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Effect of the Spray Droplet Size and Herbicide Physiochemical Properties on Pre-Emergence Herbicide Efficacy for Weed Control in Soybeans

Pedro Henrique Urach Ferreira

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Effect of the spray droplet size and herbicide physicochemical properties on pre-emergence herbicide efficacy for weed control in soybeans.

By

Pedro Henrique Urach Ferreira

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Effect of the spray droplet size and herbicide physicochemical properties on pre-emergence herbicide efficacy for weed control in soybeans.

By

Pedro Henrique Urach Ferreira

Approved:

Jason Connor Ferguson
(Major Professor)

Daniel B. Reynolds
(Committee Member)

Greg R. Kruger
(Committee Member)

Jon Trenton Irby
(Committee Member)

Michael S. Cox
(Graduate Coordinator)

George Hopper
Dean
College of Agriculture and Life Sciences

Name: Pedro Henrique Urach Ferreira

Date of Degree: December 14, 2018

Institution: Mississippi State University

Major Field: Plant and Soil Sciences

Major Professor: Jason Connor Ferguson

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Candidate for Degree of Master of Science

Field studies conducted in Missouri and Mississippi, in 2017 and 2018, respectively, indicated no droplet size effect on PRE herbicide efficacy, regardless of the herbicide, weed, soil, crop residue and weather conditions during spraying. Nozzle type enhanced herbicide efficacy for one location and herbicide. The TTI60 dual fan nozzle increased pendimethalin weed control, up to 91%, in a high organic matter (OM) soil with large clods and substantial weed pressure. Pendimethalin efficacy was reduced under high OM soils (> 2%) while metribuzin efficacy was reduced under low OM (< 0.7%), low cation exchange capacity (<13.1%) soils and 12.2 mm of rain three days after application. The greenhouse studies indicated that increasing crop residue levels reduced velvetleaf control by 7%. Simulated rainfall eight days after herbicide application decreased johnsongrass dry weight reductions by 29% in comparison to two day rainfall.

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CHAPTER I

INTRODUCTION

Pre-emergence herbicides

Weed control is of great importance to achieve optimal crop yields. By definition, weeds are every plant that causes ecological damage or economical losses, creates health problems for humans and animal or is undesirable where it grows (WSSA, 2016). Weeds compete for light, nutrients and water in the same space as cultivated plants, impacting crop development, yield and harvest. Gantoli et al. (2013) observed up to 65% yield losses in corn (*Zea mays* L.) due to weed competition. In soybeans (*Glycine max* (L.) Merr.), Soltani et al. (2017) estimated a 52% crop loss due to weed interference with a potential economic loss of $16.2 billion dollars in the US. Integrated Weed Management (IWM), an ideal weed management program, integrates all possible methods to optimize control. Examples include soil conservation practices, crop rotation, variety selection, seed purity, crop establishment and nutrition, biological control and herbicide applications (Naylor et al., 2002). Chemical weed control is the most commonly used method use by farmers worldwide due to its effectiveness. A herbicide demand and adoption review by Hossain (2015) showed yield increases of 20% in corn and 62% in soybeans when using herbicides in the US.

Craigmyle et al. (2013) observed that, prior to glyphosate-resistant (GR) crops, farmers used to apply pre-emergence herbicides (PREs) like the dinitroanilines (e.g. trifluralin and pendimenthalin) and the imidazolinones (e.g. imazaquin and imazethapyr) every year. In 1990, the top four herbicides applied were PREs: trifluralin, metribuzin, imazaquin and pendimethalin accounting for 37, 19, 16 and 14% of applied US soybean hectares respectively (USDA, 1991). After the launch of GR soybeans in 1996, farmers quickly adopted a strategy relying almost entirely on glyphosate alone (Figure 1.1). Although chemical control is the most efficient weed management tool, use of the same mode of action over time leads to weed resistance to that particular mode of action (Gazziero et al., 1998; Gelmini et al., 2001). The repetitive use of glyphosate over many years accelerated observation of GR weeds (Knezevic, 2007). By 2017, 37 weed species were documented as resistant to EPSP synthase inhibitors (Heap, 2017).

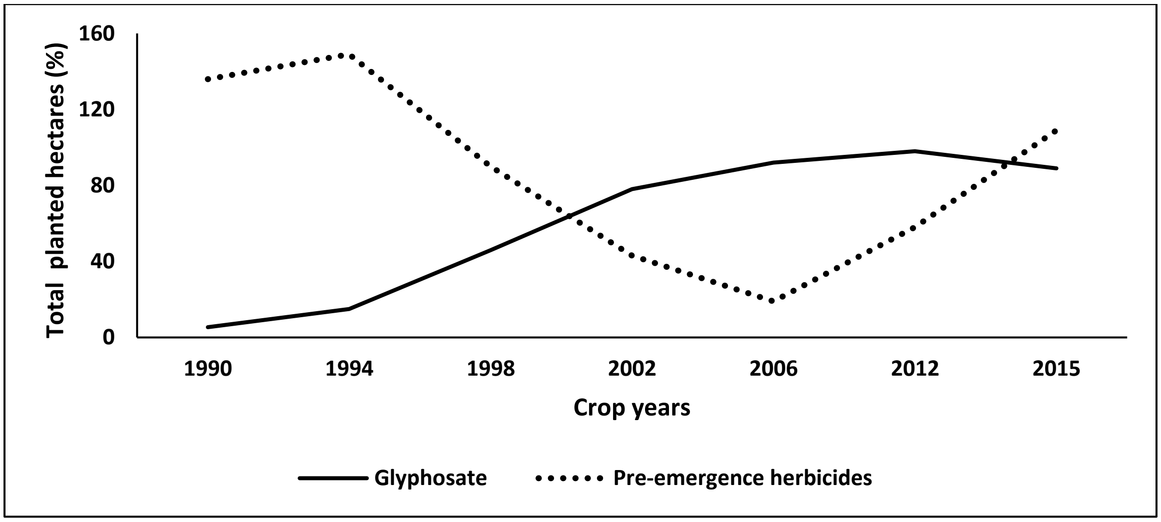

Figure 1.1 Sum of PREs applied (e.g. % of planted acres of PRE A + % PRE B) and the total glyphosate applied as percentage of planted hectares per crop year (USDA, 2017).

Although glyphosate applications covered 98% of US soybean hectares in 2012, applied hectares of PRE herbicides, after a 12 year decline, began to increase in 2006. In 2015, the total use of PRE herbicides surpassed the total glyphosate usage as shown in Figure 1.1 (USDA, 2017). The usage of PRE herbicides are important to control troublesome weeds and lessen weed resistance, especially when combined with other products and herbicide mode of action rotation. Prince et al. (2012) conducted a survey with 1,299 farmers in the US regarding crop practices to manage glyphosate resistant weeds from 2006 to 2009. The researchers observed increased crop scouting, crop rotation, herbicide applications at their maximum labeled rate, and number of applications using both post-emergence (POST) and PRE herbicides. The positive aspects of PRE herbicides include: source of alternative herbicide mode of action (MOA); decreased weed pressure as well as cost and time savings eliminating the need for future POST applications (GRDC, 2015). In Australia, the New South Wales Department of Primary Industries, NSW DPI (2012), calculated an average return of investment of 1084% from the use of PRE herbicides in five different locations. Kapusta (1979) found that using PRE herbicides alone or as tank-mixtures of alachlor, metribuzin, linuron, metolachlor, pendimethalin obtained sufficient control for weeds like large crabgrass (*Digitaria sanguinalis* L.), fall panicum (*Panicum dichotomiflorum* Michx.), giant foxtail (*Setaria faberi* Herrm.), redroot pigweed (*Amaranthus retroflexus* L.) and horseweed (*Erigeron Canadensis* L.). When proposing a series of management options to fight weed resistance, Cerdeira et al (2011) included the application of PRE herbicides to enhance cropping systems. Knezevic et al. (2009) evaluated soybean weed control of glyphosate tank-mixtures with PRE herbicides in Nebraska and found that tank mixtures provided over 80% control of troublesome weeds. Ellis and Griffin (2002) observed a decreased weed density and increased growth in soybeans over three years when PRE herbicides were adopted. They concluded that using PRE herbicides could reduce glyphosate usage to one application instead of two or three. Mahoney et al. (2014), showed that when using a tank-mixture of flumioxazin and pyroxasulfone in soybeans, the POST herbicide application could be omitted.

A wide range of variables influence PRE herbicide efficacy: photochemical decomposition, temperature, chemical breakdown, microbial decomposition, soil adsorption, product evaporation, and soil moisture. Some of these environmental pathways can be understood through specific herbicide physicochemical properties given as adsorption, volatility and solubility.

Adsorption

Herbicide adsorption is the adhesion of the herbicide in its liquid phase with the surface of solid soil particles (Vieira et al., 1999; Peterson et al., 2015), indicating how tightly a herbicide will bind to the soil. Herbicide adsorption is influenced by organic matter (OM) content where soils with high OM may require higher rates of a herbicide while a sandy or low organic matter soil will have greater product availability. According to Linde (1994), most pesticides are hydrophobic, non-polar, and are attracted to the lightly charged surface of the organic matter. Herbicide adsorption is positively correlated with soil moisture. Surface soil and organic matter particles are distributed between water and herbicide molecules. Under dry soil conditions, herbicides are strongly adsorbed onto soil and OM fragments. Because of that, plant uptake is minimal. In order to quantify adsorption a coefficient K_{oc} is used. The K_{oc} is the soil organic carbon-water partitioning coefficient and measures the chemical binding force and mobility of soil organic carbon. High K_{oc} values indicate low mobility and low K_{oc} values indicate high mobility in the soil (Vogue et al., 1994; EPA, 2012). With a lower K_{oc} more herbicide will be available in soil-solution (Schreiber, 2012). The standard mobility classification is given as the logarithm of K_{oc} due to its wide value range (Table 1.1).

Surface residues, like crop stubble and straw, also affect chemical adsorption. Hodges and Talbert (1990) studying the adsorption of diuron, terbacil and simazine on blueberry mulches, concluded that herbicide adsorption in mulches was up to five times greater than soil alone. Thus, crop residue may capture the herbicide through adsorption resulting in reduced soil deposition and reduced weed control (GRDC, 2015; Borger et al. 2013). Herbicides with high adsorption may bind tightly to crop residue and not be available for plant uptake. Toth and Milham (1975) observed similar surface residue effects on herbicide adsorption and plant uptake with diuron.

Table 1.1 Classification of herbicide mobility (FAO, 2000).

Log K_{oc}	Classification
> 4.5	Very strong sorption to soil
3.5 – 4.4	Strong sorption to soil
2.5 – 3.4	Moderate sorption to soil
1.5 – 2.4	Low sorption to soil
< 1.5	Negligible sorption to soil

Volatility

The volatilization process is another way a herbicide is degraded and dispersed in the environment. Vapor drift of volatile herbicides may rapidly occur once released in the atmosphere. Vapor drift, the off-target pesticide movement as a gas (Hanson et al., 2016), which may result in herbicide losses and plant injury. Studying the effect of dicamba volatility, Behrens and Lueschen (1979) observed soybean injury and yield losses due to vapor drift with increased damage in applications during high temperatures and low air humidity conditions. Egan et al. (2014) observed the same influence of weather conditions when studying the effects of 2,4-D and dicamba on cotton and soybeans. In addition to weather conditions, the product's physicochemical properties, its formulation type and the presence of crop residue on soil also affects the degree of losses to the atmosphere. Alachlor and atrazine applications in no-tillage corn had lower volatilization losses when compared to conventional tillage systems (Wienhold and Gish, 1994). Additionally, Glotfelty and Schomburg (1989) observed that greater surface area and crop residue increased herbicide volatilization. Schreiber et al. (2015) observed less phytotoxicity from volatilization for microencapsulated formulations of clomazone. Less loss from encapsulated formulations was also observed by Wienhold and Gish (1994).

Vapor pressure is an important measurement to evaluate volatilization and estimate the probability of a pesticide to change from a solid or liquid phase to the gaseous phase (Hornsby et al., 1996). Vapor pressure is commonly provided in millimeters of mercury (mmHg) at 25°C. Low values of vapor pressure indicate low volatility and high vapor pressure values indicate high volatility (Table 1.2).

Soil applied herbicides with high vapor pressure values, like trifluralin (1.1 x 10^{-4}) and ethalfluralin (8.2 x 10^{-5}) require soil incorporation after application to avoid product degradation. Other PRE herbicides (e.g. *S*-metolachlor; pendimethalin; pyroxasulfone; metribuzin and clomazone) require water activation through rain or irrigation soon after application to ensure optimum herbicide efficacy. Generally, PRE herbicides have better plant uptake under adequate soil moisture conditions due to reduced soil colloid adsorption and greater herbicide availability (Loux et al., 2015). Soil moisture has the opposite effect for volatile herbicides. Schneider et al. (2013) studied the volatilization of trifluralin and triallate at different soil moistures and observed up to an 8x increase in volatilization when controlled humidity within the soil was increased. When simulating a rain event, the same author observed a 3x increase in volatilization after the rain event compared with the volatilization before the rain event. The same trend was observed by Smith et al. (1997) where the authors observed increased volatility fluxes of ethalfluralin, trifluralin and triallate during rain events and no volatility from the dry surface soil. Under high soil moisture, organic molecules (such as herbicide molecules) are not adsorbed on mineral surfaces due to greater attraction from water molecules. Thus, volatilization is lower at lower soil moistures (Goss, 2004; Reichman et al., 2011; Schneider et al., 2013). Additionally, temperature influences vapor pressure as temperature increases vapor pressure increases. When temperatures increased from 15 to 35°C, volatility increased for both alachlor and atrazine (Wienhold et al., 1993). Atrazine volatilization doubled while alachlor volatility increased by 10x at 35°C compared to15°C. Henry's Law constant is another way to estimate volatility by considering the relationship between volatility and solubility.

Table 1.2 Classification of volatility based on vapor pressure from water (Silva, 2004).

Vapor Pressure (mm Hg)	Classification
$> 10^{-2}$	Very volatile from water
$10^{-4} – 10^{-3}$	Moderately volatile from water
$10^{-7} – 10^{-5}$	Slightly volatile from water
$< 10^{-8}$	Non-volatile

Solubility

Among the known physicochemical characteristics affecting the herbicide environment pathway, the solubility of herbicides helps to understand the availability, breakdown, plant uptake, movement and persistence of herbicides in the soil. Weed control, for example, is affected by the interaction between the product solution and the solid soil phase in which the solubility of herbicides and their adsorption to soil particles are directly related. Low solubility herbicides are strongly adsorbed to the soil colloids and are less likely to leach than highly soluble herbicides (Carter, 2000). Adsorption and solubility are inversely related, where high sorption corresponds to low solubility and low sorption corresponds to high solubility (Hartley, 1976). Thus, the solubility in water is used to evaluate the herbicide interaction with adsorption. Schwarzenbach (1993) explains that when a substance is broken down and perfectly divided in two (absolute pure material and aqueous solution) the aqueous solution is the same as water solubility. This represents the maximum value that a herbicide concentration can be added to pure water and still be dissolved at any temperature. Consequences of highly soluble molecules may include rapid herbicide dissipation to the water cycle resulting in ground water contamination potential through leaching and herbicide runoff (Lavorenti, 1996). The classification of herbicides by solubility in water is given in mg L^{-1} (Table 1.3). Water lipophilicity also influences solubility and a coefficient is adopted to estimate the lipophilic forces of a given solution. The n-octanol/water partition coefficient (K_{ow}) represents the relation of n-octanol concentration with the water concentration. Higher K_{ow} values indicate greater lipophilic properties such as affinity to the organic matter in the soil solution while low values are related to low adsorption and greater availability (Oliveira Jr. and Bacarin, 2011). The polarity of substances are directly correlated with solubility, where high polarity commonly indicates high solubility while non-polar substances often indicates low solubility (Schreiber, 2012).

Table 1.3 Classification of herbicide solubility in water (FAO, 2000).

