ENVIRONMENTAL AND HUMAN IMPACTS ON OFF-TARGET MOVEMENT OF DICAMBA

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by
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The undersigned, appointed by the Dean of Graduate School, have examined the dissertation entitled:

ENVIRONMENTAL AND HUMAN IMPACTS ON OFF-TARGET MOVEMENT OF DICAMBA

Presented by Jerri Lynn Henry,

A candidate of the degree of doctor of philosophy,

And hereby certify that, in their opinion, it is worthy of acceptance.

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DEDICATION

For Jerry and Kathy Henry

Thank you for not only telling me I could be anything I wanted to be when I grew up but for teaching me to work hard to make it a reality.

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ABSTRACT:

IMPACT OF SIMULATED DICAMBA DRIFT ONTO SENSITIVE SOYBEANS

Widespread use of dicamba on tolerant soybeans (*Glycine max* L.) since 2017 has resulted in reports of off-target movement. Although symptomology is quite striking, the relationship of sensitive soybean damage to crop yield is unclear. Field studies were established in 2018 and 2019 at three locations in central Missouri to assess the response of sensitive soybean to driftable concentrations of dicamba. Effects of dicamba were observed as early as 7 days after treatment (DAT). Apical meristem growth was reduced 10 to 54% and visual injury ranged from 15 to 47% at 21 DAT. Average soybean yield was significantly reduced by dicamba concentrations as low as 25 ppm and influenced by the developmental stage (V3 and R1) at the timing of dicamba exposure. Model statements were generated to predict yield reduction based on known dicamba concentrations and visual injury ratings 21 days after dicamba exposure. Statistical analysis of the prediction equations found the dicamba concentrations and soybean injury were adequate and accurate to predict soybean yield reductions in response to dicamba. Lastly, a subset of soybeans exposed to dicamba concentrations (0, 150, and 300 ppm dicamba) were collected prior to harvest, extracted using the rapid and effective (QuEChERS) method, and quantified by high-performance liquid chromatography with tandem mass spectrometry (HPLC-MS/MS). Using HPLC, mean dicamba residues in soybean samples were 0.0, 0.72, and 0.81 mg kg^{-1} following exposure to 0, 150, and 300 ppm dicamba, respectively. Location significantly impacted residual dicamba concentrations, averaging 0.70, 0.35, and 0.54 mg kg^{-1} at Bradford (2018), Boonville

(2018), and Bradford (2019), respectively. Individual samples did not exceed 10 mg kg^{-1} but samples with dicamba concentrations exceeding 0.5 mg kg^{-1} dicamba could violate residue limits for USDA National Organic Program standards. This study would suggest that sensitive soybeans that were injured by dicamba drift and allowed to go to yield would be safe for human consumption in the United States but could potentially violate the USDA regulations if driftable concentrations of dicamba moved off-target onto soybeans produced organically.

Chapter 1: Literature Review

Introduction.

Dicamba (2-methoxy-3,6-dichlorobenzoic acid) is a broadleaf selective auxin mimicking herbicide that was registered in the United States in 1967 (Environmental Protection Agency 2005). Dicamba was initially released to control broadleaf weeds in lawns, cereal grains, grazing lands, and other grass crops (Hartzler and Hartzler 2020, Soltani et al. 2018, United States Department of Agriculture 1967). Monocots quickly metabolize dicamba into 5-hydroxy-2-methoxy-3,6-dichlorobenzoic acid (5-hydroxy), a non-harmful metabolite, minimizing harm to the plant (Broadhurst et al. 1966). Dicamba can be found in products such as Banvel® (Micro Flo Company LLC, Memphis, TN, USA) and Clarity® (BASF Corporation, Research Triangle Park, NC, USA), and was one of the most used corn herbicides from its induction until the introduction of herbicide-tolerant crops.

Dicamba is considered a group 4, synthetic auxin, or plant growth regulator (PGR) herbicide because it mimics natural plant auxins and influences cellular protein receptors (Grossmann 2010). Natural plant auxins regulate cell division, elongation, differentiation, and the development of meristematic and reproductive tissues. PGRs affect plants similar to natural auxins but produce intense, long lasting effects. Natural plant auxins are conjugated into inactive metabolites (Woodward and Bartel 2005), work effectively at low concentrations, and are strictly regulated by the plant. However, when auxin concentrations become disproportionate, growth becomes hyperactive and lethal.

PGR herbicides are dose-dependent, with increasing concentrations resulting in greater effects. Symptoms of dicamba exposure include chlorosis of young terminal leaves, leaf cupping, epinasty, swollen petioles, growth reduction, and necrosis (Griffin et al. 2013; Shaner 2014; Soltani, Nurse, and Sikkema 2016). The timing of exposure to dicamba is significant, especially in soybeans; plants are more sensitive throughout reproductive stages compared to vegetative stages (Griffin et al. 2013). Exposure of soybeans and other broadleaf crops to dicamba and other PGR herbicides can result in partial or complete crop yield losses to plant death.

Dicamba stewardship became increasingly important when dicamba-tolerant (DT) crops were introduced to the market in 2016. Dicamba-tolerant (DT) soybeans were developed as high yielding varieties, exceeding Roundup Ready 2® (Bayer, St. Louis, MO, USA) soybean yields, and to control glyphosate-resistant (GR) weeds with postemergent applications of dicamba. GR crops have dominated the market since 1996, accounting for approximately 90 percent of U.S. soybeans in 2006 (Duke 2018). Furthermore, the estimated annual glyphosate use in the United States increased 10-fold in the 20 years following the introduction of glyphosate-tolerant (GT) soybeans (1996) (Duke 2018). However, as glyphosate use increased the number of active ingredients used for weed control and the total non-glyphosate herbicide areas treated decreased (Kniss 2018a, Young 2019), as well as research and development of new herbicides with alternative modes of action.

Over-reliance on glyphosate, due to its high efficacy and decreasing cost, led to a consistent increase in weed species biotypes with confirmed glyphosate resistance (Duke and Powles 2008). Currently, 50 different plant species are glyphosate resistant (Heap 2020), some of which are problematic in soybean fields including horseweed (*Conyza Canadensis* (L.) Cronq.), common waterhemp (*Amaranthus rudis* Sauer), Palmer amaranth (*Amaranthus palmeri* S. Wats.), giant ragweed (*Ambrosia trifida* L.), and common ragweed (*Ambrosia artemisiifolia* L.) (Behrens et al. 2007). Management of GR weed species has increased the cost of weed control up to $86.50 per hectare (Nandula 2010) and without proper control, GR weeds can cause significant yield losses.

Dicamba is an effective tool to combat GR weed species; therefore, the adoption of DT-soybeans was rapid, similar to that of GT-soybeans, with 43% of soybeans planted in the United States being DT by 2018 (Wechsler et al. 2019). Prompt adoption of DT soybeans resulted in increased use of dicamba nationwide and new, less volatile dicamba formulation (XtendiMax™ with VaporGrip (Bayer, St. Louis, MO, USA), Engenia® (BASF Corporation, Research Triangle Park, NC, USA), FeXapan™) were developed for POST application onto DT crops. These formulations were less volatile compared to older dicamba formulations like Clarity® or Banvel® (Gavlick et al. 2016) and were the only formulations approved for in-season applications onto DT crops.

Despite the use of new, less volatile formations of dicamba, the off-target movement of dicamba prompted complaints nationwide. In 2017, dicamba affected approximately 4.16 million hectares throughout the United States and over 445 thousand hectares by mid-season (July 15th) 2018 (Bradley 2017, 2018). In the first two years of POST applications onto DT crops, dicamba caused remarkable visual damage, causing industry leaders and legislators to reconsider dicamba label requirements. Label restrictions in 2017, for both Engenia and XtendiMax with VaporGrip Technology, were considered strict and adequate to mitigate the risks of off-target movement. No applications were supposed to be made at high wind speeds, utilize nozzles other than very coarse to ultra-coarse, at booms higher than 61 cm above the crop canopy, and applications should not be made when a temperature inversion was present (Anonymous 2019a, 2019b). Substitutional changes were made to the label registration in 2018 due to the large number of off-target dicamba claims in 2017. Only certified pesticide applicators may apply dicamba, POST applications were prohibited 45 days after planting (DAP), application windows were narrowed to 1 hour after sunrise and 2 hours before sunset, and modified downwind buffers to 33.5 meters for applications near endangered species (Environmental Protection Agency 2018).

Overall, commercial applicators carefully followed application restrictions, yet the off-target movement of new formulations of dicamba still ensued. State agriculture departments were overwhelmed with reports of dicamba damage; however, the causal factors of the off-target dicamba damage was unclear in many cases. The scope of dicamba damage caused concerns about the effectiveness and practicality of the use of new formations of dicamba. Because sensitive plants have physiological and metabolic responses leading to plant damage when exposed to minute concentrations of dicamba, any amount of off-target movement is unwelcome.

Mechanism of action.

Dicamba is traditionally applied via a water carrier onto plant leaves, followed by adsorption and translocation to plant meristems. Auxin is absorbed through the stomata of the leaves and transported to the vascular system (Kroin 2009). Dicamba, in solution, is translocated systemically throughout the plant (Grossmann 2010), mainly via mass flow in the phloem (Kroin 2009). The speed of movement can be as fast as a few centimeters per hour, which can infiltrate an entire plant quickly (Kroin 2009).

Dicamba damage occurs in three phases: stimulation, inhibition, and the decay phase. The stimulation phase occurs within the first few hours after exposure. Activation of metabolic processes like ethylene formation, membrane ion channels, and H^+-ATPases, and accumulation of abscisic acid (ABA) lead to the deregulation of growth, tissue swelling, and epinasty. Ethylene biosynthesis is active through the induction of 1-aminocyclopropane-1-carboxylic acid (ACC) synthase in shoot tissue. Dicamba binds to the chemical receptor, Auxin Binding Protein 1 (ABP1) (Hertel et al. 1972), and strongly induces proton pump activity in the plasmalemma. The hyperactivity of the proton pump generates a pH imbalance between the apoplast and the symplast, lowering extracellular pH (Tromas et al. 2010). The accumulation of H^+ ions in the apoplast leads to the acidification and hydration of the cell wall (Rayle and Cleland 1970). Cell wall acidification triggers the activation of potassium (K) pumps and expansin proteins, an influx of K^+, and increased cell turgidity causing chemical bonds between cellulose and hemicellulose of the cell wall break (Wolf et al. 2012), resulting in more water uptake and cellular expansion. Subsequent, calcium (Ca) osmo-sensitive channels are opened due to the rearrangement of membrane phospholipids caused by increases in turgor pressure (Monshausen and Gilroy 2009). The increases of intercellular Ca halt cell wall expansion by inhibiting ATPase and H^+ efflux, induce alkalization of the apoplast, and inhibition of expansin proteins, or by the activation of enzymes that phosphorylate NADPH oxidase and produce reactive oxygen species (ROS). Rapid changes and deregulation of the cell membrane and wall expansion cause twisting, epinasty, and swelling of plant tissues. The stimulation phase is represented, visually, by the petiole and stem twisting and curling of apical meristems.

Inhibition, the second phase, occurs 24 hours after exposure. This phase is characterized by decreased root and shoot growth (Grossmann 2010), decreased internode elongation, leaf expansion, intensified pigmentation, and stomatal closure. Growth inhibition and phytotoxic response occur due to the overproduction of ABA. Accumulation of ABA induces stomal closure, with consequent inhibition of transpiration, carbon assimilation, plant growth, and progressive foliar tissue damage. Decreased carbon assimilation and photosynthetic activity leads to the overproduction of ROS, like hydrogen peroxide, causing the oxidation of membrane lipids and signaling cell senescence.

The third phase is characterized by tissue decay and senescence. ROS accelerate the peroxidation of the cellular membranes, thus damaging chloroplasts, and disrupting membrane and vascular system integrity. Damage of the vascular and photosynthetic systems leads to wilting, necrosis, and finally cell death.

Dicamba symptomology is dose-dependent for sensitive plants, however, many monocots are resistant to dicamba. Resistance has been attributed to rapid metabolism of dicamba in grasses; conjugating dicamba to 5-OH dicamba and 3,6-dichlorobenzene-dioxane-acetic acid (DCSA), non-herbicidal metabolites of dicamba (Broadhurst et al. 1966, Chang and Vanden Born 1971). For comparison, wheat metabolizes nearly one-half of the applied dicamba in the first day, whereas Tartary buckwheat (*Fagopyrum tataricum* (L.) Gaertn.) only detoxifies 10% of the applied dicamba by 20 DAT (Chang and Vanden Born 1971). Additionally, absorption and translocation of dicamba are slower in Tartary buckwheat and wild mustard (*Sinapis arvensis* L.) than in barley (*Hordeum vulgare* L.)

and wheat (*Triticum vulgare* L.), giving the monocot species additional resistance mechanisms to dicamba (Chang and Vanden Born 1971).

Alterations of the soybean genome enable DT soybean to actively metabolize dicamba (Chang and Vanden Born 1971) into 3,6-dichlorosalicylic acid (DCSA) (Behrens et al. 2007). A soil-borne bacterium, *Pseudomonas maltophilia*, was inserted into the soybean gene that converts dicamba into DCSA, a non-herbicidal compound, via dicamba monooxygenase (DMO) (Behrens et al. 2007). The DMO gene found in *P. maltophilia* encodes for a Rieske protein that metabolizes dicamba in transgenic plants. In field trials, soybeans with the DMO gene express complete resistance to dicamba up to 5.8 kg ha^{-1} (Behrens et al. 2007).

DT technology was highly anticipated by producers battling GR weeds. In fields planted with DT soybean, dicamba can be used for both pre-plant and post-emergence weed control. However, many producers were concerned that dicamba applications onto DT crops could have impacts on nearby non-DT crops.

Dicamba damage.

Unintended, off-target, dicamba exposure can be detrimental to sensitive soybeans. Symptoms of dicamba injury are highly visible; leaf crinkling or cupping, swollen petioles, leaf and stem epinasty, growth reduction, wilting, and chlorosis of the terminal bud (Auch and Arnold 1978, Griffin et al. 2013, Sciumbato et al. 2004, Wax et al. 1969, Weidenhamer et al. 1989). Behrens and Lueschen (1979) devised a rating scale for dicamba injury, ranging from 0 to 100, which corresponds from no injury to complete plant death. This scale has become standard for evaluating dicamba injury.

