

**DROPLET SIZE EFFECT ON HERBICIDE USED IN CEREALS
TO CONTROL DICOTYLEDONOUS WEEDS**

**A Thesis
Submitted to the Graduate Faculty
of the
North Dakota State University
of Agriculture and Applied Science**

By

Andrew Nathan Fillmore

**In Partial Fulfillment
for the Degree of
MASTERS OF SCIENCE**

**Major Department:
Plant Sciences**

January 2014

Fargo, North Dakota

North Dakota State University
Graduate School

Title

Droplet Size Effect on Herbicide Used in Cereals to Control
Dicotyledonous Weeds

By

Andrew Nathan Fillmore

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

MASTER OF SCIENCE

SUPERVISORY COMMITTEE:

Kirk Howatt
Chair

Richard Zollinger

Ted Helms

Samuel Markell

Approved:

1/17/14
Date

Richard Horsley
Department Chair

ABSTRACT

Experiments were conducted to evaluate the effect of droplet size on the efficacy of translocated and non-translocated herbicides. Translocated and non-translocated herbicides provided similar control when comparing droplet size effect on efficacy. Medium and very coarse droplet sizes gave the greatest visible injury whereas coarse-sized gave the lowest visible injury assessments for most species. However, droplet size generally did not affect contact herbicide efficacy. Overall, droplet size was not a strong factor contributing to herbicide efficacy and often, differences were only between herbicides.

Non-ionic surfactant solutions measured by a Sympatec droplet analysis system gave the highest percent of volume in droplets <150 μ m compared to other adjuvants. The lowest percent of volume in droplets <150 μ m was a 0.5x rate. A liquid herbicide formulation gave the largest percent of volume in droplets <150 μ m whereas an emulsifiable concentrate formulation was lowest. Percent volume in droplets <150 μ m was often related to the solution VMD.

ACKNOWLEDGMENTS

I would like to extend my appreciation and gratefulness to my major advisor, Kirk Howatt, for the patience, guidance, tutelage and funding that he provided for the extent of this research. In addition, I give thanks to Richard Zollinger, Ted Helms and Sam Markell for assisting as committee members and for their instruction and guidance.

Special thanks goes to Ron Roach, Sandy Mark, Mark Ciernia and all of our summer interns for their assistance with my field research. I would also like to thank the members of WinField Solutions; Andrea Clark, Lillian Magidow and Greg Dahl, for their support, professionalism and for the use of their WinField Product Development Center.

Furthermore, I would like to thank my internship mentors, Jamie Kloster and Tom Klevens, as well as my high school activities director Brad Skogerboe, for influencing my decision to pursue a graduate degree.

Thanks to all of my fellow graduate students and department staff, both past and present, for your assistance when needed. And lastly to my family, I especially thank you for your support, understanding and love while we were apart. I would not be where or who I am today without you

TABLE OF CONTENTS

ABSTRACT	iii
ACKNOWLEDGMENTS	iv
LIST OF TABLES	viii
LIST OF FIGURES	x
CHAPTER ONE: LITERATURE REVIEW	1
Introduction	1
Environmental Protection Standards	2
Plant Characteristics	3
Spray Droplet Size	5
Droplet Size and Herbicide Efficacy	9
Spray Retention	11
Herbicide Formulation	13
Literature Cited	16
CHAPTER TWO: DROPLET SIZE EFFECT ON EFFICACY OF WHEAT HERBICIDES TO FOUR SPECIES	20
Introduction	20
Materials and Methods	21
Results and Discussion	27
Summary	40
Literature Cited	41
CHAPTER THREE: HERBICIDE FORMULATION, ADJUVANT TYPE, AND NOZZLE EFFECT ON DROPLET SIZE USING SPRAY SPECTRUM LASER ANALYZER	43
Introduction	43
Materials and Methods	44
Results and Discussion	47
Summary	53
Literature Cited	55

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1. Planting, treatment and harvest dates, and plant height at application for experiments at Dalrimple Experiment Plots at the Agronomy Seed Farm in Casselton, ND	23
2. Planting, treatment and harvest dates, and plant height at application for experiments at North Dakota State University, Fargo, ND	24
3. TeeJet nozzle treatment settings for application by experiment	25
4. Visible injury on three species as influenced by droplet size 28 DAT.....	28
5. Visible injury of plant growth regulator herbicides on three species at 14 and 28 DAT as influenced by herbicide and droplet size	30
6. Fresh weights of three species 28 DAT as influenced by plant growth regulator herbicides and droplet size	31
7. Visible injury of ALS herbicides on three species 28 DAT as influenced by herbicide and droplet size.....	32
8. Fresh weights of three species 28 DAT as influenced by ALS herbicides and droplet size	33
9. Visible injury of non-translocated herbicides on four species as influenced by herbicide and droplet size at 14 and 28 DAT.	35
10. Visible injury of four herbicide treatments on four species 14 DAT as influenced by nozzle orifice size.	37
11. Visible injury of four herbicide treatments on four species 28 DAT as influenced by nozzle orifice size.	38
12. Fresh weight of four species 28 DAT with herbicides as influenced by nozzle orifice size.	39
13. Percentage of volume in droplets <150µm of four adjuvant and two nozzle types influenced by adjuvant rate averaged across two nozzle types and two runs.	48
14. Spray characteristics of four adjuvants averaged across rate and nozzle type.	49
15. Volume mean diameter of four adjuvants and two nozzles influenced by adjuvant rate for each of two runs.....	50

16. Percent of volume in droplets <150µm and volume mean diameter of adjuvants influenced by nozzle type, averaged across adjuvant rate.	51
17. Percent of volume in droplets <150µm averaged across herbicide rate.....	53

LIST OF FIGURES

<u>Table</u>	<u>Page</u>
1. Turbo TeeJet® nozzle by Spraying Systems, Inc, P.O. Box 7900, Wheaton, Illinois	8
2. Extended Range Flat Fan and Air Induction Flat Fan nozzles by Spraying Systems, Inc	8

CHAPTER ONE: LITERATURE REVIEW

Introduction

Environmental contamination by pesticides can result from a number of sources. Off-target particle drift is one source of contamination considered preventable through adjustment of application equipment for droplet size. Problems such as these are investigated extensively by chemical companies and universities to ensure environment safety by advocating farmer stewardship. Droplet size of herbicide spray is affected by many factors and can influence environmental movement through airborne particles called spray drift. Manipulating droplet size in addition to other droplet control measures may be able to provide an effective means to kill weeds, minimize drift and satisfy regulations. Chemical drift has long been a concern which could be minimized by adjustments to produce larger droplets. However, weed control could be reduced if spray droplet size becomes too large.

Herbicide spray droplet experiments have been conducted but provided limited information on the relationship between droplet sizes and weed control (Prasad and Cadogen 1992). Also, the complexities of herbicide chemistry, formulation components and adjuvants could have a range of influences to herbicide efficacy. Understanding the role of spray droplet size in herbicide efficacy could improve consultant recommendations. Outdated studies contribute to a lack of knowledge with current herbicide formulations and technologies. Comprehensive understanding of droplet size effects across herbicides could result in refined nozzle tip choices and droplet size ranges for specific herbicides. This could result in greater efficiency for farmers and a platform for the EPA to enact manageable regulations.

Environmental Protection Standards

The Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) defines pesticide as any substance or mixture of substances intended for preventing, destroying, repelling or mitigating any pest, and any substance or mixture of substances intended for use as a plant growth regulator, defoliant or desiccant (Horne 1992). Pesticide drift to unintended areas can cause exposure to humans, animals, water sources, and other unintended consequences. The Environmental Protection Agency (EPA) sets the tolerance levels for all pesticides that accumulate on raw commodities consumed by humans or animals or potentially impact the environment (Merrill and Schewel 1980). For this reason, the focus on herbicide drift reduction is in the hands of the EPA and the Food and Drug Administration (FDA) to maintain healthy food supplies by setting safe tolerances and assuring marketed food meets these designated tolerances while minimizing complaints of off-target crop injury and damage to the environment. Crop injury by off-target movement is addressed on pesticide labels through company statements to reduce drift; increasingly these statements include recommendations for large droplet size. The EPA's focus in developing standards was for the public health of the United States, but in recent years, foreign markets have become the target of interest to consider when setting tolerance levels (Fein 2003). Therefore, United States regulatory members are urged to take foreign standards for health into account.

EPA regulations, until recently, were based upon original historic toxicology studies presented by pesticide companies. Data were evaluated to determine the tolerance levels for human consumption. With the development of the Food Quality Protection Act (FQPA), the EPA was to reassess most pesticide toxicity by 2006 (Oleskey et al. 2004). This included retesting nearly 9000 pesticides on the market. The FQPA prioritized the regulations to focus on

human health and publishing of human tolerance findings before release dates. The use of humans for toxicity levels became the standard for testing. This use helped to defend “no observed effect levels” (NOELs). These NOELs refer to the maximum tested dose at which pesticides did not produce biological effect. To complete the necessary studies of the pesticides, the spray drift task force (SDTF) was jointly formed by multiple registrant companies (Hewitt 2000). Extensive review was performed by government, academic and industrial scientists.

Many attempts to develop assessment models that define safe distances from pesticide application have been made in an effort to reduce drift exposure to bystanders. Models such as the Bystander and Residential Exposure Assessment Model (BREAM) and the Silsoe spray drift model have been used in the United Kingdom to estimate measurements (Butler Ellis et al. 2010). Other drift models have been supported and jointly developed by the EPA, the SDTF, and the United States Department of Agriculture (USDA) (Anonymous 2001). Predictions of particle movement are based on nozzle type, orifice size, fan angles, discharge angle relative to airstream, spray pressure and physical properties of the spray mixture.

Plant Characteristics

Retention of herbicide droplets on leaves is dependent upon many factors but is a contributor to leaf coverage and herbicide efficacy. To determine efficacy difference between droplet sizes, plants that represent a range of characteristics and offer practical evaluation are used in field experiments. Range of characteristics refers to commonly occurring weed species with both horizontally and vertically orientated leaf surfaces. Variation in leaf surface texture and morphological structures can influence retention of droplets as well as movement through the cuticle.

Amaranthus species are common broadleaf weeds spreading across the United States (Gossett and Toler 1999). Palmer amaranth (*Amaranthus palmeri* S. Wats) and redroot pigweed (*Amaranthus retroflexus* L.) are closely related and invade cropland. Both are troublesome weeds in much of North America and cause yield reduction in corn, soybean, wheat and many other annual crops. The prevalence of Amaranth weed species has rebounded after the adoption of reduced-till practices, the development of herbicide resistance and variable herbicide susceptibility. Palmer amaranth is capable of aggressively competing with corn based upon its emergence in relation to corn emergence dates (Rafael et al. 2001). Similarities between cultivated Amaranth species and palmer amaranth make Amaranth a suitable species to include in studies of spray droplet size because of glabrous leaf texture and horizontal leaf orientation (Bond and Oliver 2006).

Other indicator species have desirable characteristics for herbicide droplet studies as well. Quinoa (*Chenopodium quinoa* L.) is a member of the *Chenopodium* genus that contains more than 120 species (Aellen 1960). This genus is part of the Goosefoot family known as *Chenopodiaceae* (Mitich 1988). Quinoa is a cultivated crop in some parts of the world and originated in South America where it is still widely grown (Heiser 1979). Quinoa is a part of the same genus as the problematic weed common lambsquarters (*Chenopodium album* L.) and has many of the same characteristics, plant morphology, and physiology pertaining to weed control. Common lambsquarters is a major problem in many agricultural fields, especially in potato and sugar beet (Mitich 1988). It also has very high occurrence in soybean and corn in North America. Common lambsquarters has variable leaf placement with a horizontal orientation and leaves contain a mealy leaf texture produced by waxy beads.

Common buckwheat (*Fagopyrum esculentum* Moench. 'Mancan') is a relative to the cultivated tartary buckwheat (*F. tartaricum* (L.) L.J. Gaertn.) (Friesen and Campbell 1986). Tartary buckwheat is cultivated throughout Canada but also is a relative to the weed wild buckwheat (*Polygonum convolvulus*). Buckwheat species have very waxy leaf cuticles that can repel herbicide solutions. The waxy leaf cuticle possesses differing wetting ability than either Amaranth, glabrous, or Quinoa, mealy leaf texture produced by waxy beads. Buckwheat is similar to both Amaranth and Quinoa with horizontal leaf orientation and upright stem growth competitive to most agricultural crops.