Solubility (mg L^{-1})	Classification
> 10,000	Highly soluble
1,000 – 10,000	Readily soluble
100 – 1,000	Moderately soluble
0.1 – 100	Slightly soluble
< 0.1	Negligibly soluble

Modes of Action

The research and technology development in chemical weed control accelerated with new molecule discoveries beginning in 1950s. Atrazine, trifluralin and ametryne were some of the first identified herbicides in the years of 1959, 1963, and 1964 respectively (Timmons, 2005). New herbicides and modes of action (MOA) were discovered through the years and currently, according to the Weed Science Society of America (Senseman, 2007), seventeen MOAs are available. Among all seventeen MOA available, twelve include pre-emergence herbicide products.

ALS inhibitors

Inhibitors of acetolactate synthase ALS/AHAS (WSSA Group 2) are a common mode of action for PRE herbicides. This group of herbicides, first discovered in 1975, (Green, 2007), inhibits the acetolactate synthase (ALS) also known as the acetohydroxyacid synthase (AHAS) which is an essential enzyme in the production of branched-chain amino acids (BCAA) such as valine, leucine and isoleucine (Senseman, 2007). According to Corbett and Tardif (2006), ALS affects BCAA production in two ways, first by condensing two pyruvates molecules into acetolactate and secondly by condensing α-ketobutyrate and pyruvate into acetohydroxybutyrate. These herbicides will bind and inhibit ALS, leading to a reduction in cell division and consequently, plant death (Corbett and Tardif, 2006). The main stages affected by the ALS inhibitors are plant growth development and reproduction, with almost no influence on germination of seeds (Blair and Martin, 1988; Fletcher et al., 1993). Symptomology on plants include growth reduction, necrosis, chlorosis, internode shortening, leaf deformations and abscission, leaf purpling and root growth inhibition (Whitcomb, 1999) – all directly related to reductions in cell division rate. Zimdahl (1999) observed lateral root growth inhibition and purpling of vein symptoms. The ALS inhibitor herbicides are divided in five different chemical families: the sulfonylureas, imidazolinones, triazolopyrimidines, pyrimidinylthiobenzoates and the sulfonylamino-carbonyl-triazolinones (Green, 2007). Each group differs in rates and ways of absorption, translocation and metabolism. Li et al. (2016) observed higher absorption and translocation of halosulfuron (sulfonylurea group) in adzuki beans (*Vigna angularis*) compared to white beans (*Phaseolus vulgaris*). Besançon et al. (2017) testing the same herbicide, halosulfuron, in cucumber (*Cucumis sativus*) and summer squash (*Curcubita pepo*), observed greater basipetal translocation in velvetleaf (*Abutilon theophrast*i Medik.) than acropetal translocation. Another finding was the different rates of absorption, 45% in summer squash and 80% in pitted morning-glory (*Ipomoea lacunosa* L.) and low absorption in the root system, regardless of weed species. Imazethapyr (imidazolinone group) in contrast is quickly absorbed by roots and leaves as it transported by the phloem and xylem to young plant tissues (Plaza et al., 2006). Other examples of common ALS inhibitor herbicides include nicosulfuron, chlorimuron-ethyl (sulfonylureas); imazapic, imazapyr (imidazolinones); cloransulam-methyl, diclosulam (triazolopyrimidines); bispyribac-sodium (pyrimidinylthiobenzoates) and flucarbazone-Na (sulfonylamino-carbonyl-triazolinones).

Mitosis inhibitors

Both the microtubule assembly inhibitors (WSSA Group 3) and the mitosis inhibitors through the very long chain fatty acids (VLCFA) (WSSA Group 15) are modes of action affecting mitosis. Group 3 herbicides were first discovered in 1959 with DCPA (chlorthal dimethyl) followed by trifluralin in 1963 (Timmons, 2005). Microtubule assembly inhibitors are products that inhibit the polymerization of the microtubules resulting in the absence of the spindle apparatus and therefore, blocking the alignment chromosome separation during the mitosis process. Cell wall synthesis may also be affected leading to poor root tip formation (Senseman, 2007). These microtubules structures are formed by tubulin proteins and are important to cellular mitosis and plant development. The microtubules are related to cellular differentiation and its structure maintenance, cellulose fiber arrangement, cell wall synthesis and plasma transport (Fernandes et al., 2013). According to Hansen et al. (1998), when studying herbicides such as amiprophos-methyl, trifluralin, pronamide and oryzalin, the microtubule polymerization was blocked due to these herbicides binding to the tubulin protein. Moreover, Fernandes et al. (2013) indicated that microtubule inhibitors may also affect Ca^{2+} concentrations in the cytoplasm and therefore disturb cell membrane permeability, polymerization and mitochondrial activities. This group includes the following chemicals: ethalfluralin, pendimethalin, trifluralin and oryzalin (dinitroaniline family); amiprophos-methyl (phosphoroamidate family) and the dithiopyr and thazophyr (pyridine family). The main plant symptoms from application of these herbicides are swelling and cracking of hypocotyls, and base callus formation after emergence. In grasses, common symptoms are stunted plants with incomplete emergence, lateral rooting, and increased thickening and decreased length of roots (Gunsolus and Curran, 2002). As a consequence of reduced root systems in susceptible plants, additional drought and nutrition deficiency symptoms may occur. Dinitroaniline herbicides will mainly inhibit root and shoot development and are absorbed by the roots; pronamide herbicide uptake is also by roots and may be absorbed by leaves to some extent (Ware and Whitacre, 2004).

Group 15 herbicides inhibit VLCFA synthesis, typically chain lengths of 20 or more carbons, with consequential effects prior to weed emergence (Senseman, 2007). Schmalfuß et al. (1998) stated that this group affects germination, and controls mostly annual grasses and some small-seeded broadleaves. According to Böger et al. (2002) allidochlor was one of the first VLCFA inhibitors to be discovered in 1958 followed by diphenamid in 1963 and propachlor in 1965 (Timmons, 2005). The VLCFA are very important in plants as they are precursors and components of epicuticle waxes, membranes and lipids stored in plants. Metolachlor in rapeseed (*Brassica napus*) reduced wax synthesis, alcohol and long chain alkanes concentrations inhibiting plant embryos (Matthes et al., 1998). Schmalfuß et al. (1998), studying the effect of chloroacetamides in green algae (*Scenedesmus acutus*) observed the phytotoxicity of VLCFA inhibitors was caused by the breakdown of oleic acid and fatty acid elongases being inhibited and then resulting in the degradation of crucial cellular structures and biomembranes. Moreover, this group inhibits the protein synthesis in meristematic regions in leaves, shoots and roots, blocking plant growth and development (Oliveira Jr. and Bacarin, 2011). Examples of VLCFA inhibitors are alachlor, acetolachlor, flufenacet, dimethenamid-*p*, *S*-metolachlor and pyroxasulfone, each of which are absorbed by the root and shoot tissues. Injury symptoms in plants include poor leaf formation with incomplete leaf formation, crinkling and shortening of the mid vein (Gunsolus and Curran, 2002). Tanetani et al. (2009) studied the mechanism of action of pyroxasulfone in rice (*Oryza sativa*), barnyard millet (*Echinochloa esculenta*) and Italian ryegrass (*Lolium perenne ssp. multiflorum*) and confirmed that the herbicide inhibits shoot growth and inhibits the activity of the VLCFAs.

Carotenoid Biosynthesis Inhibitors

The carotenoid biosynthesis inhibitors also called the bleaching herbicides (WSSA Group 13 and Group 27) are an important herbicide mode of action including several important PRE herbicides. In the WSSA Group 13, clomazone was first discovered in 1986 (Witschel et al., 2012). Clomazone is metabolized to an active form, the 5-keto clomazone, which inhibits an important precursor of plastid isoprenoids, the deoxyxylulose 5-phosphate synthase (DXP synthase) (Ferhatoglu and Barret, 2006; Senseman, 2007). Studying the effect of clomazone on corn mutants, Vencil et al. (1989) discovered the influence of clomazone on gibberellin (GA) biosynthesis when comparing dwarf mutant corn (lower ent-kaurene – gibberellin conversion) to normal corn. Duke et al. (1991) when studying the effects of clomazone on cotton observed the reduction of carotenoid production by inhibiting the synthesis of terpenoids followed by the production of farnesyl pyrophosphate. Norman et al. (1990) observed clomazone inhibiting the production of chlorophyll and plastoquinones. In the same study, the authors also discovered the site of clomazone activity, between the geranylgeranyl pyrophosphate (GGPP) and mevalonate (MEV) pathways. Classical symptoms of this group include whitening, bleaching and/or yellowing of leaves sometimes initiating in between the leaf veins (Bauman et al., 2008; Schreiber et al., 2015).

Inhibitors of Photosynthesis at the Photosystem II

In 1958, simizine was the first herbicide discovered that inhibits photosystem II (WSSA Group 5). Atrazine followed in 1959 and bromacil in 1969 (Timmons, 2005). This mode of action stops the production of ATP and $NADPH_2$ and the fixation of CO_2, halting plant growth. These are consequences of a blockage on electron transports from Q_A to Q_B due to the herbicide binding on a D1 protein present in the chloroplast thylakoid membranes of the photosystem II complex. Plant death is often associated with chlorophyll and carotenoid loss and weakening of cell membranes resulting in rapid disintegration and cell water loss and its structures. This loss is the result of triplet state chlorophyll forming a singlet oxygen that produces a lipid radical driving to a chain reaction of lipid peroxidation. This peroxidation will end on the oxidation of proteins and lipids (Senseman, 2007). As Trebst (2008) indicated, the first mechanism of action leads to the second and principal one: the singlet oxygen formation is the reason of the final interruption in the system and causes the chlorophyll bleaching; but the main reason of photosynthesis shutdown is the plastoquinone replacement at the Q_B. The majority of herbicides are absorbed by roots and leaves; the main transport is through xylem and the CO_2 absorption rates decline after a few hours of application in susceptible plants (Oliveira Jr. and Bacarin, 2011). Differences in the metabolism and conjugation processes are the principal way of increased tolerance in plants (Trebst, 2008). Phytotoxicity varies depending on the herbicide and plant species but generally the typical symptomology includes leaf and mid vein chlorosis such as general yellowing, slow growth and necrosis (Trebst, 2008). As Gunsolus and Curran (2002) elucidated, herbicides of this group will not prevent plant emergence and germination and symptoms occur after cotyledon and leaf formation. Dayan et al. (2009) compared weed control with atrazine and amicarbazone and observed the same classical symptoms in susceptible plants and the ready absorption through leaves and root when applied as a PRE or as a POST application. Common herbicides within the mode of action are divided in five chemical families: triazines, including herbicides like ametryne, atrazine, simazine; triazinones with hexazinone, metamitron and metribuzin; triazolinone family with amicarbazone; the uracils such as bromacil and terbacil; the pyridazinones with chloridazon and finally the phenyl-carbamates like desmedipham.

Droplet size effect on pesticide control

Pesticide spray efficacy is influenced by numerous factors which may or may not be controlled. Uncontrolled variables in spray applications include, for example, the weather, the environment and the distribution and incidence of pests. Among the characteristics that can be managed, nozzle selection, spray pressure and tank-mixture formulation are examples that directly affect droplet size. The influence of droplet size on pesticides has been studied for a long time by several authors. With insecticides, for example, the effect of droplet size on tobacco budworm (*Heliothis virescens*) sprayed with bifenthrin and oil was observed by Womac et al. (1994). Two droplet sizes were selected, 96 and 337 µm ($D_{V0.5}$), with coarser droplets increasing larvae mortality and accelerating its process. Reed and Smith (2001) observed, however, that increasing droplet size indicated reduced midcanopy tobacco budworm mortality when spraying lambda-cyhalothrin in cotton. Lešnik et al (2005), compared the control of codling moth (*Cydia pomonella*), green apple aphid (*Aphis pomi*) and apple leaf miner (*Leucoptera malifoliella*) using air induction and standard nozzles. Despite many variables affecting the control of these pests, the authors observed lower control with coarser droplets (air induction nozzles) than with finer ones.

Similarly to insecticides, the general recommendation for fungicides is to adopt finer sprays for contact products and medium to larger sprays for systemic ones. That is what Prokop and Veverka (2006) observed when studying the influence of droplet size on both contact and systemic fungicides on *Phytophthora infestans*. Six droplet sizes were selected, from 183 to 939 μm ($D_{V0.5}$) and greater contact fungicide control efficacy with finer than the coarser droplets was observed. Washington (1997), working with aerial application of fungicides to control *Mycosphaerella fijiensis*, used different droplet sizes and concluded the need of sprays with $D_{V0.5}$ between 300 to 400 μm and deposit of 30 droplets cm^{-2}, to provide adequate pest control and drift reduction.

Numerous authors have also shown the influence of spray droplet size on herbicide control, especially for POST herbicides (Ennis and Williamson, 1963; Douglas, 1968; McKinlay et al., 1972; McKinlay et al., 1974; Wolf et al., 1992; Knoche, 1994; Liu et al., 1996; Etheridge et al., 1999; Smith et al., 2000; Shaw et al., 2000; Ramsdale and Messersmith, 2001; Etheridge et al., 2001; Feng et al., 2003; Brown et al., 2007; Creech et al., 2016; Ferguson et al., 2018; Butts et al., 2018). Usually the effect of droplet size on POST herbicide weed control depends on the weed species and the herbicide used. Brown et al. (2007) concluded that not only nozzle but carrier volume and spray pressure are herbicide and weed specific. Etheridge et al. (1999), for instance, compared weed controls of glufosinate, glyphosate and paraquat using two air induction nozzles with coarse droplets (RU and AI) and a standard flat-fan with finer droplets (XR) applied to broadleaf signalgrass (*Urochloa platyphylla*) and common cocklebur (*Xanthium strumarium*). The AI nozzle with $D_{V0.5}$ of 450 μm and the XR with $D_{V0.5}$ of 175 μm had similar herbicide efficacy while the larger $D_{V0.5}$ produced by the RU nozzle had lower weed control. Feng et al. (2003), found that increasing droplet size increased glyphosate absorption and translocation in corn leaves. Using three droplet sizes (Fine, Medium and Coarse) to spray glyphosate in corn, the authors observed great retention but low absorption and translocation with fine droplets. According to the study, the absorption on leaves was higher with coarser droplets due to larger disrupted cuticle areas produced with those droplets. Shaw et al. (2000) studied the effect of droplet sizes and spray volume on acifluorfen deposition and control of common cocklebur. Three droplet sizes of 250, 350 and 450 μm and three carrier volumes of 56, 112 and 169 L ha^{-1} were used. Similar weed control was achieved for both the 250 and the 450 μm droplets. The authors hypothesized that finer droplets had better spray coverage while the 450 μm droplets had greater local leaf injury, just as Feng et al. (2003) observed. Creech et al. (2016) and Butts et al. (2018) studied the effects of droplets sizes on common POST herbicides such as 2,4-D, atrazine, cloransulam-methyl, dicamba, glufosinate and saflufenacil. Creech et al. (2016) observed different droplet size responses depending on the herbicide and weed species. In that study, coarse droplets increased weed control with 2,4-D while weed control with cloransulam-methyl increased almost 80% when changing from Extremely

Coarse to Fine sprays. Butts et al. (2018) observed improved weed control with Ultra Coarse droplets (900 µm) for dicamba and Extremely Coarse droplets (605µm) for glufosinate. Additionally, the leaf morphology of different weed species on droplet size can affect herbicide control. Smith et al. (2000) studied those effects on pesticide deposition. The study included droplet sizes of 140, 280, 420, 560 and 720 µm sprayed with spinning discs on 6 different weed species. The authors concluded significant leaf morphology effect on spray deposition and predicted up to 16% decrease of spray deposit for every 100 µm increase on droplet size. The effects of leaf morphology over deposition can be explained by factors like the leaf angle, hydrophilicity and the presence of trichrome. Therefore, spray droplets can bounce or shatter depending on the target but, as observed by Dorr et al. (2014), other physical and spray properties are crucial for optimum leaf spray retention. A model developed by Dorr et al. (2014) predicted the interception, shatter, bounce and retention of droplets on cotton, wheat and common lambsquarters (*Chenopodium album* L.) leaves. The authors concluded that, generally, as tank-mixture surface tension, static contact angle, droplet size and droplet velocity decreased, leaf retention increased.