While dicamba damage is dose-dependent, only minute concentrations are required to adversely affect plant biomass accumulation. Sublethal doses of dicamba, at rates as low as 0.01% of the labeled rate (560 g ae ha^{-1}) of dicamba can reduce soybean yield 10% (Weidenhamer et al. 1989). Similarly, Osipitan et al. (2019) and Griffen et al. (2013) noted 10% yield loss when V3 soybeans were exposed to sub-lethal dicamba concentrations of 1.85 and 4.4 g ae ha^{-1}, respectively.

Dicamba injury also depends on the soybean growth stage. Exposure to 4.4 g ae ha^{-1} dicamba has been shown to reduce soybean yields 4 and 23 % for V3 and R1 growth stages, respectively (Wax et al. 1969). Auch and Arnold (1978) found soybeans exposed to 11 g ae ha^{-1} dicamba had yield reductions ranging from 2% higher to 9% lower when exposed at V3 and R1 growth stages, respectively. Griffin et al. (2013) noted yield reductions of 4 to 15% for soybeans exposed to 4.4 to 17.5 g ae ha^{-1} dicamba at V3, but noted a 10 to 36% yield reduction when R1 soybeans were exposed to similar rates. A 7-year meta-analysis of dicamba drift by Egan et al. (2014) noted no yield losses for V3 soybeans and approximately 1% for R1 for soybeans exposed to 5.6 g ha^{-1}. Similarly, Solomon and Bradley (2014) found yield losses ranging from 2 to 67% when soybeans were exposed at R2 but had no significant yield loss when soybeans were exposed to similar rates at V3. These studies concluded that soybeans exposed to dicamba in the reproductive growth stage were injured more than soybeans exposed to similar concentrations at a vegetative growth stage. Therefore, the off-target movement of dicamba, even at sublethal concentrations, can have devastating economic repercussions.

Several factors contribute to the off-target movement of dicamba. This includes sprayer tank contamination (Cundiff et al. 2017, Luke et al. 2017, Soltani et al. 2016, Steckel and Thompson 2005), spray drift (Guilherme et al. 2017, Hanks 1995, Wolf et al. 2012), and vapor drift (Behrens and Lueschen 1979, Mueller et al. 2013).

Drift. Spray drift is the movement of herbicides in liquid form during a spray application (Ross and Lembi 1999). Drift occurs at the time of application and can be identified by the pattern throughout an impacted field, with greater damage occurring closer to the application point and decreasing with distance. Ensuring dicamba reaches its target site is critical for reducing dicamba damage to sensitive soybeans. Between 1 and 8% of applied herbicides drift beyond the spray swath (Maybank et al. 1978) and can be influenced by several factors including droplet size, nozzle type, carrier volume, boom height, application pressure, and spray additives (Bird et al. 1996, Guilherme et al. 2017, Klein et al. 2008, Miller and Butler Ellis 2000, Miller and Tuck 2005, Nuyttens et al. 2006, Van de Zande et al. 2004).

Appropriate nozzle selection reduces dicamba drift. Coarse droplet nozzle tips, such as air induction nozzles, decrease the incidence of small droplets (Bird et al. 1996). Guilherme et al. (2017) showed that the generation of larger droplets reduced drift of dicamba up to 24-fold compared to traditional nozzle tips. Compared to TeeJet XR8004 flat fan nozzles, RA-6 Raindrop nozzles reduced drift by 55% at 90 to 210 cm downwind from the application by increasing the average droplet size from 269 to 330 µm (Hatterman-Valenti et al. 1995). Coarse droplet nozzles create denser, heavier droplets that reduce the likelihood droplets are picked up by the wind and maximizes the likelihood droplets reach the intended target site.

Applicators can minimize drift during application. By increasing the carrier volume from 47 to 187 L ha^{-1} fine droplets are reduced (less than 105 µm) from 7.6 to 6.8% of the applied solution (Creech et al. 2014). Lowering boom height from 80 to 40 cm decreases drift from 3.2 to 1.0% (Nordby and Skuterud 1974) and lowing application pressure from 10 to 2.5 bars reduces drift from 2.9 to 1.4%. Reducing sprayer speed is also effective at mitigating drift during application (Creech et al. 2014, Guilherme et al. 2017, Klein et al. 2008, Long 2017).

Adjuvants may be added to reduce spray drift. Adjuvants are added to improve spray retention, penetration into plant tissues, increase spray droplet size, and reduce the amount of spray solution dispersed as small, driftable sized particles (Hanks 1995, Hull et al. 1982, McWorter 1982). Spray modifier adjuvants increase herbicide activity by reducing surface tension, increasing cuticular penetration, and improving herbicide absorption (McWorter 1982, Young and Hart 1998). Addition of a spray modifier adjuvant to dicamba solutions can increase herbicidal efficacy on broadleaf weed species, including Palmer amaranth (*Amaranthus palmeri*), common lambsquarters (*Chenopodium album*), and ivyleaf morningglory (*Ipomoea hederacea*) (Long 2017). Additionally, adjuvants alter the viscoelastic properties of the spray solution (Hewitt 1993) and produce coarser spray droplets with a lower driftable fraction (McMullan 2000).

Spray drift is a function of both droplet size and wind. Wind greatly influences herbicide drift (Creech et al. 2014, Jones et al. 2019, Nordby and Skuterud 1974); wind speeds during dicamba applications are restricted between

4.8 and 16.1 kilometers per hour (Anonymous 2019a, 2019b, 2020, Enz et al. 2017) and applications are off label when exceeding 16.1 kph (Johnson et al. 2012). Higher wind speeds negate steps taken to mitigate the off-target movement, such as low-drift nozzles, low spray pressure, and drift retardants (Hartzler 2017).

Application restrictions have been implemented to mitigate dicamba drift onto neighboring sensitive crops. No additional pH buffering solutions or acidifiers, like ammonium sulfate (AMS), other than a non-ionic surfactant (NIS) are to be added with new formulations of dicamba. Only coarse or ultra-coarse droplet nozzles are to be used and they should be operated at pressures greater than 30 psi. Applications should be made at no less than 94 liters per hectare (LPH) carrier volume, at speeds less than 24 kph, and with a boom height less than 61 cm above crop canopy. Lastly, applications should not be made at low relative humidity or at high temperatures (Anonymous 2019b, 2019a, 2020).

Volatility. Volatilization occurs after an herbicide reaches its intended target, where chemical properties such as vapor pressure can result in active herbicide moving off-target as a gas. Risks of volatility are higher for herbicides with larger vapor pressures, surface characteristics of the target site, higher temperatures, lower humidity (Mortensen et al. 2012), and higher wind speeds. The free acid of dicamba is particularly susceptible to volatility, with a vapor pressure of 4.5×10^{-3} mm Hg compared to a non-volatile herbicide like glyphosate that has a vapor pressure of 2.45×10^{-8} mm Hg (Ross and Lembi 1999, Shaner 2014). The volatility of dicamba is also dependent on the active ingredient (salt) of the formulation (Zimdahl 2013). Dicamba in its active form is an acid but is stabilized by being formulated as a salt. The cation used for the salt impacts the likelihood of volatility (Petersen et al. 1985). Under field conditions, Mueller et al.

(2013) found that older formulations of dicamba, including the DMA salt (Banvel®) and diglycolamine (DGA) salt (Clarity®), were 2-fold more volatile than newer formulations. Under lab conditions, dicamba volatility with a new formulation (Xtendimax with VaproGrip) was reduced by 5505 and 97% compared to older formulations, Banvel and Clarity, respectively (Gavlick et al. 2016). The vapor drift of dicamba is strongly affected by environmental factors such as air temperature. Numerous studies have documented higher vapor concentrations of dicamba with increased air temperatures (Miller and Tuck 2005, Mueller and Steckel 2019a, Ouse et al. 2018). Burnside and Lavy (1966) found that soybeans yielded up to 50% of the dry weight of untreated soybeans when exposed to 0.125 ppm dicamba at 32˚C ambient temperature, as compared to 75% of the dry weight of untreated soybeans when exposed to 0.125 ppm dicamba at 21 C. Mueller and Steckel (2019) quantified <5% dicamba volatiles when applications were made at 15 C compared to 30 C. Both Mortensen et al. (2012) as well as Behrens and Lueschen (1979) reported reduced dicamba vapors at lower air temperatures. Additionally, Behrens and Lueschen (1979) noted reduced dicamba vapors at higher relative humidity. Hence, current recommendations for reducing vapor drift include avoiding application during periods of high temperature and low relative humidity (Burnside and Lavy 1966, Mortensen et al. 2012, Ouse et al. 2018).

Because air temperatures and wind are frequently lowest around sunrise and sunset, growers avoid herbicide applications in the middle of the day. However, environmental conditions known to increase dicamba volatility can occur early and late in the day, often due to the formation of temperature inversions. A temperature inversion is a naturally occurring phenomenon, characterized by stable air masses, cooler air near the earth’s surface, and a layer of warmer air trapped above (Enz et al. 2017). Inversions are often formed close to sunset and sunrise and are typically characterized by the presence of dew (Bish and Bradley 2017). The air stability caused by inversions poses an increased risk for the suspension of fine particles in the air as applicators apply agrochemicals. As the temperature inversion dissipates, fine particles freely flow with the wind and descend. While the dissipation of temperature inversions may facilitate the movement of fine particles, the environmental conditions present during an inversion influence the conversion of dicamba to a gaseous form, enabling vapor drift (Enz et al. 2017).

The link of increased dicamba volatility with temperature inversions under field conditions was made by Farrell et al. (2018). Using air samplers, they measured airborne dicamba particles between 16 to 24 HAT, under conditions when temperature inversions were present. This confirmed previous research suggesting environmental conditions present during a temperature inversion could exacerbate the volatilization of dicamba (Foster 2018). An increase in volatilization in an inversion can create a concentration of fine, gaseous dicamba particles that will be moved off-target when the temperature inversion dissipates.

Dew is an indicator of temperature inversions (Bish and Bradley 2017, Enz et al. 2017, Farrell et al. 2018); however, the formation and persistence of dew have yet to be studied as it relates to dicamba volatility. Dew forms on a surface when the air temperature drops below the dew-point (Agam and Berliner 2006), and is dictated by the leaf microclimate boundary layer (Sutton 1953). This boundary layer for soybean differs from other plants because of a broad leaf area, heavily ridged surfaces, and adaxial trichomes that are optimal for dew formation (Vogel 1970). Thus, soybean leaf characteristics escalate diurnal radiative cooling and dew formation when exposed to the cool, humid air masses present during a temperature inversion.

Sprayer tank contamination. In addition to off-target movement, spray equipment following applications of dicamba can remain contaminated (Boerboom 2004). Applicators typically use the same field sprayer equipment to apply herbicides to all crops, relying on proper cleansing to reduce injury to subsequently treated crops (Browne et al. 2020, Cundiff et al. 2017, Davis et al. 2015, Griffin et al. 2013, Johnson et al. 1997, Osborne et al. 2015, Steckel and Thompson 2005).

Traditionally, sprayer tanks are cleansed using a triple-rinse method including the use of either ammonia or a commercial cleaning agent (Steckel and Thompson 2005). However, Osborne et al. (2015) found that after three rinses, only 98% of dicamba residues were removed from some spray equipment, leaving sufficient residue concentrations to cause damage to sensitive crops. When examining sprayer tank rinsate solutions, Luke et al. (2017) noted that commercial cleaning agents, like Cleanse® (Universal Crop Protection Alliance, Eagan, MN, USA) and Erase® (Precision Laboratories, Waukegan, IL,USA), remove more dicamba residue than water or ammonia alone from commercial spray tanks. These studies suggest that three rinses, using a detergent, are necessary to effectively cleanse dicamba residues from commercial spray equipment.

Effective removal of dicamba residues from spray systems can be difficult because application equipment consists of an extensive network of hoses and fittings. Despite dicamba being formulated as a water-soluble product, it readily adheres to many sprayer components, including plastic parts, rubber hoses, the tank, and nozzles

(Boerboom 2004, Browne et al. 2020, Cundiff et al. 2017, Osborne et al. 2015, Steckel and Thompson 2005). Additionally, the wear and tear of constant use creates additional cracks, nodes, and pockets, increasing the likelihood of adhered dicamba following cleanout (Cundiff et al. 2017). Cleanout methods become important for PGR herbicides, which are active at minute concentrations. Current dicamba labels require a triple rinse cleanout procedure following application, however, not all require the use of a commercial cleaning agent.

The role of cleaning agents is to solubilize or displace herbicides to permit the removal from the sprayer. Solubilizers like ammonia increase the water solubility of the herbicide and allow it to be flushed through the system upon rinsing (Johnson et al. 1997), whereas cleaning agents are composed of phosphate groups that attach water molecules to hydrophobic herbicides and allow water to flush the herbicide out of the system.

There is limited published research on effective cleanout procedures and sensitive soybean response to residual dicamba in rinsate. Luke et al. (2017) and Browne et al. (2020) both noted no significant yield reductions when soybeans were exposed to the third rinse of a commercial spray system following dicamba applications. However, sprayer contamination is a primary source of dicamba off-target movement, and more research is needed to examine the effectiveness of cleanout procedures used by commercial applicators following dicamba applications.

Prediction of yield loss due to dicamba damage.

Due to the persistent risk of off-target movement of dicamba by drift and commercial spray systems threatening sensitive crops, it would be beneficial for producers, agronomists, and cooperators to be able to predict yield losses based on dicamba associated injury before harvest (Kniss 2018b). Foster et al. (2019) offered a predictive model for yield loss for soybeans exposed to dicamba using a rating system (1-5) for dicamba damage symptoms; lower stem base lesions/ cracking, terminal leaf chlorosis, leaf petiole base swelling, stem, epinasty, terminal leaf necrosis, and terminal leaf cupping. Each dicamba injury symptom receives a 1-5 rating for these predictive models. While the models are relatively accurate at predicting yield loss, the model statements proposed by Foster et al. (2019) use various physiological injury observations that vary depending on the soybean growth stages and the time passed since exposure, making the models complex.

A simple tool used by agronomists to access dicamba injury is the rating scale devised by Behrens and Lueschen (1979) for dicamba injury, from 0 (no damage) to 100% (plant death). A model that uses the standard Brehens-Luechen dicamba injury scale may be beneficial and practical for agronomists to quickly estimate yield loss resulting from dicamba.

