is a dimensionless parameter that estimates the spread of a distribution

[4] Droplet size classification in accordance with the reference nozzles (ASABE S572.3): F - Medium, C – Coarse, VC – Very Coarse, EC – Extremely Coarse

List of Figures

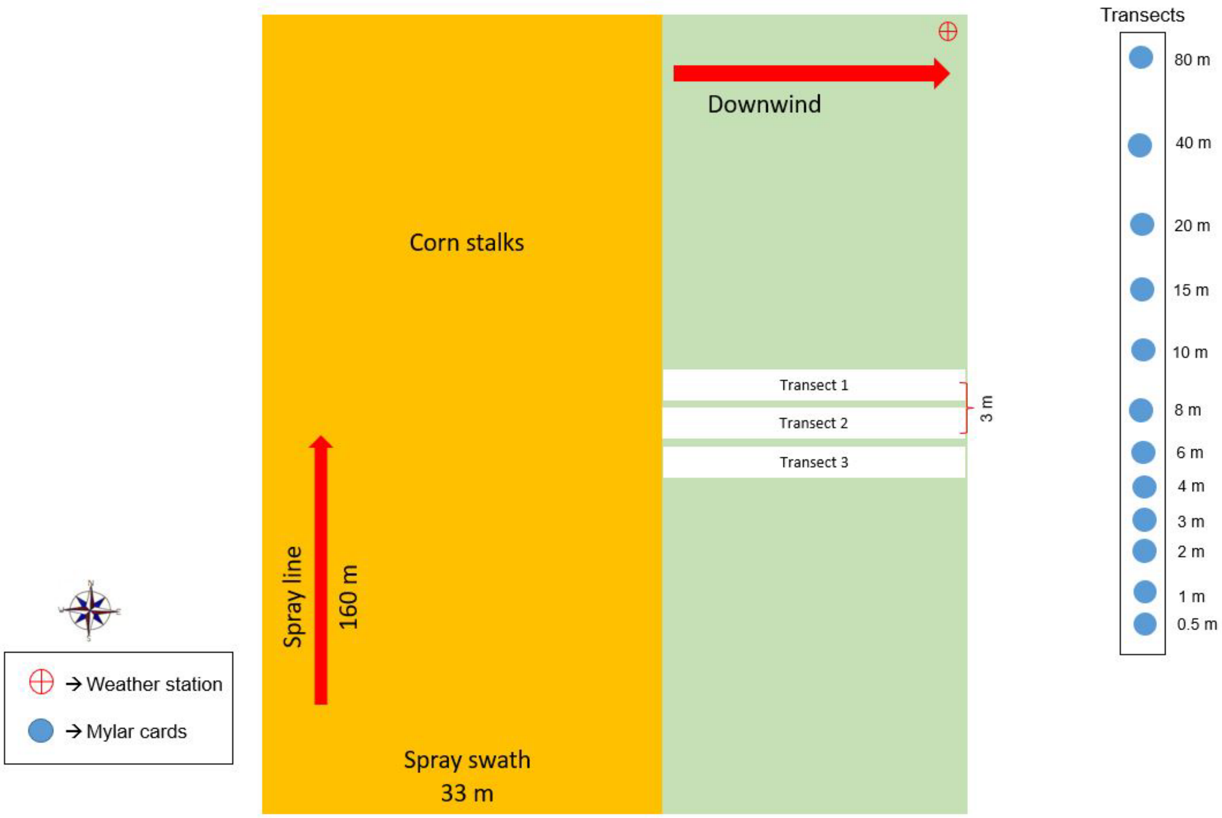

Figure 1. Field layout at the time of applications.