Despite many studies showing the different responses of POST herbicide for droplet sizes, only a few authors have conducted research showing the influence of droplet size on PRE herbicides efficacy (Merry, 1986; Derksen et al., 2012; Borger et al., 2013). For instance, Merry's (1986) study on the influence of droplet size and application methods on PRE herbicide activity was one of the first to connect spray droplet sizes to PREs, soil type, soil moisture, spraying methods and weed control. The study compared different application methods and the droplet sizes produced by each system regarding weed control. The spraying systems were: controlled application method (CDA), Electrodyne (electrostatic sprayer) and conventional hydraulic. Among the systems tested, the hydraulic nozzle system was the one that provided improved and more consistent weed control. Finer sprays did not result in improved weed control even with reduced carrier volume compared to coarser sprays. According to the author, as long as the full herbicide dose was delivered on the target under appropriate weather conditions, suitable weed control should be achieved. Despite its importance, the study compared droplet size within different spray systems, pressures and volumes instead of comparing under same conditions. Additionally, only two PRE herbicides were studied, isoproturon and atrazine. Thus, including different nozzles, droplet sizes and herbicides with distinct physicochemical properties is necessary to better address the importance of droplet size on PRE herbicide efficacy. Borger et al. (2013), conducted a research on PRE herbicides control of rigid ryegrass (*Lolium rigidum*) with increased carrier volume in no-till systems. Two nozzles were used, a TT110015, producing Medium droplets and a TTI110015, producing Extremely Coarse droplets. No nozzle effect on rigid ryegrass control was observed. The PRE herbicides used were trifluralin, and pyroxasulfone. According to the author, it would be more advantageous to adopt the Extremely Coarse spray since it would better reduce drift when compared with finer sprays. In another study conducted by Derksen et al. (2012), the spray deposit on the canopy of potted hydrangeas spray deposit on the and ground were assessed using droplet sizes ($D_{V0.5}$) ranging from 188 to 440 µm with the TeeJet® nozzles XR and AI. The coarser the droplets, the greater the ground deposit and the better the delivery through plant canopy. In addition, nozzles and droplet sizes were compared in different herbicide programs for peanuts (*Arachis hypogaea*), including PRE and POST herbicides, using the TTI11002 (Ultra Coarse), AIXR11002 (Coarse) and DG11002 (Medium) nozzles by Carter et al. (2017). Grass control was reduced by 6%, using the TTI compared to the other nozzles but no significant difference for Palmer amaranth (*Amaranthus palmeri*) control and peanut yield was observed.

Thereupon, limited data are available regarding the influence of droplet sizes on different PRE herbicides in comparison with POST herbicides, fungicides or insecticides. The few studies that tried to better understand its relation failed to include more nozzles, herbicides, soil types and environmental conditions. The recommendation and adoption of coarser sprays for PRE herbicides is, however, common among applicators and nozzle manufacturers even without conclusive research showing better weed control with coarser sprays (Klein and Kruger, 2011; Teejet®, 2011; Hypro®, 2016; Greenleaf Technologies, 2018).

This study intends to show the effect of droplet sizes on PRE herbicide weed control efficacy through different herbicides based on physicochemical characteristics (adsorption, volatility and solubility), spray nozzle type, soil types, crop residues and precipitation.

CHAPTER II

DROPLET SIZE MEASUREMENTS FOR DIFFERENT HYDRAULIC NOZZLES AND PRE-EMERGENCE HERBICIDES

Abstract

Herbicide efficacy depends on numerous factors, including nozzle type and droplet size. However, little information is known regarding the effect of droplet size on pre-emergence herbicide efficacy. Four nozzle types and six pre-emergence (PRE) herbicides were selected for droplet size measurement in wind tunnel and to further support herbicide efficacy studies. The nozzles XR11002, ULD12002, TTI6011002, and TTI11002 and the herbicides pendimethalin, metribuzin, clomazone, imazethapyr, pyroxasulfone and *S*-metolachlor were selected. The TTI had the coarsest spray quality while the XR had the finest. Herbicide tank-mixtures affected droplet formation where the TTI had the highest variation among herbicides followed by the TTI60. Among all tank-mixtures, the nozzles sprayed with imazethapyr solution produced largest droplet sizes. Additionally, herbicide concentration affected droplet size where the concentrated *S*-metolachlor tank-mixture increased droplet size for all nozzles except the XR.

Introduction

Understanding atomization of spray droplets produced by hydraulic nozzles is fundamental to ensure effective pesticide applications and to reduce spray drift potential. According to the American Society of Agricultural and Biological Engineers (ASABE, 2013), droplet size classification ranges from Extremely Fine (< 60 µm) to Ultra Coarse (> 665 µm) spray quality (Table 2.1.)

Table 2.1 ASABE S572.1 droplet size classification category, symbol, nozzle color code and approximate $D_{V0.5}$ in microns (µm).

Spray Quality	Symbol	Color Code
Extremely Fine	XF	Purple
Very Fine	VF	Red
Fine	F	Orange
Medium	M	Yellow
Coarse	C	Blue
Very Coarse	VC	Green
Extremely Coarse	XC	White
Ultra Coarse	UC	Black

Several authors have studied many aspects of nozzle types that affect spray quality, ranging from droplet velocity studies, product formulation effects on surface tension, nozzle spray angle alteration, spray droplet air inclusions and spray pressure influence on drift potential studies (Butler Ellis et al., 2002; Czaczyk et al., 2012; Dorr et al., 2013; Fritz et al., 2014; Ferguson et al., 2015; Ferguson et al., 2016; Henry et al., 2016). Dorr et al. (2013), for example, compared the spray characteristics of a standard flat-fan nozzle, XR, a non-Venturi anvil nozzle, TT, and three air-induction nozzles, the AI, TDCFFC and TTI. They observed a negative correlation between nozzle droplet size and droplet velocity. The XR produced the smallest droplets and highest velocity while the air induction nozzle produced the coarsest droplets and the lowest droplet velocity. The study also demonstrated the influence of spray tank-mixture on droplet size. The nozzles tested with glyphosate at 1%, when compared with water alone and non-ionic surfactant plus water, produced smaller droplets, reduced spray angle and low liquid density, due to lower surface tension when compared to water only. Similarly, another study included three nozzles: XR, AIXR and TTI; two pressures: 207 and 414 kPa; three pesticide formulations: soluble liquid concentrate, emulsifiable concentrate and water dispersible granules; and three adjuvant formulations: microemulsion, high surfactant oil concentrate and crop oil concentrate. Nozzle type had the greatest influence on droplet size but spray tank-mixture and nozzle pressure also affected droplet size (Henry et al., 2016). Miller and Butler Ellis (2000) observed the same formulation effect on droplet size, but they also observed a reduced nozzle type effect. Air induction nozzles were more sensitive to liquid physical property changes than standard hydraulic nozzles due to the air inclusion mechanism, found in these Venturi nozzles. The Venturi process creates an internal pressure drop with different chamber diameters and once combined with air induction ports creates an air suction, incorporating air into the nozzle and eventually in the droplets (Dorr et al., 2013). Larger droplets are formed with these air inclusions when compared to other standard flat-fan nozzles, producing fewer droplets prone to drift and consequently reducing the drift potential. This has been observed by many authors

(Johnson et al., 2006; Sikkema et al., 2008; Ferguson et al., 2015; Ferguson et al., 2016, Alves et al., 2017)

In order to better understand the effect of droplet size on pesticide efficacy, it is necessary to measure the droplet size produced by the nozzles using actual spray tank-mixtures. Womac et al. (1994) observed that droplets of 337 µm increased tobacco budworm (*Heliothis virescens*) larvae mortality in comparison with 96 µm droplet sizes when spraying bifenthrin and oil. In another study, six droplet sizes ranging from 183 to 939 µm were adopted when spraying contact and systemic fungicides on *Phytophthora infestans* and the fine sprays provided better fungicide control than the coarser ones (Prokop and Veverka, 2006). Attempting to maximize herbicide efficacy and mitigate drift with dicamba and glufosinate, Butts et al. (2018) observed acceptable control results using Ultra Coarse droplets for dicamba and Extremely Coarse droplets for glufosinate. The objective of this study was to compare the droplet size of nozzles and PRE herbicides to support subsequent field and greenhouse studies.

Materials and Methods

Droplet size measurements were obtained in a low speed wind tunnel in July, 2017 in North Platte, Nebraska, USA, in the Pesticide Application Technology Lab (PAT) at the University of Nebraska-Lincoln West Central Research and Extension. A SympaTec Helos Vario (SympaTec Inc., Clausthal, Germany) laser diffraction instrument with an R7 lens with particle size range of 0.5 to 3500 µm was used. Following the standard droplet size classification methodology by ASABE (2013), reference nozzles with water at pre-determined spray angles, flow rates and pressures were used in order to develop the classification category threshold (Table 2.2). The nozzles tested were the XR11002, TTI6011002, TTI11002 (Turbo Teejet® Induction, Spraying Systems Inc. Wheaton, Illinois, USA) and the ULD12002 (Ultra-Lo Drift, Hypro LLC, New Brighton, Minnesota, USA). Each nozzle was sprayed using the following herbicides: pendimethalin, (Prowl H_2O®, BASF Corp., Florham Park, NJ, USA) at 1062 g a.i. ha^{-1}, metribuzin (Sencor®, Bayer CropScience, Research Triangle Park, NC, USA) at 701 g a.i. ha^{-1}, clomazone (Command 3ME®, FMC Corp., Philadelphia, PA, USA) at 1122 g a.i. ha^{-1}, imazethapyr (Pursuit®, BASF Corp., Florham Park, NJ, USA) at 70 g a.i. ha^{-1}, pyroxasulfone (Zidua®, BASF Corp., Florham Park, NJ, USA) at 179 g a.i. ha^{-1} and *S*-metolachlor (Brawl®, Tenkoz, Inc., Alpharetta, GA, USA) at 1421 g a.i. ha^{-1}. Three *S*-metolachlor concentrations were used to simulate herbicide concentrations at three volumes: 47, 94 and 140 L ha^{-1}.

The wind tunnel was equipped with a traversing arm positioned inside the section of 1.25 m^2 with the nozzle attached at the end. The nozzle was located 0.3 m from the diffraction laser beam. An electric motor drive was used to traverse the nozzle allowing the entire spray plume to pass through the beam. Compressed CO_2 air cylinders provided the air pressure, and a calibrated pressure gauge with a capacity of 2500 kPa was located near the nozzle to measure spray pressure through a capillary. Solenoid valves were used to start and stop spraying. The internal wind speed was maintained at 6.7 s^{-1} for all the laser diffraction measurements. Droplet size measurements were collected at 276 kPa. The spray system was cleaned between each tank mixture to limit contamination. Droplet diameters at which 10, 50 and 90% of the spray volume was contained in smaller droplets were given in values as $D_{V0.1}$, $D_{V0.5}$ and $D_{V0.9}$, respectively, in µm. The percent of droplets smaller than 150 µm and the relative span (RS) were also measured. RS is a dimensionless value of the distribution of the droplet spectra and is calculated:

$$RS = (Dv0.9 - Dv0.1)/Dv0.5$$

Data Analysis

Droplet size and RS data were submitted to an analysis of variance in SAS v.9.4 (SAS Institute, Cary, NC, USA) using least squares means to fit the general linear model (PROC GLM) at $^{*}P<0.05$ using Sidak's multiple comparison test. Run replication was treated as a random effect. Tank mixture, nozzle and its interaction were treated as fixed effects.

Results and Discussion

A classification category threshold was plotted using reference nozzles in order to classify the spray quality of four selected nozzles. Based on the reference nozzles, a spray quality ($D_{V0.5}$) over 140 µm is categorized as Fine and a spray quality greater than 645 µm is categorized as an Ultra Coarse (Table 2.2).

As expected, the XR nozzle produced the finest droplets with a $D_{V0.5}$ of 207 µm, while the TTI produced the coarsest droplets with a $D_{V0.5}$ of 704 µm (Table 2.3). The nozzles producing the coarsest droplets to the finest droplets were: TTI > TTI60 > ULD > XR across tank-mixtures. Henry et al. (2016) observed similar results, especially for the TTI and XR nozzles where the TTI had the largest and the XR had the smallest droplet size spectra. The XR had the highest droplet size distribution across nozzles, represented by the RS value (Table 2.3).

Additionally, herbicide tank-mixture influenced droplet size and RS. The $D_{V0.5}$ and RS values differed across herbicides within the same nozzle. The TTI sprayed with pyroxasulfone had $D_{V0.5}$ of 794 µm while when sprayed with pendimethalin, a $D_{V0.5}$ of 710 µm (Table 2.2). The RS also differed across herbicides. Miller and Butler Ellis (2000) observed that air induction nozzle droplet size formation would respond differently than standard flat-fan nozzles with different tank-mixture, especially for inhomogeneous mixtures like emulsions and dispersions, due to changes in the air induction ports of those nozzles. The XR sprayed with metribuzin and pendimethalin had a RS of 1.28 and 1.18, respectively (Table 2.3) while, for the TTI60 nozzle, for example, with metribuzin and pendimethalin had a RS of 0.94 and 0.91, respectively.

Comparing the herbicide effect on droplet size across nozzles, imazethapyr had larger droplet size, excluding the XR, than other solutions. *S*-metolachlor at 140 L ha^{-1} had the smallest droplet size distribution.

Herbicide concentration also affected droplet size. *S*-metolachlor was tested at three concentrations due to different carrier volumes used. The TTI60 droplet size, for example, was 494 µm at the highest concentration (47 L $ha^{-}1$) while it was 518 µm at the lowest concentration (140 L ha^{-1}). Increasing the carrier volume and decreasing the herbicide concentration led to finer sprays for all nozzles except for the XR.

It is important to evaluate droplet size and spray quality changes among nozzles, and tank-mixtures to mitigate drift and increase herbicide efficacy. Great droplet size reduction can increase drift potential, droplet evaporation, reduce spray coverage and reduce weed control.

Table 2.2 Droplet size spectrum and percent of droplets smaller than 150 µm for the reference nozzles and the spray quality classification based on the reference nozzles[a].

Nozzle	Pressure	$D_{V0.1}$	$D_{V0.5}$	$D_{V0.9}$	% < 150 µm	Classification
	kPa	----------------	µm	----------------		
11001	450	63	140	244	55.55	Fine
11003	300	109	246	412	19.87	Medium
11006	200	157	355	594	8.93	Coarse
8008	250	183	420	718	6.40	Very Coarse
6510	200	222	508	857	4.11	Extremely Coarse
6515	150	296	645	1039	1.84	Ultra Coarse

[a] Measurements were collected according to the ASABE 2572.1 guidelines.

Table 2.3 Droplet size ($D_{V0.5}$) per nozzle and herbicide and classification according to the reference nozzle threshold at 276 kPa[ab].

Herbicide	Formulation[c]	XR11002		ULD12002		TTI6011002		TTI11002	
		------------------	------------	------------	µm	------------	------------	------------	------------
clomazone	ME	201 ^{s}	F	474 ^{m}	VC	626 ^{h}	XC	721 ^{d}	UC
imazethapyr	SC	204 $^{s, r}$	F	479 ^{m}	VC	663 ^{e}	UC	782 ^{b}	UC
metribuzin	DF	197 ^{s}	F	470 ^{m}	VC	639 $^{f, g}$	XC	740 ^{c}	UC
pendimenthalin	CS	213 $^{q, r}$	F	451 ^{n}	VC	610 ^{i}	XC	710 ^{d}	UC
pyroxasulfone	DF	204 $^{s, r}$	F	468 ^{m}	VC	646 ^{f}	UC	794 ^{a}	UC
S-metolachlor[d]	EC	205 $^{s, r}$	F	419 ^{o}	VC	518 ^{j}	XC	639 ^{f,g}	XC
S-metolachlor[e]	EC	213 $^{q, r}$	F	402 ^{p}	C	506 ^{k}	VC	625 ^{h}	XC
S-metolachlor[f]	EC	219 ^{q}	F	399 ^{p}	C	494 ^{l}	VC	628 ^{h,g}	XC

[a] LS-means followed by same letter are not significantly different at $P \leq 0.05$.

[b] F – Fine, C – Coarse, VC – Very Coarse, XC – Extremely Coarse, UC – Ultra Coarse.