Flax (*Linum usitatissimum* L.) is an oil seed crop that is also grown for its fiber qualities. The scientific name, *Linum usitatissimum*, translates to “linen most useful”, describing the importance and long standing history (Hamilton 1986). The use of flax as an agronomic crop optimized fiber production in flax (Akin 2012). The durability of flax as a fiber crop made it a suitable candidate for herbicide difference evaluation as well its ability to grow in colder climates. Resilient stems and complex composition could deter absorption and facilitates solution run off. Flax leaves can have a horizontal to diagonal orientation providing a suitable leaf surface to observe herbicide droplet retention characteristics.

Spray Droplet Size

Pesticide droplet and spray formation are dependent on a variety of system operation characteristics. Variations of these components will alter properties of droplet formation and the spray droplet size spectrum. Droplet formation is dependent on nozzle size and type, pressure exerted on the solution and droplet physical properties (Hanks 1995). An important measurement with which the spray spectrum is measured is referred to as the volume median diameter (VMD).

VMD is the most common measurement of spray droplet size (Matthews 1979). VMD is the droplet size for which half of the volume of spray is in smaller droplets than the VMD and half of the volume is in larger droplets than the VMD.

Pressure exerted to the spray solution is an important influence on droplet sizes. Studies showed that VMD of spray spectrums decreased as pressure increased (Hanks 1995). Inversely, VMD increased as pressure exertion decreased. Research also showed that VMD increased as the flow rates (orifice size) of a nozzle increased, indicating that application pressure and primary orifice size have significant influence on droplet size (Hanks 1995; Nuyttens et al. 2007).

Although VMD is widely used to describe a droplet spectrum, additional spray characteristics are withheld. VMD does not categorize droplets prone to drift or of extremely large size. Consequently, in addition to VMD, other measurements are necessary for describing spray spectrum characteristics: $Dv_{0.1}$, $Dv_{0.25}$, $Dv_{0.75}$, $Dv_{0.9}$ and relative span. For example, $Dv_{0.1}$ represents the droplet diameter in μm with which smaller droplets constitute 10% of the spray volume (Nuyttens et al. 2007). Relative span represents variation in the spray spectrum and is calculated by subtracting the $Dv_{0.1}$ value from the $Dv_{0.9}$ value and dividing by the $Dv_{0.5}$. A smaller number represents less variation within the spray spectrum, or a narrower distribution peak. Hanks and McWhorter (1993) identified that the addition of an oil adjuvant compared to water alone provided a narrower relative span. A narrower relative span indicates that droplets will be more similar in size to the VMD.

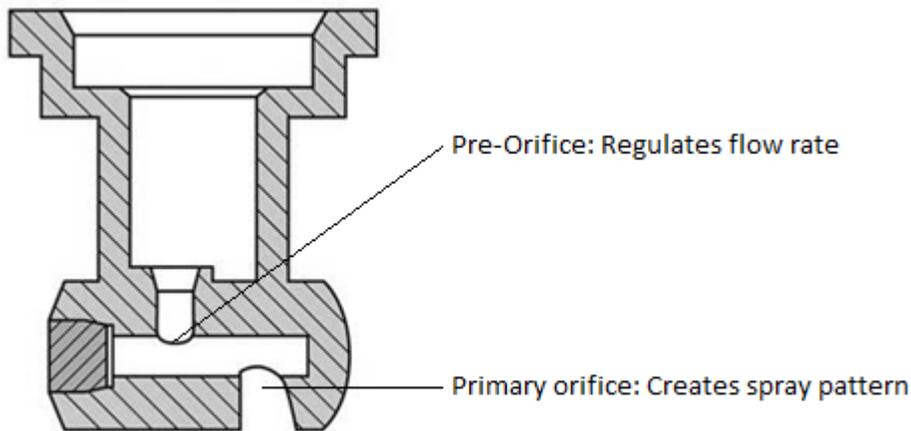
There are different spectrums of spray solution classification. The American Society of Agricultural and Biological Engineers (ASABE) organized standards for advancement of agricultural engineering. ASABE had developed universal droplet size categories to be used in reference to pesticide application. Nozzles classified as producing very fine ($<136 \mu\text{m}$), fine

(136-177 μm), medium (177-218 μm), coarse (218-349 μm), very coarse (349-428 μm), extremely coarse (428-622 μm) or ultra-coarse (>622 μm) spray droplets (ASAE 2009). When addressing problems of drift, fine droplets are of concern. Although a universal droplet size is not consistent among research, <100 μm droplet size often is targeted as driftable. Farooq et al. (2001) indicated that droplets less than 100 μm were separated from larger droplets and were moved downwind from larger droplets. Droplet sizes of 150 to 200 μm have been investigated as a threshold for minimizing droplet movement by airflow (Bode 1987). Similar interpretations of the driftable portion are followed by commercial spray system producers. Wind tunnels are used to investigate and evaluate droplets prone to drift. Also, water-sensitive paper is used in applied situations to show deposition of spray droplets and classify sizes of droplets applied (Matthews 2000).

Nozzle body types that incorporate a pre-orifice are believed to reduce the pressure on solutions exiting the primary orifice (Figure 1). This concept is practiced to reduce the number of droplets in the spray spectrum that are prone to drift. Use of nozzles with a pre-orifice such as a TurboTee reduced the percent of spray volume in droplets <191 μm by 18.7% with glyphosate formulations (Mueller and Womac 1997).

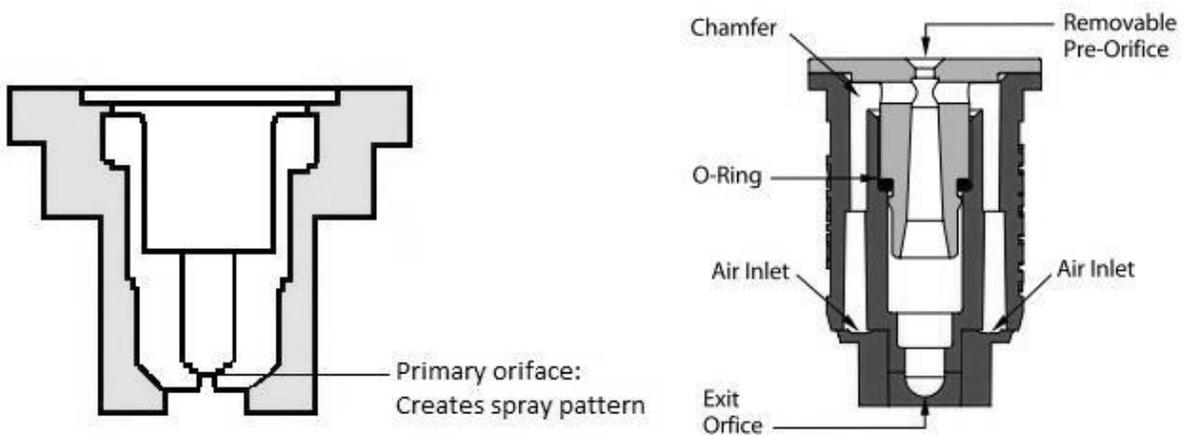
Smaller orifice size could result in a portion of the droplet spectrum as fine droplets due in part to smaller liquid sheet thickness. Prior work with flat fan nozzles, which lack a pre-orifice, suggested that sheet thickness was strongly correlated with droplet size, with shorter sheet lengths resulting in larger droplets (Figure 2) (Butler Ellis et al. 1997). Air induction (AI) nozzles are recognized as drift reducing technology. AI nozzles can reduce drift by 34% when compared to an extended range (XR) standard nozzle tip (Johnson et al. 2006). Nozzles such as these also incorporate a pre-orifice design which reduces the production pressure before reaching

the primary orifice without reducing solution flow rate. Primary orifices vary for certain application conditions and pesticides applied. For herbicides applied to row crops, fan, flat spray or flat fan type nozzles are used and produce a flat sheet by use of an elliptical orifice (ASAE 1997).



Turbo Wide Angle Flat Fan

Figure 1. Turbo TeeJet® nozzle by Spraying Systems, Inc, P.O. Box 7900, Wheaton, Illinois.



Extended Range Flat Fan

Air Induction Flat Fan

Figure 2. Extended Range Flat Fan and Air Induction Flat Fan nozzles by Spraying Systems, Inc.

Volume of spray applied per area also can have an effect on the properties of a pesticide spray. Low volume applications are common as greater area can be treated with the same initial

volume. Ultra low volume applications require a smaller spray nozzle orifice size, lower pressure, faster travel speed or a combination of these factors and often times result in smaller droplet sizes. Ultra low volume spray systems were characterized by Hanks and McWhorter (1993) as producing large proportions of the spray volume in droplet sizes smaller than 220 μm .

Spray formation also includes the atomization of the droplet. Properties that affect the atomization process include the dynamic surface tension, shear viscosity, and extensional viscosity (Hewitt 2008). Sheet length is a re-occurring diagnostic property that encompasses these properties. Sheet length is believed to likely be responsible for the spray droplet size distribution (Butler Ellis and Tuck 1999). The sheet length was determined by surface tension of the liquid; thus, formulation could have an effect on the droplet distribution. Emulsion formulations changed the droplet size distribution pattern compared to water-soluble formulations at lower pressures. Emulsions are responsible for inhomogeneous mixtures that cause earlier sheet breakup. This results in a shorter sheet length and a more uniform and larger droplet distribution. Many types of nozzles are available for different types of agricultural applications such as herbicide, fungicide, insecticide and liquid fertilizer. Many spray characteristics are determined shortly after exiting the nozzle indicating a strong influence by the orifice and solution properties.

Droplet Size and Herbicide Efficacy

Current spray volumes per area and concurrent droplet size are based on a few fundamental factors. These include the nozzle tip, application ground speed and the force exerted onto the solution to exit the nozzle. Each spray component can be adjusted to affect volume output and droplet size. Droplet size is influential on the efficacy and potency of applied

chemical (Prasad and Cadogen 1992). Droplets of 150 to 450 μm were more phytotoxic than 660 μm droplets presumably because of greater coverage. However, droplet size was nullified when herbicide concentration was increased. Experiments showed similar results with common lambsquarters and wild mustard (*Sinapis arvensis* (L.)) across a wide range of volumes (10, 25, 50, 100 and 200 l ha⁻¹) with both bromoxynil and 2,4-D (Scoresby and Nalewaja 1984).

A spray spectrum that is effective under a variety of conditions is often used to meet changing field conditions. Accordingly, droplet spectrums are neither fine (100 to 150 μm) nor ultra-coarse (450 μm) and located within the extremes of droplet sizes but will provide adequate coverage and minimize drift. One nozzle can achieve a range of droplet sizes with changes in application pressure. Use of higher pressure often is undesirable because smaller droplets prone to drift could be generated. However, higher pressure in the spray system resulted in greater weed control because of smaller droplet sizes (McMullen 1995). Smaller droplet sizes provided greater coverage which reportedly increased efficacy. Lower pressure systems operating at approximately 100 kPa resulted in less drift but wild oat (*Avena sativa* L.) control was decreased by as much as 36%. Low pressure produced large droplets, which may have been poorly retained on the leaf surface. Spray systems operated at 400 kPa produced more droplets less than 100 μm that had a much greater tendency to drift but provided much better coverage. Similarly experiments targeting a larger droplet provided less control when compared to smaller droplet spray patterns (Prasad and Cadogen 1992). Larger droplet size also show decreased activity at extended assessment periods compared to smaller droplets.

Knoche (1994) presented in a review that 71% of experiments showed increased herbicide performance at smaller droplet sizes. Decreasing droplet size and increasing leaf coverage increased systemic herbicide efficacy more than non-systemic herbicides. Many studies

suggest smaller droplets provide better efficacy coinciding with greater leaf coverage and retained volume. However, larger droplet VMD in some field studies (Feng et al. 2003) provided better absorption despite lower plant retention of medium and coarse droplets. Greater leaf surface disruption, an increase in droplet evaporation time or differences in nozzle spray spectrum characteristics could be a contributing factor to greater uptake.

Spray Retention

The retention or ability of foliar applied pesticide droplets to remain on the leaf surface is dependent on many factors. Formulation, spray characteristics, application method, carrier volume and leaf cuticle characteristics all contribute to effective spray retention. Combinations of these components make spray retention a difficult aspect to predict and quantify. Leaf morphology plays an important role in droplet retention. Presence of trichomes, epicuticular waxes and leaf orientation could affect the interaction between droplet and leaf and influence droplet retention.