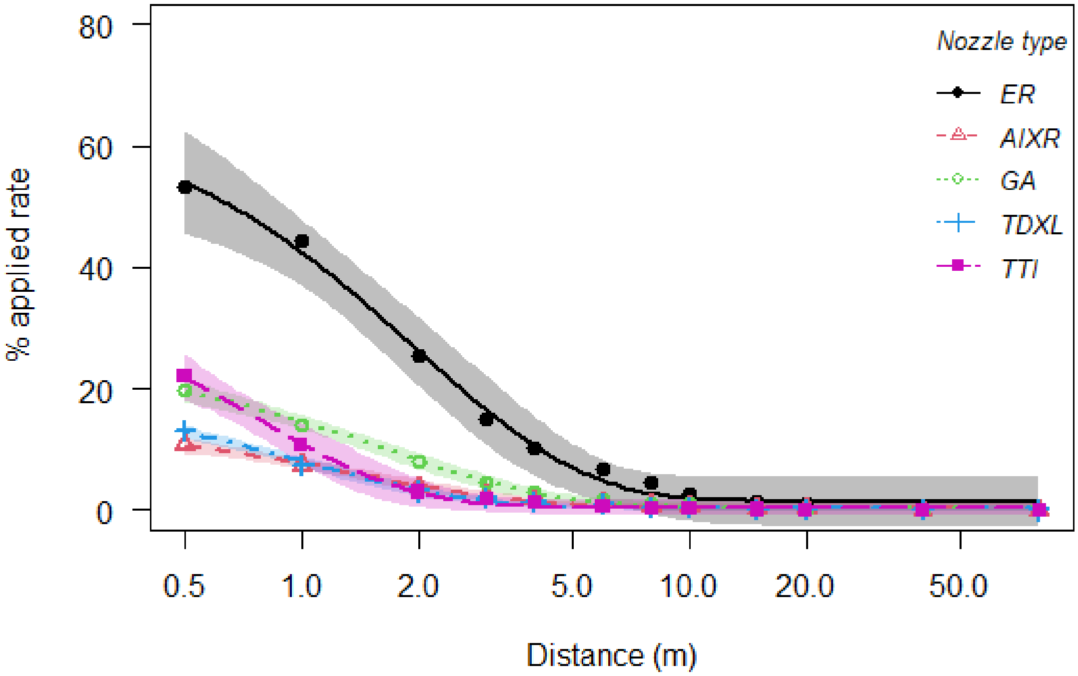

Figure 2. Percentage of applied measured across downwind distances for ER11004, GA11004, AIXR11004, TDXL11004 and TTI11004 with water and PTSA dye (5 g L^{-1}) sprayed at 140 L ha^{-1}.

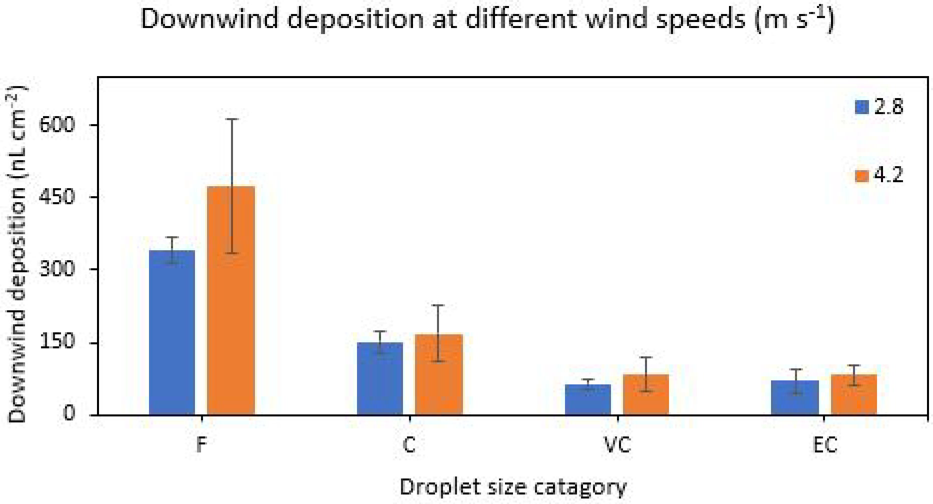

Figure 3. Downwind deposition averaged across 3-15 m downwind distances for F – fine, C – coarse, VC – very coarse and EC – extremely coarse spray (ASABE S572.3) at 2.8 and 4.2 m s^{-1} wind speed.