[c] CS – capsule suspension, DF – dry flowable, ME – microemulsion, SL – soluble concentrate, EC – emulsifiable concentrate.

[d] Herbicide rate for 47 L ha^{-1}, [e] Herbicide rate for 94 L ha^{-1}, [f] Herbicide rate for 140 L ha^{-1}.

Table 2.4 Relative span (RS) per nozzle and herbicide at 276 kPa[a].

Herbicide	Formulation[b]	XR11002	ULD12002	TTI6011002	TTI11002
clomazone	ME	$1.27^{a,b}$	$0.97^{i,j,k}$	$0.93^{m,n}$	$0.94^{l,m,n}$
imazethapyr	SC	1.24^{b}	$1.06^{e,f}$	$0.94^{l,m,n}$	$0.93^{m,n}$
metribuzin	DF	1.28^{a}	$0.99^{h,i}$	$0.94^{k,l,m}$	$0.94^{l,m,n}$
pendimenthalin	CS	1.18^{c}	$0.98^{i,j}$	0.91^{n}	$0.93^{m,n}$
pyroxasulfone	DF	1.24^{b}	$1.03^{f,g}$	$0.94^{l,m,n}$	$0.93^{m,n}$
S-metolachlor[c]	EC	1.18^{c}	$1.09^{e,d}$	$0.95^{j\text{-}m}$	$1.02^{g,h}$
S-metolachlor[d]	EC	1.16^{d}	$0.94^{l,m,n}$	$0.96^{j,k,l}$	$1.04^{f,g}$
S-metolachlor[e]	EC	$1.09^{e,d}$	$0.95^{j\text{-}m}$	$0.94^{k,l,m}$	$1.04^{f,g}$

[a] LS-means followed by same letter are not significantly different at $P \leq 0.05$.

[b] CS – capsule suspension, DF – dry flowable, ME – microemulsion, SL – soluble concentrate, EC – emulsifiable concentrate.

[c] Herbicide rate for 47 L ha^{-1}.

[d] Herbicide rate for 94 L ha^{-1}.

[e] Herbicide rate for 140 L ha^{-1}.

Conclusion

Droplet size was influenced by nozzle type, tank-mixture and herbicide concentration. The air induction nozzles had a smaller droplet size distribution while the XR nozzle had the largest RS values among herbicides and nozzles. The TTI nozzle had the largest droplet size across herbicides, followed by the TTI60, ULD and XR. Distinguishing droplet size differences among nozzles and herbicides will help to support future PRE herbicide efficacy and nozzle studies involving the same nozzles and herbicides.

CHAPTER III

EFFECT OF DROPLET SIZE, VOLATILITY, SOLUBILITY AND ADSORPTION ON HERBICIDE EFFICACY OF PRE-EMERGENCE HERBICIDES IN SOYBEANS

Abstract

Unlike post-emergence herbicides, little is known about droplet size effect on pre-emergence herbicide (PREs) efficacy. Four nozzle types were used to spray different PRE herbicides on eight soybean fields in Missouri and Mississippi in 2017 and 2018, respectively. Pendimethalin, metribuzin, clomazone, imazethapyr and pyroxasulfone were selected based on their physicochemical characteristics (adsorption, volatility and solubility) and were sprayed with the XR11002, ULD12002, TTI6011002 and TTI11002 nozzles. The XR nozzle produced the smallest droplet size ($D_{V0.5}$), 204 µm, followed by the ULD, TTI60 and TTI with $D_{V0.5}$ of 468, 646 and 794 µm, respectively. Droplet size, spray coverage, nozzle type or physicochemical characteristics did not affect PRE herbicide efficacy, except in the Monroe County, MS, field, with pendimethalin. The TTI60 twin fan nozzle enhanced pendimethalin weed control (up to 91%) in comparison with pendimethalin sprayed with the TTI nozzle (64%), in a high organic matter (OM) soil comprised of large clods and high weed pressure. This was due to improved herbicide penetration assisted by the TTI60 dual fan pattern increasing herbicide-moisture contact and clod coverage by the herbicide. Under soils with higher OM content

(> 2%) pendimethalin weed control was reduced. In soils with low OM (< 0.7%), low cation exchange capacity (< 13.1%) and rainfall of 12.2 mm within 3 days after application, metribuzin also resulted in reduced weed control. The results indicate that droplet size does not affect PRE herbicide efficacy.

Introduction

Pre-emergence herbicides (PREs) are an important tool for an optimal weed control program (Palmer et al., 1999; Hasty et al., 2004). Among the variables affecting herbicide efficacy, nozzle selection is critical due to direct impacts on droplet size, spray coverage and deposition, drift control and herbicide efficacy. The influence of droplet size on pesticides, especially for post-emergence herbicides (POSTs), has been studied by several authors (Ennis and Williamson, 1963; Douglas, 1968; McKinlay et al., 1972; McKinlay et al., 1974; Wolf et al., 1992; Knoche, 1994; Liu et al., 1996; Etheridge et al., 1999; Smith et al., 2000; Shaw et al., 2000; Ramsdale and Messersmith, 2001; Etheridge et al., 2001; Feng et al., 2003; Brown et al., 2007; Creech et al., 2016; Butts et al., 2018; Ferguson et al., 2018). The droplet size effect on POST herbicide efficacy depends on the herbicide used and the weed species. In a non-selective herbicide control comparison with glufosinate, glyphosate and paraquat, two air induction nozzles (RU and AI) and a standard flat-fan (XR) were used for broadleaf signalgrass (*Urochloa platyphylla*) and common cocklebur (*Xanthium strumarium*) applications (Etheridge et al., 1999). The AI nozzle with $D_{V0.5}$ of 450 µm and the XR with $D_{V0.5}$ of 175 µm had similar herbicide controls while the RU nozzle with $D_{V0.5}$ of 650 µm had lower weed control (Etheridge et al., 1999). Creech et al. (2016) and Butts et al. (2018) studied droplet size effects on weed control of common POST herbicides like 2,4-D, atrazine, cloransulam-methyl, dicamba, glufosinate and saflufenacil. Creech et al. (2016) observed different droplet size responses depending on herbicide and weed. Coarse droplets tended to increase weed control with 2,4-D while application of cloransulam-methyl resulted in nearly 80% weed control increase when droplet size decreased from Extremely Coarse ($D_{V0.5}$ of 637 μm) to Fine ($D_{V0.5}$ of 228 μm). Butts el al. (2018) observed reduced drift and greater weed control for dicamba and glufosinate with droplet sizes of 900 μm and 605 μm ($D_{V0.5}$) respectively.

Despite all the research with POST herbicides, few studies have shown the droplet size effect on PRE herbicide efficacy (Merry, 1986; Borger et al., 2013). Merry (1986) compared application methods (CDA - Controlled Application Method, electrostatic sprayer and hydraulic nozzle system) and droplet sizes produced by each system and the impact they had on weed control. The hydraulic nozzle system provided better and more consistent weed control and the finer sprays reduced control when compared to coarser sprays. According to the author, ensuring the correct herbicide dose on the target under appropriate weather conditions should provide suitable weed control. Borger et al. (2013) conducted a study on PRE herbicide control of rigid ryegrass (*Lolium rigidum*) in no-tillage systems using TT110015 and TTI110015 nozzles producing Medium and Extremely Coarse droplets, respectively. For both the herbicides used, trifluralin and pyroxasulfone, no nozzle effect on rigid ryegrass control was observed and according to the authors, adopting Extremely Coarse sprays would be wiser since it would reduce drift more when compared to the Medium spray. Derksen et al. (2012)

using droplet sizes ($D_{V0.5}$) ranging from 188 to 440 µm with the TeeJet® nozzles XR and AI, observed that the coarser the droplets, the greater the ground deposit and better delivery through the plant canopy resulted.

Herbicide efficacy is also directly related to the environment. Variables affecting herbicide environment fate include photochemical decomposition, chemical breakdown, microbial decomposition, soil adsorption, product evaporation and soil moisture. Physicochemical characteristic like adsorption, volatility and solubility are important herbicide properties to estimate its environment fate. The adsorption coefficient K_{oc} is the partitioning between soil organic carbon and water and is interpreted as the binding force of a chemical to the soil. A high K_{oc} indicates low soil mobility (Vogue et al., 1994; EPA, 2012), while a low K_{oc} indicates greater herbicide availability in the soil-solution (Schreiber, 2012). Variables like soil organic matter (OM) and crop residue also affects herbicide adsorption. Crop residues can capture herbicides through adsorption and physical obstruction resulting in reduced spray coverage, deposit and weed control (GRDC, 2015; Borger et al., 2013). The vapor pressure is another important tool to estimate the probability of a pesticide changing from the solid/liquid to the gaseous phase (Hornsby et al., 1996). Several authors have observed greater herbicide volatilization under higher soil moisture and higher temperature conditions (Wienhold et al., 1993; Goss, 2004; Reichman et al., 2011; Schneider et al., 2013). The solubility of products also influences the availability, breakdown, plant uptake, movement and persistence of herbicides in the soil. Highly soluble products can rapidly dissipate through herbicide runoff and leaching, potentially causing ground water contamination and reduced weed control (Lavorenti, 1996).

The effects that physicochemical herbicide properties on droplet sizes and their effect on PRE herbicide efficacy is not clear. It is known, though, that particle size influences the rate of dissolution of substances. Reducing a particle size results in surface area increase and consequently dissolution rate increase (Florence and Attwood, 1981; Richards, 1988; Chu et al., 2012). Droplet sizes will also affect the evaporation rate of a volatile solution. According to Raoult's Law, the partial vapor pressure of each component in the solution is directly proportional to its mole fraction. Dalton's Law, for instance, states that the total pressure of a mix of gases is the sum of the partial pressures of each gas (Freed et al., 1967). Therefore, a solution consisting of water and a volatile herbicide (with higher vapor pressure than water) will have a combined single vapor pressure, greater than the vapor pressure of water or herbicide alone. Yu et al. (2009a) and Holterman (2003), for example, observed faster evaporation of smaller droplets and spray mixtures with lower surface tension. Merry (1986) also did not observe increased efficacy from smaller droplets with isoproturon. Additionally, droplet size affects the adhesion, bouncing, and shattering on solid surfaces (Dorr et al., 2014; Cock et al., 2017) Therefore, droplet physical processes could affect herbicide efficacy, for example, through droplet contact on hydrophilic surfaces as on plant residues.

Thus, this research aims to better address nozzle and droplet size recommendations for PRE herbicide applications based on different environmental and physicochemical characteristics.

Materials and Methods

Studies were conducted in 2017 and 2018, respectively, across eight locations in two states, Missouri and Mississippi. In 2017, four fields were selected in three different counties in northwest Missouri: Nodaway, Atchison and Gentry Counties. In 2018, four fields were selected in four different counties in Mississippi: Washington, Oktibbeha, Noxubee and Monroe Counties. The experimental design was a randomized complete block design with four replications. Each plot measured 2.25 by 3 m in 2017 and 3 by 9m in 2018. Soil samples were collected in all fields and soil analyses were conducted by the Mississippi State University Soil Testing Laboratory. Crop residue quantification was only conducted for the fields with a minimum amount of residue, all four fields in Missouri and none in Mississippi. The quantification of crop residue was conducted using a 1 square meter frame and by randomly selecting three points in the field and collecting all the residue from within those three points. Residues were dried at 55°C for 3 days and weighed using the methodology in Al-Kaisi & Yin (2005) and Brye et al. (2007). Field location, soil type, organic matter, cation exchange capacity, pH, plant residue quantity and rainfall for each field is shown in Table 3.1. All fields in Missouri were sprayed with glyphosate (Roundup PowerMax®, Monsanto Co., St. Louis, MO, USA) at 351 g a.i. ha^{-1} one to two days prior to soybean (*Glycine max* (L.) Merr.) planting. In Mississippi a shallow soil cultivation was conducted prior to planting for all locations. Pre-emergence herbicides were selected from those labeled for soybeans based on the attribute values of adsorption, volatility and solubility. Herbicide rates and physicochemical properties and classification are listed in Table 3.2. An untreated control treatment was included in each block at each field location. The nozzle types selected for comparison were the XR11002, TTI6011002, TTI11002 (Turbo Teejet® Induction, Spraying Systems Inc. Wheaton, Illinois, USA) and the ULD12002 (Ultra-Lo Drift, Hypro LLC, New Brighton, Minnesota, USA).

Table 3.1 Soil analysis, crop residue amount and stubble height, first rain event after application and total rainfall from 7 days before application until 21 days after application.

	2017, Missouri, USA			
Location	Atchison County	Nodaway County	Gentry County	Nodaway County
Soil Type	Napier silt loam	Higginsville silty clay loam	Lamoni clay loam	Lamoni clay loam
Organic Matter	1.59%	1.94%	1.49%	2.02%
CEC	19.6	23.4	24.0	25.3
pH ($CaCl_2$)	6.6	7.9	7.0	6.9
Residue	9,573 kg ha^{-1}	5,636 kg ha^{-1}	3,150 kg ha^{-1}	4,733 kg ha^{-1}
Residue Height	0 cm	30.3 cm	26.3 cm	18.3 cm
First Rain Event	0.3 mm (6 DAA)	2.8 mm (0 DAA)	19.3 mm (1 DAA)	11.9 mm (2 DAA)
Rainfall	97.8 mm	68.8 mm	52.6 mm	79.7 mm

	2018, Mississippi, USA			
Location	Washington County	Oktibbeha County	Noxubee County	Monroe County
Soil Type	Bosket very fine sandy loam	Leeper silty clay loam	Brooksville silty clay	Vaiden silty clay
Organic Matter	0.70%	0.60%	2.10%	2.30%
CEC	13.1	7.61	30.1	26.1
pH ($CaCl_2$)	6.7	6.5	7.6	6.0
Residue	---------- 0 kg ha^{-1} ----------			
First Rain Event	12.2 mm (3 DAA)	12.9 mm (1 DAA)	40.9 mm (7 DAA)	1.52 mm (5 DAA)
Rainfall	48.8 mm	42.4 mm	55.88 mm	136.4 mm

Table 3.2 Herbicide treatments and each corresponding value and classification regarding volatility, adsorption and solubility characteristics[a].

Herbicide	Rate	Trade name	Manufacturer	Volatility	Adsorption[b]	Solubility
	g a.i. ha^{-1}			mm Hg	Log K_{oc}	mg L^{-1}
pendimethalin	1062	Prowl H_2O®	BASF Corp., Research Triangle Park, NC	9.4 x 10^{-6} [c] Slightly volatile	4.23[d] Strong sorption	0.275 [e] Slightly soluble
metribuzin	701	Sencor®	Bayer CropScience, Research Triangle Park, NC	4.35 x 10^{-7} [f] Slightly volatile	1.77 [g] Low sorption	1100 [g] Readily soluble
clomazone	1122	Command 3ME®	FMC Corp., Philadelphia, PA	1.44 x 10^{-4} [e] Moderately volatile	2.47 [h] Moderate sorption	1100 [e] Readily soluble
imazethapyr	70	Pursuit®	BASF Corp., Research Triangle Park, NC	2.1 X 10^{-11} [I] Non-volatile	2.45 [g] Moderate sorption	1400 [g] Readily soluble
pyroxasulfone	178	Zidua®		1.8 x 10^{-8} [j] Non-volatile	2.05 [k] Low sorption	3.49 [l] Slightly soluble

[a] Classifications for volatility, adsorption and solubility according to Silva (2004), FAO (2000) and FAO (2000), respectively.

[b] K_{oc} values were converted to the logarithm value.

[c] Ahrens (1994), [d] Shaner (2012), [e] Meister (1992), [f] Gangolli (1999), [g] Gillespie et al. (2011), [h] Schreiber et al. (2015), [i] Lyman (1985), [j] MDA (2013), [k] Westra (2012), [l] Yamaji et al. (2016).