Leaf characteristics are important when understanding wettability of a leaf surface. Wettability refers to the droplet spread on the leaf surface as measured by the contact angle (Forster and Zabkiewicz 2001). The wettability of a leaf has been shown to change as the plant matures. Wheat, barley and oat horizontal leaf wettability increased as growth stage increased (Henning-Gizewski and Wirth 2000). As age increased wettability increase because of switching-over to amorphous wax content in the leaf cuticle. Older wheat plants also were shown to have greater spray deposition compared to younger plants because of plant growth characteristics such as a denser canopy and greater leaf surface area (Butler Ellis et al. 2004).

In addition to leaf waxes, plants also possess small surface structures called trichomes that affect droplet retention. The use of microscopy has given us a closer look at the topography and trichome structure and density of a leaf surface. Microscopy was used to detect three types of trichomes on common ragweed (*Ambrosia artemisiifolia* (L.)) (Grangeot et al. 2005). Variation in trichome structure ranged from long and sharp to medium-sized to spherical shaped. Droplet contact with the leaf epidermis was affected by the fine trichomes on a leaf surface after deposition (Xu et al. 2011). Solutions amended with crop oil concentrate (COC) remained separated from leaf surfaces by trichome structures. Addition of a non-ionic surfactant (NIS) to reduce droplet surface tension and initiate droplet spread was needed for the droplet to reach the leaf epidermis. Droplet spread is facilitated by the decreased surface tension, thus, bypassing trichome defense. Droplets containing modified seed oil (MSO) spread across hairy leaf surfaces better when compared to droplets without. Droplets that were amended with adjuvant spread more on leaves containing trichomes than on waxy leaf surfaces. Droplets without an MSO amendment remained spherical and suspended on trichomes as with COC. Evaporation time of droplets also was longer for droplets on leaves with greater trichome density. A longer evaporation time could relate to greater herbicide bypass through the plant cuticle, resulting in greater efficacy if epidermis contact is achieved.

Droplet size is a significant component of spray retention but should remain appropriate for application conditions. Large droplet spray spectrums have less chance of drifting off target but also are less likely to obtain desirable leaf coverage. Sprays that included a larger droplet spectrum demonstrated lower retention on giant foxtail (Wolf et al. 2000). Nozzles that produced smaller droplets were more often retained which was measured as a larger volume deposited on leaf surfaces (Peng et al. 2005). Although smaller droplets had greater retention in these studies,

other studies showed small differences in retention between fine (175 μm) and coarse (491 μm) droplet sizes in grass crops (Feng et al. 2003). Retention variability could be linked to differences in the plants targeted. For example, leaf surfaces with rough texture could lead to similar retention between small and large droplet sizes.

Large droplets can rebound and scatter after impact with leaf surfaces resulting in less pesticide absorption because of less retention. Droplets intended to contact the leaf do not control weeds if they rebound off the surface. Droplet impaction can be influenced by leaf structures as was wettability. Certain studies indicate that rough leaf surfaces rebound droplets more than hard, smooth surfaces (Reichard 1988). Among grass weed species there were differences of rebounded droplets. Yellow nutsedge and witchgrass, which had waxy microstructures on the leaf surface, had very low droplet rebound compared to smooth crabgrass and green foxtail, which have smooth leaf surfaces.

Herbicide Formulation

With limited new modes of action coming to market, herbicides are being reformulated and redesigned to offer better efficacy and facilitate better mixing. Widely used herbicides such as glyphosate, 2,4-D and dicamba, along with many others, are available in multiple formulations. Experiments containing the same herbicide but of different formulations have been conducted to establish differences in spray characteristics (Mueller and Womac 1997; Sciumbato et al. 2005; Xie et al. 1994). Frequently, herbicides are formulated with other components to minimize crop damage, increase mixing ability, optimize efficacy and decrease amount of chemical used. For example, adding the safener mefenpyr diethyl to fenoxaprop-ethyl or fenoxaprop p-ethyl significantly increased tolerance of wheat to the herbicide (Huff et al. 1989).

Herbicide formulation refinement can increase activity of an existing molecule. Wide use of glyphosate has resulted in significant formulation development. Change in formulation has resulted in droplet sizes as well. Glyphosate-IPA II sprays produced larger volumes of droplets in 5 to 91 μm sizes compared with glyphosate-trimesium and glyphosate-IPA I (Mueller and Womac 1997).

Industry nozzle classification is established by using water alone (ASAE 2009). It is important to understand that inclusion of a herbicide, adjuvant or both can change the droplet size spectrum. Use of different herbicide formulation can affect spray quality, activity and spray droplet characteristics. Spray droplet size spectrum of suspension concentrate (SC) and emulsifiable concentrate (EC) herbicides has been shown to be different than for water alone (Stainier et al. 2006). The VMD of SC and EC herbicides were 78% and 37% larger than water alone when sprayed through a flat fan nozzle. Although the formulation of a herbicide can be an underlying factor of droplet size, some studies also suggest that formulation does not correlate to droplet size when using certain spray nozzles (Nicetic et al. 2004).

Formulation effect can be as influential as nozzle size on herbicide droplet size. When using flat fan nozzle designs, herbicide formulation was the most important factor when determining spray formation (Miller and Butler Ellis 2000). Also, water-soluble liquid formulations resulted in finer sprays than emulsions because of longer sheet length. Long sheet length correlates to larger numbers of smaller droplets and short sheet length to larger droplets. Shorter sheet lengths, a result of sheet perforation attributed to emulsion particles, have consistent sized droplets because of consistent solution properties. Sheet length is a component that is determined by dynamic surface tension and the solution particle. Emulsion formulations produced a more coarse droplet spectra than other formulations included because of sheet

perforation (Butler Ellis and Tuck 2000). However, when considering nozzle type, there is wide variation between air inclusion and fluid nozzles with emulsion formulations. Micro emulsions have been shown to facilitate air intake when applied using an air induction nozzle (McMullen et al. 2006). When comparing liquid, dry and emulsion formulations of 2,4-D, Sciumbato et al. (2005) found that the VMD of liquid and emulsion formulations were similar but greater than dry formulation when sprayed at 380 and 760 ml/min. In fact, solutions with dry formulation herbicide had VMD and other spray characteristics similar to water. Similar results were measured for percentage of droplets $<191 \mu\text{m}$. This research also indicated that many dry herbicide formulations could have similar VMD and droplets $<191 \mu\text{m}$.

The effect of formulation type on spray characteristics has been studied previously (Butler-Ellis and Tuck 2000; Mueller and Womac 1997; Nicetic et al. 2004; Sciumbato 2005; Stainier et al. 2006). However, studies comparing phytotoxicity of different herbicide formulations are limited. Canadian experiments showed that a soluble powder formulation of imazamethabenz had greater phytotoxicity when compared to liquid concentrate and suspension concentrate formulations at 100 g ai ha^{-1} (Xie et al. 1994). This was not consistent when the rate was increased to 200 g ai ha^{-1} under well watered conditions. An increased rate of either dry, liquid or oil formulation herbicide has nullified the spray droplet characteristics as it had with herbicide efficacy. Dynamic surface tension was noted to decrease with higher emulsion concentrations which were counteractive to lower herbicide concentration effect with spray droplet size (Dexter 2001). Droplet deposition and retention on leaf surfaces is affected by surface tension of the droplet which also influences spray droplet size (Hanks 1995). Similar findings state high surfactant concentrations found in soluble liquid formulations will increase the amount of droplets considered fine (Miller et al. 2008).

Literature Cited

- Aellen P (1960) *Chenopodium*. G. Hegi, ed., *Illustrierte Flora von Mitteleuropa*. 3:533-657
- Akin DE (2012) Flax fiber. *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, New York, NY, USA
- Anonymous (2001) "A summary of tank mix and nozzle effects on droplet size." *Spray Drift Task Force*. 2001. Web. 22 May. 2013. www.agdrift.com/PDF_FILES/Tankmix.pdf
- ASAE *Standards*. (1997) S.327.2: Terminology and definitions for agricultural chemical application. St. Joseph, Mich ASAE
- ASAE (2009) S572.1 Spray Tip Classification by Droplet Spectra. Developed by the Pest Control and fertilizer Application Committee; Approved by the Power and Machinery Division Standards Committee; Adopted by ASAE PM41
- Bode LC (1987) Spray application technology. *In* C. G. McWhorther. And M. R. Gebhardt, ed. *Methods of Applying Herbicides*. Champaign, IL: Weed Science Society of America. 85-121
- Bond JA, Oliver LR (2006) Comparative growth of Palmer Amaranth (*Amaranthus palmeri*) accessions *Weed Sci* 54(1):121-126
- Butler Ellis MC, Webb DA, Western NM (2004) The effect of different spray liquids on the foliar retention of agricultural sprays by wheat plants in a canopy. *Pest Manag Sci* 60:786-794
- Butler Ellis MC, Lane AG, O'Sullivan CM, Miller PCH, Glass CR (2010) Bystander exposure to pesticide spray drift: New data for model development and validation. *Biosystem Engineering* 107:162-168
- Butler Ellis MC, Miller PCH, Tuck CR (1997) The effect of some adjuvants on sprays produced by agricultural flat fan nozzles. *Crop Protect* 16:41-50
- Butler Ellis MC, Tuck CR (1999) How adjuvants influence spray formation with different hydraulic nozzles. *Crop Protect* 18:101-109
- Butler Ellis MC, Tuck CR (2000) The variation in characteristics of air-included sprays with adjuvants. *Aspects Appl Biol* 57:155-161
- Dexter RW (2001) The effect of fluid properties on the spray quality from a flat fan nozzle. *In*: *Pesticide Formulations and Application Systems*. ASTM STP 1400 14:27-43
- Farooq M, Balachandar R, Wulfsohn D, Wolf TM (2001) Agricultural sprays in cross flow and drift. *Journal of Agric. Eng Res* 78:347-358

Fein R (2003) Should the EPA regulate under TSCA and FIFRA to protect foreign environments from chemicals used in the United States? *Stanford Law Rev* 55:2153-2193

Feng PCC, Chiu T, Sammons RD, Ryerse JS (2003) Droplet size affects glyphosate retention, absorption, and translocation in corn. *Weed Sci* 51:443-448

Forster WA, Zabkiewicz JA (2001) Improved method for leaf surface roughness characterisation. In: De Ruiter, H. (Ed.), *Proceedings of the Sixth International Symposium on Adjuvants for Agrochemicals*, pp. 113–118.

Friesen H, Campbell CG (1986) Common buckwheat (*Fagopyrum esculentum*) tolerance to herbicides. *Weed Sci* 34:435-439

Gossett BJ, Toler JE (1999) Differential control of Palmer amaranth (*Amaranthus palmeri*) and smooth pigweed (*Amaranthus hybridus*) by postemergence herbicides in soybean (*Glycine max*). *Weed Technol* 13:165-168

Grangeot M, Chauvel B, Gauvrit C (2005) Spray retention, foliar uptake and translocation of glufosinate and glyphosate in *Ambrosia artemisiifolia*. *Weed Res* 46:152-162

Hamilton IT (1986) Linen. *Textiles* 15:30-34

Hanks JE (1995) Effect of drift retardant adjuvants on spray droplet size of water and paraffinic oil applied at ultralow volume. *Weed Technol* 9:380-384

Hanks JE, McWhorter CG (1993) Spray droplet size for water and paraffinic oil applied at ultralow volume. *Weed Technol* 7:799-807

Heiser CB (1979) Origins of some cultivated new world plants. *Annu Rev Ecol Syst* 10:309-326

Henning-Gizewski S, Wirth W (2000) Changes in the biosynthesis of epicuticular waxes in maize and their influence on wetting properties. *Planzenschutz-Nachrichten Bayer* 53:105-125

Hewitt AJ (2000) Spray drift: impact of requirements to protect the environment. *Crop Protect* 19:623-627

Hewitt AJ (2008) Spray optimization through application and liquid physical property variables-I. *Environmentalist* 28:25-30

Horne DM (1992) EPA's response to resistance management and herbicide-tolerant crop issues. *Weed Technol* 6:657-661

Huff P, Schumacher H, Von Olfers H, Banks M (1989) Hoe 7113 – Worldwide results on selectivity and grass weed efficacy. *Proc Br Crop Prot Conf Weeds* 2:723-728

Johnson AK, Roeth FW, Martin AR, Klein RN (2006) Glyphosate drift management with drift-reducing nozzles and adjuvants. *Weed Technol* 20:893-897

Knoche M (1994) Effect of droplet size and carrier volume on performance of foliar-applied herbicides. *Crop Protect* 13:163-178

Matthews GA (1979) *Pesticide application methods*. Longman, Inc., New York, NY. 306 p.