Purpose of research.

The rapid adoption of DT crops has resulted in a significant increase in POST applications of dicamba, resulting in a multitude of off-target cases of dicamba damage. Consequently, registration for dicamba was revoked by the Ninth Circuit Court of Appeals on June 3rd, 2020. Dicamba sales ceased immediately and only provisional applications of dicamba were made thereafter. Re-registration of dicamba products was accessed by the EPA in December 2020 and granted a 5-year extension with additional restrictions.

On top of the yield impacts associated with the off-target movement of dicamba, there is rising public concern regarding pesticide residue in the food supply. Tolerance levels for acceptable concentrations of dicamba in soybeans, 10 mg kg^{-1}, is listed in 40 CFR § 180.227 from the United States Environmental Protection Agency (EPA 2010). However, the USDA organic regulations only allow up to 5% pesticide residue tolerance (USDA National Organic Program and USDA Science and Technology Programs 2012). Few reports exist on dicamba residues found in soybean seed following exposure to off-target dicamba movement. The Pesticide Residue Monitoring Program from the Federal Department of Agriculture (FDA) inspects domestic and imported commodity samples entering the food market for herbicide residues. Of the 1,799 domestic and 4,270 import human food samples collected and analyzed for pesticide residues, only 3 samples contained quantifiable concentrations of dicamba (U.S. FDA 2019). However, with the increased use of dicamba herbicides in coordination with DT-crops, and the increased number of cases of off-target dicamba damage, the public has become increasingly interested in the off-target movement of dicamba and potential pesticide residues in the food supply.

Therefore, the objective of the first study is three-fold: 1) quantify apical meristem elongation, visual injury, and yield after being exposed to dicamba; 2) create a simple yield reduction model statement based on Behrens-Luechen 0-100 dicamba injury scale; and 3) to quantify potential dicamba residues in soybean seed following exposure to simulated off-target movement of dicamba.

A second study was conducted to determine if dew increases the volatility of dicamba products from DT soybean leaves. Under simulated field conditions using growth chambers and micro-climate boxes, the objective of this research was to determine if the formation and evaporation of dew on dicamba treated DT soybeans can influence the volatilization of dicamba.

Lastly, a third study was conducted to determine the efficacy of commercial sprayer tank cleanout procedures. Sprayer tank rinsate was collected across Missouri, Illinois, and Nebraska from 2017 to 2020 and cooperators were asked to fill out a survey regarding the cleanout procedures used. The objective of this study was to analyze the efficacy of cleanout procedures being used following dicamba applications and to report quantified dicamba concentrations back to individual applicators so as to improve cleanout efficacy and further mitigate the risk of off-target movement of dicamba.

Literature Cited

BASF. 2018. BASF has created a better dicamba rom the molecule up: Engenia® herbicide. http://agproducts.basf.us/campaigns/engenia/ Accessed January 17, 2018

Agam N, Berliner PR (2006) Dew formation and water vapor adsorption in semi-arid environments - A review. J Arid Environ 65:572–590

AGCO (2020) Weed control efficacy. https://www.croplife.com/iron/sprayers/sprayer-setup-best-practices-maximize-weed-control-efficacy/

Ahmadi MS, Haderlie LC, Wicks GA (1980) Effect of growth stage and water stress on barnyardgrass (*Echinochloa crus-galli*) control and on glyphosate absorption and translocation. Weed Sci 28:277–282

Akey WC, Morrison IN (1983) Effect of moisture stress on wild oat (*Avena fatua*) response to diclofop. Weed Sci 31:247–253

Anastassiades M, Lehotay SJ, Stajnbaher D, Schenck FJ (2003) Fast and easy multiresidue method employing acetonitrile extraction/partitioning and “dispersive solid-phase extraction” for the determination of pesticide residues in produce. J AOAC Int 86:412–431

Anonymous (2010) Clarity label. Research Triangle, NC: BASF Corporation

Anonymous (2019a) Engenia herbicide product label. Research Triangle, NC: BASF Corporation

Anonymous (2019b) XtendiMax with vaporgrip technology herbicide product label. St. Louis, MO: Bayer

Anonymous (2020) FeXapan plus vaporgrip technology herbicide product label.

Indianapolis, IN

Auch DE, Arnold WE (1978) Dicamba use and injury on soybeans (*Glycine max*) in South Dakota. Weed Sci 26:471–475

Babiker AGT, Duncan HJ (1975) Penetration of bean leaves by asulam as influenced by adjuvants and humidity. Pestic Sci 6:655–664

Basler E, Todd GW, Meyer RE (1961) Effects of moisture stress on absorption, translocation, & distribution of 2,4-dichlorophenoxyacetic acid in bean plants. Plant Physiol 36:573–576

Behrens MR, Mutlu N, Chakraborty S, Dumitru R, Jiang WZ, Lavallee BJ, Herman PL, Clemente TE, Weeks DP (2007) Dicamba resistance: enlarging and preserving biotechnology-based weed management strategies. Science (80-) 316:1185–1189

Behrens R, Lueschen WE (1979) Dicamba volatility. Weed Sci 27:486–493

Benbrook CM (2016) Trends in glyphosate herbicide use in the United States and globally. Environ Sci Eur 28:1–15

Beysens D, Lekouch I, Mileta M, Milimouk I, Muselli M (2019) Dew and rain collection in South Croatia. Int J Civ Environ Eng 1:64–70

Bird SL, Esterly DM, Perry SG (1996) Off-target deposition of pesticides from agricultural aerial spray applications. J Agric Food Chem 14:585–588

Bish M, Bradley K (2017) Knowing when to spray: monitoring the weather. https://weedscience.missouri.edu/Missouri Weather Analysis_2017.pdf

Bish MD, Farrell ST, Lerch RN, Bradley KW (2019) Dicamba losses to air after applications to soybean under stable and nonstable atmospheric conditions. J Environ Qual 48:1675–1682

Boerboom C (2004) Field case studies of dicamba movement to soybeans. Page *in* Wisconsin Crop Management Conference

Boydston R (1990) Soil water content affects the activity of four herbicides on green foxtail (*Setaria viridis*). Weed Res 38:578–582

Bradley K (2017) Integrated pest 2017. 1–2 p

Bradley K (2018) July 15 dicamba injury update. different year, same questions:1–2

Broadhurst NA, Montgomery ML, Freed VH (1966) Metabolism of 2-methoxy-3,6-dichlorobenzoic acid (dicamba) by wheat and bluegrass plants. J Agric Food Chem 14:585–588

Browne FB, Li X, Price KJ, Wang J, Wang Y, Kruger GR, Golus J, De Castro Macedo G, Vieira BC, Sandlin T (2020) Dicamba retention in commercial sprayers following triple rinse cleanout procedures, and soybean response to contamination concentrations. Agronomy 10:1–15

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

Burnside OC, Lavy TL (1966) Dissipation of dicamba. Weeds 14:211–214

Celen IH (2010) The effect of spray mix adjuvants on spray drift. Bulg J Agric Sci 16:105–110

Cenkci S, Yildiz M, Ciĝerci IH, Bozdaĝ A, Terzi H, Terzi ESA (2010) Evaluation of 2,4-D and dicamba genotoxicity in bean seedlings using comet and RAPD assays. Ecotoxicol Environ Saf 73:1558–1564

Chang FY, Vanden Born WH (1968) Translocation of dicamba in Canada thistle. Weed Sci 16:176–181

Chang FY, Vanden Born WH (1971) Dicamba uptake, translocation, metabolism, and selectivity. Weed Sci 19:113–117

Christoffoleti PJ, Figueiredo MRA de, Peres LEP, Nissen S, Gaines T (2015) Auxinic herbicides, mechanisms of action, and weed resistance: a look into recent plant science advances. Sci Agric 72:356–362

Creech CF, Henry RS, Fritz BK, Kruger GR (2014) Influence of herbicide active ingredient, nozzle type, orifice size, spray pressure, and carrier volume rate on spray droplet size characteristics. Weed Sci 62:193–206

Cundiff GT, Reynolds DB, Mueller TC (2017) Evaluation of dicamba persistence among various agricultural hose types and cleanout procedures using soybean (*Glycine max*) as a bio-indicator. Weed Sci 65:305–316

Davis FS, Merkle MG, Bovey RW (1968) Effect of moisture stress on the absorption and transport of herbicides in woody plants. Bot Gaz 129:183–189

Davis J, Barber T, Max C (2015) Tank clean-out recommendations for common herbicides. 1–2 p

Dickson RL, Andrews M, Field RJ, Dickson EL (1990) Effect of water stress, nitrogen, and gibberellic acid on fluazifop and glyphosate activity on oats (Avena sativa). Weed Sci 38:54–61

Dill GM (2005) Glyphosate-resistant crops : history , status and future †. Pest Manag Sci 224:219–224

Dintelmann BR, Warmund MR, Bish MD, Bradley KW (2019) Investigations of the sensitivity of ornamental, fruit, and nut plant species to driftable rates of 2,4-D and dicamba. Weed Technol:1–11

Do-Thanh CL, Vargas JJ, Thomas JW, Armel GR, Best MD (2016) Design, synthesis, and evaluation of novel auxin mimic herbicides. J Agric Food Chem 64:3533–3537

Duke SO (2018) The history and current status of glyphosate. Pest Manag Sci 74:1027–1034

Duke SO, Powles SB (2008) Glyphosate: a once-in-a-century herbicide. Pest Manag Sci 63:1100–1106

Egan JF, Barlow KM, Mortensen DA (2014a) A meta-analysis on the effects of 2,4-D and dicamba on soybean and cotton. Weed Sci 62:193–206

Egan JF, Barlow KM, Mortensen DA (2014b) A meta-analysis on the effects of 2,4-D and dicamba drift on soybean and cotton. Weed Sci 62:193–206

Environmental Protection Agency (2005) Reregistration eligibility decision (RED) document for nitrapyrin. 1–38 p

Environmental Protection Agency (2018) EPA announces changes to dicamba registration. https://archive.epa.gov/epa/newsreleases/epa-announces-changes-dicamba-registration.html

Environmental Protection Agency (2019) Food and pesticides. https://www.epa.gov/safepestcontrol/food-and-pesticides. Accessed October 25, 2020

Environmental Protection Agency (2020) Dicamba training requirements. https://www.epa.gov/ingredients-used-pesticide-products/dicamba-training-requirements-frequently-asked-questions#components

Enz JW, Hofman V, Thostenson A (2017) Air temperature inversions causes, characteristics, and potential effects on pesticide spray drift. NDSU Ext 1705:1–16

EPA (2010) Index to pesticide chemical names, part 180 tolerance information, and food and feed commodities (by commodity). Environ Prot Agency:1–314

Ester A, Strachan SD, Casini MS, Heldreth KM, Scocas JA, Nissen SJ, Bukun B, Lindenmayer RB, Shaner DL, Westra P, Ester A, Strachan SD, Casini MS, Heldreth KM, Scocas JA, Nissen SJ, Bukun B, Lindenmayer RB, Shaner DL, Westra P, Brunk G (2010) Vapor movement of synthetic auxin herbicides : Aminocyclopyrachlor-methyl ester, dicamba, and aminopyralid. Weed Sci 58:103–108

Farrell S, Lerch RN, Bish M (2018) Influence of formulations and application time of day on dicamba air concentrations following treatment. Page *in* Proceedings of the 73rd Annual Meeting of the North Central Weed Science Society

Foster MR (2018) Soybean response to dicamba : Associated injury criteria and development of a model to predict yield loss. Louisiana State University

Foster MR, Griffin JL, Copes JT, Blouin DC (2019) Development of a model to predict soybean yield loss from dicamba exposure. Weed Technol 33:287–295

Gałek G, Sobik M, Błaś M, Polkowska Z, Cichała-Kamrowska K, Wałaszek K (2015) Dew and hoarfrost frequency, formation efficiency and chemistry in Wroclaw, Poland. Atmos Res 151:120–129

Gauvrit C (2003) Glyphosate response to calcium, ethoxylated amine surfactant, and ammonium sulfate. Weed Technol 17:799–804

Gavlick WK, Wright DR, MacInnes A, Hemminghaus JW, Webb JK, Yermolenka VI, Su W (2016) A method to determine the relative volatility of auxin herbicide formulations.pdf. Pestic Formul Deliv Syst 35:24–32

Grafstrom LD, Nalewaja JD (1986) Uptake and translocation of fluazifop in green goxtail (*Setaria viridis*). Weed Sci 108:115–123

Griffin JL, Bauerle MJ, Stephenson DO, Miller DK, Boudreaux JM (2013) Soybean response to dicamba applied at vegetative and reproductive growth stages. Weed Technol 27:696–703

Grossmann K (2010) Auxin herbicides: Current status of mechanism and mode of action. Pest Manag Sci 66:113–120

Guilherme A, Alves S, Kruger GR, Paulo J, Cunha AR, Denise G, Santana D, Pinto LAT (2017) Dicamba spray drift as influenced by wind speed and nozzle type dicamba spray drift as influenced by wind speed and nozzle type. Weed Technol 31:724–731

Hall GJ, Hart CA, Jones CA (2000) Plants as sources of cations antagonistic to glyphosate activity. Pest Manag Sci 56:351–358

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

Hartzler R (2017) Wind speed and herbicide application. https://crops.extension.iastate.edu/cropnews/2017/01/wind-speed-and-herbicide-application

Hartzler R, Hartzler R (2020) 2020 Herbicide guide for Iowa corn and soybean production. Page Iowa State University Extension and Outreach Integrated Crop Management

Hatterman-Valenti H, Owen MD, Christians NE (1995) Comparison of spray drift during postemergence herbicide applications to turfgrass. Weed Technol 9:321–325

Hauser EW (1955) Absorption of 2,4-dichlorophenoxyacetic acid by soybean and corn plants. Agron J 47:32

Heap I (2020) International herbicide-resistant weed database. http://weedscience.org/Home.aspx

Hertel R, Thomson KS, Russo VEA (1972) In-vitro auxin binding to particulate cell fractions from corn coleoptiles. Planta 107:325–340

Hewitt AJ (1993) Droplet size spectra produced by air-assisted atomizers. J Aerosol Sci 24:155–162