Droplet size measurements for all nozzles and herbicides were obtained in a low speed wind tunnel in July, 2017 in North Platte, Nebraska, USA, in the Pesticide Application Technology Lab (PAT) at the University of Nebraska-Lincoln West Central Research and Extension. Because spray coverage was collected with pyroxasulfone tank-mixture, the droplet spectrum data is given for the measurements with the same herbicide. Data readings of the droplet diameters at which 50% of the spray volume was contained in smaller droplets were given in values as $D_{V0.5}$ in μm. Herbicide treatments were applied one to two days after soybean planting with a 4 nozzle boom, CO_2 sprayer calibrated to deliver 140 L ha^{-1} at 276 kPa with boom height of 0.5 m. Wind speed, air humidity and temperature were collected using a WeatherFlow WEATHERmeter (WeatherFlow Inc., CO, USA). Spraying dates and average meteorological conditions at the time of application for each field are listed in Table 3.3.

Spray Coverage Measurement

Spray coverage assessment was conducted at all field locations, in Missouri and Mississippi, in 2017 and 2018, respectively. Before treatment applications Syngenta water sensitive papers, 52 mm x 76 mm, (Spraying Systems Inc. Wheaton, IL, USA) were placed in the center of the treatment plots. Water sensitive papers were collected in individual plastic bags after spraying to ensure cards were completely dry, preventing humidity contamination. Cards were then scanned (Figure 3.1) and analyzed using Image J (National Institute of Health Washington DC, USA) (Rasband, 2008). Following same methodology as in Ferguson et al. (2016), the image was cropped removing the background, image scale was set to the real dimensions, converted in 8-bit grayscale, transformed in binary black & white and analyzed in percent coverage and droplet density per cm^2.

Weed Control Rating

Weed control ratings were conducted at 7, 14, 21 and 28 days after application (DAA). The untreated checks were the first plots to be rated followed by the treated plots. Due to the selectivity of each herbicide used, the ratings consisted of counting weed plants by species on the center of each plot. The treated plot ratings would then be based on the untreated treatments as:

$$\text{Weed control} = 100 - \left(\frac{T}{U} \times 100\right)$$

where T is the weed count for a treated individual experimental unit and U is the mean weed count for the untreated control replicates. If a herbicide treatment had the same or higher count number as the untreated plots for one weed species, 0% control would be rated for that particular species. If the determined species was absent in a herbicide treatment, 100% control would be rated. Each herbicide label was examined to ensure only the weeds controlled at the applied herbicide rate were included in the control rating. Therefore, a weed species would not be included in the control rating if it was not listed on the herbicide label. In addition, only weeds emerged after application were considered in the control ratings.

Table 3.3 Weather conditions at the time of herbicide application.

		2017, Missouri, USA		
Location	Atchison County	Nodaway County	Gentry County	Nodaway County
Application Date	05/09/2017	05/11/2017	05/18/2017	05/26/2017
Temperature	27°C	22.3°C	24.3°C	25.4°C
Relative Humidity	39.3%	49.3%	55.3%	57%
Wind Speed	2.4 m s^{-1}	3.2 m s^{-1}	4.1 m s^{-1}	2.3 m s^{-1}
		2018, Mississippi, USA		
Location	Washington County	Oktibbeha County	Noxubee County	Monroe County
Application Date	05/01/2018	05/04/2018	05/09/2018	06/07/2018
Temperature	26.2°C	28.8°C	27.7°C	34.4°C
Relative Humidity	33%	54%	44%	38%
Wind Speed	2.6 m s^{-1}	1.6 m s^{-1}	1.44 m s^{-1}	1.15 m s^{-1}

Data Analysis

Weed control and spray coverage data were submitted to an analysis of variance in SAS v.9.4 (SAS Institute, Cary, NC, USA) using least squares means to fit the general linear mixed-model (PROC GLIMMIX) at *$P<0.05$ using Tukey's multiple comparison test. Field location was treated as independent variable and run replication was treated as a random effect. Intending to see the overall herbicide and nozzle effect on weed control and spray coverage across sites, field location was intentionally pooled.

Results and Discussion

Spray Coverage

The largest droplet size was produced by the TTI11002 nozzle ($D_{V0.5}$ 794 µm) followed by the TTI6011002 ($D_{V0.5}$ 646 µm), ULD12002 ($D_{V0.5}$ 468 µm) and the XR11002 produced the smallest droplet size ($D_{V0.5}$ 204 µm) as observed in previous studies (Wolf, 2009; Dorr et al., 2013; Ferguson et al., 2015; Henry et al., 2016). The XR nozzle produced the greatest water sensitive coverage and droplet density while the TTI had the least (Table 3.4; Figure 3.1). Borger et al. (2013) observed similar coverage improvements with nozzles producing Medium sprays compared Extremely Coarse sprays but without PRE herbicide efficacy improvement. In all field locations, both the TTI and TTI60 nozzles had similar weed control results, but not similar droplet size results. Among the air induction nozzles, the ULD produced the greatest spray coverage and droplet density as also observed in Wolf (2009). Application conditions (Table 3.3) had a direct effect on coverage and density. The field with lowest wind speed during herbicide application, the Monroe County field, had better results when compared to other locations, even under high temperatures and low relative humidity.

The XR nozzle for example, had 43% coverage and 161 droplets cm^{-2}. At the Gentry County field, however, which had the strongest winds during application, both coverage and density were low, for all nozzles. The XR nozzle had 27.5% coverage and 77 droplets cm^{-2}. The wind speed effect on drift has been widely studied by the Spray Drift Task Force (STDF, 1997) with over 300 application studies and Arvidsson et al. (2011) with 67 field studies, showing the wind speed as the most decisive factor impacting drift and consequently spray coverage.

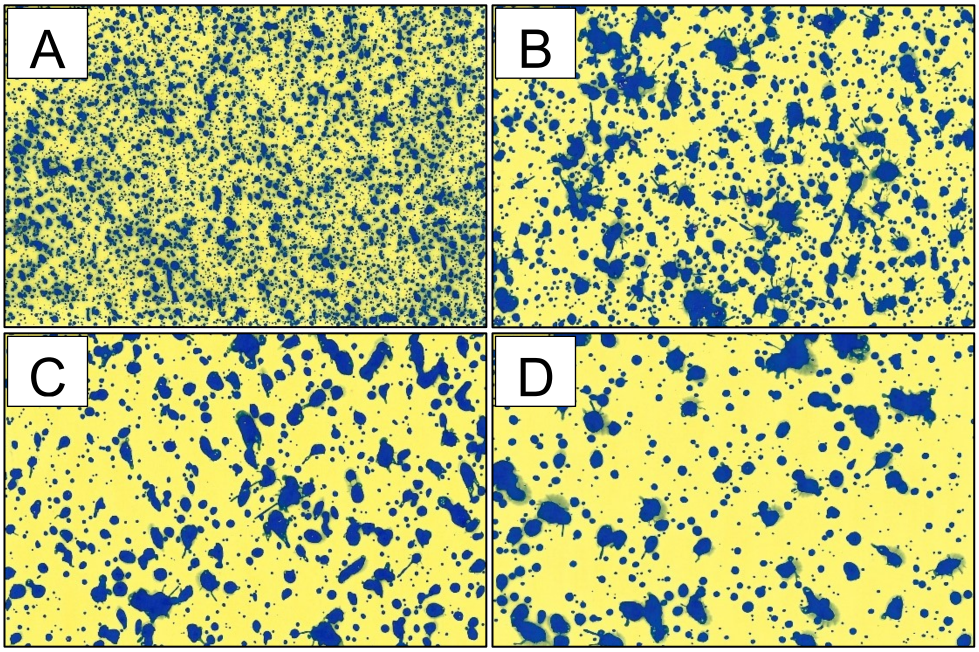

Figure 3.1 Water sensitive papers showing the spray coverage for nozzles XR11002 (A); ULD12002 (B); TTI6011002 (C) and TTI11002 (D).

Table 3.4 Droplet size, spray coverage and droplet density for each nozzle at each field location sprayed with pyroxasulfone[a].

2017, Missouri, USA									
		Atchison County		Nodaway County		Gentry County		Nodaway County	
Nozzle	$D_{V0.5}$ (µm)	Coverage (%)	Density (cm^{-2})	Coverage (%)	Density (cm^{-2})	Coverage (%)	Density (cm^{-2})	Coverage (%)	Density (cm^{-2})
XR11002[c]	204 ^{a}	29.8 ^{a}	78.8 ^{a}	42.5 ^{a}	50.8 ^{a}	27.5 ^{a}	76.8 ^{a}	36.4 ^{a}	95.0 ^{a}
ULD12002[d]	468 ^{b}	24.9 ^{a}	36.6 ^{b}	29.1 ^{b}	30.2 ^{b}	20.4 ^{a}	28.5 ^{b}	27.2 ^{b}	31.2 ^{b}
TTI6011002[c]	646 ^{c}	17.7 ^{a}	23.4 ^{b}	22.2 ^{bc}	18.2 ^{c}	23.0 ^{a}	21.8 ^{b}	23.6 ^{b}	27.0 ^{b}
TTI11002[c]	794 ^{d}	17.0 ^{a}	23.0 ^{b}	18.2 ^{c}	19.9 ^{bc}	18.0 ^{a}	18.4 ^{b}	24.0 ^{b}	20.5 ^{b}

2018, Mississippi, USA									
		Washington County [b]		Oktibbeha County		Noxubee County		Monroe County	
Nozzle	$D_{V0.5}$ (µm)	Coverage (%)	Density (cm^{-2})	Coverage (%)	Density (cm^{-2})	Coverage (%)	Density (cm^{-2})	Coverage (%)	Density (cm^{-2})
XR11002[c]	204 ^{a}	24.0 ^{a}	63.3 ^{a}	37.3 ^{a}	138.0 ^{a}	34.7 ^{a}	115.9 ^{a}	43.6 ^{a}	161.5 ^{a}
ULD12002[d]	468 ^{b}	30.3 ^{a}	60.7 ^{a}	30.5 ^{a}	36.9 ^{b}	23.5 ^{b}	29.8 ^{b}	28.6 ^{b}	51.5 ^{b}
TTI6011002[c]	646 ^{c}	13.5 ^{a}	9.5 ^{a}	22.7 ^{b}	23.0 ^{b}	17.4 ^{b}	15.2 ^{b}	29.0 ^{b}	37.3 ^{b}
TTI11002[c]	794 ^{d}	18.3 ^{a}	21.0 ^{a}	21.4 ^{b}	18.1 ^{b}	18.2 ^{b}	15.8 ^{b}	29.6 ^{b}	28.7 ^{b}

[a] LS-means within same location and variable ($D_{V0.5}$, coverage and density) followed by same letter are not significantly different at $P \leq 0.05$.

[b] Fewer cards were analyzed for this location due to wind carrying.

[c] Spraying Systems Inc. Wheaton, IL, USA.

[d] Hypro LLC, New Brighton, MN, USA.

Droplet Size Effect

Droplet size had no effect on weed control for all PRE herbicides (P value = 0.66) regardless of the herbicide physicochemical characteristics, soil texture, OM, crop residue levels, weed species and rainfall across the eight locations. Location was intentionally pooled in order to evaluate the overall effect of changing droplet sizes for PRE herbicide applications. Therefore, despite of the PRE herbicide's solubility, volatility or adsorption, herbicide efficacy was not be affected by droplet size changes.

Pendimethalin

Nozzle type was not different for pendimethalin efficacy and weed control for all sites. Borger et al. (2013) observed similar results with trifluralin where droplet size did not affect herbicide efficacy and weed control. In the Monroe County, MS, the TTI60 nozzle had higher weed control than the TTI nozzle, 91% to 64% control respectively, at 28 DAA, as observed in Table 3.7. Both nozzles produce large droplets, similar spray coverage and both had similar weed control across all other locations. The Monroe County field, however, was a pasture for several years and it had exceptionally high weed pressure, mostly composed of goosegrass (*Eleusine indica*), broadleaf signalgrass (*Urochloa platyphylla*), southern crabgrass (*Digitaria ciliaris*), yellow foxtail (*Setaria pumila*), velvetleaf (*Abutilon theophrasti*) and spotted spurge (*Chamaesyce maculata*). The TTI60 nozzle was the only dual fan nozzle used in the study, and even though its water sensitive paper coverage and droplet density did not differ among nozzles, the dual fan pattern improved the deposit under the soil clods, increasing the pendimethalin contact surface area through the hidden seedbank (Figure 3.2). The Monroe County location also had the highest OM concentration of all fields, 2.3%. As a strongly adsorptive herbicide, pendimethalin is highly affected by the OM and soil moisture (Linde, 1994). Under dry soil conditions, pendimethalin adsorption to soil colloids is enhanced and herbicide activity reduced. Because the moisture below soil clods was higher compared to the top soil surface, spraying pendimethalin under the clods as assisted by the twin fan nozzle increased the herbicide availability in comparison to spraying on top of drier soil particles.

The OM content effect was also significant on pendimethalin weed control for other locations. This effect was more apparent when nozzle type was pooled for all locations to emphasize the herbicide effect. When the OM content was close to 2%, weed control would drop from 90% to below 80% (Table 3.5). Similar results were observed by several authors (Sparks, 1995; De Jonge et al., 2000; Đurović et al., 2009). Crop residue, however, did not influence efficacy to the same extent. The location with the highest residue, Atchison County, MO field with 9.573 kg ha^{-1}, for example, had satisfactory control (92%). Additionally, pendimethalin had the lowest weed control when compared with the other herbicides when locations and nozzles were intentionally pooled. In both Nodaway County, MO fields and the Noxubee County, MS field pendimethalin control was the lowest (Table 3.6 and 3.7).

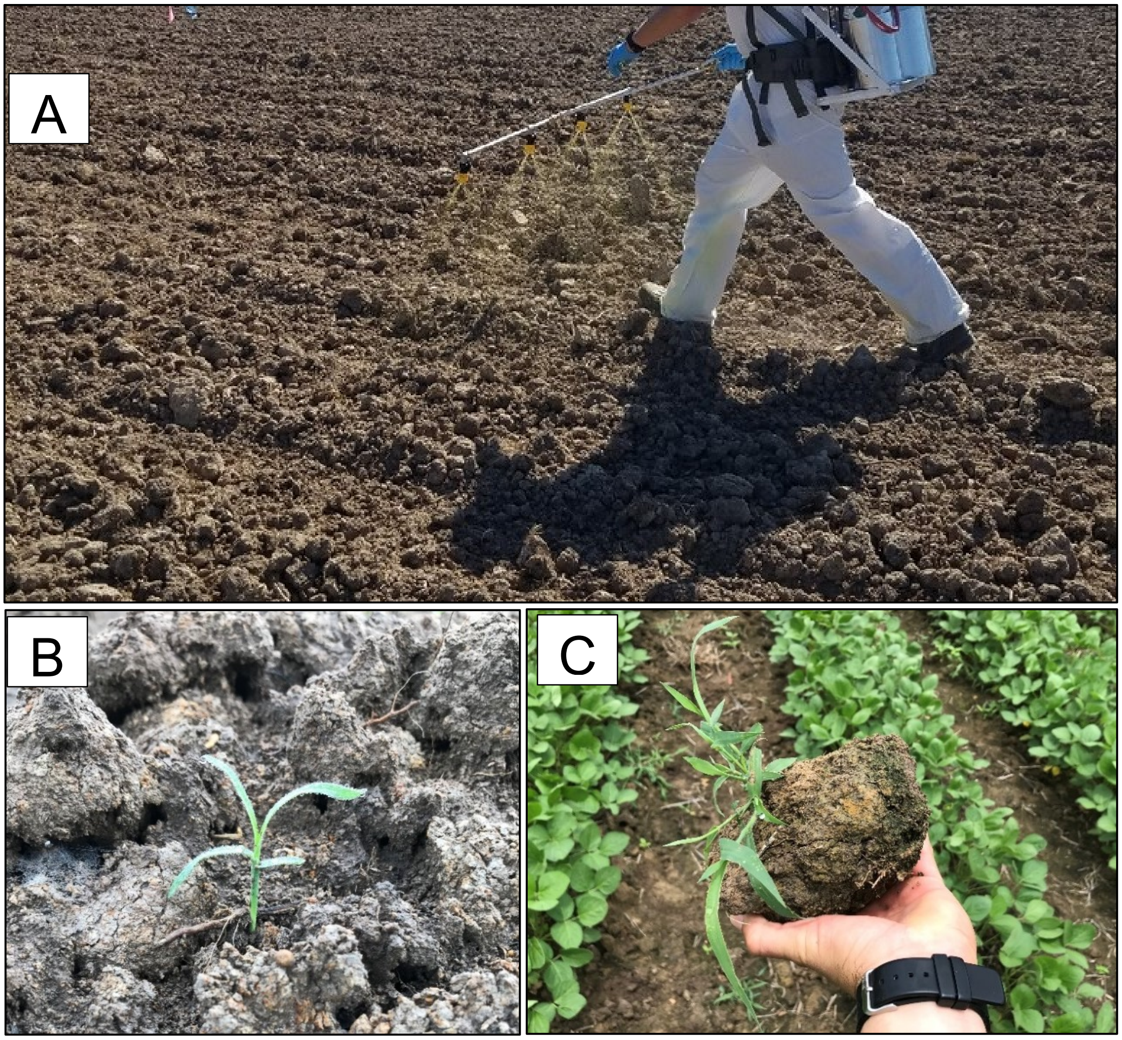

Figure 3.2 Pendimethalin application with the TTI60 dual fan nozzle in the Monroe County, MS, field with large soil clods (A), weed emergence between (B) and under (C) the clods.