Matthews GA (2000) *Pesticide application methods*, 3rd E. Osney Mead, Oxford.: Blackwell Science Ltd P. 91

McMullen PM (1995) Effect of spray volume, spray pressure and adjuvant volume on efficacy of sethoxydim and fenoxaprop-p-ethyl. *Crop Prot* 14:549-554

McMullen PM, Thurman S, McManic G, Brigance M (2006) Nozzle-adjuvant formulation interactions: implications on herbicide efficacy. *J ASTM Int.* 3:1-6

Merrill R, Schewel M (1980) FDA regulation of environmental contaminants of food. *Virginia Law Rev* 8:1357-1441

Miller PCH, Butler Ellis MC (2000) Effects of formulation on spray nozzle performance for applications from ground-based boom sprayers. *Crop Prot* 19:609-615

Miller PCH, Tuck CR, Murphy S, da Costa Ferreira M (2008) Measurements of the droplet velocities in sprays produced by different designs of agricultural spray nozzles. In: *Proceedings of 22nd European Conference on Liquid Atomization and Spray Systems (ILASS-Europe)*, Como Lake, Italy, pp. 1-8. Paper ID ILASS08-8-5

Mitich LW (1988) Common Lambsquarter. *Weed Technol* 2:550-552

Mueller TC, Womac AR (1997) Effect of formulation and nozzle type on droplet size with isopropylamine and trimesium salts of glyphosate. *Weed Technol* 11:639-643

Nicetic O, Dorr G, Woods N, Beattie GAC (2004) Influence of agricultural mineral oil on droplet spectra and spray drift. In: *Proceedings of 7th International Symposium on Adjuvants for Agrochemicals (ISAA 2004)*, Cape Town, South Africa, pp. 136-142

Nuyttens D, Baetens K, De Schampheleire M, Sonck B (2007) Effect of type, size and pressure on spray droplet characteristics. *Biosystems Engineering* 97:333-345

Oleskey C, Fleischman A, Goldman L, Hirschhorn K, Landrigan PJ, Lappe M, et al. (2004) Pesticide testing in humans: ethics and public policy. *Environmental Health Perspectives* 112:914-919

Prasad R, Cadogan BL (1992) Influence of droplet size and density on phytotoxicity of three herbicides. *Weed Technol* 6:415-423

- Rafael AM, Randall CS, Horak MJ, Boyer Jr J (2001) Interference of Palmer amaranth in corn. *Weed Sci* 49:202-208
- Peng G, Wolf TM, Beyer KN, Caldwell B (2005) Spray retention on green foxtail (*Setaria viridis*) and its effect on weed control efficacy by *Pyricularia setariae*. *Weed Technol* 19:86-93
- Reichard DL (1988) Drop formation and impaction on the plant. *Weed Technol.* 2:82-87
- Sciumbato AS, Senseman SA, Ross J, Mueller TC, Chandler JM, Cothren JT, Kirk IW (2005). Effects of 2,4-D formulation and quinclorac on spray droplet size and deposition. *Weed Technol* 19:1030-1036
- Scoresby JR, Nalewaja JD (1984) Herbicides in various size droplets and spray volumes. *Proc 39th North Central Weed Control Conf* 39:60
- Stainier C, Destain MF, Schiffers B, Lebeau F (2006) Droplet size spectra and drift effect of two phenmedipham formulations and four adjuvants mixtures. *Crop Protect* 25:1238-1243
- Wolf TM, Harrison SK, Hall FR, Cooper J (2000) Optimizing postemergence herbicide deposition and efficacy through application variable in no-till systems. *Weed Sci* 48:761-768
- Xie HS, Quick WA, Hsiao AI (1994) Effect of drought and formulation on wild oat (*Avena fatua*) control with imazamethabenz and fenoxaprop. *Crop Protect* 13:195-200
- Xu L, Zhu H, Ozkan HE, Bagley WE, Krause CR (2011) Droplet evaporation and spread on waxy and hairy leaves associated with type and concentration of adjuvants. *Pest Manag Sci* 67:842-851

CHAPTER TWO: DROPLET SIZE EFFECT ON EFFICACY OF WHEAT HERBICIDES TO FOUR SPECIES

Introduction

EPA regulation may soon incorporate expectation and remedy of pesticide spray drift through application system parameters or drift reduction technologies (DRTs). Current drift-reducing nozzles have shifted the droplet spectrum to larger sizes, yet the uniformity of spray droplets has not improved (Lafferty and Tian 2001). Many herbicide labels now include recommended buffer zones for application near water and residential areas. Also, ideal droplet sizes to reduce drift are included. However, reducing drift may also compromise herbicide efficacy. DRTs incorporate the use of pre-orifice and air-inlet designs that reduce the amount of fine droplets (Lafferty and Tian 2001). Large droplets present other problems such as less coverage and lower retention (Reichard 1988). Many factors could contribute to reducing drift such as type and concentration of adjuvants, nozzle performance, and herbicide used.

Herbicide mobility in the plant is classified as non-translocated and translocated. Non-translocate herbicides refer to localized movement in the plant tissue. Many protoporphyrinogen oxidase inhibiting herbicides are non-translocated and cause rapid desiccation of foliage in the presence of light (Senseman 2001). Translocated herbicides, such as plant growth regulators, affect areas besides the initial application location within the plant. Translocated herbicide passes through plant cuticles and cell walls to affect critical plant processes after relocation via phloem and xylem translocation. Non-translocated herbicides enter the plant through the cuticle and enter plant cells and organelles. They differ from translocated herbicides in that they remain relatively close to initial entry point.

Located in an economically important wheat producing area, the objective of these experiments was to evaluate the effect of different droplet sizes on efficacy of several translocated and non-translocated herbicides used to control broadleaf weeds in *Triticum aestivum* L.

Materials and Methods

Four field experiments were conducted to evaluate droplet size effect on herbicide efficacy in four species. Three experiments focused on herbicides with specific characteristics. The fourth experiment investigated the influence of nozzle type and orifice size with common herbicide mixtures. Experiments were conducted at the North Dakota State University research centers at 432 40th Ave. North, Fargo, ND on a Fargo silty clay soil (fine, emectitic, and frigid Typic Natraquerts) with a pH of 7.6 and 7.0% organic matter and the Dalrimple Experiment Plots at the Agronomy Seed Farm, Casselton, ND on Bearden clay loam soil with a pH of 7.7 and 7.6% organic matter. Field experiments took place in the summer of 2012 and 2013.

Plant species included for evaluation of herbicides in all experiments were common buckwheat (*Polygonum convolvulus* L.), flax (*Linum usitatissimum* L.), amaranth (*Amaranthus hybridus* L.), and quinoa (*Chenopodium quinoa* L.). On occurrence, natural infestation of Venice mallow (*Hibiscus trionum* L.) also was included because of poor emergence of quinoa. Buckwheat, amaranth and quinoa provide a horizontal leaf surface with differing leaf cuticle composition. Flax provided a diagonal leaf angle. These species were used to obtain a range of injury necessary for evaluation.

Plant species, except Venice mallow, were seeded parallel to each other within each replication. Venice mallow emerged from the native seed bank throughout both research sites.

Plots were 3.5 m wide by 10 m long. Species were seeded perpendicular to direction of treatment application in a strip that was 1.5 m wide with rows spaced 18 cm apart. Seeding, treatment and harvest dates of species were included for experiments in Casselton (Table 1) and Fargo (Table 2).

Herbicide treatments were applied through a CO₂-pressurized system attached to an all-terrain vehicle with an attached spraying boom. The boom had four nozzles spaced 50 cm apart that were approximately 50 cm above plants to achieve a 2-m-wide treatment width. An attached speedometer was used to achieve required speeds for application of the correct volume.

Application pressure and speed varied to maintain application volume at 79.5 L ha⁻¹ with various nozzle tips (Table 3). The experimental design for all experiments was a randomized complete block with four replicates. Treatments were organized in a factorial arrangement of herbicide and nozzle droplet spectrum. A control was included that consisted of an untreated plot.

The studies were conducted with one herbicide rate for each herbicide. Herbicides were separated into four experiments of droplet effect on efficacy of 1) translocated plant growth regulators 2) translocated ALS inhibitors, 3) non-translocated herbicides, and 4) herbicides to evaluate nozzle type and orifice. Four droplet spectra were evaluated for each herbicide in experiments 1, 2 and 3 and two droplet sizes for experiment 4 (Table 3). Spray nozzles for Experiments 1, 2, and 3 were Turbo TeeJet® nozzles (Spraying Systems, P.O. Box 7900 Wheaton, Illinois). Nozzles targeted VMD distributions of medium (200 µm), coarse (300 µm), very coarse (400 µm) and extra coarse (500 µm). Experiment 4 included XR and AIXR (Spraying Systems Inc., Wheaton, IL.) to achieve medium or extra coarse droplet spectra.

Table 1. Planting, treatment and harvest dates, and plant height at application for experiments at Dalrimple Experiment Plots at the Agronomy Seed Farm in Casselton, ND.

Experiment	Planting date	Treatment date	Harvest date	Species	Height cm
1	June 18, 2012	July 10, 2012	August 8, 2012	Quinoa	20 to 25
				Amaranth	20 to 25
				Flax	10 to 18
				Buckwheat	30 to 45
	June 20, 2013	July 9, 2013	August 7, 2013	Quinoa	7 to 10
				Amaranth	7 to 10
				Flax	7 to 10
				Buckwheat	10 to 15
2	June 18, 2012	July 10, 2012	August 8, 2012	Quinoa	20 to 25
				Amaranth	20 to 25
				Flax	10 to 18
				Buckwheat	30 to 45
	June 20, 2013	July 9, 2013	August 8, 2013	Quinoa	7 to 10
				Amaranth	7 to 10
				Flax	7 to 10
				Buckwheat	10 to 15
3	June 18, 2012	July 10, 2012	August 9, 2012	Quinoa	20 to 25
				Amaranth	20 to 25
				Flax	10 to 18
				Buckwheat	30 to 45
	June 20, 2013	July 9, 2013	August 8, 2013	Quinoa	7 to 10
				Amaranth	7 to 10
				Flax	7 to 10
				Buckwheat	10 to 15
4	June 18, 2012	July 10, 2012	August 9, 2012	Quinoa	20 to 25
				Amaranth	20 to 25
				Flax	10 to 18
				Buckwheat	30 to 45
	June 20, 2013	July 9, 2013	August 7, 2013	Quinoa	7 to 10
				Amaranth	7 to 10
				Flax	7 to 10
				Buckwheat	10 to 15

Table 2. Planting, treatment and harvest dates, and plant height at application for experiments at North Dakota State University, Fargo, ND.

Experiment	Planting date	Treatment date	Harvest date	Species	Height cm
1	June 14, 2012	July 3, 2012	August 1, 2012	Quinoa	20 to 25
				Amaranth	20 to 25
				Flax	10 to 18
				Buckwheat	30 to 45
	July 11, 2013	July 30, 2013	September 4, 2013	Quinoa	7 to 10
				Amaranth	7 to 10
				Flax	7 to 10
				Buckwheat	10 to 15
2	June 14, 2012	July 3, 2012	August 1, 2012	Quinoa	20 to 25
				Amaranth	20 to 25
				Flax	10 to 18
				Buckwheat	30 to 45
	July 11, 2013	July 30, 2013	September 4, 2013	Quinoa	7 to 10
				Amaranth	7 to 10
				Flax	7 to 10
				Buckwheat	10 to 15
3	June 14, 2012	July 3, 2012	August 2, 2012	Quinoa	20 to 25
				Amaranth	20 to 25
				Flax	10 to 18
				Buckwheat	30 to 45
	July 11, 2013	July 31, 2013	September 3, 2013	Quinoa	7 to 10
				Amaranth	7 to 10
				Flax	7 to 10
				Buckwheat	10 to 15
4	June 20, 2012	July 3, 2012	August 2, 2012	Quinoa	20 to 25
				Amaranth	20 to 25
				Flax	10 to 18
				Buckwheat	30 to 45
	July 11, 2013	July 31, 2013	September 3, 2013	Quinoa	7 to 10
				Amaranth	7 to 10
				Flax	7 to 10
				Buckwheat	10 to 15

Table 3. TeeJet nozzle treatment settings for application by experiment

Experiment	Nozzle	Application			VMD ^a µm	Droplet spectrum
		pressure kPa	Speed kph	Volume L ha ⁻¹		
1,2,3	TT110015	345	9.5	79.5	177-218	Medium
	TT11002	138	8	79.5	218-349	Coarse
	TT11003	138	10.5	79.5	349-428	Very coarse
	TT11004	105	13.5	79.5	428-622	Extra coarse
4	XR800015	138	6.5	79.5	177-218	Medium
	XR8004	138	16	79.5	177-218	Medium
	AIXR110015	138	6.5	79.5	428-622	Extra coarse
	AIXR11004	207	19	79.5	428-622	Extra coarse

^a Predicted based on TeeJet catalogue classification

Droplet Size Effect within Herbicide Mode of Action (Experiment 1, 2 and 3).