Holly K (1956) Penetration of chlorinated phenoxyacetic acid into leaves. Pages 195–199 *in* Annals of Applied Biology

Hughes EE (1968) Hygroscopic additives to phenoxy herbicides for control of saltcedar. Weed Sci 16:486–488

Hughes RE, Freed VH (1961) The role of surfactants in the foliar absorption of indole-3-acetic acid (IAA). Weeds 9:54–59

Hull HM, Davis DG, Stolzenberg GE (1982) Action of adjuvants on plant surfaces. Pages 26–67 *in* Adjuvants for Herbicides. Weed Science Society of America

Jhala A, Knezevic S, Klein RN (2017) Dicamba injury symptoms on sensitive crops

Jiries A (2001) Chemical composition of dew in Amman, Jordan. Atmos Res 57:261–268

Johnson WG, Casady B, Peterson D, Kuhlman D (1997) Cleaning field sprayers to avoid crop injury. MU Extension, Univ Missouri-Columbia

Johnson WG, Hallett SG, Legleiter TR, Whitford F, Weller SC, Bordelon BP, Lerner BR (2012) 2,4-D and dicamba-tolerant crops- some facts to consider. Page Purdue Extension. 1–7 p

Jones GT (2018) Evaluation of dicamba off-target movement and subsequent effects on soybean offspring. University of Arkansas

Jones GT, Norsworthy JK, Barber T, Gbur E, Kruger GR (2019) Off-target movement of DGA and BAPMA dicamba to sensitive soybean. Weed Technol 33:51–65

Kabela ED, Hornbuckle BK, Cosh MH, Anderson MC, Gleason ML (2009) Dew frequency, duration, amount, and distribution in corn and soybean during SMEX05. Agric For Meteorol 149:11–24

Kelley KB, Wax LM, Hager AG, Riechers DE (2005) Soybean response to plant growth regulator herbicides is affected by other postemergence herbicides. Weed Sci 53:101–112

Kidder DW, Behrens R (1988) Plant responses to haloxyfop as influenced by water stress. Weed Sci

Klein RN, Schulze L, Ogg CL (2008) Factors affecting spray drift of pesticides. Crop Soils:19–23

Klevorn TB, Wyse DL (1984) Effect of soil temperature and moisture on glyphosate and photoassimilate distribution in quackgrass (*Agropyron repens*). Weed Sci 32:402–407

Kniss AR (2018a) Genetically engineered herbicide-resistant crops and herbicide-resistant weed evolution in the United States. Weed Sci 66:260–273

Kniss AR (2018b) Soybean response to dicamba: a meta-analysis. Weed Technol 32:507–512

Knoche M, Petracek PD (2014) Foliar uptake of PGRs: barriers, mechanisms, model systems, and factors. Acta Hortic 1042:125–141

Kroin J (2009) Auxins and the pathways for foliar application. 53–59 p

Lakhani A, Parmar RS, Prakash S (2012) Chemical composition of dew resulting from radiative cooling at a semi-arid site in Agra, India. Pure Appl Geophys 169:859–871

Lauridson TC, Wilson RG, Haderlie LC (1983) Effect of moisture stress on Canada thistle (*Cirsium arvense*) control. Weed Sci 31:674–680

Lehotay SJ, Son KA, Kwon H, Koesukwiwat U, Fu W, Mastovska K, Hoh E, Leepipatpiboon N (2010) Comparison of QuEChERS sample preparation methods for the analysis of pesticide residues in fruits and vegetables. J Chromatogr 1217:2548–2560

Lekouch I, Mileta M, Muselli M, Milimouk-Melnytchouk I, Šojat V, Kabbachi B, Beysens D (2010) Comparative chemical analysis of dew and rain water. Atmos Res 95:224–234

Lin LI-K (1989) A concordance correlation coefficient to evaluate reproducibility. Biometrics 45:255–268

Long J (2017) Infuence of application factors on dicamba volatility. Purdue. 98 p

Long J, Basler E (1973) Some factors regulating auxin translocation in intact bean seedlings. Plant Physiol 51:128–135

Luke AJ, Weirich JW, Smeda RJ (2017) Dicamba residues in spray equipment reduces soybean (*Glycine max*) growth and yield. University of Missouri

Madeira AC, Kim KS, Taylor SE, Gleason ML (2002) A simple cloud-based energy balance model to estimate dew. Agric For Meteorol 111:55–63

Marth PC, Davis FF, Mitchell JW (2018) Herbicidal properties of 2,4-dichlorophenoxyacetic acid applied in dusts containing hygroscopic agents. Bot Gaz 107:129–136

Maybank J, Yoshida K, Grover R (1978) Spray drift from agricultural pesticide applications. J Air Pollut Control Assoc 28:1009–1014

McMullan PM (2000) Utility adjuvants. Weed Technol 14:792–797

McWhorter CG, Jordan TN, Wills GD (1980) Translocation of 14 C-glyphosate in soybeans (Glycine max) and johnsongrass (*Sorghum halepense*). Weed Sci 28:113–118

McWorter CG (1982) The use of adjuvants. Pages 10–25 *in* Adjuvants for Herbicides. Weed Science Society of America

Merkle MG, Davis FS (1967) Effect of moisture stress on absorption and movement of picloram and 2,4,5-T in beans. Weeds 15:10–12

Miller A, Donnie K, Robert G, Roger B, Merritt E, Steve T, Miller DK, Downer RG, Leonard BR, Kelly ST (2003) Response of non-glufosinate-resistant cotton to reduced rates of glufosinate. Weed Sci 51:781–785

Miller PCH, Butler Ellis MC (2000) Effects of formulation on spray nozzle performance for applications from ground-based boom sprayers. Page *in* Crop Protection

Miller PCH, Tuck CR (2005) Factors influencing the performance of spray delivery systems: A review of recent developments. J ASTM Int 2:1–13

Mills MS, Thurman EM (1994) Reduction of nonpoint source contamination of surface water and groundwater by starch encapsulation of herbicides. Environ Sci Technol 28:73–79

Monshausen GB, Gilroy S (2009) Feeling green: mechanosensing in plants. Trends Cell Biol 19:228–235

Morgan J V, Tukey Jr. HB (1964) Characterization of leachate from plant foliage. Plant

Physiol 39:590–593

Morrison RG, Lownds NK, Sterling TM (1995) Picloram uptake, translocation, and efficacy in relation to water status of Russian knapweed (*Acroptilon repens*). Weed Sci 43:34–39

Mortensen DA, Egan JF, Maxwell BD, Ryan MR, Smith RG (2012) Navigating a critical juncture for sustainable weed management. Bioscience 6:75–84

Mueller TC, Steckel LE (2019a) Dicamba volatility in humidomes as affected by temperature and herbicide treatment. Weed Technol 33:1–6

Mueller TC, Steckel LE (2019b) Spray mixture pH as affected by dicamba, glyphosate, and spray additives. Weed Technol 33:547–554

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

Mueller TC, Wright DR, Remund KM (2013) Effect of formulation and application time of day on detecting dicamba in the air under field conditions. Weed Sci 61:586–593

Nandula VK (2010) Glyphosate resistance in crops and weeds: History, development, and management. Page Glyphosate Resistance in Crops and Weeds: History, Development, and Management. 1–33 p

Nath S, Yadav S (2018) A comparative study on fog and dew water chemistry at New Delhi, India. Aerosol Air Qual Res 18:26–36

National Center for Biotechnology Information (2020) PubChem compound summary for CID 3030, dicamba. https://pubchem.ncbi.nlm.nih.gov/compound/Dicamba. Accessed December 11, 2020

Natural Resources Conservation Services (n.d.) Official soil series descriptions.

https://soilseries.sc.egov.usda.gov/osdname.aspx. Accessed April 9, 2020

Nordby A, Skuterud R (1974) The effects of boom height, working pressure and wind speed on spray drift. Weed Res 14:385–395

Nuyttens D, Schampheleire M, Steurbaut W, Baetens K (2006) Experimental study of factors influencing the risk of drift from field sprayers, part 2: spray application technique. Asp Appl Biol 77:1–9

Osborne PP, Xu Z, Swanson KD, Walker T, Farmer DK (2015) Dicamba and 2,4-D residues following applicator cleanout: a potential point source to the environment and worker exposure. J Air Waste Manag Assoc 65:1153–1158

Ouse DG, Gifford JM, Schleier J, Simpson DD, Tank HH, Jennings CJ, Annangudi SP, Valverde-Garcia P, Masters RA (2018) A new approach to quantify herbicide volatility. Weed Technol 32:691–697

Pallas, JE, Williams GG (1962) Foliar absorption and translocation of P32 and 2,4-dichlorophenoxyacetic acid as affected by soil-moisture tension. Bot Gaz 123:175–180

Peachey E (2009) Tank cleaners: why and when they work

Peregoy R, Kitchen L, Jordan P, Griffin JL (1990) Moisture stress effects on the absorption, translocation, and metabolism of haloxyfop in johnsongrass (*Sorghum halepense*) and large crabgrass (*Digitaria sanguinalis*). Weed Sci 38:331–337

Perry ED, Ciliberto F, Hennessy DA, Moschini GC (2016) Genetically engineered crops and pesticide use in U.S. maize and soybeans. Sci Adv 2:1–8

Petersen PJ, Haderlie LC, Hoefer RH, McAllister RS (1985) Dicamba absorption and translocation as influenced by formulation and surfactant. Weed Sci 33:717–720

Ramsey RJL, Stephenson GR, Hall JC (2005) A review of the effects of humidity, humectants, and surfactant composition on the absorption and efficacy of highly water-soluble herbicides. Pestic Biochem Physiol 82:162–175

Rayle DL, Cleland R (1970) Enhancement of wall loosening and elongation by acid solutions. Plant Physiol 46:250–253

Rice EL (1948) Absorption and translocation of ammonium 2,4-dichlorophenoxyacetate by bean plants. Bot Gaz 109:301–314

Ross MA, Lembi CA (1999) Applied Weed Science. 3rd ed. Minneapolis, Minnesota: Burgess Pub Co

Sargent JA (1965) The penetration of growth regulators into leaves. Annu Rev Plant Physiol 16:1–12

Sciumbato AS, Chandler JM, Senseman SA, Bovey RW, Smith KL (2004) Determining exposure to auxin-like herbicides. I. quantifying injury to cotton and soybean. Weed Technol 18:1125–1134

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

Sharma MP, Born WH Vanden (1970) Foliar penetration of picloram and 2,4-D in aspen and balsam poplar. Weed Sci 18:57–63

Skelton JJ (2015) Uptake, translocation, and metabolism 2,4-D in enlist crops and control of drought-stressed waterhemp (*Amaranthus tuberculatus*) with 2,4-D and glyphosate. University of Illinois at Urbana-Champaign

Solomon CB, Bradley K (2014) Influence of application timings and sublethal rates of synthetic auxin herbicides on soybean. Weed Technol 28:454–464

Soltani N, Brown L, Sikkema PH (2018) Control of glyphosate-resistant common ragweed in corn with preemergence herbicides. Can J Plant Sci 98:959–962

Soltani N, Nurse RE, Sikkema PH (2016) Response of glyphosate-resistant soybean to dicamba spray tank contamination during vegetative and reproductive growth stages. Can J Plant Sci 96:160–164

Steckel L, Thompson A (2005) Cleaning plant growth regulator (PGR) herbicides out of field sprayers. UT Extension

Sutton OG (1953) Micrometeorology. Q J R Meteorol Soc:333–335

Szabo SS, Buchholtz KP (1961) Penetration of living and non-living surfaces by 2 ,4-D as influenced by ionic additives. Weeds 9:177–184

Tedeschi LO (2006) Assessment of the adequacy of mathematical models. Agric Syst 89:225–247

Thelen KD, Jackson EP, Penner D (2020) The basis for the hard-water antagonism of glyphosate activity 43:541–548

Tromas A, Paponov I, Perrot-Rechenmann C (2010) Auxin binding protein 1: functional and evolutionary aspects. Trends Plant Sci 15:436–446

Tukey HB (1970) The leaching of substances from plants. Annu Rev Plant Physiol 21:305–324

U.S. FDA (2019) Pesticide residue monitoring program fiscal year 2017 pesticide report:48

United States Department of Agriculture (1967) Suggested guide for weed control

USDA National Organic Program, USDA Science and Technology Programs (2012) Pilot study pesticide residue testing of organic produce. 34 p

Vogel S (1970) Convective cooling at low airspeeds and the shapes of broad leaves. J Exp Bot 21:91–101

Waldecker MA, Wyse DL (1985) Soil moisture effects on glyphosate absorption and rtanslocation in common milkweed (*Asclepias syriaca*). Weed Sci

Wax LM, Knuth LA, Slife FW (1969) Response of soybeans to 2,4-D, dicamba, and picloram. Weed Sci 17:388–393

Wechsler SJ, Smith D, Mcfadden J, Dodson L, Williamson S (2019) The use of genetically engineered dicamba-tolerant soybean seeds has increased quickly, benefting adopters but damaging crops in some fields. https://www.ers.usda.gov/amber-waves/2019/october/the-use-of-genetically-engineered-dicamba-tolerant-soybean-seeds-has-increased-quickly-benefiting-adopters-but-damaging-crops-in-some-fields/. Accessed April 9, 2020

Weidenhamer JD, Triplett GB, Sobotka FE (1989) Dicamba injury to soybean. Agron J 81:637–643

Whisenant SG, Bouse LF, Crane RA, Bovey RW (1993) Droplet size and spray volume effects on honey mesquite mortality with clopyralid. J Range Manag 46:257

Wolf S, Hématy K, Höfte H (2012) Growth control and cell wall signaling in plants. Annu Rev Plant Biol 63:381–407

Woodward AW, Bartel B (2005) Auxin: regulation, action, and interaction. Ann Bot 95:707–735

Xu Y, Zhu H, Tang J, Lin Y (2015) Chemical compositions of dew and scavenging of particles in Changchun, China. Adv Meteorol:1–11

Young BG (2019) Changes in herbicide use patterns and production practices resulting from glyphosate-resistant crops. Weed Technol 20:301–307

Young BG, Hart SE (1998) Optimizing foliar activity of isoxaflutole on giant foxtail (*Setaria faberi*) with various adjuvants. Weed Sci 46:397–402