Table 3.5 Pendimethalin weed control at 28 DAA and organic matter content per site[a].

Site	Organic Matter	Weed Control
	-------------------------------- % --------------------------------	
Oktibbeha County, MS	0.60	94^{a}
Atchison County, MO	1.59	92^{ab}
Washington County, MS	0.70	92^{ab}
Gentry County, MO	1.49	91^{abc}
Nodaway County, MO	1.94	79^{bdc}
Monroe County, MS	2.30	78^{dc}
Nodaway County, MO	2.02	77^{d}
Noxubee County, MS	2.10	72^{d}

[a] Abbreviations: DAA, days after application.

[b] LS-means within followed by same letter are not significantly different at $P \leq 0.05$.

Metribuzin

Nozzle type and droplet size was not different across fields. For some locations, however, metribuzin weed control was lower than other herbicides. In the Oktibbeha County, MS, field, for example, metribuzin resulted in lower weed control compared to clomazone and pyroxasulfone (Table 3.7). The Oktibbeha County field had the least OM content and the least cation exchange capacity (CEC) across all fields and the first rain event (12.9 mm) only one day after application. Metribuzin is very mobile in soils because it is readily soluble in water (1100 mg L^{-1}) with low adsorption (Log K_{oc} of 1.77). The low OM concentrations, CEC and rainfall within less than 24 hours of application enhanced the product mobility in the soil, moving it under the seedbank layer and reducing the weed control. Liu and Cibes-Viadé (1973) observed, for instance, that CEC and OM were the main variables affecting metribuzin adsorption. Sharom and Stephenson (1976) also observed reduced metribuzin weed control in low organic soils with considerable rainfall as explained by the soil adsorption capacity affecting herbicide leaching potential and the rainfall amount. For that reason, metribuzin is widely known for contamination risks in surface and ground water (EPA, 1992; Dores et al., 2008; Jacobsen et al., 2008). The Washington County, MS, field, second lowest in OM (0.70%), CEC (13.1) and with 12.2 mm of rain 3 DAA had weed control under 90% for all nozzles when compared to other herbicides and fields. The sites with higher CEC and OM had over 90% control, regardless of the rainfall amount, reinforcing the CEC and OM influence on metribuzin efficacy as observed by Liu and Cibes-Viadé (1973).

Table 3.6 Weed control at 28 DAA by herbicide and nozzle per site location in Missouri, 2017.[a]

Site	Herbicide	Nozzle[b]			
		XR11002[c]	ULD12002[d]	TTI6011002[c]	TTI11002[c]
		%			
Atchison County, MO	pendimethalin	82 a	95 a	92 a	86 a
	metribuzin	95 a	97 a	97 a	94 a
	clomazone	97 a	97 a	97 a	94 a
	imazethapyr	97 a	97 a	97 a	97 a
	pyroxasulfone	85 a	95 a	75 a	97 a
Nodaway County, MO	pendimethalin	77 c	87 c	75 c	76 c
	metribuzin	94 ab	99 ab	93 ab	99 ab
	clomazone	95 a	98 a	100 a	97 a
	imazethapyr	95 ab	87 ab	92 ab	88 ab
	pyroxasulfone	89 bc	83 bc	90 bc	88 bc
Gentry County, MO	pendimethalin	92 a	96 a	86 a	97 a
	metribuzin	92 a	99 a	92 a	84 a
	clomazone	100 a	100 a	100 a	100 a
	imazethapyr	92 a	90 a	89 a	99 a
	pyroxasulfone	98 a	100 a	100 a	95 a
Nodaway County, MO	pendimethalin	78 c	77 c	72 c	75 c
	metribuzin	93 a	97 a	99 a	97 a
	clomazone	91 ab	91 ab	87 ab	89 ab
	imazethapyr	97 ab	96 ab	88 ab	92 ab
	pyroxasulfone	89 b	88 b	88 b	87 b

[a] Abbreviations: DAA, days after application.

[b] LS-means within same location and same herbicide followed by same letter are not significantly different at $P \leq 0.05$.

[c] Spraying Systems Inc. Wheaton, IL, USA.

[d] Hypro LLC, New Brighton, MN, USA.

Table 3.7 Weed control at 28 DAA by herbicide and nozzle per site location in Mississippi, 2018.[a]

Site	Herbicide	Nozzle[b]			
		XR11002[c]	ULD12002[d]	TTI6011002[c]	TTI11002[c]
		---------------------------	%	---------------------------	
Washington County, MS	pendimethalin	89^{ab}	87^{ab}	81^{ab}	77^{ab}
	metribuzin	87^{ab}	88^{ab}	88^{ab}	88^{ab}
	clomazone	92^{a}	92^{a}	92^{a}	92^{a}
	imazethapyr	80^{b}	84^{b}	71^{b}	80^{b}
	pyroxasulfone	89^{ab}	91^{ab}	80^{ab}	89^{ab}
Oktibbeha County, MS	pendimethalin	85^{ab}	95^{ab}	88^{ab}	92^{ab}
	metribuzin	83^{b}	90^{b}	90^{b}	85^{b}
	clomazone	95^{a}	95^{a}	96^{a}	96^{a}
	imazethapyr	91^{ab}	95^{ab}	95^{ab}	92^{ab}
	pyroxasulfone	95^{a}	95^{a}	96^{a}	94^{a}
Noxubee County, MS	pendimethalin	75^{c}	69^{c}	75^{c}	63^{c}
	metribuzin	95^{a}	98^{a}	96^{a}	96^{a}
	clomazone	95^{ab}	83^{ab}	94^{ab}	79^{ab}
	imazethapyr	79^{b}	78^{b}	88^{b}	87^{b}
	pyroxasulfone	80^{ab}	88^{ab}	94^{ab}	91^{ab}
Monroe County, MS[e]	pendimethalin	74^{bc}	83^{bc}	91^{ab}	64^{c}
	metribuzin	96^{ab}	95^{ab}	95^{ab}	100^{a}
	clomazone	90^{ab}	62^{c}	100^{a}	95^{ab}
	imazethapyr	92^{ab}	95^{ab}	95^{ab}	93^{ab}
	pyroxasulfone	99^{a}	98^{a}	100^{a}	100^{a}

[a] Abbreviations: DAA, days after application.

[b] LS-means within same location and same herbicide followed by same letter are not significantly different at $P \leq 0.05$.

[c] Spraying Systems Inc. Wheaton, IL, USA.

[d] Hypro LLC, New Brighton, MN, USA.

[e] LS-means across herbicides and nozzles followed by same letter are not significantly different at $P \leq 0.05$.

Clomazone

Nozzle type and droplet size did not differ for clomazone efficacy and weed control for all locations, except in the Monroe County, MS. The use of the ULD12002 nozzle resulted in reduced weed control, 62%, in comparison with the XR11002, TTI11002 and TTI6011002, with 90, 95 and 100% control respectively (Table 3.7). The ULD nozzle produced Very Coarse sprays and consistent spray coverage and droplet density for air induction type nozzles as observed by Wolf (2009). The ULD produces a wider spray angle of 120° in comparison with the other 110° nozzles, but this characteristic did not affect the weed control with clomazone in other fields. Analyzing the control mean values from 7 to 28 DAA for each Monroe County, MS, field plot treated with clomazone (Table 3.8), it was observed a gradual weed control reduction from the first to the last ULD nozzle sprayed plot, while the other nozzles had consistently higher control. The hypothesis is that an application issue like clogged nozzles or pressure drop occurred and reduced the correct herbicide rate and distribution on soil.

The moderately volatile herbicide clomazone, was not affected by nozzle type, application conditions or field characteristics, since over 90% control was obtained for almost all locations, regardless of OM, CEC, rainfall, temperature, humidity and wind speed.

Imazethapyr

Neither nozzle type nor droplet size affected weed control. Imazethapyr application resulted in low control for two locations, the Washington and Noxubee County, MS, fields (Table 3.7). In the Washington County, MS, located in the Mississippi Delta, the mean weed control was lower due to spotted spurge, with poor control for all nozzles. Spotted spurge is not considered a noxious species but its dispersion, dormancy and germination capacity makes it a troublesome weed throughout the US (Elmore and McDaniel., 1986; Asgarpour et al., 2010; McCullough et al., 2016). Elmore and McDaniel (1986) identified spotted spurge populations in 15 of the 17 counties in the Mississippi Delta in 1983 and 1985, when conducting that survey.

Table 3.8 Clomazone weed control mean value per plot and control rating date after application at the Monroe County field, MS, 2018.

		Weed Control[a]			
Nozzle	Plot number	7 DAA[b]	14 DAA	21 DAA	28 DAA
		%			
XR11002	1	100	100	100	88
	2	100	85	84	72
	3	100	100	100	100
	4	100	100	100	100
ULD12002	1	100	76	69	33
	2	100	67	62	72
	3	100	83	67	58
	4	100	100	83	83
TTI6011002	1	100	100	93	100
	2	100	100	99	100
	3	100	83	83	83
	4	100	98	98	98
TTI11002	1	100	100	100	100
	2	100	100	100	98
	3	100	100	98	100
	4	100	100	96	100

[a] Mean control value for barnyardgrass (*Echinochloa crus-galli*), bermudagrass (*Cynodon dactylon)*, broadleaf signalgrass (*Urochloa platyphylla*), goosegrass (*Eleusine indica*), prickly sida (*Sida spinosa*) and velvetleaf (*Abutilon theophrasti*).

[b] Abbreviations: DAA, days after application.

Spotted spurge competiveness is assured by its seed dormancy, sporadic germination and its temperature and water requirement adaptability (Hope, 1982). Imazethapyr is an imidazolinone herbicide and inhibits acetolactate synthase ALS/AHAS. Its constant use has led to several cases of weed resistance and tolerance (Saari et al., 1994; Bernasconi et al. 1995). Several weed species are resistant to ALS herbicides in Mississippi, including pigweed species (*Amaranthus* spp.), barnyardgrass (*Echinochloa crus-galli*), large crabgrass (*Digitaria sanguinalis*), Italian ryegrass (*Lolium perenne ssp. multiflorum*), annual bluegrass (*Poa annua*) and common cocklebur (*Xanthium strumarium*) (Heap, 2018). Therefore, ALS herbicide overuse could have caused spotted spurge to develop imazethapyr tolerance or resistance in the Washington County, MS, as already observed in Georgia by McCullough et al. (2016). Further research should be conducted to confirm tolerance or resistance cases in the Mississippi Delta. Similarly, the reduced mean weed control in the Noxubee County, MS, was mostly caused by poor tall waterhemp control (*Amaranthus tuberculatus*), possibly due to ALS resistance, where less than 75% waterhemp control was obtained for all nozzles at 28 DAA. Pigweed species resistant to ALS herbicides in Mississippi include tall waterhemp (*Amaranthus tuberculatus*), Palmer amaranth (*Amaranthus palmeri*), redroot pigweed (*Amaranthus retroflexus*) and spiny amaranth (*Amaranthus spinosus*) Heap (2018). No herbicide physicochemical properties and environmental characteristic affected imazethapyr weed control.

Pyroxasulfone

Weed control was not affected by nozzle type and droplet size. Borger et al. (2013) observed similar results in Australia using the XR and AI nozzles to spray pyroxasulfone for rigid ryegrass control. Pyroxasulfone application resulted in reduced control compared to other herbicides in both Nodaway County, MO fields (Table 3.6). For both locations, the weeds with reduced control were yellow foxtail, tall waterhemp and barnyardgrass (*Echinochloa crus-galli*). Hausman et al. (2013) observed similar pyroxasulfone waterhemp control at 30 DAA, below 90%. Yamaji et al. (2016) observed reduced green foxtail (*Setaria viridis*) and giant foxtail (*Setaria faberi*) control, less than 62%, with rainfall under 12.5 mm within 7 DAA, and observed control over 88% with rainfall over 12.5 mm within 7 DAA. Both locations had up to 12.5 mm of rain within 7 DAA and yellow foxtail control was still less than 80%. Other studies showed improved barnyard and Amaranthus spp. control (Yamaji et al. 2014; Yamaji et al. 2016). Pyroxasulfone adsorption and efficacy is also affected by soil OM content (Tidemann et al., 2014). As observed by Odero and Wright (2013), the labeled rate of 214 g a.i. ha^{-1} for high OM soils was enough to provide sufficient control. The rate of 178.5 g a.i ha^{-1} followed the label recommendations for both Nodaway County, MO locations, with 1.94 and 2.02% OM, respectively, and yet, did not provided acceptable control for yellow foxtail, barnyard and tall waterhemp, while in the Monroe County, MS field with 2.30% OM, the weed control was over 98% for all nozzles.

Conclusion

The results of field experiments indicate that PRE herbicide weed control is not affected by droplet size, spray coverage and nozzle type regardless of physicochemical herbicide properties like adsorption, volatility and solubility. Merry (1986) and Borger et al. (2013) observed similar results. The TTI60 twin nozzle, however, increased pendimethalin weed control in specific field conditions (high OM content, large-sized soil clods, high weed pressure) due to better herbicide deposit on moist soil surfaces and greater herbicide clod coverage. Further research should consider herbicide soil deposit and weed control studies with twin-fan nozzles with the potential to enhance PRE herbicide efficacy. Environmental factors affected pendimethalin and metribuzin efficacy. Pendimethalin control was reduced (< 80%) in high OM content soils as observed in other studies (Sparks, 1995; De Jonge et al., 2000; Đurović et al., 2009). Under high OM content soils (> 2%), additional pendimethalin tank-mixture combination should be considered. Metribuzin weed control was reduced due to increased soil mobility in low OM and low CEC soil with >12 mm rain within 3 DAA as described in

Liu and Cibes-Viadé (1973) and Sharom and Stephenson (1976). Based on the results, metribuzin applications should be avoided in low OM (< 0.7%) and CEC soils (< 13.1%) with chance of rain of (12.2 mm) within three days after application. Overall, clomazone, imazethapyr and pyroxasulfone provided acceptable weed control independent of soil type, OM, CEC, pH, crop residue and rainfall. Imazethapyr, however, provided reduced spotted spurge and tall waterhemp control (< 90%) in two locations in Mississippi, possibly due to ALS tolerance or resistance as recorded by Heap (2018) and McCullough et al. (2016). Further investigation is necessary to confirm ALS tolerance or resistance in both locations.

CHAPTER IV

RAINFALL TIMING AND CROP RESIDUE EFFECT ON PRE-EMERGENCE HERBICIDES EFFICACY FOR DIFFERENT SPRAY NOZZLES

Abstract

Pre-emergence (PRE) herbicide weed control success is affected by environmental factors including rainfall and herbicide-plant residue interaction. Two greenhouse experiments were conducted in 2017 and will be continued in 2018, studying the effect of crop residue amounts (2500 and 5000 kg ha^{-1}) and the effect of simulated rain at two, four and eight days after herbicide application (DAA). Applications were made over weed species treated with five PRE herbicides and sprayed with four different nozzle types. The preliminary results have shown no nozzle type effect across plant residue amounts. With rain at eight DAA, however, the use of the XR nozzle provided reduced johnsongrass weight, up to 17% weight reduction increase in comparison to the TTI nozzle. Johnsongrass and velvetleaf were affected by crop residue amount where 5000 kg ha^{-1} of residue decreased johnsongrass fresh weight reduction and 2500 kg ha^{-1} increased velvetleaf control and weight losses. Pendimethalin consistently provided low velvetleaf and johnsongrass control throughout the studies. The 5000 kg ha^{-1} residue amount increased pendimethalin control of johnsongrass while rain at eight DAA decreased johnsongrass fresh and dry weight reductions. Rain at 2 DAA decreased velvetleaf response to pendimethalin in comparison to 4 and 8 DAA.