Experiments 1, 2 and 3 treatments consisted of four nozzle types and three herbicides at one spray volume. Nozzles were Turbo TeeJet® that provided a wide angle flat-fan pattern for uniform coverage in broadcast spraying. Turbo nozzles incorporate a pre-orifice before the primary nozzle orifice. The pre-orifice regulates liquid volume flow allowing for lower pressure upon exiting the primary orifice. A reduction in pressure at the primary orifice will minimize percentage of fine droplets in the spray pattern.

All treatments were sprayed at equipment settings based on desired droplet spectra (Table 3). Experiment 1 consisted of translocated herbicides 2,4-D amine, dicamba and fluroxypyr. These 3 herbicides are all members of the group 4 plant growth regulator mode of action. Application rates were 2,4-D applied at 560 g ae ha⁻¹, dicamba applied at 140 g ae ha⁻¹ and fluroxypyr at 140 g ae ha⁻¹.

Experiment 2 consisted of translocated ALS-inhibiting herbicides flucarbazone, imazamox and thifensulfuron. Application rates were flucarbazone at 24.5 g ai/ha, imazamox at 35 g ai/ha and thifensulfuron at 17.5 g ai/ha. Adjuvants added were a basic pH blend (alcohol

ethoxylate and ammonium nitrate) at 1% v/v with flucarbazone, nonionic surfactant at 0.25% v/v for imazamox and nonionic surfactant at 0.125% v/v for thifensulfuron.

Experiment 3 consisted of non-translocated herbicides bromoxynil, carfentrazone and saflufenacil. Bromoxynil was applied at 560 g ai ha⁻¹, carfentrazone at 9 g ai ha⁻¹ and saflufenacil at 25.2 g ai ha⁻¹. Adjuvants added were nonionic surfactant at 0.25% v/v for carfentrazone and methylated seed oil (MSO) at 2.3 L ha⁻¹ plus ammonium sulfate at 9.5 kg ha⁻¹ for saflufenacil.

Droplet Size Effect with Nozzle Tip Type and Orifice Size (Experiment 4).

Treatments for experiment 4 consisted of four nozzle tips and four herbicide treatments at one volume. Nozzles were chosen to target two droplet sizes but with different orifice size/flow rate (Table 3). Operation pressure and speed were adjusted to achieve desired droplet size and volume.

Treatments contained one representative herbicide from the previous three experiments and one common mixture of two previously used herbicides. Herbicides used were 2,4-D amine, thifensulfuron, bromoxynil and bromoxynil plus 2,4-D. 2,4-D was applied at 560 g ae ha⁻¹, thifensulfuron at 17.5 g ai ha, bromoxynil at 560 g ai/ha and 2,4-D plus bromoxynil at 19.6 g ai/ha. Nonionic surfactant at 0.125% v/v was added with thifensulfuron.

Treatments were evaluated visually to determine percent injury at 14 and 28 days after treatment (DAT) for all experiments. Injury was documented from 0 to 100% control. A visual evaluation of no injury was documented as 0% and completely dead plants were documented as 100%. Species were harvested after the 28 DAT evaluation and fresh weights were recorded in the field using a portable scale. Plants were harvested by clipping at the soil surface with shears. A 0.5- by 1.0-m area quadrat was harvested from each plot for Venice mallow, quinoa, and amaranth. A 1 m length of row was harvested for flax and buckwheat.

Data from each experiment was analyzed as a factorial arrangement of herbicide and spray nozzle. Each species was evaluated individually due to differences in herbicidal efficacy for each species type. Each experiment was repeated and experimental runs were combined when error mean squares were homogeneous. Herbicide and spray nozzle treatment variables were considered fixed and experimental runs random. ANOVA with Fisher's protected LSD test ($P < 0.05$) for mean separation was used. Statistical analysis system (SAS, SAS Institute, Inc.) was used to analyze all data.

Results and Discussion

Less than favorable growing conditions affected the development of multiple bioassay species. This resulted in variable emergence, low plant population and inconsistent plant sizes. The variability in plant population and size resulted in an insufficient plant population for reliable visible injury assessment of quinoa in 2012 and 2013. Inconsistent size of quinoa during herbicide application noticeably affected the harvest weights of treatments across repetitions. Environments that were largely inconsistent were not harvested. Environments with low emergent quinoa were withheld from evaluation and statistical analysis. Also, environments with error mean squares which were not homogeneous were analyzed separately and not included in combined data. Although visible injury assessments were effected by excessive environmental variation among plots, visible injury was more consistent than fresh weight values.

Plant Growth Regulator Herbicides (Experiment 1). No interaction occurred between droplet size and herbicide for plant growth regulator herbicide visible injury assessments (Table 4). Although mean separation showed a significant difference between some treatments, an interaction was not present. This was due to variation of visual assessments among combined

data. Since main effects of herbicide and droplet spectra did not interact, main effects were averaged across levels of other factors. Changes in magnitude between herbicides occurred but mainly, differences among droplet sizes were not significant.

Table 4. Visible injury on three species as influenced by droplet size 28 DAT

Herbicide	Droplet size	Visible injury ^a		
		Amaranth	Buckwheat	Flax
		%		
2,4-D	Medium	83	63	27
	Coarse	84	57	21
	Very coarse	87	65	20
	Extra coarse	80	60	15
Dicamba	Medium	58	43	23
	Coarse	43	39	16
	Very coarse	57	48	16
	Extra coarse	54	44	16
Fluroxypyr	Medium	20	62	80
	Coarse	23	57	83
	Very coarse	33	73	84
	Extra coarse	26	59	81
LSD (0.05)		16	8	11

^a Visible injury in based on a 0 to 100% plant death scale. 0=no injury and 100=entire plant death.

When comparing droplet spectra averaged across plant growth regulator herbicides, a medium sized droplet provided better control of flax than other droplet sizes, although differences were small (Table 5). A very coarse droplet size provided better control of both amaranth and buckwheat species compared to medium, coarse and extra coarse droplet sizes when averaged across herbicide. Amaranth and buckwheat visible injury were similar at both 14 and 28 DAT. Medium and extra coarse droplet spectra provided similar control of amaranth and buckwheat at both visible injury assessments. Coarse sized droplets (300-350µm) have been

shown to provide less control than compared to other sizes. Results showed that 250 μ m and 450 μ m droplets provided better control of common cocklebur than an intermediate size of 350 μ m droplets at volumes of 56 and 112 L/ha (Shaw et al. 2000). Conversely, conventional and drift-reducing nozzles (150 μ m VMD) provided better coverage and efficacy when applied without adjuvants than Turbo TeeJet, TurboDrop and AI TeeJet (210 to 620 μ m VMD) (Ramsdale and Messersmith 2001). Droplets of an intermediate size may not reach leaf surfaces as efficiently as larger droplets and they may not have sufficient coverage compared to smaller droplets. Fine droplets may often have higher retention on leaf surfaces and minimize solution runoff. Glyphosate droplets had higher retention with fine droplets compared to a medium or coarse droplet (Feng et al. 2003). Although fine droplets had higher retention, coarse droplets had higher absorption into plant tissue compared to medium and fine droplets. However, greenhouse studies demonstrated similarities in spray deposition between 160 μ m (fine) and 330 μ m (coarse) spray solutions on honey mesquite when clopyralid was applied (Bovey et al. 1991). Specific observations are variable among research and a consistent trend was not obvious.

2,4-D and fluroxypyr provided similar control of buckwheat when averaged across droplet size at 14 DAT evaluation period (Table 5). This remained consistent at 28 DAT as visible injury did not change substantially. Visible injury assessments for 2,4-D and dicamba were similar when applied to flax at both 14 and 28 DAT. All other comparisons between herbicides were significantly different.

Fresh weight of amaranth was 448 grams after fluroxypyr compared to 227 grams for dicamba and 97 grams for 2,4-D (Table 6). This indicated a herbicidal difference on amaranth among the three herbicides related to inherent herbicide efficacy. Similarly, flax treated with fluroxypyr had a lower amount of fresh weight than either 2,4-D or dicamba and buckwheat had

similar fresh weights when either 2,4-D or fluroxypyr were applied but had significantly greater weights when treated with dicamba.

Table 5. Visible injury of plant growth regulator herbicides on three species at 14 and 28 DAT as influenced by herbicide and droplet size.

Treatment	Visible injury ^a					
	Amaranth		Buckwheat		Flax	
	14 DAT	28 DAT	14 DAT	28 DAT	14 DAT	28 DAT
<u>Herbicide^b</u>	%					
2,4-D	62	84	54	61	20	21
Dicamba	39	53	41	43	20	18
Fluroxypyr	24	25	51	63	71	82
LSD (0.05)	3	5	3	3	2	3
<u>Droplet size^c</u>						
Medium	41	53	48	56	37	43
Coarse	40	50	46	51	37	40
Very coarse	46	59	54	62	39	40
Extra coarse	40	54	45	54	35	37
LSD (0.05)	3	5	3	3	3	3

^a Visible injury was based on a 0 to 100% plant death scale. 0=no injury and 100=entire plant death.

^b Data averaged across droplet size.

^c Data averaged across herbicide.

Lower fresh weight, which indicated greater herbicide efficacy, occurred with very coarse droplet size compared to medium or coarse sizes on amaranth. Very coarse droplet size had the lowest fresh weight compared to medium and coarse droplet size (Table 6). Droplet size did not affect the fresh weight accumulation of buckwheat or flax when averaged over herbicide. Fresh weight when herbicide was applied with coarse sized droplet spectrum was highest for each of the three species which is consistent with the lowest visible injury assessment.

Table 6. Fresh weights of three species 28 DAT as influenced by plant growth regulator herbicides and droplet size.

Treatment	Amaranth	Buckwheat	Flax
	g		
<u>Herbicide^a</u>			
2,4-D	97	319	170
Dicamba	227	428	182
Fluroxypyr	448	309	43
LSD (0.05)	73	62	13
<u>Droplet size^b</u>			
Medium	282	329	132
Coarse	307	382	135
Very coarse	185	351	127
Extra coarse	255	346	134
LSD (0.05)	84	NS	NS

^a Data averaged across droplet size.

^b Data averaged across herbicide.

ALS Herbicides (Experiment 2). The interaction between main effects of herbicide and droplet size were not significant and will be discussed as analyzed across levels of the other factor for ALS herbicide for any measurement parameter. Therefore, each main effect will be discussed as analyzed across levels of the other factor. 14 and 28 DAT ratings had similar main effect results, thus only 28 DAT ratings were provided for discussion.

When visible injury was averaged across ALS herbicides 28 DAT, herbicide application with a medium sized droplet spectrum was less efficacious on amaranth when compared to a very coarse droplet spectrum (Table 7). Except for when applied in a very coarse sized spray spectrum to flax, herbicides in all other droplet sizes gave equal control of both buckwheat and flax indicating that droplet size may not be a significant factor influencing herbicide efficacy.

Table 7. Visible injury of ALS herbicides on three species 28 DAT as influenced by herbicide and droplet size.

Treatment	Visible injury ^a		
	Amaranth	Buckwheat	Flax
	%		
<u>Herbicide^b</u>			
Flucarbazone	62	59	63
Imazamox	82	38	18
Thifensulfuron	93	48	20
LSD (0.05)	3	3	2
<u>Droplet size^c</u>			
Medium	76	47	31
Coarse	79	48	34
Very coarse	81	48	36
Extra coarse	79	49	33
LSD (0.05)	4	NS	3

^a Visible injury was based on a 0 to 100% plant death scale. 0=no injury and 100=entire plant death.

^b Data averaged across droplet size.

^c Data averaged across herbicide.

Flucarbazone, imazamox and thifensulfuron efficacies were biologically meaningful for each species 28 DAT (Table 7). Thifensulfuron provided the greatest efficacy on amaranth with 93% control. Flucarbazone gave the greatest visible injury of buckwheat and flax with 59 and 63% control, respectively. Imazamox and thifensulfuron gave similar control of flax at 18 and 20%, respectively, but thifensulfuron provided more visible injury to buckwheat than imazamox.