Van de Zande JC, Stallinga H, Michielsen JMGP, van Velde P (2004) Effect of sprayer speed on spray drift. Annu Rev Agric Engeneering 4:11

Zimdahl R (2013) Fundamentals of Weed Science. 4th ed. Fort Collins, Colorado: Elsevier. 378–381 p

Chapter 2: Impact of Simulated Dicamba Drift onto Sensitive Soybeans

Abstract

Off-target damage attributed to dicamba has been an agronomic issue since the release of dicamba-tolerant (DT) crops in 2017. Although symptomology is quite striking, the relationship of sensitive soybean damage to crop yield is unclear. The objective of this field study was to correlate dicamba damage on sensitive soybeans with yield impacts and to quantify dicamba residues in harvested soybeans. Field studies were established in 2018 and 2019 at three locations in Central Missouri to assess soybean morphological and yield response of sensitive soybeans to driftable concentrations of dicamba. Effects of dicamba were observed as early as 7 days after treatment (DAT). Apical meristem growth was reduced 10 to 54% and visual injury ranged from 15 to 47 at 21 DAT. Average soybean yield was significantly reduced by dicamba concentrations as low as 25 ppm and influenced by the developmental stage (V3 and R1) at the timing of dicamba exposure. Model statements were generated to predict yield reduction based on known dicamba concentrations and visual injury ratings 21 days after dicamba exposure. Statistical analysis of the prediction equations found the dicamba concentrations and soybean injury were adequate and accurate to predict soybean yield reductions in response to dicamba. Lastly, a subset of soybeans exposed to dicamba concentrations (0, 150, and 300 ppm dicamba) were collected prior to harvest, extracted using the quick, easy, cheap, effective, rugged, and safe (QuEChERS) method, and quantified by high-performance liquid chromatography with tandem mass spectrometry (HPLC-MS/MS). Using HPLC, mean dicamba residues in soybean samples were 0.0, 0.72, and 0.81 mg kg^{-1} following exposure to 0, 150, and 300 ppm dicamba, respectively. Sites significantly impacted residual dicamba concentrations, averaging 0.70, 0.35, and 0.54 mg kg^{-1} at Bradford (2018), Boonville (2018), and Bradford (2019), respectively. Individual samples did not excess 10 mg kg^{-1} but samples with dicamba concentrations exceeding 0.5 mg kg^{-1} dicamba could violate USDA National Organic Program standards. This study would suggest that sensitive soybeans that were injured by dicamba drift and allowed to go to yield would be safe for human consumption in the United States but could potentially violate the USDA regulations if driftable concentrations of dicamba move off-target onto an organic operation.

Keywords: *Glycine max*, injury, yield model, off-target movement, spray drift, residue analysis

Introduction

Dicamba (2-methoxy-3,6-dichlorobenzoic acid) is a plant growth regulator (PGR) herbicide traditionally used to control broadleaf weeds in lawns, cereal grains, grazing lands, and other monocot crops (United States Department of Agriculture 1967). Dicamba is selectively active on broadleaves and is rapidly metabolized by monocots into non-injurious metabolites (Broadhurst et al. 1966). Prior to 2017 dicamba products such as Banvel® and Clarity® were restricted to pre-plant conditions in broadleaf crops (Anonymous 2010).

The introduction of dicamba-tolerant (DT) crops in 2017 resulted in significant changes in dicamba use. DT crops are an attractive option for producers with fields populated by glyphosate-resistant (GR) weeds, following over-reliance on glyphosate (Duke and Powles 2008). Roughly 85% of soybean hectares in the United States are planted with glyphosate-tolerant (GT) varieties (Benbrook 2016, Dill 2005, Perry et al. 2016) and glyphosate continues to be widely utilized due to its low cost and high efficacy, leading to a continual increase in resistant weed biotypes.

Dicamba effectively combats GR weed species and adoption of DT-soybeans was rapid, similar to that of GT-soybeans, occupying 43% of soybeans planted in the US by 2018 (Wechsler et al. 2019). DT crops are often planted in close proximity to dicamba sensitive species. These species are injured at extremely low concentrations of dicamba (Cenkci et al. 2010, Dintelmann et al. 2019) because dicamba mimics the natural plant hormone indole-3-acetic acid

(IAA) (Grossmann 2010). Rates as low as 0.01% of the labeled rate (560 g ae ha^{-1}) have reduced soybean yields by 10% (Weidenhamer et al. 1989).

Amongst broadleaf species, soybeans are highly sensitive to sublethal doses of dicamba (Foster et al. 2019, Jhala et al. 2017, Jones 2018, Kniss 2018b, Solomon and Bradley 2014) and injury is dependent on the concentration of dicamba exposure and the soybean growth stage. Exposure to 4.4 g ae ha^{-1} dicamba have been shown to reduce soybean yields 4 and 23% for V3 and R1 growth stages, respectively (Wax et al. 1969). Auch and Arnold (1978) found soybeans exposed to 11 g ae ha^{-1} dicamba had yield reductions ranging from 2 higher to 9% lower when exposed at V3 and R1 growth stages, respectively. Griffin et al. (2013) noted yield reductions of 4 to 15% for V3 soybeans exposed to 4.4 to 17.5 g ae ha^{-1} dicamba, respectively, but noted a 10 to 36% yield reduction when R1 soybeans were exposed to similar rates. In a 7 year meta-analysis of simulated dicamba drift, Egan et al. (2014) noted negligible yield losses for V3 soybeans and approximately 1% for R1 for soybeans exposed to 5.6 g ha^{-1}. Similarly, Solomon and Bradley (2014) found yield losses ranging from 2 to 67% when soybeans were exposed at R2 but had no significant yield loss when soybeans were exposed to similar rates at V3. These studies concluded that soybeans exposed to dicamba in the reproductive growth stage were injured more than soybeans exposed to similar concentrations at a vegetative growth stage. Therefore, the off-target movement of dicamba, even at sublethal concentrations, can have significant economic repercussions.

Following release of DT soybeans there were many reports of off-target damage. Widespread dicamba damage was associated with increased use of dicamba in DT crops. In the first year of using the DT technology, Bradley (2017) reported in excess of 2,700 cases of off-target movement (Bradley 2017), affecting over 1.45 million hectares nation-wide. Despite numerous reports of dicamba damage, the associated of damage to crop yields is relatively unknown.

A source for dicamba trespassing onto sensitive fields with soybeans is particle drift. Particle drift (drift) can be influenced by many factors including droplet size, nozzle type, nozzle spray angle, carrier volume, solution properties, boom height, and application wind speed (Bird et al. 1996, Guilherme et al. 2017, Klein et al. 2008, Miller and Butler Ellis 2000, Miller and Tuck 2005, Nuyttens et al. 2006, Van de Zande et al. 2004); so the current dicamba labels require specific application equipment and instructions to minimize drift. Dicamba drift decreases with appropriate nozzle selection for proper droplet size (Bird et al. 1996, Whisenant et al. 1993). Coarse droplet nozzle can be used to reduce the risk of dicamba drift, as coarse droplet nozzles create heavier droplets that are less likely to be picked up by the wind and more likely to reach the intended target site (Creech et al. 2014, Guilherme et al. 2017, Mueller and Womac 1997, Whisenant et al. 1993). Additionally, increasing carrier volume from 47 to 187 L ha^{-1} decreases the percentage of fine droplets (less than 105 µm) from 7.6 to 6.8% of the applied solution (Creech et al. 2014). Lower boom heights and application speeds also mitigate drift (Creech et al. 2014, Guilherme et al. 2017, Klein et al. 2008, Long 2017).

Wind is a primary factor that moves herbicide droplets from their intended target (Creech et al. 2014, Jones et al. 2019, Nordby and Skuterud 1974). To minimize drift, wind speeds between 4.8 and 16.1 $km{\cdot}hr^{-1}$ are recommended for dicamba applications (Anonymous 2019a, 2019b, 2020, Enz et al. 2017); applications are restricted when wind speeds exceed 16.1 kph (Johnson et al.

2012). Higher wind speeds can override steps taken to mitigate off target movement, such as low-drift nozzles, low spray pressure, and drift retardants (Hartzler 2017), as greater wind speeds allow small, suspended particles to be carried further downwind, damaging nearby sensitive plants.

In the event dicamba moves off-target, questions abound regarding the extent of impact on non-target crops. Due to the risk of off-target movement of dicamba onto sensitive crops, it would be beneficial to predict yield losses based on dicamba associated injury prior to harvest (Kniss 2018b). Foster et al. (2019) offered a predictive model for yield loss for soybeans exposed to dicamba using symptoms of dicamba damage; lower stem base lesions/ cracking, terminal leaf chlorosis, leaf petiole base swelling, stem, epinasty, terminal leaf necrosis, and terminal leaf cupping; with each dicamba injury symptom receiving a 1-5 rating. The proposed models are relatively accurate at predicting yield loss, however, the model proposed uses various physiologic injury observations that vary depending on the soybean growth stages and the time passed since exposure, making the models complex.

On top of the yield impacts associated with off-target movement of dicamba, there is rising public concern over pesticide residue in the food supply. The tolerance level for acceptable concentrations of dicamba in soybeans, 10 mg kg^{-1}, is listed in 40 CFR § 180.227 from the United States Environmental Protection Agency (EPA 2010). However, few reports exist on dicamba residues found in soybean seed following exposure to off-target dicamba movement. The Pesticide Residue Monitoring Program from the Federal Department of Agriculture (FDA) inspects domestic and imported commodity samples entering the food market for herbicide residues. Of the 1,799 domestic and 4,270 import human food samples collected and analyzed for pesticide residues, only 3 samples contained quantifiable concentrations of dicamba (U.S. FDA 2019). However, with the increased use of dicamba herbicides in coordination with DT-crops, and the increased number of cases of off-target dicamba damage, the public has become increasingly interested in pesticide residues in the food supply (Environmental Protection Agency 2019).

A simple tool used by agronomists to access dicamba injury is the rating scale devised by Behrens and Lueschen (1979) , which ranges from 0 (no damage) to 100% (plant death). A model correlating this dicamba injury scale to sensitive soybean crop yield may be beneficial and practical for agronomists to quickly estimate yield loss caused by dicamba. The objective of this study was twofold: to assess dicamba damage on sensitive soybeans and associated yield impacts based on Behrens-Lueschen dicamba injury scale; and to quantify potential dicamba residues in soybean seeds.

Materials and Methods

Site selection and field establishment.

Field trials were established in 2018 and 2019 at two locations in central Missouri. Locations in 2018 included the Bradford Research and Extension Center (Bradford) near Columbia (38.89°N, 92.19°W), and the Kendall Kircher farm near Boonville (Boonville) (38.99°N, 92.67°W). Initially the 2019 locations were the same as 2018, however, flooding from the Missouri River caused the Boonville location to be inaccessible. Therefore, the 2019 locations were Bradford and Anderson Acres near Williamsburg (38.93°N, 91.73°W). The soil type at Bradford was a Mexico silt loam (fine, smectitic, mesic Vertic Epiaqualfs), Boonville was Lowmo silt loam (coarse-silty, mixed, superactive, mesic Fluventic Hapludolls), and Williamsburg was a Mexico silt loam (fine, smectitic, mesic Vertic Epiaqualfs).

At each location, a glufosinate-tolerant (LibertyLink 3944) variety of soybean was planted (76 cm rows), except Williamsburg, which was planted with a glufosinate and glyphosate-tolerant (Stine GT27 38GA12) variety (38 cm rows). Conventional tillage was used at Boonville (2018) and Bradford (2019) and no tillage was used at Bradford (2018) and Williamsburg (2019). Planting occurred on May 24, 2018 at Boonville, June 6, 2018 and May 31, 2019 at Bradford, and May 30, 2019 at Williamsburg. All locations were planted to a population of 345,800 seeds per hectare, except Williamsburg in 2019, which was planted to a population of 407,550 seeds per hectare.

Experimental areas were maintained weed-free to properly assess the effects of dicamba-exposure. At Boonville, applications of 0.30 kg ai ha^{-1} sulfentrazone + 0.02 kg ai ha^{-1} chlorimuron ethyl and 1.26 kg ai ha^{-1} acetochlor + 1.26 kg ai ha^{-1} glyphosate were timed at planting. Escape weeds were removed with POST applications of 0.68 kg ai ha^{-1} glufosinate-ammonium on June 12 and July 30, 2018. At Bradford an application of 0.28 kg ai ha^{-1} sulfentrazone + 1.67 kg ai ha^{-1} S-metolachlor was applied at planting in 2018 and 0.13 kg ai ha^{-1} flumioxazin + 1.67 kg ai ha^{-1} S-metolachlor were applied at planting in 2019. Escape weeds were removed with POST applications of 0.68 kg ai ha^{-1} glufosinate-ammonium on July 2, 2018. At Williamsburg, PRE applications of 0.110 kg ai ha^{-1} pyroxasulfone + 0.003 kg ai ha^{-1} fluthiacet-methyl + 0.66 kg ai ha^{-1} glufosinate-ammonium were made at planting. Escape weeds were removed with POST applications of 1.93 kg ai ha^{-1} glyphosate on July 30 and August 29, 2019. All pesticide treatments were applied with a CO_2 pressurized backpack sprayer and 3 m boom at a carrier volume of 140 L ha^{-1}.

Plots (7.6 X 3 m) were arranged at each location as a split plot design, with six replications. The main plot factor was soybean growth stage at the time of dicamba application, V3 or R1, and the sub-plot factor consisted of 9 dicamba concentrations (0, 10, 25, 50, 100, 150, 200, 250, and 300 ppm dicamba). Dicamba treatments were made using a diglycolamine salt of dicamba (XtendiMax with VaporGrip; Bayer) in deionized water with 0.5% v/v Impetro II™ (MFA Inc., Columbia, MO, USA). Dicamba treatments were applied at 4.8 km h^{-1} with a CO_2 pressurized backpack sprayer through a 1.52 m boom equipped with TTI 11003 (TeeJet® Spraying Systems, Wheaton, IL) nozzles tips calibrated to deliver 140 L ha^{-1}. V3 dicamba treatments were applied on June 14 and 28 for Boonville and Bradford, respectively, in 2018 and July 2 for Williamsburg and

Bradford in 2019. R1 dicamba treatments were applied on July 3 and 17 for Boonville and Bradford, respectively, and on July 17 for Williamsburg and Bradford in 2019.