Introduction

The fate and efficacy of herbicides in the environment is directly affected by variables like herbicide volatilization, leaching, microbial decomposition, chemical breakdown and soil adsorption (Toth and Milham, 1975; Hodges and Talbert, 1990; Borger et al., 2013; GRDC, 2015). Rainfall, for example, influences soil applied herbicide performance by activating and distributing the active ingredient throughout the soil. Generally, pre-emergence herbicides (PREs) are better available for plant uptake when soil moisture is present (Loux et al., 2015). Most herbicides are hydrophobic and are attracted to low charged organic matter (OM) particles and the soil colloids. Under dry soils, herbicide adsorption to soil and OM particles is increased, reducing herbicide activity and weed control (Linde, 1994). On the other hand volatile herbicides may have the opposite effect. Schneider et al. (2013) observed trifluralin and triallate volatilization increasing up to eight times when controlled humidity within the soil was increased and up to three times when a rain event was simulated. Smith et al. (1997) observed similar results with increased ethalfluralin, trifluralin and triallate volatility during rain events and no volatility with a dry soil surface. Additionally, rain may affect highly soluble PRE herbicide efficacy through herbicide runoff and leaching, potentially contaminating ground water and reducing control (Lavorenti, 1996).

The amount of crop residue covering the soil surface can also affect PRE herbicide efficacy from reduced spray coverage, herbicide deposit interception and herbicide adsorption, reducing its availability for plant uptake (Borger et al., 2013; GRDC, 2015). Studying the adsorption of diuron, terbacil and simazine on blueberry (*Vaccinium ssp*.) residue, Hodges and Talbert (1990) observed up to a five times greater herbicide-residue adsorption than herbicide-soil adsorption. Highly adsorptive products may bind to the residue thereby reducing availability for plant uptake. The volatilization process may also be enhanced or reduced with crop residue depending on conditions. Wienhold and Gish (1994) observed lower alachlor and atrazine volatility losses in no-till corn (*Zea mays*) in comparison to a conventionally tilled corn field. Erbach and Lovely (1975), however, observed no significant corn residue effect on weed control for alachlor but, observed increased velvetleaf (*Abutilon theophrasti*) and foxtail millet (*Setaria italica*) control when simulated rain was conducted after herbicide treatment.

The weed control herbicide efficacy, which is affected by complex interactions between herbicide pathways and environment variables, is a result of satisfactory spray coverage and correct active ingredient deposits. Correct nozzle selection, for instance, will impact spray quality, spray coverage and deposit, drift control and consequently, herbicide efficacy. Few authors have, however, studied the effects of nozzle type selection on PRE herbicides efficacy (Merry, 1986; Derksen et al., 2012; Borger et al., 2013), when compared to spray nozzle studies on post-emergence (POST) herbicides influence over weed control (Ennis and Williamson, 1963; Douglas, 1968; McKinlay et al., 1972; McKinlay et al., 1974; Wolf et al., 1992; Knoche, 1994; Liu et al., 1996; Etheridge et al., 1999; Smith et al., 2000; Shaw et al., 2000; Ramsdale and Messersmith, 2001; Etheridge et al., 2001; Feng et al., 2003; Brown et al., 2007; Creech et al., 2016; Butts et al., 2018; Ferguson et al., 2018). Therefore, this study aims to evaluate the weed control of PRE herbicides at different rainfall timings and crop residue amounts with different nozzles types.

Materials and Methods

Two greenhouse studies were conducted at the Rodney Foil Plant Science Research Center, Starkville, MS in December, 2017 and will be replicated in November, 2018. Herbicides were selected based on the physicochemical characteristic of each product, specifically for adsorption, volatility and solubility. The herbicides, rates, formulations and physicochemical properties of each product used in both studies are listed in Table 4.1. Both experiments were conducted in a factorial arrangement of treatments in a completely randomized design with four untreated control trays per treatment. Herbicide applications were applied with a two boom research spray chamber generation III (DeVries Manufacturing Inc., Hollandale, MN) calibrated to deliver 140 L ha^{-1} at 276 kPa and a nozzle height of 0.5 m. Nozzles selected for comparison were: XR11002, ULD12002, TTI6011002 and the TTI11002. The weed species selection was conducted through examining each herbicide label and by choosing three weeds species commonly controlled by all herbicides and one controlled specifically by each herbicide treatment, as listed in Table 4.2. Each tray had twenty manually selected seeds per weed species, including the three common weeds and the herbicide-specific one, totaling eighty seeds planted per tray. Marestail (*Erigeron canadensis*) seeds, however, were the only species weighed, where 1 gram of seed was added to the pyroxasulfone treatment. The seeds were planted in trays measuring 24 cm x 24 cm x 6.3 cm with potting mix Sungro Horticulture® (Sun Gro Horticulture Ltd., Agawam, MA) consisting of ingredients like Canadian sphagnum peat moss, composted pine bark, vermiculite and dolomitic limestone. Field corn residue was collected in October, 2017, in a field near Egypt, MS and in September, 2018, in Starkville, MS. Weed emergence and weed control ratings were collected at 7, 14, 21 and 28 days after application (DAA).

Weed emergence per species was calculated based on twenty planted seeds and the number of plants emerged per tray (*N*) as:

$$\text{Weed emergence} = \frac{N}{20} \text{ x } 100$$

except for marestail which the emergence was visually estimated based on the untreated trays. The emergence equation was used to calculate the weed control rating per species based on the untreated and treated weed emergence values where *T* was the mean weed emergence for a treated experimental unit and *U* was the mean weed emergence for the untreated control replicates as:

$$\text{Weed control} = 100 - (\frac{T}{U} \text{ x } 100)$$

Zero control was rated for the treatments with same or higher emergence as the untreated trays for the specific weed. Complete control (100%) was rated for the treatments with no weed emergence. Fresh matter weight data were at 30 DAA while dry matter weight was collected after drying plants at 65°C for 72 hours. Fresh weight reduction (FWR) and dry weight reduction (DWR) were both calculated based on the untreated weight results of each species and converted in percent of weight reduction as shown in Creech et al. (2016). Johnsongrass and velvetleaf were the only species included in the control results and the fresh and dry weight reduction results due to regular and higher plant emergence across treatments than the other weed species.

Table 4.1 Herbicide treatments and each corresponding value and classification regarding volatility, adsorption and solubility characteristics[a].

Herbicide	Rate	Trade name	Manufacturer	Volatility	Adsorption[b]	Solubility
	g a.i. ha^{-1}			mm Hg	Log K_{oc}	mg L^{-1}
pendimethalin	1062	Prowl H_2O®	BASF Corp., Research Triangle Park, NC	9.4×10^{-6} [c] Slightly volatile	4.23[d] Strong sorption	0.275 [e] Slightly soluble
metribuzin	701	Sencor®	Bayer CropScience, Research Triangle Park, NC	4.35×10^{-7} [f] Slightly volatile	1.77 [g] Low sorption	1100 [g] Readily soluble
clomazone	1122	Command 3ME®	FMC Corp., Philadelphia, PA	1.44×10^{-4} [e] Moderately volatile	2.47 [h] Moderate sorption	1100 [e] Readily soluble
imazethapyr	70	Pursuit®	BASF Corp., Research Triangle Park, NC	$2.1 \text{ X } 10^{-11}$ [i] Non-volatile	2.45 [g] Moderate sorption	1400 [g] Readily soluble
pyroxasulfone	178	Zidua®		1.8×10^{-8} [j] Non-volatile	2.05 [k] Low sorption	3.49 [l] Slightly soluble

[a] Classifications for volatility, adsorption and solubility according to Silva (2004), FAO (2000) and FAO (2000), respectively.

[b] K_{oc} values were converted to the logarithm value.

[c] Ahrens (1994), [d] Shaner (2012), [e] Meister (1992), [f] Gangolli (1999), [g] Gillespie et al. (2011), [h] Schreiber et al. (2015), [i] Lyman (1985), [j] MDA (2013), [k] Westra (2012), [l] Yamaji et al. (2016).

Table 4.2 List of weeds included in each herbicide treatment represented by an X in the herbicide column[a].

Weed Species		Herbicides				
Common name	Scientific name	pendimethalin	metribuzin	clomazone	imazethapyr	pyroxasulfone
johnsongrass	*Sorghum halepense*	X	X	X	X	X
barnyardgrass	*Echinochloa crus-galli*	X	X	X	X	X
velvetleaf	*Abutilon theophrasti*	X	X	X	X	X
Palmer amaranth	*Amaranthus palmeri*	X				
waterhemp	*Amaranthus tuberculatus*		X			
common ragweed	*Ambrosia artemisiifolia*			X		
common lambsquarters	*Chenopodium album*				X	
marestail	*Erigeron canadensis*					X

[a] Johnsongrass, barnyard and velvetleaf are included in all herbicide treatments.

Rainfall Study

Corn residue was placed on top of the potting mix at the amount of 2000 kg ha^{-1} (11.64 g $tray^{-1}$). On December 11th, 2017, trays were weed-planted in the top 2 cm of the soil surface and watered with 10 mm. Herbicide treatments were applied with each nozzle type two days after planting (DAP). The XR11002, ULD12002 and TTI11002 nozzles were used in the study. The rainfall treatments included 10 mm of simulated rain at two, four and eight days after application (DAA) and were conducted using the two boom research spray chamber III (DeVries Manufacturing Inc., Hollandale, MN) with the Combo-Jet® UR 11010 nozzle (Wilger Inc., Lexington, TN) producing Ultra Coarse spray quality as in Figure 4.1. After the simulated rainfall treatment, trays were watered every ten days until harvest.

Crop Residue Study

Two corn residue quantities were used as treatments: 5000 kg ha^{-1} (29.11 g $tray^{-1}$) and 2500 kg ha^{-1} (14.55 g $tray^{-1}$) as shown on Figure 4.2. Weed seeds were planted on December 10th, 2017, in the top 2 cm of the soil surface, then the corn residue was evenly distributed across each treatment, followed by tray watering with 10 mm. Herbicide treatments were sprayed with each nozzle type at two DAP and trays were watered at two, twelve and twenty-one DAA with 10 mm. The XR11002, ULD12002, TTI6011002 and TTI11002 nozzles were used in the study.

Figure 4.1 Rainfall timing experimental units being treated in the rain simulator.

Figure 4.2 Corn residue treatments of 5000 kg ha^{-1} (Left) and 2500 kg ha^{-1} (Right).

Data Analysis

In each study, weed control, FWR and DWR results were submitted to an analysis of variance in SAS v.9.4 (SAS Institute, Cary, NC, USA) using least squares means to fit the general linear mixed-model (PROC GLIMMIX) at $*P<0.05$ using Tukey's multiple comparison test. Weed species was treated as independent and run replication was treated as a random effect. A factor would be considered random effect if it was not statistically significant in the primarily model.

Results and Discussion

Crop Residue Effect on Velvetleaf

The amount of crop residue impacted velvetleaf response to herbicides. Velvetleaf control, fresh weight, and dry weight reductions were greater under low crop residue, 2500 kg ha^{-1}, than under 5000 kg ha^{-1}, despite the nozzle type or herbicide used (Table 4.3). Velvetleaf DWR increased 8% from the low to high residue level. Cardina et al. (1995) observed similar results when studying the competition of velvetleaf in corn under no-till and conventional tillage systems. The authors observed greater velvetleaf competitiveness in the no-till system when compared to the bare soil conventionally tilled system. Correia and Durigan (2004) also observed an emergence increase of the large-seeded weed cypressvine (*Ipomoea quamoclit*) when increasing sugarcane residues from 5000 kg ha^{-1} to 15000 kg ha^{-1}.

Velvetleaf control, FWR and DWR were also affected by herbicide treatment as listed in Table 4.4. Pendimethalin and imazethapyr followed by pyroxasulfone provided reduced control and little FWR and DWR regardless of the residue amount and nozzle type. Walsh et al. (2015) also observed lower velvetleaf controls with imazethapyr sprayed alone in comparison to additional tank-mixture herbicides. Similarly, Belfry et al. (2015) observed reduced pyroxasulfone control on velvetleaf (< 32% control). Reduced pendimethalin efficacy can be explained by its strong adsorption to the soil organic matter (OM). Pendimethalin is an adsorptive herbicide (log K_{oc} of 4.23) and can strongly bind to OM and residue. The decrease in control and weight reduction for velvetleaf with pendimethalin can be accounted for due to the high OM concentration of the potting mix. The potting mix contained high concentrations of peat moss among other highly concentrated OM ingredients which decreased the pendimethalin availability for weed uptake due to OM adsorption. Several authors have observed reduced pendimethalin weed control under elevated OM content soils (Sparks, 1995; De Jonge et al., 2000; Đurović et al., 2009). Clomazone and metribuzin provided complete velvetleaf control and weight reduction regardless of the residue amount or nozzle type.

Nozzle type did not affect velvetleaf control and weight reductions, regardless of the residue level or herbicide used. Borger et al. (2013) also observed no droplet size and nozzle type influence on PRE herbicide efficacy in wheat fields containing 1573 and 2267 kg ha^{-1} of crop residue respectively. Merry (1986) also did not observe droplet size and nozzle effects in PRE herbicide weed control.

Crop Residue Effect on Johnsongrass

Johnsongrass fresh weight reduction was reduced at the 5000 kg ha^{-1} level, a 78% reduction in comparison with 71% reduction under 2500 kg ha^{-1} of residue (Table 4.3). Oliveira el al. (2001) observed similar results in an experiment including corn residue levels ranging from 0 to 12000 kg ha^{-1} treated with a tank-mixture of metolachlor and atrazine. Herbicide control of the grass species increased with the higher residue levels.

The different amounts of residue will directly impact soil surface light interception. Therefore, the reduced light penetration under greater residue amounts may affect the germination and emergence of small-seeded weeds such as johnsongrass (Crutchfield et al., 1986; Mohler, 1996).

Johnsongrass FWR and DWR were affected by herbicide treatment specifically for pendimethalin, regardless of the residue amount and nozzle type (Table 4.4). Pendimethalin reduced activity is accounted for due to the strong herbicide binding to the potting mix OM particles as similarly observed in previous studies (Sparks, 1995; De Jonge et al., 2000; Đurović et al., 2009). Clomazone and metribuzin provided the greatest johnsongrass weight reduction (FWR of 87%, DWR of 90%) across nozzle type or residue amount.

Crop residue and herbicide treatment interacted to increase johnsongrass control and weight reductions (Table 4.5). Under 2500 kg ha^{-1} of residue, clomazone provided greater control than both metribuzin and pendimethalin. Pendimethalin weight reductions were reduced with the low residue amount (2500 kg ha^{-1}), a 28% reduction on dry weight, in comparison to the high residue treatments (5000 kg ha^{-1}) with 74% of dry weight reduction despite the nozzle type used to spray pendimethalin. Pendimethalin activity was enhanced under greater corn residue levels due to increased soil moisture. The plant residue tended to decrease temperature and increase moisture in soil (Van Wijk et al., 1959) increasing the herbicide availability for plant uptake under greater moisture (Loux et al., 2015).

Nozzle type did not affect johnsongrass FWR and DWR when treated with the same herbicide despite the crop residue level. However, clomazone sprayed with the XR nozzle provided greater johnsongrass control than imazethapyr sprayed with the TTI60 nozzle, 71% and 15% controls, respectively, when nozzle type and herbicide interacted (Table 4.6).

Table 4.3 Johnsongrass and velvetleaf responses to different crop residue amounts across all nozzles and herbicides used in the study[a].