Fresh weight results were in agreement with 28 DAT visible injuries as higher efficacy levels resulted in lower fresh weight for amaranth, buckwheat or flax (Table 8). Differences in herbicide efficacy on fresh weight accumulation were measured for amaranth, buckwheat and flax for all herbicides. Thifensulfuron applied to amaranth had the highest visible injury and

resulted in 53 grams of fresh weight compared to imazamox at 124 grams and flucarbazone at 347 grams. Inversely, flucarbazone applied to flax had the highest visible injury and resulted in the lowest fresh weight with 89 grams compared to 190 grams for imazamox and 205 grams for thifensulfuron.

Table 8. Fresh weights of three species 28 DAT as influenced by ALS herbicides and droplet size.

Treatment	Amaranth	Buckwheat	Flax
	g		
<u>Herbicide^a</u>			
Flucarbazone	347	257	89
Imazamox	124	355	190
Thifensulfuron	53	309	205
LSD (0.05)	90	44	17
<u>Droplet size^b</u>			
Medium	200	318	160
Coarse	162	306	159
Very coarse	167	298	169
Extra coarse	168	307	156
LSD (0.05)	NS	NS	NS

^a Data averaged across droplet size.

^b Data averaged across herbicide.

ALS-inhibiting herbicides represent translocated mobility within plants. This may contribute to the lack of droplet size influence on herbicide activity as expressed by visible injury evaluations or fresh weight accumulation. Imazamox has been shown to be equally efficacious regardless of nozzle type (droplet spectrum) and other factors such as adjuvant or volume (Ramsdale and Messersmith 2001). Additionally, greenhouse studies showed that when herbicide droplet concentrations were equal, one large droplet had similar phytotoxicity as four smaller droplets when overall herbicide dose was the same (Ramsdale and Messersmith 2002).

Non-Translocated Herbicides (Experiment 3). Significant interaction was not detected between droplet size and herbicide. Therefore, each main effect will be discussed as analyzed across levels of the other factor.

Herbicide in coarse-sized droplets tended to give the lowest visible injury for all species. When averaged across herbicide, herbicide in a coarse droplet spectrum applied to amaranth gave 66% control compared to 72% with either very coarse or extra coarse droplets 14 DAT (Table 9.). This difference was not present 28 DAT although herbicide in coarse droplets gave the least control numerically. Medium, very coarse and extra coarse droplets were similar in control for all plant species 14 DAT. Buckwheat and Venice mallow control were not affected by changes in droplet sizes for herbicide application at either 14 or 28 DAT.

Differences in herbicide efficacy were observed on all species. Saflufenacil provided the greatest efficacy across all plant species indicating plants were very susceptible and responded rapidly with as much as 99% control 14 DAT (Table 9). High susceptibility may mask droplet differences if active ingredient rates are too high. Separation of means is expected at sub lethal rates of herbicide but too low of herbicide rate may be undetectable as well because of lack of response. Bromoxynil and carfentrazone gave similar efficacy when applied to either buckwheat or Venice mallow. Carfentrazone had greater efficacy than bromoxynil when applied to either amaranth or flax.

Visible injury ratings 28 DAT were either similar to/or less than 14 DAT ratings for all species (Table 9). New growth from axillary meristems and continuation of apical meristem growth was responsible for less control at 28 DAT compared with initial evaluation 14 DAT. Venice mallow control when averaged across droplet size or across herbicide decreased by 2 to 9 times from 14 to 28 DAT. Venice mallow control was not sufficiently maintained by contact

herbicides as its rate of recovery was high. Similar observations have been noted in other research.

Table 9. Visible injury of non-translocated herbicides on four species as influenced by herbicide and droplet size at 14 and 28 DAT.

Treatment	Amaranth		Buckwheat		Flax		V. mallow		
	14 DAT	28 DAT	14 DAT	28 DAT	14 DAT	28 DAT	14 DAT	28 DAT	
	-----%								
<u>Herbicide^a</u>									
Bromoxynil	47	42	53	54	29	25	24	4	
Carfentrazone	63	62	53	58	42	28	26	3	
Saflufenacil	99	96	91	85	86	77	90	40	
LSD (0.05)	5	6	2	6	7	6	4	2	
<u>Droplet size^b</u>									
Medium	70	69	66	68	53	40	49	15	
Coarse	66	63	64	64	50	48	46	17	
Very coarse	72	68	68	68	54	45	46	16	
Extra coarse	72	67	65	62	52	41	45	14	
LSD (0.05)	6	NS	-----	NS	-----	NS	6	-----	NS

^a Data averaged across droplet size.

^b Data averaged across herbicide.

Saflufenacil applied to 5-to 10-cm tall Palmer amaranth only gave 77% control at 28 DAT compared to 92% control 7 DAT (Morichetti et al. 2012). Control ratings behaved similar in this research as herbicide efficacy often decreased from 14 to 28 DAT. Significant herbicidal effects of coarse-sized droplets applied to amaranth at 14 DAT were not present at the 28 DAT assessments. Flax control by herbicides in coarse-sized droplets 28 DAT had decreased from the 14 DAT assessments. Even though coarse-sized droplets gave greater herbicide injury at 28 DAT than a medium or extra coarse sized droplet when applied to flax, the general trend for herbicide

control in coarse droplet spectra was toward less control than when herbicides were applied in other droplet sizes.

Fresh weights of many treatments were not informative because of differences in plant herbicide efficacy. Plants with high sensitivity to saflufenacil resulted in near complete control of plant biomass and were not different from plots with low plant population (data not shown). High efficacy of saflufenacil resulted in complete plant death and not different values between droplet sizes. Conversely, bromoxynil or carfentrazone provided so little control that biomass accumulation was the same across treatments. In addition to high efficacy and low plant population, high densities of native Venice mallow outcompeted species seeded in rows. All of these factors contributed to nonsignificant effect of spray droplet size on herbicide efficacy.

Droplet Size Effect of Nozzle Tip Type and Orifice Size (Experiment 4). Interaction between herbicide and nozzle type was not detected, allowing for discussion of main effects. Visible injury of amaranth and Venice mallow was not affected by droplet size when averaged across herbicides indicating that orifice size and spray spectrum did not influence efficacy 14 DAT (Table 10). Although the AIR110015 nozzle tip (extra coarse droplet and small orifice size) had significantly lower control when applied to buckwheat compared to other droplet sizes 14 DAT, the same droplet size with greater tip flow gave similar control to medium droplet size treatments. In general, the AIR110015 nozzle resulted in the lowest efficacy for all species. Other results have shown that liquid sheet thickness correlates to droplet size (Miller and Butler Ellis 2000). Smaller orifice size could result in a portion of the droplet spectrum as fine droplets, due in part to smaller liquid sheet thickness.

Bromoxynil control at 14 DAT was lower than all other herbicides for amaranth and Venice mallow but was a poor herbicide for buckwheat or flax control as well (Table 10).

Addition of 2,4-D to improved efficacy on buckwheat, flax and venice mallow compared with either herbicide alone. However, 2,4-D alone resulted in higher efficacy when applied to amaranth. Thifensulfuron efficacy was greatest for all species except buckwheat, which was most effectively controlled by bromoxynil plus 2,4-D.

Table 10. Visible injury of four herbicide treatments on four species 14 DAT as influenced by nozzle orifice size.

Treatment	Visible injury ^a			
	Amaranth	Buckwheat	Flax	V. mallow
	%			
<u>Herbicide^b</u>				
2,4-D	74	64	23	40
2,4-D+bromoxynil	66	71	30	49
Bromoxynil	50	48	21	29
Thifensulfuron	80	50	34	50
LSD (0.05)	4	4	3	4
<u>Droplet size^{cd}</u>				
M015 (XR80015)	70	57	28	43
M04 (XR8004)	65	59	28	39
XC015 (AIXR110015)	64	53	24	39
XC04 (AIXR11004)	66	59	26	39
LSD (0.05)	NS	4	3	NS

^a Visible injury was based on a 0 to 100% plant death scale. 0=no injury and 100=entire plant death.

^b Data averaged across droplet size.

^c Data averaged across herbicide.

^d M=Medium, XC=Extremely coarse, XR=Extended range, AIXR=Air induction extended range, 015=0.15 gallon per minute flow rate, 04=0.4 gallon per minute flow rate.

Orifice size was not a determining factor in herbicide efficacy when applied to amaranth or Venice mallow when averaged over herbicides 28 DAT (Table 11). There was not a difference in control between 015 and 04 orifice size for medium or extra coarse droplet size when applied to amaranth, flax or Venice mallow. Similar to 14 DAT assessments, use of the AIXR110015 nozzle tip to apply herbicide to buckwheat resulted in the lowest control 28 DAT.

Table 11. Visible injury of four herbicide treatments on four species 28 DAT as influenced by nozzle orifice size.

Treatment	Visible injury ^a			
	Amaranth	Buckwheat	Flax	V. Mallow
	%			
<u>Herbicide^b</u>				
2,4-D	88	62	28	46
2,4-D+bromoxynil	74	57	25	39
Bromoxynil	38	40	18	20
Thifensulfuron	93	57	30	51
LSD (0.05)	7	5	3	4
<u>Droplet size^c</u>				
M (XR80015)	76	53	24	41
M (XR8004)	73	55	25	39
XC (AIXR110015)	72	50	24	37
XC (AIXR11004)	72	57	27	39
LSD (0.05)	NS	4	NS	3

^a Visible injury was based on a 0 to 100% plant death scale. 0=no injury and 100=entire plant death.

^b Data averaged across droplet size.

^c Data averaged across herbicide.

Herbicide efficacy averaged over droplet size responded consistently with previous experiments when comparing 14 DAT to 28 DAT. Treatments containing a translocated herbicide, 2,4-D, thifensulfuron and 2,4-D+bromoxynil, had increased numerical efficacy values from 14 to 28 DAT whereas bromoxynil, a non-translocated herbicide, had numerically lower herbicide efficacy values 28 DAT compared with 14 DAT (Table 10 and 11). Bromoxynil control 28 DAT was significantly lower than other herbicides for each species (Table 11). Also different from 14 DAT, 2,4-D alone performed better on each species compared to a mixture of 2,4-D plus Bromoxynil 28 DAT.

Fresh weights, in general, did not behave similarly to 28 DAT visible injury values for any species. Amaranth fresh weight was similar compared to 28 DAT visible injury values as 2,4-D and thifensulfuron had significantly lower weights when compared to 2,4-D+Bromoxynil and bromoxynil (Table 12). Bromoxynil applied to buckwheat had the highest fresh weight compared to other herbicides. High bromoxynil fresh weight correlates to low levels of efficacy at 14 and 28 DAT.

Table 12. Fresh weight of four species 28 DAT with herbicides as influenced by nozzle orifice size.

Treatment	Amaranth	Buckwheat	Flax	V. mallow
	g			
<u>Herbicide^a</u>				
2,4-D	52	173	175	202
2,4-D+bromoxynil	174	127	179	193
Bromoxynil	272	225	176	305
Thifensulfuron	34	136	200	332
LSD (0.05)	64	26	18	55
<u>Droplet size^b</u>				
M015 (XR80015)	117	182	190	279
M04 (XR8004)	128	161	186	262
XC015 (AIXR110015)	128	159	179	262
XC04 (AIXR11004)	159	158	173	230
LSD (0.05)	NS	NS	NS	NS

^a Data averaged across droplet size.

^b Data averaged across herbicide.

Thifensulfuron provided the greatest control of amaranth, flax and venice mallow which was consistent with 14 DAT. 2,4-D efficacy was greatest when applied to buckwheat compared to other herbicides which was similar to the 14 DAT data for both the orifice size experiment (Table 10) and previous experiments containing 2,4-D (Table 5).

Summary

Interactions between herbicide and droplet size or herbicide and nozzle type were not identified for visible control at 14 DAT and 28 DAT or for fresh weight for any of the four field experiments. Therefore, analysis of main effects was reported.

Plant growth regulators, averaged across herbicide, provided greatest efficacy for flax when applied at a medium sized droplet for both 14 and 28 DAT assessments. Smaller droplet size probably provided better control of flax because of the smaller leaf area available for contact surface. Amaranth and buckwheat demonstrated the greatest injury when plant growth regulators were applied through a very coarse droplet size at 14 and 28 DAT. Medium and extra coarse droplet size spectra gave similar control when applied to amaranth or buckwheat. Fresh weight rankings affected by herbicide efficacy did not entirely follow visible injury assessments. This could be characteristically influenced by the effect of increased growth caused by plant growth regulator herbicides. Ferrell et al. (1989) reported that addition of plant growth regulator herbicides increased shoot fresh weight of leafy spurge compared to plants with no herbicide application. Depending on the level of plant response, a plant with greater injury may also have greater amounts of accumulated fresh weight.