Crop injury and yield.

Data collection on soybean response began 7 days after treatment (DAT) and concluded at harvest. Visual injury ratings were taken at 7, 14, 21, and 28 DAT and were based on the Behrens-Lueschen scale, with 0 indicating no visible injury and 100 indicating complete plant death (Behrens and Lueschen 1979). Apical meristem height was measured at 7, 14, 21, and 28 DAT. Height was considered from the ground level to the top of the apical meristem from four randomly selected plants from each of the center two rows of each plot. Yield was determined by harvesting the two center rows of each plot with an 8 XP Massey Ferguson Multi Plot Combine (Kincaid Equipment Manufacturing, Haven, KS) on October 18 and November 17 at Boonville and Bradford, respectively, in 2018 and at Bradford on October 16, 2019. Owing to the nature of the location, yield for the Williamsburg site was collected by hand on October 24, 2019. Yields were corrected to 13% moisture content and expressed as kilograms per hectare. Seed samples from 3 different treatments (0, 150, and 300 ppm dicamba) at Bradford (2018 and 2019) and Boonville were collected at harvest and frozen following collect to be analyzed for dicamba residues. Seed samples were not collected from Williamsburg due to the extended environmental exposure at harvest.

Residue analysis.

Frozen soybean samples (approximately 30g) were placed into a Toastmaster® 5-Speed Blender (Toastmaster®, Englewood, CO, USA) and beans were homogenized without dry ice. Samples were placed in labeled sample containers and were stored frozen for further analysis. To prevent cross contamination between samples, countertops, workspace, glass blender, and blender blade were triple rinsed with deionized (DI) water and followed by a triple acetone rinse. The blender lid was rinsed with DI water then triple rinsed with methanol.

The quick, easy, cheap, effective, rugged, and safe (QuEChERS) extraction method (Anastassiades et al. 2003, Lehotay et al. 2010) for multiclass, multiresidue analysis of pesticides was used to extract dicamba from soybean samples. QuEChERS materials were obtained from commercial suppliers. Chopped soybeans (5g) were transferred into a 50 mL Falcon tube (Fisher Scientific, Hanover Park, IL, USA) and 10 mL ultrapure water was added. Sodium hydroxide solution (5N) (300 µL) (Fisher Scientific, Hanover Park, IL, USA) was added and the solution was shaken vigorously for 1 minute. After 30 minutes, 300 µL of a 5N sulfuric acid solution (Fisher Scientific, Hanover Park, IL, USA) and 10 mL of acetonitrile were added, and samples shaken vigorously for 1 minute. After shaking, 4 g magnesium sulfate (Fisher Scientific, Hanover Park, IL, USA), 1 g sodium chloride (Fisher Scientific, Hanover Park, IL, USA), 1 g trisodium citrate dihydrate (Sigma-Aldrich, St. Louis, MO. USA), and 0.5 g disodium citrate sesquilhydrate (Sigma-Aldrich, St. Louis, MO, USA) were added and the Falcon tubes were vigorously shaken for 1 minute. Falcon tubes were centrifuged for 5 minutes at 3000 rpm and the supernatant was removed and filtered through a Whatman® Anotop® 0.2 µM membranous filter (Millipore Sigma, Burlington, MA, USA).

Dicamba concentrations, in solution, were quantified using a Waters Alliance 2695 High Performance Liquid Chromatography (HPLC) system coupled with Waters Acquity TQ triple quadrupole mass spectrometer (MS/MS). Compounds were chromatographically separated by a Phenomenex® (Torrance, CA, USA) Kinetex C18 (100mm x 4.6 mm; 2.6 µm particle size) reverse-phase column with an attached Phenomenex (Torrance, CA, USA) SecurityGuard™ ULTRA (2 mm X 4.6 mm) reverse-phase guard cartridge. The mobile phase consisted of 10 mM ammonium acetate and 0.1% formic acid in water (A) and 100% acetonitrile (B). The gradient conditions were 0 to 0.5 minutes, 2% B; 0.5 to 7.0 minutes, 2 to 80% B; 7.0 to 9.0 minutes, 80 to 98% B; 9.0 to 10.0 minutes, 2% B; 10 to 15 minutes, 2% B at a flow rate of 0.5 mL per minute. The system was operated with electrospray ionization (ESI) in the negative ion mode with capillary voltage of 1.5 kV. The ionization source was programmed at 150°C and the desolvation temperature was programmed at 450°C. The MS/MS system was operated in the single ion recording (SIR) mode, and the spectrum of fragmented product ions were determined by injecting 30 µL of a standard solution containing 1000 µg L^{-1} of the analytical standards ionized by electrospray ionization in negative ion mode (ES^{-}, Figure 2.1). Analytical data were processed using Waters Empower 3 software (Waters, CA, USA). The ion m/z 174.72 $[M\text{-}H\text{-}COO]^{-}$ was used for the quantification of dicamba (Figure 2.2)

Quality assurance. Homogenous soybean samples were spiked with 200, 250, 500, 1000, or 2000 ng mL^{-1} dicamba and extracted with the QuEChERS method to determine the extraction efficiency of the method. Samples were analyzed using HPLC-MS/MS methods, as previously described, and quantified using standard dicamba concentrations of 10, 50, 100, 500, and 1000 ppb. Spiked dicamba (85 to 100%) was recovered using the QuEChERS and HPLC-MS/MS methods previously described. No adjustments were made to soybean residues to correct for extraction efficiencies.

Limits of detection (LOD) were evaluated by injecting standard solutions of 10, 50, 100, and 500 ng mL^{-1} dicamba in methanol. The LOD was set as the value where the intensities for the dicamba peaks were significantly higher than the background, and where the signal-to-noise ratio was greater than 3. For the matrixes in this study, the LOD was established at 10 ng mL^{-1} dicamba (data not shown).

Statistical analysis. Data were subjected to ANOVA using PROC GLIMMIX in SAS 9.4 (SAS Institute Incorporated, Cary, NC) for analysis of apical meristem elongation, visual injury, yields, and yield reductions. Treatment, time, and treatment by time were considered fixed factors, while replication within time by site was considered random. Means were separated at using P|Diff lines at $\alpha \geq 0.05$.

To generate regression equations, data were subjected to PROC REG in SAS 9.4 (SAS Institute Inc., Cary NC 27513). Regression equations were compared using R^2 values, Akaike Information Criterion Values (AIC), factor significance, and consistency with biological principles. Normality was assessed using the Shapiro-Wilks test and residual values were analyzed using the UNIVARIATE procedure within SAS 9.4. Regression models were analyzed for goodness of fit using the model evaluation system (http://nutritionmodels.com/mes.html; Tedeschi 2006).

Dicamba residue concentrations quantified in harvested soybeans were subjected to ANOVA using PROC GLIMMIX in SAS 9.4. Treatment, time, and site were considered fixed factors, while replication within site by application timing were considered random factors. All possible pairs of means were compared using Scheffe’s procedure and considered significant when $p \leq 0.05$.

Results and Discussion

Field observations.

Reductions in apical meristem growth were found as early as 7 DAT and stunting persisted up to 28 DAT (Table 2.1). Apical meristem growth was reduced from 7 to 28%, 9 to 43, 10 to 54%, and 13 to 59% when compared to the untreated control at 7, 14, 21, and 28 DAT, respectively. Similar to studies from Behrens and Lueschen (1979), Weidenhamer et al. (1989), Solomon and Bradley (2014), Soltani el at. (2016), and Foster (2018), the pattern of growth reduction with increased dicamba concentrations was consistent over the rating period.

Like growth measurements, soybean injury concomitantly increased with greater concentrations of dicamba (Table 2.2). Soybean injury was visible at concentrations as low as 10 ppm. [Visual injury following dicamba exposure was observed as early as 7 DAT]. Injury ratings ranged from 14 to 44, 16 to 48, 15 to 47, and 13 to 43% at 7, 14, 21, and 28 DAT, respectively (Table 2.2). Interestingly, soybean injury was greater for R1 versus V3 plants at the same dicamba concentrations at 7 and 14 DAT, but not by 21 and 28 DAT (Table 2.3).

Although treatments caused visual and measurable responses of soybean to dicamba, that did not necessarily translate into yield impacts (Table 2.4). Soybean yield varied based on the year and site. The average yields for V3 untreated control plots ranged between 3,542 to 4,262 kg ha^{-1} and 3,2701 to 4,575 kg ha^{-1} in untreated R1 control plots. Yield losses were observed as low as 25 ppm dicamba at three of four site years at V3 and two of four site years at R1. Significant yield reductions were observed when exposed to as low as 25 ppm dicamba In 2018, Bradford yields were reduced 41 and 53% by 300 ppm when compared to the untreated control at V3 and R1, respectively; whereas Boonville yields were reduced 52 and 55% at V3 and R1, respectively. In 2019, Bradford yields were reduced by 41 and 55% by 300 ppm compared to the untreated control at V3 and R1, respectively, whereas Williamsburg yields were reduced by 4 and 46% at V3 and R1. Averaged over the growth stages, soybean yield was reduced by dicamba concentrations as low as 25 ppm. At 300 ppm, yield losses reached almost 50%. Soybeans yields for R1 treated plants were significantly reduced compared to V3 soybeans when exposed to the same concentrations of dicamba (Figure 2.3). Environmental conditions varied between sites and years. The 2018 growing season was significantly drier than the 30-year average leading to lower yields throughout the Midwest, whereas 2019 was a wet growing season. Parts of the Williamsburg site experienced flooding, impacting crop stands. Bradford did not experience any flooding, drought, or weed control issues that would have led to significant yield limitations in 2019. Additionally, the soil types and soil chemical characteristics differ between different sites. These factors could explain some of the yield variation.

Soybean yield losses in response to low rates of dicamba have been widely documented. Compared to our results, similar responses were noted in sensitive soybeans by Wax et al. (1969), Auch and Arnold (1978), and Griffin et al. (2013). Wax el al. (1969) noted yield losses of 4 and 23% when 4.4 g ha^{-1} dicamba was applied during vegetative and reproductive growth stages, respectively, while Griffin et al. (2013) found yield reductions 52% with 70 g ha^{-1} dicamba applied at V3/V4 compared to 73% when similar rates were applied at R1.

Yield reductions also depend on the time of dicamba exposure (V3 or R1). Compared to our results, Wax et al. (1969) reported similar responses with an 11% yield reduction with 17.5 g ha^{-1} dicamba. Weidenhamer et al. (1989) also found that 40 to 80 g ha^{-1} dicamba reduced soybean yield 20 to 40% of the maximum observed yields. More recently, Solomon and Bradley (2014) noted yield reductions of 6 to 67% following dicamba applications to R1 soybeans; these findings were echoed by Jones et al. (2018) noted yield reductions when dicamba was applied with or without glyphosate to sensitive soybeans. Similar to the present study, previous studies found soybean yield reductions increase and dicamba concentrations increase and greater yield reductions when soybeans were exposed during reproductive development.

Prediction model analysis.

Many studies examining soybean yield responses to dicamba simulate some fraction of a labeled rate but including rates sufficient to kill soybeans. This research intentionally focused on multiple rates at low concentrations. These data may be useful for agronomists, farmers, and the insurance agency in predicting potential soybean yield losses from in-season exposure to dicamba. For instances of contaminated spray equipment, rinsate samples will be expressed in ppm; this study was established on using concentrations in ppm for direct comparison.

In the following section, predictive equations for yield losses are shown for different scenarios. In situations where dicamba exposure was known to occur for vegetative or reproductive growth stages, distinct yield loss equations were generated because losses vary depending upon growth stage. However, for instances where the timing of dicamba exposure was not known for soybeans, a prediction model averaged over the growth stages was generated.

Combined over each growth stage (V3 and R1), soybean yield in response in increasing dicamba concentrations can be expressed based upon Figure 2.4. The equation with the best fit was:

$$\text{Yield reduction (\% control)} = 0.46\ (\text{ppm}) - 0.002\ (\text{ppm})^{2} + 0.000004\ (\text{ppm})^{3} \qquad \textbf{[1]}$$

Predictive soybean yield equations for both V3 and R1 treated soybeans in response in increasing dicamba concentrations can also be expressed based upon Figure 2.5 (A and B). That equation is:

$$\text{V3 yield reduction (\% control)} = 0.40\ (\text{ppm}) - 0.002\ (\text{ppm})^{2} + 0.000004\ (\text{ppm})^{3} \qquad \textbf{[2]}$$

$$\text{R1 yield reduction (\% control)} = 0.53\ (\text{ppm}) - 0.003\ (\text{ppm})^{2} + 0.000004\ (\text{ppm})^{3} \qquad \textbf{[3]}$$

Each prediction model can be used to accurately predict soybean yield losses in response to dicamba when dicamba concentrations can be quantified, however, the dicamba concentration that soybeans were previously exposed to is rarely known. Usually, dicamba injury is not identified until seven to fourteen days after initial exposure and injury is typically quantified using the Behrens-Lueschen injury scale. The Behrens-Lueschen injury scale was used in this study to predict yield losses in response to dicamba exposure.

For instances of off-target damage injury where the developmental stage at the time of dicamba exposure is questionable, a prediction model that does not take developmental stage into account would be best suited. The prediction equation for cases where soybeans are injured by off-target movement of dicamba at any developmental stage (Figure 2.6, [4]) and rated using the Behrens-Lueschen dicamba injury scale 21 DAT is:

$$\text{Yield reduction (\% control)} = 0.91\ \text{(injury)} \qquad \textbf{[4]}$$

However, yield reductions in response to dicamba exposure vary based on soybean developmental stage. Therefore, if the developmental stage of the soybeans at the time of dicamba exposure is known prediction models for vegetative (V3) or reproductive stages (R1) would be more accurate. Predictive soybean yield equations for both V3 and R1 soybean in response to Behrens-Lueschen injury ratings at 21 DAT can be expressed based upon Figure 2.7 (A and B). That equation is:

$$\text{V3 yield reduction (\% control)} = 0.79\ \text{(injury)} \qquad \textbf{[5]}$$

$$\text{R1 yield reduction (\% control)} = 1.02\ \text{(injury)} \qquad \textbf{[6]}$$

The model evaluation system (Tedeschi 2006) was used to determine the goodness of fit for the predictive equations. Shapiro-Wilk’s W statistical analysis suggests that each of the above equations is a good fit for predicting yield reductions to sensitive soybeans exposed to dicamba ($p \leq 0.001$). Equation accuracy was assessed by the evaluation of the bias correction factor (Cb), a factor of the concordance correlation coefficient (CCC) described by (Lin 1989). The CCC provides an assessment of both the accuracy and precision of the model. All equations above [1 – 6] were assessed as highly accurate (Cb of ≥ 0.90), and the mean square error of prediction (MSEP) indicated that random errors were the main contributing factor associated with the lack of prediction power.