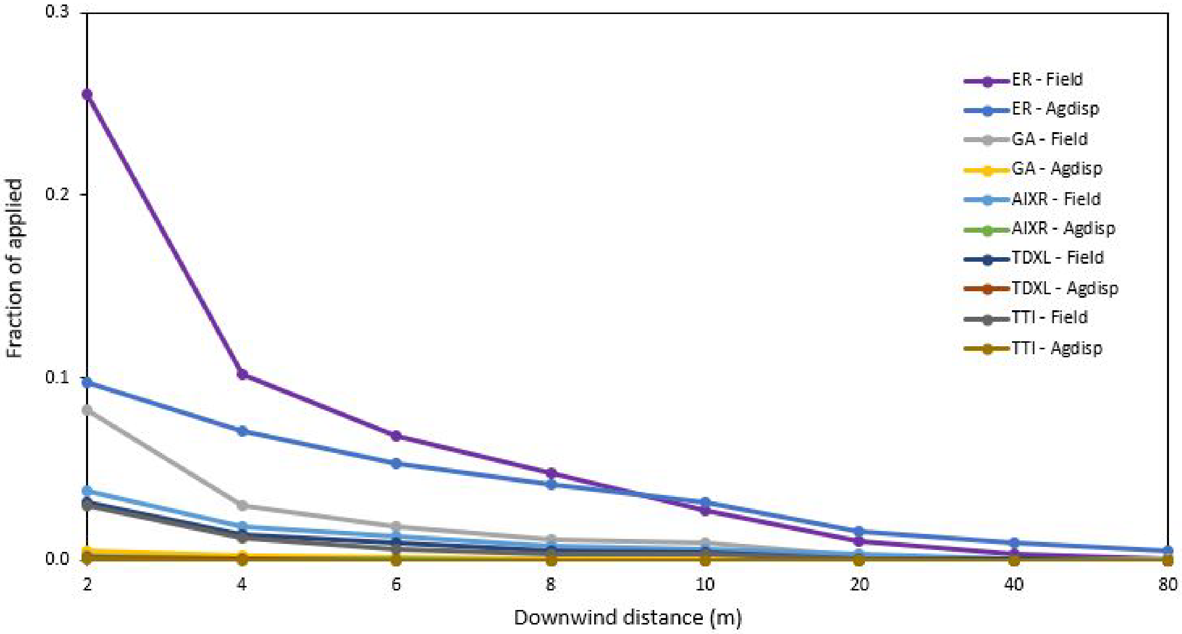

Figure 4. Field vs AGDISP downwind deposition expressed as fraction of applied for 140 L ha^{-1}.

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Thesis Summary

Water often comprises at least 95% of the spray solution. Its effect on product efficacy can be reflected in the success of the spray operation. Water is usually viewed as a clean input, and not a lot of thoughts are given on its purity. However, some water properties, such as water hardness and pH, can skew the herbicide application process. Previous research has shown that weak acid herbicides, such as 2,4-D and glyphosate, have reduced activity on weed control in hard water and high pH, and that the response is weed species-, herbicide- and water hardness dependent. Hard water contains dissolved minerals, with Ca^{2+} and Mg^{2+} being predominant, which can be problematic when used as a carrier for weak acid herbicide applications. These cations can easily react with the herbicide, which leads to decreased herbicide penetration into the plant cuticle or can cause precipitation of the herbicide from the solution. To prevent the formation of the hard water cation-herbicide complex, addition of water conditioning adjuvant is recommended. Ammonium sulfate (AMS) is most used water conditioner. Ammonium ions build a complex with a weak acid herbicide and outcompete the antagonistic cations which leads to enhanced herbicide absorption and translocation. The sulfate anions bind with the antagonistic cations preventing the formation of hard water cation-herbicide complex which is less readily absorbed. The addition of AMS also increases ammonium accumulation in the cell which alters the pH. The increase of hydrogen inside the cell decreases cellular pH if allowed to accumulate. To maintain cytoplasmic pH in the range of 7.5-8, hydrogen ions are pumped across the cell membrane into the cell wall. This causes the cell wall pH to become more acidic. For weak acid herbicides, acidic conditions cause more of the herbicide molecules to be present in non-ionized, lipophilic form which allows for passing through the cell membrane.