Species response to ALS herbicide or droplet size differences had similar results at 14 and 28 DAT for ALS herbicides indicating the effect on plants progress similarly over time. At 28 DAT, a very coarse sized droplet spectrum gave better visible control than medium for both amaranth and flax. Buckwheat response to ALS herbicides was unaffected by changes in droplet size. Fresh weights for species treated with ASL herbicides agreed with 28 DAT visible injury assessments in rank and magnitude of differences when differences were observed. Flucarbazone

had the greatest 28 DAT visible injury for buckwheat and flax which resulted in the lowest accumulated fresh weight.

Visible injury assessments, when averaged across non-translocated herbicide treatments, were similar for all droplet sizes when applied to buckwheat or Venice mallow at either 14 and 28 DAT. Visible injury 28 DAT was either equal to or less than 14 DAT assessments for all species. Limited movement within the plant likely is responsible for the ability of new plant growth to initiate after application. Visible injury 7 DAT may have been beneficial for droplet size effect separation. Coarse-sized droplets gave the lowest control values across all species 14 DAT. However, these differences were not present 28 DAT. Fresh weight was not a reliable means of measuring droplet size effect as some plots were completely absent of plant material because of high herbicide efficacy or overgrown from plant regrowth.

Amaranth and Venice mallow were not affected by droplet size 14 or 28 DAT when comparing orifice size. No difference was observed in visible injury between 015 and 04 orifice size for medium or extra coarse droplet size when applied to amaranth, flax or Venice mallow. An AIXR110015 nozzle type had the least visible injury for any species at 14 or 28 DAT. Although fresh weight differences were not significant, the AIXR110015 nozzle type did not correlate to the largest fresh weight. Fresh weight treatment means for nozzle type were not different for any species.

Literature Cited

Bovey RW, Stermer RA, Bouse LF (1991) Spray deposition of clopyralid on Honey Mesquite (*Prosopis glandulosa*). *Weed Technol* 5: 499-503

Feng PCC, Chiu T, Sammons RD, Ryerse JS (2003) Droplet size affects glyphosate retention, absorption, and translocation in corn. *Weed Sci* 51: 443-448

Ferrell MA, Whitson TD, Alley HP (1989) Control of leafy spurge (*Euphorbia esula*) with growth regulator-herbicide combinations. *Weed Technol* 3:479-484

Lafferty CL, Tian LF (2001) The impacts of pre-orifice and air-inlet design features on nozzle performance. ASAE paper number 01-1079. 2001 ASAE Annual International Meeting, Sacramento, CA, July 30-Aug 1

Miller PCH, Butler Ellis MC (2000) Effects of formulation on spray nozzle performance for applications from ground-based boom sprayers. *Crop Prot* 19:609-615

Morichetti S, Ferrell J, MacDonald G, Sellers B, Rowland D (2012) Weed management and peanut response from applications of saflufenacil. *Weed Technol* 26:261-266

Ramsdale BK, Messersmith CG (2001) Nozzle, spray volume, and adjuvant effects on carfentrazone and imazamox efficacy. *Weed Technol* 15: 485-491

Ramsdale BK, Messersmith CG (2002) Adjuvant and herbicide concentration in spray droplets influence phytotoxicity. *Weed Technol* 16: 631-637

Reichard DL (1988) Drop formation and impaction on the plant. *Weed Technol.* 2:82-87

Senseman SA, ed. 2007. *Herbicide Handbook*. 9th ed. Lawrence, KS: Weed Science Society of America 458 p

Shaw DR, Morris WH, Webster EP, Smith DB (2000) Effects of spray volume and droplet size on herbicide deposition and common cocklebur (*Xanthium strumarium*) control. *Weed Technol* 14: 321-326

CHAPTER THREE: HERBICIDE FORMULATION, ADJUVANT TYPE, AND NOZZLE EFFECT ON DROPLET SIZE USING SPRAY SPECTRUM LASER ANALYZER

Introduction

Herbicide efficacy can be influenced by many factors apart from the herbicide mode of action within the plant. Adjuvants, nozzle type, formulation of herbicide, and adsorption to leaf surfaces can influence herbicide efficacies. A portion of the effects of these factors may be related to changes in droplet size of the spray. Alterations of a spray spectrum to achieve better retention could result in an increase in droplet sizes that are prone to drifting off target. Different formulations and adjuvant activity have been studied in field trials to comprehend their efficacy and droplet size. However, these experiments primarily look at plant injury instead of physical spray spectrum characteristics.

A systematic approach for droplet spectrum analysis is now available for herbicide solutions. Laser diffraction systems situated in wind tunnels are capable of analyzing spray particle size. The diffraction system calculates the diameter and volume of each droplet encounter by the laser beam and counts the number of droplets of each size. Laser analysis interprets a nozzle output and gives a computational output of VMD, droplet micrometer (μm) ranges and percentages of droplets in a particular size spectrum. Laser analysis gives an accurate characterization of droplet output by determining important performance characteristics.

The objective of this research was to compare the droplet spectrum caused by widely used adjuvants and different herbicide formulations, using a laser droplet analyzer.

Materials and Methods

A series of experiments to compare droplet sizes were conducted in 2013 at WinField Product Development Center, 2777 Prairie Drive, River Falls, WI 54022. Two different experiments were conducted based on adjuvant type and concentration and herbicide formulation and concentration. Run one of experiments was completed on February 11 and February 12, 2013 and run two on December 17 and December 18, 2013.

WinField Product Development Center houses the WinField Solutions Spray Analysis System, which is a low speed wind tunnel and laser droplet analyzer measuring particle size distribution. This is a patent pending combination of compressed-air fluid delivery, Sympatec HELOS-KR laser diffraction particle size sensor (Sympatec, PO Box 7527, Princeton, NJ), low speed recirculating wind tunnel and waste management system. The particle size sensor was a 632.8 nm He-Ne laser with 0.5-3500 μm range (R7) lens. Fluid was sprayed with the nozzle oriented so that the tunnel air movement was in the same direction as the spray, meaning the nozzle was rotated 90° (sideways) from the ground with the broad side or the spray fan perpendicular to the laser path. Wind speed was 12.9 ± 0.8 kph during sampling. The nozzle was affixed to a moving spray arm that allowed the laser to sample the full width of the spray fan pattern up to 140°. The laser can be oriented to traverse the spray pattern at 0-92 cm from the nozzle orifice, with standard sampling distance of 30 cm.

Water temperature was adjusted to 20 ± 1 °C, and air temperature was held at 20 ± 1 °C. Standard treatments use tap water, 200 ppm CaCO_3 equivalency. The flow rate of each nozzle was tested with water at the desired pressure before beginning the study. Operator pressure was adjusted to account for pressure loss within the system until the nominal flow rate of the nozzle

was reached (ex. 11003 nozzle at 0.3 gallons per minute, 1.1 L/minute). A system cleanout running water through the spray system was performed after every treatment.

Data was collected with the Sympatec software WINDOX 5.0.0.7. Standard measurements included x10, x50 (Volume Median Diameter), x90, and relative span (Dv0.1). Data analyzed included percent of volume less than 150 μ m, percent of volume greater than 633 μ m also were recorded.

Drift reduction technologies (DRT) are evaluated for percent reduction in fines over reference standard glyphosate at 1240g ae ha⁻¹ in 93.5 L ha⁻¹, using TeeJet XR11003 at 300 kPa. If no active ingredient is used, comparisons were made against water. Percent reduction in fines = $100 * (V_{ai} - V_{DRT})/V_{ai}$ where V = % particles < 105 μ m. Treatments were mixed in an 11.4 liter stainless steel pressurized spray canister and attached to the wind tunnel spray system via spray tubing.

Adjuvant Type by Nozzle Tip by Adjuvant Rate (Experiment 1). Treatments were organized in a factorial arrangement of four adjuvants, three adjuvant rates and two nozzle tips. An additional control treatment was analyzed of water alone as a comparison. All treatments were sprayed at 300 kpa to achieve 93.5 L/ha. Adjuvant rates were incremental of half, full and twice the recommended field rates.

Adjuvant types used were nonionic surfactant (NIS), methylated seed oil (MSO), high surfactant oil concentrate (HSMOC) and ammonium sulfate (AMS) water conditioner. Chemicals used were a mixture of alkylphenol ethoxylate, butyl alcohol and dimethylpolysiloxane for NIS, nonylphenol ethoxylate for MSO, methylated soybean oil, high fructose corn syrup, sorbitan fatty acid esters for HSMOC and granular ammonium sulfate for AMS. NIS was sprayed at 0.25%, 0.5% and 1% v/v, MSO at 0.9, 1.8 and 3.5 L/ha, HSMOC at

0.7, 1.5 and 2.9 L/ha and granular AMS at 0.45, 0.9 and 1.8 kg/ha. Spray volume of 93.5 L/ha was achieved with XR11003 and TT11003 nozzles (TeeJet®, Spraying Solutions Inc., Wheaton, IL.).

Herbicide Formulation by Nozzle Type by Herbicide Rate (Experiment 2).

Treatments were organized in a factorial arrangement of five herbicides of different formulation type, four nozzles and three rates. Herbicides were selected to compare a range of commonly used formulations in wheat. Herbicide formulations selected were liquid (2,4-D amine), soluble granule (thifensulfuron), emulsifiable concentrate (2,4-D ester), soluble concentrate (flucarbazone plus fluroxypyr) and oil dispersion (pyroxsulam plus fluroxypyr plus florasulam). 2,4-D amine was sprayed at a rate of 280, 560 and 1120 g ae ha⁻¹. Thifensulfuron was sprayed at 8.75, 17.5 and 35 g ai ha⁻¹. 2,4-D ester was sprayed at 336, 672 and 1344 g ae ha⁻¹. Flucarbazone plus fluroxypyr was sprayed at 245, 490 and 980 g ai ha⁻¹. Pyroxsulam plus fluroxypyr plus florasulam were sprayed at 560 g ae ha⁻¹. To determine formulation type effect on spray solution, recommended adjuvants were not added to solutions.

Data Collection and Analysis. All data were collected with the Sympatec software WINDOX 5.0.0.7 into Excel data sheet form. Treatment variables were all considered fixed effects. Experiment treatments were organized in a factorial arrangement of herbicide, nozzle and rate with five replications taken of each treatment. Data were combined between run one and run two when error mean squares were homogenous. Runs with heterogeneous error mean squares were presented separately. These values were subject to analysis of variance and mean separation occurred with Fisher's-protected LSD at (P<0.05). Analysis was conducted with separate LSD for main affect and interaction comparison.

Results and Discussion

Wind tunnel operation was modified following the February 2013 experiments affecting the measurements of data for the December 2013 experiments. Modification of the system was conducted to increase wind speed to reduce the amount of fine droplets traveling back through the laser diffraction particle size sensor. However, Bouse (1994) found that increasing wind tunnel speed at very fast speeds (193 to 241 km/h) resulted in smaller droplet size and a higher percent of spray volume in droplets prone to drift in the field. Volume in droplets $<200\mu\text{m}$ decreased from 11.42 to 6.42%. Consequently, measurements were different for run one and run two. In general, percent volume in droplets $<150\mu\text{m}$ were lower and VMD was higher for run 2 across most treatments. Treatment means were different, error mean squares between runs were within a factor of ten allowing data to be combined across runs.

Adjuvant Influence on Spray Spectrum. A significant interaction between adjuvant type and rate was observed for percent volume of solution in droplets $<150\mu\text{m}$. When averaged across nozzle type, percent volume in droplets $<150\mu\text{m}$ for NIS was greater than other adjuvants at 0.5x, 1.0x and 2.0x of the recommended rate (Table 1). NIS adjuvants are used for lowering surface tension of spray solutions to enhance leaf wetting. Reduced surface tension of the spray solution upon exiting the nozzle could result in delayed droplet breakup causing more fine droplets in the spray spectrum. Previous research has shown that lowering dynamic surface tension would delay spray sheet breakup upon exiting the nozzle orifice and a thinner spray sheet is produced resulting in smaller droplets (Miller 1998). 1.0x and 2.0x the recommended field rate of NIS were similar and gave the highest percentage of volume in droplets $<150\mu\text{m}$. MSO, HSMOC and AMS produced similar driftable fraction volumes at 0.5x or 1.0x the recommended field rate. HSMOC had a lower volume of droplets $<150\mu\text{m}$ when sprayed at 2.0x the

recommended rate compared to the other adjuvants. However, HSMOC and MSO rate did not affect driftable volume while AMS, similar to NIS, had greater volume in droplets <150µm at 2.0x compared to 0.5x.