Species	Crop Residue	Control[bc]	FWR[cd]	DWR[cd]
		----------------------	%	----------------------
johnsongrass	2500 kg ha^{-1}	44 [a]	71 [b]	76 [a]
	5000 kg ha^{-1}	47 [a]	78 [a]	77 [a]
velvetleaf	2500 kg ha^{-1}	58 [a]	72 [a]	64 [a]
	5000 kg ha^{-1}	51[b]	63 [b]	56 [b]

[a] No significant interaction among crop residue, nozzle and herbicide was observed.

[b] Control at 28 days after application.

[c] LS-means within each species and column followed by same letter are not significantly different at $P \leq 0.05$.

[d] Abbreviations: FWR, fresh weight reduction; DWR, dry weight reduction.

Table 4.4 Johnsongrass and velvetleaf responses to different herbicide treatments across all nozzles and crop residue amounts used in the study[a].

Species	Herbicide	Control[bc]	FWR[cd]	DWR[cd]
		-------------------------	%	-------------------------
johnsongrass	pendimethalin	38 [a]	44 [b]	51 [b]
	metribuzin	46 [a]	82 [a]	89 [a]
	clomazone	55 [a]	87 [a]	90 [a]
	imazethapyr	42 [a]	80 [a]	75 [a]
	pyroxasulfone	47 [a]	81 [a]	75 [a]
velvetleaf	pendimethalin[e]	4 [c]	12 [d]	7 [d]
	metribuzin	100 [a]	100 [a]	100 [a]
	clomazone	100 [a]	100 [a]	100 [a]
	imazethapyr[e]	14 [c]	49 [c]	25 [c]
	pyroxasulfone[e]	57 [b]	76 [b]	68 [b]

[a] No significant interactions among crop residue, nozzle and herbicide was observed

[b] Control at 28 days after application.

[c] LS-means within each species and column followed by same letter are not significantly different at $P \leq 0.05$

[d] Abbreviations: FWR, fresh weight reduction; DWR, dry weight reduction.

[e] Suppression or partial control (Anonymous, 2017a; Anonymous, 2017b; Anonymous, 2017c).

Table 4.5 Johnsongrass response to different herbicides at two crop residue amounts across all nozzle types used in the study.

Crop Residue	Herbicide	Control[ab]	FWR[bc]	DWR[bc]
			%	
	pendimethalin	27^{b}	17^{b}	28^{c}
	metribuzin	31^{b}	81^{a}	89^{ab}
2500 kg ha^{-1}	clomazone	71^{a}	95^{a}	99^{a}
	imazethapyr	38^{ab}	79^{a}	79^{ab}
	pyroxasulfone	56^{ab}	84^{a}	82^{ab}
	pendimethalin	50^{ab}	72^{a}	74^{ab}
	metribuzin	61^{ab}	82^{a}	89^{ab}
5000 kg ha^{-1}	clomazone	40^{ab}	78^{a}	81^{ab}
	imazethapyr	47^{ab}	82^{a}	72^{b}
	pyroxasulfone	37^{ab}	78^{a}	67^{b}

[a] Control at 28 days after application.

[b] LS-means within each column followed by same letter are not significantly different at $P \leq 0.05$.

[c] Abbreviations: FWR, fresh weight reduction; DWR, dry weight reduction.

Table 4.6 Johnsongrass control with different herbicides and nozzles across all crop residue amounts used in the study[ab].

	Nozzle			
Herbicide	XR11002[c]	ULD12002[d]	TTI6011002[c]	TTI11002[c]
		%		
pendimethalin	30^{ab}	47^{ab}	27^{ab}	49^{ab}
metribuzin	34^{ab}	48^{ab}	68^{ab}	36^{ab}
clomazone	71^{a}	68^{ab}	60^{ab}	24^{ab}
imazethapyr	53^{ab}	49^{ab}	15^{b}	53^{ab}
pyroxasulfone	48^{ab}	43^{ab}	56^{ab}	39^{ab}

[a] Control at 28 days after application.

[b] LS-means followed by same letter are not significantly different at $P \leq 0.05$

[c] Spraying Systems Inc. Wheaton, IL, USA.

[d] Hypro LLC, New Brighton, MN, USA.

Crop residue and nozzle type did not affect Palmer amaranth, waterhemp and marestail treated with pendimethalin, metribuzin and pyroxasulfone, respectively. The other weed species used in the study (common ragweed, barnyardgrass and lambsquarters) were not included in the results due to low weed emergence in all treatments, including the untreated checks.

Rainfall Timing Effect on Velvetleaf

Velvetleaf FWR was affected by the timing of rainfall for the PRE herbicides used in the study. The eight day rainfall treatment resulted in reduced FWR compared to the two day rainfall (Table 4.7).

Herbicide treatment affected velvetleaf control, FWR and DWR despite the rainfall timing after application and nozzle type selected. Pendimethalin control and DWR was the lowest across herbicides followed by imazethapyr (Table 4.8). Low velvetleaf control and low DWR with pendimethalin was a consequence of high adsorption between OM potting mix particles and the herbicide. The decrease of imazethapyr control on velvetleaf was also observed by Walsh et al. (2015) where imazethapyr sprayed alone provided reduced control compared to imazethapyr plus additional herbicides. Clomazone and metribuzin provided complete weed control.

Both rainfall timings and herbicides affected velvetleaf control and velvetleaf dry weight reduction as shown in Table 4.11. The pendimethalin and imazethapyr treatments provided reduced control and DWR for all rainfall timings. Pendimethalin control and weight reductions in velvetleaf were not significant among rainfall timings. Velvetleaf control and DWR at the two day rainfall were considerably reduced, 1% control and 8% dry weight reduction, possibly due better plant emergence under higher soil moisture, even though, pendimethalin adsorption should be reduced under soil moisture in comparison to dry soils. As observed by Taylor-Lovell et al. (2002) and Erbach and

Lovely (1975) where velvetleaf control with pendimethalin were increased with greater moisture availability.

Rainfall Timing Effect on Johnsongrass

The timing of rainfall after herbicide application affected johnsongrass control, FWR and DWR to the PRE herbicides used in the study. Johnsongrass control and dry weight reductions were decreased at the eight day rainfall application across nozzle types and herbicides (Table 4.7). Johnsongrass DWR decreased 29% from the two to eight day rainfall treatment. This reduced herbicide efficacy in johnsongrass at the eight day rainfall application is a consequence of less herbicide availability in the soil-solution (Loux et al., 2015), possibly due to soil surface temperature changes and increased water competition. Acciaresi et al. (2012) observed johnsongrass high water competition under low moisture soil conditions. Krenchinski et al. (2015) observed, for instance, that increasing soil temperatures to up to 30 °C increased germination of both species of johnsongrass (*S. halepense and S. arundinaceum*). The four day rainfall treatment reduced johnsongrass FWR and DWR in comparison to the two day rainfall. Defelice et al. (1987) also observed greater herbicide control in johnsongrass under no-till when moisture was available.

Johnsongrass control, FWR and DWR were affected by herbicide treatments regardless of the rainfall timing after application and nozzle used. Pendimethalin provided the lowest FWR and DWR while johnsongrass control was reduced with pendimethalin, imazethapyr and metribuzin treatments (Table 4.8). Reduced johnsongrass control with pendimethalin can be explained by the potting mix OM content (mainly consisted of peat moss) likely increasing the herbicide molecule adsorption.

Additionally, johnsongrass biotypes resistant to imazethapyr have already been reported in Texas and Arkansas, specifically in the Delta region of Arkansas (Johnson et al., 2014; Heap, 2018). Therefore, the possibility that imazethapyr-resistant johnsongrass seeds were included in the experiment, explaining the reduced imazethapyr efficacy, should be further evaluated. Clomazone provided greater johnsongrass control, FWR and DWR than the other herbicides (Table 4.8).

Johnsongrass control was affected by nozzle type while no weight reduction effect was observed (Table 4.9). Based on previous field and wind tunnel studies (Chapter II and III) the TTI11002 nozzle produces Extremely Coarse spray quality ($D_{V0.5}$ 794 μm) and spray coverage of 21% (average of water sensitive papers in eight field locations), producing the lowest coverage when compared to the ULD and the XR nozzles, with 27% and 34% of spray coverage, respectively. Therefore, even though no significant weight reduction was noticed, decreased johnsongrass control is possibly the consequence of reduced spray coverage. Several studies have shown the influence of spray coverage over weed control using POST herbicides (Oliver et al., 1983; McKinlay et al., 1974; Wolf, 2009; Knoche, 1994; Shaw et al., 2000; Etheridge et al., 2001) while no research has shown the same effect in PRE herbicides. Borger et al. (2013) did not observe improved rigid ryegrass (*Lolium rigidum*) control when spraying PRE herbicides with the TT and TTI nozzle, despite different spray coverages.

When nozzle type and rain timing interacted, the spray coverage also seemed to impact johnsongrass fresh weight reduction (Table 4.10). With rain at eight days after application, the TTI nozzle provided the lowest weight reduction, 56% followed by the ULD nozzle with 58% and the XR nozzle with greater reduction of 73% regardless of the herbicide used, producing up to a 17% increase in fresh weight reduction. At both two and four days after application, nozzle type had no effect. Therefore, the increase on spray coverage on soil with low moisture for extended periods had a significant impact on johnsongrass weight reduction. Based on these results, it is possible to presume that the smaller droplets produced by the XR nozzle were better distributed on top and throughout the corn residue in comparison with the ULD and TTI nozzles, ensuring herbicide activity when moisture became available. Even though small droplets are known to evaporate faster than larger droplets (Houghton, 1933; Holterman, 2003; Yu et al., 2009[A]; Yu et al., 2009[B]). Thus, further research will be conducted to investigate the effect of nozzle and droplet sizes on johnsongrass control.

Table 4.7 Johnsongrass and velvetleaf responses to different rain timings after herbicide application across all nozzles and herbicides used in the study[a].

Species	Rain timing	Control[bc]	FWR[cd]	DWR[cd]
		%		
johnsongrass	2 DAA[d]	61 a	90 a	93 a
	4 DAA	57 a	70 b	59 b
	8 DAA	38 b	62 b	64 b
velvetleaf	2 DAA	64 a	77 ab	69 a
	4 DAA	70 a	80 a	75 a
	8 DAA	68 a	73 b	69 a

[a] No significant interaction among rain timing, nozzle and herbicide was observed.

[b] Control at 28 days after application.

[c] LS-means within each species and column followed by same letter are not significantly different at $P \leq 0.05$.

[d] Abbreviations: FWR, fresh weight reduction; DWR, dry weight reduction; DAA, days after application.

Table 4.8 Johnsongrass and velvetleaf responses to different herbicides across all rain timings and nozzles used in the study[a].

Species	Herbicide	Control[bc]	FWR[cd]	DWR[cd]
		-----------------------	%	---------------------------
johnsongrass	pendimethalin	37^{c}	48^{c}	48^{c}
	metribuzin	45^{bc}	73^{b}	77^{ab}
	clomazone	74^{a}	93^{a}	93^{a}
	imazethapyr	42^{c}	80^{ab}	68^{b}
	pyroxasulfone	61^{ab}	77^{ab}	73^{b}
velvetleaf	pendimethalin[e]	16^{d}	27^{b}	21^{c}
	metribuzin	100^{a}	100^{a}	100^{a}
	clomazone	99^{a}	100^{a}	100^{a}
	imazethapyr[e]	38^{c}	65^{b}	45^{b}
	pyroxasulfone[e]	85^{b}	92^{a}	89^{a}

[a] No significant interaction among rain timing, nozzle and herbicide was observed.

[b] Control at 28 days after application.

[c] LS-means within each species and column followed by same letter are not significantly different at $P \leq 0.05$.

[d] Abbreviations: FWR, fresh weight reduction; DWR, dry weight reduction.

[e] Suppression or partial control (Anonymous, 2017a; Anonymous, 2017b; Anonymous, 2017c).

Table 4.9 Johnsongrass responses to different nozzles across all rain timings and herbicides used in the study[a].

Nozzle	Control[bc]	Fresh Weight Reduction[c]	Dry Weight Reduction[c]
	-------------------------------	%	--
XR11002[d]	51^{ab}	76^{a}	74^{a}
ULD12002[e]	59^{a}	76^{a}	71^{a}
TTI11002[d]	46^{b}	71^{a}	70^{a}

[a] No significant interactions among rain timing, nozzle and herbicide was observed.

[b] Control at 28 days after application.

[c] LS-means within each column followed by different letter are significantly different at $P \leq 0.05$.

[d] Spraying Systems Inc. Wheaton, IL, USA.

[e] Hypro LLC, New Brighton, MN, USA

Table 4.10 Johnsongrass fresh weight reduction for different nozzles at both rain timings across all herbicides used in the study[a].

Rain timing	Nozzles		
	XR11002[b]	ULD12002[c]	TTI11002[b]
	---------------------------------- %	------------------------------------	
2 DAA[d]	91^{ab}	98^{a}	82^{abc}
4 DAA	64^{dc}	71^{bdc}	$76^{a\text{-}d}$
8 DAA	73^{ab}	58^{dc}	56^{d}

[a] LS-means followed by same letter are not significantly different at P ≤ 0.05.

[b] Spraying Systems Inc. Wheaton, IL, USA.

[c] Hypro LLC, New Brighton, MN, USA.

[d] Abbreviation: DAA, days after application.

Table 4.11 Velvetleaf responses to different herbicides at both rain timings across all nozzle types used in the study[a].

Rain timing	Herbicide	Control[bc]	FWR[cd]	DWR[cd]
		--------------------------	%	---------------------------
2 DAA	pendimethalin[e]	1^{e}	22	8^{cd}
	metribuzin	100^{a}	100	100^{a}
	clomazone	99^{ab}	100	100^{a}
	imazethapyr[e]	25^{cd}	64	37^{bc}
	pyroxasulfone[e]	96^{ab}	99	98^{a}
4 DAA	pendimethalin	23^{de}	37	32^{bcd}
	metribuzin	99^{ab}	99	100^{a}
	clomazone	98^{ab}	99	99^{a}
	imazethapyr	47^{c}	69	54^{b}
	pyroxasulfone	84^{ab}	93	88^{a}
8 DAA	pendimethalin	24^{cde}	22	21^{cd}
	metribuzin	100^{a}	100	100^{a}
	clomazone	100^{a}	100	100^{a}
	imazethapyr	41^{cd}	60	44^{bc}
	pyroxasulfone	75^{b}	83	81^{a}

[a] No significant interactions of rain timing and herbicide was observed.

[b] Control at 28 days after application.

[c] LS-means within each column followed by same letter are not significantly different at P ≤ 0.05.

[d] Abbreviations: FWR, fresh weight reduction; DWR, dry weight reduction.

[e] Suppression or partial control (Anonymous, 2017a; Anonymous, 2017b; Anonymous, 2017c).

Similarly to the crop residue study, rainfall and nozzle type did not affect Palmer amaranth, waterhemp and marestail control with the specific herbicides in Table 4.2. Common ragweed, barnyardgrass and lambsquarters results were also not included due to reduced plant emergence in all treatments, including the untreated checks.

Conclusion

The preliminary results have shown that the amount of crop residue affected PRE herbicide efficacy to both johnsongrass and velvetleaf, where johnsongrass showed increased FWR under higher crop residue while velvetleaf response to herbicides was reduced under low corn residue. Pendimethalin provided the lowest weed responses regardless of the residue amount when compared to other herbicides, and provided increased johnsongrass control under greater crop residue, possibly due to greater soil moisture. Nozzle type within the same herbicide did not affect weed response for both plant amounts of plant residue of 2500 and 5000 kg ha^{-1}.

Johnsongrass had reduced control and weight reduction in the eight day rainfall for all herbicides while pendimethalin provided the lowest control for johnsongrass and velvetleaf. The XR nozzle increased johnsongrass control in comparison with the ULD and TTI nozzles when rain timing was not considered. When rain timing was considered, the XR nozzle only improved FWR at the eight day rainfall.

Based on these initial results, the influence of crop residue amount and rainfall timing on herbicide weed control depends specifically on the herbicide and weed species while nozzle type, generally, will not affect PRE herbicide efficacy regardless of the residue amount and rain timing.

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