Additionally, residual values for all equations using ppm dicamba to predict soybean yield reduction were determined to be normally distributed by the Shapiro-Wilks ($p = 0.6522$) and the Kolmogorov-Smirnov ($p > 0.1500$) tests for normality [equations 1 – 3]. However, for equations using visual injury to predict soybean yield reductions [4 – 6] the Shapiro-Wilks test for normality determined the residual factors to not be normally distributed ($p = 0.0152$), whereas the Kolmogorov-Smirnov test for normality determined the residual factors to be normally distributed.

Statistical analyses indicate these prediction equations are adequate and accurately predict soybean yield reductions based upon both the applied ppm concentration of dicamba and visual injury response of soybeans, as assigned by the Behrens-Lueschen scale. Predictive yield loss models can help producers and agronomist assess damage as well as forecast economic losses prior to harvest. Few other prediction models have been proposed (Foster et al. 2019, Kniss 2018b, Weidenhamer et al. 1989) that rate injury based on morphological responses or plant height, but to our knowledge there are none that use the Behrens-Lueschen rating scale commonly used to access visual dicamba damage.

Residue analysis.

Dicamba was quantified in soybeans exposed to driftable (low) concentrations of dicamba. In the absence of dicamba, soybean seeds for both the V3 and R1 treated growth stages contained no detectable dicamba concentrations, despite untreated plots being in close proximity to dicamba treated soybeans (Table 2.5). However, soybean samples treated with 150 and 300 ppm dicamba contained and average of 0.72 and 0.81 mg kg^{-1} dicamba at harvest (Table 2.5). Soybeans treated with 300 ppm dicamba contained 11% more dicamba compared to soybeans treated with 150 ppm dicamba; however, the dicamba concentrations quantified were not significantly different (p=0.5650). Surprisingly, the timing of the dicamba application did not significantly impact residual dicamba concentrations (Table 2.6) (p=0.4938). Although soybeans exposed to dicamba at the V3 growth stage had longer to recover from dicamba applications and yields were less affected by dicamba treatments than R1 treated soybeans, this study suggested that dicamba concentrations remained consistent in the soybean from the time of exposure up to pod fill.

While the subsample of dicamba treatments selected from this study for residue analysis did not correlate with applied dicamba, site year significantly impacted residual dicamba concentrations. Average dicamba residue in harvested soybeans following dicamba exposure was 0.70, 0.35, and 0.54 mg kg^{-1} at Bradford (2018), Boonville (2018), and Bradford (2019), respectively. Dicamba residues were significantly higher at Bradford (2018) compared to Boonville (2018) (p=0.0015); whereas dicamba residues at Bradford (2019) were not significantly different from those at Bradford (2018) (p=0.1190) or Boonville (2018) (p=0.0668) (Table 2.7).

Due to the polarity of dicamba, the compound in situ will translocate from the point of application to meristematic tissues including roots, shoots, and seeds (Chang and Vanden Born 1968, 1971). However, auxin translocation can be negatively affected by drought (Basler et al. 1961, Hauser 1955, Merkle and Davis 1967, Pallas, and Williams 1962, Skelton 2015). Deficits of available soil water are known to decrease the translocation of other herbicides, such as glyphosate (Ahmadi et al. 1980, Davis et al. 1968, Klevorn and Wyse 1984, Lauridson et al. 1983, McWhorter et al. 1980, Waldecker and Wyse 1985), picloram (Lauridson et al. 1983, Morrison et al. 1995), haloxyfop (Boydston 1990, Kidder and Behrens 1988, Peregoy et al. 1990), 2,4-D (Hauser 1955, Hughes 1968, Lauridson et al. 1983, Long and Basler 1973, Pallas, and Williams 1962, Skelton 2015), diclorofop (Akey and Morrison 1983), fluazifop (Dickson et al. 1990, Grafstrom and Nalewaja 1986), and sethoxydim (Boydston 1990); and may cause reduced translocation of dicamba as well.

In this study, sites where harvested soybeans contained higher concentrations of dicamba residue experienced more precipitation than those with lower dicamba concentrations. In the 13 weeks following R1 dicamba applications, Bradford in 2019 received 27.5 centimeters of precipitation, whereas, in 2018 the Bradford and Boonville field sites received 28.7 and 24.7 centimeters 24.7 centimeters of precipitation, respectively (Table 2.8). In 2018, long periods without rainfall occurred around the R1 application timing. Boonville saw no significant rainfall 14 days prior and up to 14 days following R1 dicamba applications, whereas Bradford, in both 2018 and 2019, were dry

14 days prior to R1 dicamba applications but received significant rainfall within 3 days following application. Due to the higher than average air temperatures in 2018 the field site at Bradford was irrigated following the R1 dicamba application, further compounding the differences in precipitation between years. Additionally, the Lowmo silt loam soil at the Boonville site is a well-drained soil and has a greater sand content (5 to 50% sand) compared to the poorly drained Mexico silt loam (3 to 10% sand) at the Bradford site (Natural Resources Conservation Services 2020). Sites with less precipitation may have experienced reduced translocation of dicamba due to reduced photosynthesis and photoassimilate transport because less material is being loaded and transported in the phloem of drought-stressed plants (de Ruiter and Meinen 1998). This study could suggest that dicamba residue concentrations may be lower in soybeans harvested from sites experiencing greater water stress.

While concentrations of dicamba were quantified in harvested soybeans, dicamba concentrations were well below the EPA level of tolerance for dicamba in soybeans for human consumption. The highest dicamba concentration measured from this study, 2.27 mg kg^{-1} dicamba, originated from soybeans treated with 300 ppm dicamba at the Bradford field site 2018 (data not shown), but is 4.4-fold less than the 10 mg kg^{-1} level of tolerance set by the EPA. However, a residual of 2.27 mg kg^{-1} would be problematic for organic producers. The USDA National Organic Program sets strict limits for pesticide residues in food crops at 5% of the EPA level of tolerance in cases where the organic producer hasn’t directly applied the prohibited pesticide, such as off-target dicamba (USDA

National Organic Program and USDA Science and Technology Programs 2012). Therefore, the tolerance level for dicamba in organic produce is 0.5 mg kg^{-1}. Of the samples from this study, 53% exceeded the organic tolerance level. However, with limited sampling, this study suggests that conventional soybeans injured by dicamba drift and allowed to go to yield would be safe for human consumption in the United States but could potentially violate the USDA regulations for damaged, organic soybeans.

Literature Cited

Agam N, Berliner PR (2006) Dew formation and water vapor adsorption in semi-arid environments - A review. J Arid Environ 65:572–590

AGCO (2020) Weed control efficacy. https://www.croplife.com/iron/sprayers/sprayer-setup-best-practices-maximize-weed-control-efficacy/

Ahmadi MS, Haderlie LC, Wicks GA (1980) Effect of growth stage and water stress on barnyardgrass (*Echinochloa crus-galli*) control and on glyphosate absorption and translocation. Weed Sci 28:277–282

Akey WC, Morrison IN (1983) Effect of moisture stress on wild oat (*Avena fatua*) response to diclofop. Weed Sci 31:247–253

Anastassiades M, Lehotay SJ, Stajnbaher D, Schenck FJ (2003) Fast and easy multiresidue method employing acetonitrile extraction/partitioning and "dispersive solid-phase extraction" for the determination of pesticide residues in produce. J AOAC Int 86:412–431

Anonymous (2010) Clarity label. Research Triangle, NC: BASF Corporation

Anonymous (2019a) Engenia herbicide product label. Research Triangle, NC: BASF Corporation

Anonymous (2019b) XtendiMax with vaporgrip technology herbicide product label. St. Louis, MO: Bayer

Anonymous (2020) FeXapan plus vaporgrip technology herbicide product label. Indianapolis, IN

Auch DE, Arnold WE (1978) Dicamba use and injury on soybeans (*Glycine max*) in South Dakota. Weed Sci 26:471–475

Babiker AGT, Duncan HJ (1975) Penetration of bean leaves by asulam as influenced by adjuvants and humidity. Pestic Sci 6:655–664

Basler E, Todd GW, Meyer RE (1961) Effects of moisture stress on absorption, translocation, & distribution of 2,4-dichlorophenoxyacetic acid in bean plants. Plant Physiol 36:573–576

Behrens MR, Mutlu N, Chakraborty S, Dumitru R, Jiang WZ, Lavallee BJ, Herman PL, Clemente TE, Weeks DP (2007) Dicamba resistance: enlarging and preserving biotechnology-based weed management strategies. Science (80-) 316:1185–1189

Behrens R, Lueschen WE (1979) Dicamba volatility. Weed Sci 27:486–493

Benbrook CM (2016) Trends in glyphosate herbicide use in the United States and globally. Environ Sci Eur 28:1–15

Beysens D, Lekouch I, Mileta M, Milimouk I, Muselli M (2019) Dew and rain collection in South Croatia. Int J Civ Environ Eng 1:64–70

Bird SL, Esterly DM, Perry SG (1996) Off-target deposition of pesticides from agricultural aerial spray applications. J Agric Food Chem 14:585–588

Bish M, Bradley K (2017) Knowing when to spray: monitoring the weather. https://weedscience.missouri.edu/Missouri Weather Analysis_2017.pdf

Bish MD, Farrell ST, Lerch RN, Bradley KW (2019) Dicamba losses to air after applications to soybean under stable and nonstable atmospheric conditions. J Environ Qual 48:1675–1682

Boerboom C (2004) Field case studies of dicamba movement to soybeans. Page *in* Wisconsin Crop Management Conference

Boydston R (1990) Soil water content affects the activity of four herbicides on green

foxtail (*Setaria viridis*). Weed Res 38:578–582

Bradley K (2017) Integrated pest 2017. 1–2 p

Bradley K (2018) July 15 dicamba injury update. different year, same questions:1–2

Broadhurst NA, Montgomery ML, Freed VH (1966) Metabolism of 2-methoxy-3,6-dichlorobenzoic acid (dicamba) by wheat and bluegrass plants. J Agric Food Chem 14:585–588

Browne FB, Li X, Price KJ, Wang J, Wang Y, Kruger GR, Golus J, De Castro Macedo G, Vieira BC, Sandlin T (2020) Dicamba retention in commercial sprayers following triple rinse cleanout procedures, and soybean response to contamination concentrations. Agronomy 10:1–15

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

Burnside OC, Lavy TL (1966) Dissipation of dicamba. Weeds 14:211–214

Celen IH (2010) The effect of spray mix adjuvants on spray drift. Bulg J Agric Sci 16:105–110

Cenkci S, Yildiz M, Ciĝerci IH, Bozdaĝ A, Terzi H, Terzi ESA (2010) Evaluation of 2,4-D and dicamba genotoxicity in bean seedlings using comet and RAPD assays. Ecotoxicol Environ Saf 73:1558–1564

Chang FY, Vanden Born WH (1968) Translocation of dicamba in Canada thistle. Weed Sci 16:176–181

Chang FY, Vanden Born WH (1971) Dicamba uptake, translocation, metabolism, and selectivity. Weed Sci 19:113–117

Christoffoleti PJ, Figueiredo MRA de, Peres LEP, Nissen S, Gaines T (2015) Auxinic

herbicides, mechanisms of action, and weed resistance: a look into recent plant science advances. Sci Agric 72:356–362

Creech CF, Henry RS, Fritz BK, Kruger GR (2014) Influence of herbicide active ingredient, nozzle type, orifice size, spray pressure, and carrier volume rate on spray droplet size characteristics. Weed Sci 62:193–206

Cundiff GT, Reynolds DB, Mueller TC (2017) Evaluation of dicamba persistence among various agricultural hose types and cleanout procedures using soybean (*Glycine max*) as a bio-indicator. Weed Sci 65:305–316

Davis FS, Merkle MG, Bovey RW (1968) Effect of moisture stress on the absorption and transport of herbicides in woody plants. Bot Gaz 129:183–189

Davis J, Barber T, Max C (2015) Tank clean-out recommendations for common herbicides. 1–2 p

Dickson RL, Andrews M, Field RJ, Dickson EL (1990) Effect of water stress, nitrogen, and gibberellic acid on fluazifop and glyphosate activity on oats (Avena sativa). Weed Sci 38:54–61

Dill GM (2005) Glyphosate-resistant crops : history , status and future †. Pest Manag Sci 224:219–224

Dintelmann BR, Warmund MR, Bish MD, Bradley KW (2019) Investigations of the sensitivity of ornamental, fruit, and nut plant species to driftable rates of 2,4-D and dicamba. Weed Technol:1–11

Do-Thanh CL, Vargas JJ, Thomas JW, Armel GR, Best MD (2016) Design, synthesis, and evaluation of novel auxin mimic herbicides. J Agric Food Chem 64:3533–3537

Duke SO (2018) The history and current status of glyphosate. Pest Manag Sci 74:1027–

1034

Duke SO, Powles SB (2008) Glyphosate: a once-in-a-century herbicide. Pest Manag Sci 63:1100–1106

Egan JF, Barlow KM, Mortensen DA (2014a) A meta-analysis on the effects of 2,4-D and dicamba on soybean and cotton. Weed Sci 62:193–206

Egan JF, Barlow KM, Mortensen DA (2014b) A meta-analysis on the effects of 2,4-D and dicamba drift on soybean and cotton. Weed Sci 62:193–206

Environmental Protection Agency (2005) Reregistration eligibility decision (RED) document for nitrapyrin. 1–38 p

Environmental Protection Agency (2018) EPA announces changes to dicamba registration. https://archive.epa.gov/epa/newsreleases/epa-announces-changes-dicamba-registration.html

Environmental Protection Agency (2019) Food and pesticides. https://www.epa.gov/safepestcontrol/food-and-pesticides. Accessed October 25, 2020