In the effort to better understand how water quality affects herbicide performance we designed two projects investigating addition of water conditioning adjuvants and testing several levels of water hardness and pH on herbicide efficacy. The results have shown that addition of phosphoric acid to glufosinate and glyphosate increases weed biomass reduction, as well as addition of phosphoric acid and AMS to 2,4-D compared to herbicides alone in 240 ppm water hardness and 7 pH. It was also observed that herbicides applied in soft water at high carrier volume (187 L ha^{-1}) are not statistically different than herbicides applied in 1000 and 1500 ppm water hardness at low carrier volume (47 L ha^{-1}). Due to label restrictions Enlist One (2,4-D) and Liberty (glufosinate) cannot be applied at 47 L ha^{-1}. This only emphasizes that addition of water conditioning adjuvant will be important when 2,4-D and glufosinate are applied in very hard high carrier volume. It was also observed that smaller droplet size (150 µm) increases biomass reduction for waterhemp and common lambsquarters, whereas larger droplet size (900 µm) increases green foxtail biomass reduction when glufosinate and glyphosate are applied in 187 L ha^{-1}. However, when applied in 47 L ha^{-1} droplet size is not significant. Again, low carrier volume and more concentrated droplets manage to overcome the antagonistic hard water cation effect since there is far less cations to bind with the herbicides.

Before starting a tank mix, water should be tested to see if any properties need to be altered with water conditioners for maximum spray application effectiveness. If found that water has unfavorable conditions for a certain herbicide, water conditioning adjuvant should be added to the tank prior the addition of an herbicide. Since this research was conducted in the greenhouse, therefore reduced herbicide rates were used for better observing differences among treatments, it would be beneficial to repeat the studies in the field. This would allow for weeds to be more vulnerable to the environmental conditions and also use of the label recommended rates that would genuinely represent the influence of water quality on herbicide performance.

Once the spray solution characteristics are managed, applicators need to make sure they have the correct set up for optimized pesticide application. This includes nozzle selection, boom height and equipment calibration. Optimized pesticide application means making sure that most of the (already managed) solution being sprayed is deposited onto the target. Off target movement has been a concern since the introduction of pesticides. Intensive use of auxin herbicides has brought greater attention to minimizing spray drift. This resulted in changing label recommendations and label restrictions for tank-mix partners increasing the spray drift. One of the first steps in managing drift is nozzle selection. Selecting a nozzle that produces large enough droplets to resist being carried with the wind, but provide efficient coverage is crucial in pesticide applications. Introduction of air inclusion nozzles – nozzles that can provide much larger droplets than conventional flat fan nozzles under the same flow rate – allowed farmers to enhance pesticide application. Many efforts were given to understanding pesticide drift by performing field large-scale drift trials. These endeavors are challenging due to environmental conditions that cannot be controlled, time being consumed, and labor needed. However, they are crucial in building the data set that can help estimate the downwind deposition at certain conditions. The US Environmental Protection Agency uses Agricultural Dispersal (AgDISP) model for that purpose. AgDISP was initially developed for aerial applications, but overtime was updated with the ground model. However, the model needs more support with empirical data since the introduction of newer technology for broadcast applications. The purpose of our research was to collect the downwind depositions with air inclusion nozzles and compare the empirical data with the estimated depositions by AgDISP, and potentially update the model with more information on drift produced by these nozzles. The results show that the model tends to underpredict the downwind deposition across the nozzles and distances, and overpredict the deposition for the standard flat fan nozzle at greater distances (>10 m from the end of spray swath). These results were expected since the model was initially developed for aerial applications, and the ground model is more sensitive to larger droplets. Moreover, TTI nozzle produces droplets bigger in size than the model's upper limit.

It is of crucial importance that the model is handled correctly. The knowledge of the parameters in the model are essential before changing any of them. For example, choosing the Air Injection option over Flat Fan for the air inclusion nozzles is important because of the logarithms behind the model that calculate the jet velocity which is different between the two nozzle types. Also, setting the Swath Displacement to 0 under Advanced Settings since this option is for aerial applications.

The model has a great potential which was seen with numerous research on aerial applications, and the data collected in our research is beneficial for better understanding the droplets faith once they exit the air inclusion nozzle.