No significant interaction occurred between nozzle type and rate when averaged over adjuvant for percent volume of droplets <150µm (Table 13). The standard nozzle, XR11003, had 11.3 percent more of volume in droplets <150µm compared to the TT11003 nozzle (not shown). NIS, MSO and AMS percent of volume in droplets <150 increased as rate was increased from 0.5x to 2.0x. HSMOC was the only adjuvant that remained unchanged as rate was changed.

Table 13. Percentage of volume in droplets <150µm of four adjuvant and two nozzle types influenced by adjuvant rate averaged across two nozzle types and two runs.

Treatment	<150µm		
	0.5x	1.0x	2.0x
<u>Adjuvant^a</u>	%		
NIS	20.2	25.0	26.3
MSO	16.9	18.3	19.1
HSMOC	17.1	17.5	17.4
AMS	17.7	19.8	20.8
<u>LSD (0.05)</u>	2.4		

^a Averaged across nozzle type.

Error mean squares for VMD were heterogeneous across runs and treatments, thus, means were presented for treatments within each experimental run for each rate. RELSPAN for NIS was the largest compared to other adjuvants (Table 14). Data suggests that a larger RELSPAN for spray spectra may signify inconsistency and a greater distribution of different sized droplets. RELSPAN is an indicator of variation in droplet size. NIS gave the highest spray spectrum VMD at 0.5x rate (Table 15). Although NIS gave the highest percentage of volume in droplets <150µm (Table 13), it did not correlate to the smallest VMD compared to other adjuvants (Table 15). A larger percent of volume in droplets <150µm should correlate to a

smaller VMD within a treatment. However, deviation from this trend can relate to a wider span of droplet sizes represented by RELSPAN.

An increase of NIS from 0.5x to 1.0x decreased the spray VMD by 23 (Table 15). This should increase driftable spray fraction which was confirmed (Table 13). MSO sprayed at 1.0x and 2.0x resulted in the lowest spray spectrum VMD compared to MSO at 0.5x and any other combination of adjuvant and rate. VMD for AMS and HSMOC were not significantly changed by adjuvant rate.

Table 14. Spray characteristics of four adjuvants averaged across rate and nozzle type.

Treatment	<150	<622	RELSPAN	VMD	
				Run 1	Run 2
Adjuvant ^a	%	%		µm	
NIS	23.8	2.1	1.31	262	266
MSO	18.1	0.4	1.16	248	263
HSMOC	17.3	1.4	1.22	259	283
AMS	19.4	2.2	1.28	266	284
LSD (0.05)	1.5	NS	0.13	2	6

^a Averaged across nozzle type.

When averaged across adjuvants, an XR11003 nozzle gave a smaller spray spectrum VMD than a TT11003 at all rates for run 1 and run 2 (Table 15). For an XR11003 nozzle, a 0.5x rate gave the highest spray spectrum VMD for both runs. An XR11003 nozzle sprayed at 1.0x and 2.0x rates provided similar VMD for both runs. A TT1103 nozzle sprayed at 0.5x or 1.0x provided similar VMD for Run 1. There was no rate effect for a TT1103 nozzle during run 2.

When averaged across rates for combined locations, NIS sprayed through an XR11003 nozzle had the highest percentage of volume in droplets <150µm compared to the three other adjuvants or when sprayed through a TT11003 (Table 16). MSO and HSMOC gave similar volume in droplets <150µm. Driftable volume with AMS was significantly higher than with

MSO and HSMOC but was less than NIS. All adjuvants gave similar percentages of volume in droplets <150µm when applied through a TT11003 nozzle when averaged over adjuvant rates. The incorporation of a pre-orifice in the TT nozzle design is responsible for similar percentages of volume in droplets <150µm because of reduction in pressure. Although flow rates are different, spray spectra characteristics remain similar.

Table 15. Volume mean diameter of four adjuvants and two nozzles influenced by adjuvant rate for each of two runs.

Treatment	VMD					
	Run 1			Run 2		
	0.5x	1.0x	2.0x	0.5x	1.0x	2.0x
	————— µm —————			————— µm —————		
<u>Adjuvant^a</u>						
NIS	278	255	252	274	262	261
MSO	254	246	244	266	261	262
HSMOC	260	260	258	292	278	282
AMS	264	267	267	291	284	272
LSD (0.05)	————— 3 —————			————— NS —————		
<u>Nozzle^b</u>						
XR11003	224	209	210	250	233	227
TT11003	304	305	300	312	309	316
LSD (0.05)	————— 2 —————			————— 8 —————		

^a Averaged across nozzle type.

^b Averaged across adjuvant type.

Error mean squares for VMD between run 1 and run 2 were not homogeneous requiring separate presentation of data. When compared to a TT11003 nozzle, all adjuvants had lower VMDs when sprayed with an XR11003 for both run 1 and run 2 (Table 16). For both runs, NIS had the lowest VMD compared to the three other adjuvants when sprayed through the XR11003

nozzle. However, NIS had the highest VMD when applied through a TT1103 nozzle. MSO had the lowest VMD within TT11003 nozzle type for both experimental runs.

Table 16. Percent of volume in droplets <150µm and volume mean diameter of adjuvants influenced by nozzle type, averaged across adjuvant rate.

Treatment	VMD					
	<150		Run 1		Run 2	
	XR11003	TT11003	XR11003	TT11003	XR11003	TT11003
Adjuvant ^a	%		µm		µm	
NIS	34.7	12.5	189	334	211	324
MSO	19.4	16.8	225	271	247	279
HSMOC	20.8	13.8	229	290	251	319
AMS	25.9	12.6	214	318	238	330
LSD (0.05)	6.4		3		9	

Herbicide Formulation Influence on Spray Spectrum. The data for herbicide formulation influence on the spray spectrum were homogeneous allowing for combined analysis between run 1 and run 2. Rate response was not observed in this experiment so data presented were averaged across herbicide rate. XR11003 nozzle produced the largest percentage of volume in droplets <150µm compared to the three other nozzle types for each herbicide (Table 17). 2,4-D amine sprayed through the XR11003 nozzle gave the largest volume in droplets <150µm. 2,4-D amine, flucarbazone plus fluroxypyr and thifensulfuron had similar volumes in droplets <150µm when sprayed through a TT11002, TT11003 or TT11004 nozzle tips. When 2,4-D ester was sprayed, a TT11004 produced less driftable sized droplets than when sprayed through the other three smaller sized orifice TT nozzles. 2,4-D ester, an emulsifiable concentrate (EC) formulation, gave the lowest volume in droplets <150µm for the XR11003 nozzle. This corresponds with research done by Miller and Butler Ellis (2006), reporting that EC formulations have lower numbers of droplets prone to drift because of spray sheet perforation. Solutions containing emulsions are not homogeneous which results in liquid spray sheet perforation closer

to the nozzle orifice. Earlier sheet perforation and overcoming surface tension forces reduce the amount of small droplets. The percentage of volume in droplets <150µm may have remained unchanged for TT style nozzles because of the incorporation of the pre-orifice previously discussed. Use of nozzles with a pre-orifice has been shown to reduce the number of small droplets produced (Mueller and Womac 1997). Extended range (XR) nozzles are intended to produce similar spray droplet spectrums over a range of pressures; however, they do not use a pre-orifice such as TT style nozzles. Prior work with flat fan nozzles, which lack a pre-orifice, suggested that sheet length was strongly correlated with droplet size, with shorter sheet lengths resulting in larger droplets (Butler Ellis et al. 1997).

VMD of the four herbicides correlated with volume in droplets <150 when sprayed with all nozzle types, i.e. largest volume in droplets <150 and smallest VMD were recorded from the same treatment (Table 17). The TT1104 nozzles gave the largest VMD for all herbicides except when flucarbazone plus fluroxypyr was sprayed. VMD was smallest for all herbicides when sprayed through the XR11003 nozzle. 2,4-D amine resulted in the lowest VMD, 211µm, compared to all other herbicides, 218µm or more, when sprayed through the XR11003 nozzle. 2,4-D ester gave the largest VMD, 240µm, when sprayed through the same nozzle. Ranked by herbicide formulation, VMD was liquid < soluble granule < soluble concentrate < emulsifiable concentrate. This is consistent with expected percent of volume in droplets <150. Stainier et al. (2006) also showed that VMD was higher for EC herbicides when compared to other formulations.

Differences between TT nozzle sizes were negligible yet remained significantly different. TeeJet classifications offer ranges of spray spectrums which allows for variation between herbicides sprayed. XR spray nozzle data also remained narrow considering the range of

herbicide formulations sprayed. The range VMD for the XR11003 nozzle was 29µm compared to 14µm for the TT style nozzle tips.

Table 17. Percent of volume in droplets <150µm averaged across herbicide rate.

Treatment		<150	VMD
<u>Herbicide</u>	<u>Nozzle</u>	%	µm
2,4-D amine (L)	XR11003	30.6	211
	TT11002	12.3	344
	TT11003	12.3	338
	TT11004	11.4	348
2,4-D ester (EC)	XR11003	18.3	240
	TT11002	14.2	288
	TT11003	13.9	296
	TT11004	12.8	300
Flucarabzone+fluroxypyr (SC)	XR11003	26.7	222
	TT11002	11.7	334
	TT11003	11.7	332
	TT11004	11.0	329
Thifensulfuron (SG)	XR11003	29.0	218
	TT11002	12.3	326
	TT11003	12.8	329
	TT11004	12.0	336
LSD (0.05)		1.0	3

Summary

NIS gave the largest percentage of volume in droplets <150µm compared to MSO, HSMOC or AMS across rates of 0.5x, 1.0x or 2.0x, averaged across nozzle type. A 0.5x rate of NIS reduced percent of volume in droplets <150µm by 4.8 percent, averaged across nozzle type. The 0.5x rate had lower percent of volume in droplets <150µm compared to the 2.0x rate. Although NIS had the largest percent of volume in droplets <150µm, it did not have the lowest

VMD when averaged across rate and nozzle type. This is attributed to the largest RELSPAN value of 1.31. A larger RELSPAN indicates a broader spread droplet size, which would nullify the effect that percent of volume in droplets <150µm would have on the VMD.

The TT11003 nozzle had lower percent of volume in droplets <150µm and higher VMD than compared to the XR11003 nozzle. TT style nozzles incorporate a pre-orifice within the nozzle that lowers spray pressure before exiting the primary orifice. This aids in the reduction of droplets prone to drift.

Liquid herbicide formulation (2,4-D amine) gave the largest percent of volume in droplets <150µm while an emulsifiable concentrate formulation (2,4-D ester) was lowest when sprayed through an XR11003 nozzle. However, the percent of volume in droplets <150µm for the emulsifiable concentrate formulation was greater than other formulations when sprayed from any of the TT style nozzles. VMD correlated well with the percent of volume in droplets <150µm meaning sprays with less volume in droplets <150µm had larger VMD. The TT11004 nozzle gave the largest VMD for all herbicide except for when flucarbazone plus fluroxypyr was sprayed. The wind tunnel standard nozzle, XR11003, had the smallest VMD for all herbicides.

Emulsifiable concentrate herbicides reduction in droplets <150µm suggests a spray spectrum less likely to contain droplets prone to drift. Although VMD for an emulsifiable concentrate herbicide was lowest, droplets were more consistent in size overall. However, herbicide formulation was of less importance than nozzle type in reducing risk of droplets prone to drift. Although an emulsifiable concentrate herbicide reduced driftable droplets the most, this may not be appropriate under all applications. Continued research should be done to analyze the interactions of herbicide formulation with more nozzle types.

Literature Cited

Bouse LF (1994) Effect of nozzle type and operation on spray droplet size. Transactions of ASAE 37(5):1389-1400

Butler Ellis MC, Miller PCH, Tuck CR (1997) The effect of some adjuvants on sprays produced by agricultural flat fan nozzles. Crop Protect 16:41-50

Miller PCH (1998) Spray application and adjuvants: challenges and opportunities. Proceedings of fifth international symposium on adjuvants for agrochemicals. pp 367-376

Miller PCH, Butler Ellis MC (2000) Effects of formulation on spray nozzle performance for applications from ground-based boom sprayers. Crop Protect 19:609-615

Mueller TC, Womac AR (1997) Effect of formulation and nozzle type on droplet size with isopypylamine and trimesium salts of glyphosate. Weed Technol 11:639-643

Stainer C, Destain M-F, Schiffers B, Lebeau F (2006) Droplet size spectra and drift effect of two phenmeipham formulations and four adjuvants mixtures. Crop Protect 25:1238-1243