Environmental Protection Agency (2020) Dicamba training requirements. https://www.epa.gov/ingredients-used-pesticide-products/dicamba-training-requirements-frequently-asked-questions#components

Enz JW, Hofman V, Thostenson A (2017) Air temperature inversions causes, characteristics, and potential effects on pesticide spray drift. NDSU Ext 1705:1–16

EPA (2010) Index to pesticide chemical names, part 180 tolerance information, and food and feed commodities (by commodity). Environ Prot Agency:1–314

Ester A, Strachan SD, Casini MS, Heldreth KM, Scocas JA, Nissen SJ, Bukun B,

Lindenmayer RB, Shaner DL, Westra P, Ester A, Strachan SD, Casini MS, Heldreth KM, Scocas JA, Nissen SJ, Bukun B, Lindenmayer RB, Shaner DL, Westra P, Brunk G (2010) Vapor movement of synthetic auxin herbicides : Aminocyclopyrachlor-methyl ester, dicamba, and aminopyralid. Weed Sci 58:103–108

Farrell S, Lerch RN, Bish M (2018) Influence of formulations and application time of day on dicamba air concentrations following treatment. Page *in* Proceedings of the 73rd Annual Meeting of the North Central Weed Science Society

Foster MR (2018) Soybean response to dicamba : Associated injury criteria and development of a model to predict yield loss. Louisiana State University

Foster MR, Griffin JL, Copes JT, Blouin DC (2019) Development of a model to predict soybean yield loss from dicamba exposure. Weed Technol 33:287–295

Gałek G, Sobik M, Błaś M, Polkowska Z, Cichała-Kamrowska K, Wałaszek K (2015) Dew and hoarfrost frequency, formation efficiency and chemistry in Wroclaw, Poland. Atmos Res 151:120–129

Gauvrit C (2003) Glyphosate response to calcium, ethoxylated amine surfactant, and ammonium sulfate. Weed Technol 17:799–804

Gavlick WK, Wright DR, MacInnes A, Hemminghaus JW, Webb JK, Yermolenka VI, Su W (2016) A method to determine the relative volatility of auxin herbicide formulations.pdf. Pestic Formul Deliv Syst 35:24–32

Grafstrom LD, Nalewaja JD (1986) Uptake and translocation of fluazifop in green goxtail (*Setaria viridis*). Weed Sci 108:115–123

Griffin JL, Bauerle MJ, Stephenson DO, Miller DK, Boudreaux JM (2013) Soybean

response to dicamba applied at vegetative and reproductive growth stages. Weed Technol 27:696–703

Grossmann K (2010) Auxin herbicides: Current status of mechanism and mode of action. Pest Manag Sci 66:113–120

Guilherme A, Alves S, Kruger GR, Paulo J, Cunha AR, Denise G, Santana D, Pinto LAT (2017) Dicamba spray drift as influenced by wind speed and nozzle type dicamba spray drift as influenced by wind speed and nozzle type. Weed Technol 31:724–731

Hall GJ, Hart CA, Jones CA (2000) Plants as sources of cations antagonistic to glyphosate activity. Pest Manag Sci 56:351–358

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

Hartzler R (2017) Wind speed and herbicide application. https://crops.extension.iastate.edu/cropnews/2017/01/wind-speed-and-herbicide-application

Hartzler R, Hartzler R (2020) 2020 Herbicide guide for Iowa corn and soybean production. Page Iowa State University Extension and Outreach Integrated Crop Management

Hatterman-Valenti H, Owen MD, Christians NE (1995) Comparison of spray drift during postemergence herbicide applications to turfgrass. Weed Technol 9:321–325

Hauser EW (1955) Absorption of 2,4-dichlorophenoxyacetic acid by soybean and corn plants. Agron J 47:32

Heap I (2020) International herbicide-resistant weed database. http://weedscience.org/Home.aspx

Hertel R, Thomson KS, Russo VEA (1972) In-vitro auxin binding to particulate cell fractions from corn coleoptiles. Planta 107:325–340

Hewitt AJ (1993) Droplet size spectra produced by air-assisted atomizers. J Aerosol Sci 24:155–162

Holly K (1956) Penetration of chlorinated phenoxyacetic acid into leaves. Pages 195–199 *in* Annals of Applied Biology

Hughes EE (1968) Hygroscopic additives to phenoxy herbicides for control of saltcedar. Weed Sci 16:486–488

Hughes RE, Freed VH (1961) The role of surfactants in the foliar absorption of indole-3-acetic acid (IAA). Weeds 9:54–59

Hull HM, Davis DG, Stolzenberg GE (1982) Action of adjuvants on plant surfaces. Pages 26–67 *in* Adjuvants for Herbicides. Weed Science Society of America

Jhala A, Knezevic S, Klein RN (2017) Dicamba injury symptoms on sensitive crops

Jiries A (2001) Chemical composition of dew in Amman, Jordan. Atmos Res 57:261–268

Johnson WG, Casady B, Peterson D, Kuhlman D (1997) Cleaning field sprayers to avoid crop injury. MU Extension, Univ Missouri-Columbia

Johnson WG, Hallett SG, Legleiter TR, Whitford F, Weller SC, Bordelon BP, Lerner BR (2012) 2,4-D and dicamba-tolerant crops- some facts to consider. Page Purdue Extension. 1–7 p

Jones GT (2018) Evaluation of dicamba off-target movement and subsequent effects on soybean offspring. University of Arkansas

Jones GT, Norsworthy JK, Barber T, Gbur E, Kruger GR (2019) Off-target movement of DGA and BAPMA dicamba to sensitive soybean. Weed Technol 33:51–65

Kabela ED, Hornbuckle BK, Cosh MH, Anderson MC, Gleason ML (2009) Dew frequency, duration, amount, and distribution in corn and soybean during SMEX05. Agric For Meteorol 149:11–24

Kelley KB, Wax LM, Hager AG, Riechers DE (2005) Soybean response to plant growth regulator herbicides is affected by other postemergence herbicides. Weed Sci 53:101–112

Kidder DW, Behrens R (1988) Plant responses to haloxyfop as influenced by water stress. Weed Sci

Klein RN, Schulze L, Ogg CL (2008) Factors affecting spray drift of pesticides. Crop Soils:19–23

Klevorn TB, Wyse DL (1984) Effect of soil temperature and moisture on glyphosate and photoassimilate distribution in quackgrass (*Agropyron repens*). Weed Sci 32:402–407

Kniss AR (2018a) Genetically engineered herbicide-resistant crops and herbicide-resistant weed evolution in the United States. Weed Sci 66:260–273

Kniss AR (2018b) Soybean response to dicamba: a meta-analysis. Weed Technol 32:507–512

Knoche M, Petracek PD (2014) Foliar uptake of PGRs: barriers, mechanisms, model systems, and factors. Acta Hortic 1042:125–141

Kroin J (2009) Auxins and the pathways for foliar application. 53–59 p

Lakhani A, Parmar RS, Prakash S (2012) Chemical composition of dew resulting from radiative cooling at a semi-arid site in Agra, India. Pure Appl Geophys 169:859–871

Lauridson TC, Wilson RG, Haderlie LC (1983) Effect of moisture stress on Canada

thistle (*Cirsium arvense*) control. Weed Sci 31:674–680

Lehotay SJ, Son KA, Kwon H, Koesukwiwat U, Fu W, Mastovska K, Hoh E, Leepipatpiboon N (2010) Comparison of QuEChERS sample preparation methods for the analysis of pesticide residues in fruits and vegetables. J Chromatogr 1217:2548–2560

Lekouch I, Mileta M, Muselli M, Milimouk-Melnytchouk I, Šojat V, Kabbachi B, Beysens D (2010) Comparative chemical analysis of dew and rain water. Atmos Res 95:224–234

Lin LI-K (1989) A concordance correlation coefficient to evaluate reproducibility. Biometrics 45:255–268

Long J (2017) Infuence of application factors on dicamba volatility. Purdue. 98 p

Long J, Basler E (1973) Some factors regulating auxin translocation in intact bean seedlings. Plant Physiol 51:128–135

Luke AJ, Weirich JW, Smeda RJ (2017) Dicamba residues in spray equipment reduces soybean (*Glycine max*) growth and yield. University of Missouri

Madeira AC, Kim KS, Taylor SE, Gleason ML (2002) A simple cloud-based energy balance model to estimate dew. Agric For Meteorol 111:55–63

Marth PC, Davis FF, Mitchell JW (2018) Herbicidal properties of 2,4-dichlorophenoxyacetic acid applied in dusts containing hygroscopic agents. Bot Gaz 107:129–136

Maybank J, Yoshida K, Grover R (1978) Spray drift from agricultural pesticide applications. J Air Pollut Control Assoc 28:1009–1014

McMullan PM (2000) Utility adjuvants. Weed Technol 14:792–797

McWhorter CG, Jordan TN, Wills GD (1980) Translocation of 14 C-glyphosate in soybeans (Glycine max) and johnsongrass (*Sorghum halepense*). Weed Sci 28:113–118

McWorter CG (1982) The use of adjuvants. Pages 10–25 *in* Adjuvants for Herbicides. Weed Science Society of America

Merkle MG, Davis FS (1967) Effect of moisture stress on absorption and movement of picloram and 2,4,5-T in beans. Weeds 15:10–12

Miller A, Donnie K, Robert G, Roger B, Merritt E, Steve T, Miller DK, Downer RG, Leonard BR, Kelly ST (2003) Response of non-glufosinate-resistant cotton to reduced rates of glufosinate. Weed Sci 51:781–785

Miller PCH, Butler Ellis MC (2000) Effects of formulation on spray nozzle performance for applications from ground-based boom sprayers. Page *in* Crop Protection

Miller PCH, Tuck CR (2005) Factors influencing the performance of spray delivery systems: A review of recent developments. J ASTM Int 2:1–13

Mills MS, Thurman EM (1994) Reduction of nonpoint source contamination of surface water and groundwater by starch encapsulation of herbicides. Environ Sci Technol 28:73–79

Monshausen GB, Gilroy S (2009) Feeling green: mechanosensing in plants. Trends Cell Biol 19:228–235

Morgan J V, Tukey Jr. HB (1964) Characterization of leachate from plant foliage. Plant Physiol 39:590–593

Morrison RG, Lownds NK, Sterling TM (1995) Picloram uptake, translocation, and efficacy in relation to water status of Russian knapweed (*Acroptilon repens*). Weed

Sci 43:34–39

Mortensen DA, Egan JF, Maxwell BD, Ryan MR, Smith RG (2012) Navigating a critical juncture for sustainable weed management. Bioscience 6:75–84

Mueller TC, Steckel LE (2019a) Dicamba volatility in humidomes as affected by temperature and herbicide treatment. Weed Technol 33:1–6

Mueller TC, Steckel LE (2019b) Spray mixture pH as affected by dicamba, glyphosate, and spray additives. Weed Technol 33:547–554

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

Mueller TC, Wright DR, Remund KM (2013) Effect of formulation and application time of day on detecting dicamba in the air under field conditions. Weed Sci 61:586–593

Nandula VK (2010) Glyphosate resistance in crops and weeds: History, development, and management. Page Glyphosate Resistance in Crops and Weeds: History, Development, and Management. 1–33 p

Nath S, Yadav S (2018) A comparative study on fog and dew water chemistry at New Delhi, India. Aerosol Air Qual Res 18:26–36

National Center for Biotechnology Information (2020) PubChem compound summary for CID 3030, dicamba. https://pubchem.ncbi.nlm.nih.gov/compound/Dicamba. Accessed December 11, 2020

Natural Resources Conservation Services (n.d.) Official soil series descriptions. https://soilseries.sc.egov.usda.gov/osdname.aspx. Accessed April 9, 2020

Nordby A, Skuterud R (1974) The effects of boom height, working pressure and wind speed on spray drift. Weed Res 14:385–395

Nuyttens D, Schampheleire M, Steurbaut W, Baetens K (2006) Experimental study of factors influencing the risk of drift from field sprayers, part 2: spray application technique. Asp Appl Biol 77:1–9

Osborne PP, Xu Z, Swanson KD, Walker T, Farmer DK (2015) Dicamba and 2,4-D residues following applicator cleanout: a potential point source to the environment and worker exposure. J Air Waste Manag Assoc 65:1153–1158

Ouse DG, Gifford JM, Schleier J, Simpson DD, Tank HH, Jennings CJ, Annangudi SP, Valverde-Garcia P, Masters RA (2018) A new approach to quantify herbicide volatility. Weed Technol 32:691–697

Pallas, JE, Williams GG (1962) Foliar absorption and translocation of P32 and 2,4-dichlorophenoxyacetic acid as affected by soil-moisture tension. Bot Gaz 123:175–180

Peachey E (2009) Tank cleaners: why and when they work

Peregoy R, Kitchen L, Jordan P, Griffin JL (1990) Moisture stress effects on the absorption, translocation, and metabolism of haloxyfop in johnsongrass (*Sorghum halepense*) and large crabgrass (*Digitaria sanguinalis*). Weed Sci 38:331–337

Perry ED, Ciliberto F, Hennessy DA, Moschini GC (2016) Genetically engineered crops and pesticide use in U.S. maize and soybeans. Sci Adv 2:1–8

Petersen PJ, Haderlie LC, Hoefer RH, McAllister RS (1985) Dicamba absorption and translocation as influenced by formulation and surfactant. Weed Sci 33:717–720

Ramsey RJL, Stephenson GR, Hall JC (2005) A review of the effects of humidity, humectants, and surfactant composition on the absorption and efficacy of highly water-soluble herbicides. Pestic Biochem Physiol 82:162–175

Rayle DL, Cleland R (1970) Enhancement of wall loosening and elongation by acid solutions. Plant Physiol 46:250–253

Rice EL (1948) Absorption and translocation of ammonium 2,4-dichlorophenoxyacetate by bean plants. Bot Gaz 109:301–314

Ross MA, Lembi CA (1999) Applied Weed Science. 3rd ed. Minneapolis, Minnesota: Burgess Pub Co

Sargent JA (1965) The penetration of growth regulators into leaves. Annu Rev Plant Physiol 16:1–12

Sciumbato AS, Chandler JM, Senseman SA, Bovey RW, Smith KL (2004) Determining exposure to auxin-like herbicides. I. quantifying injury to cotton and soybean. Weed Technol 18:1125–1134

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

Sharma MP, Born WH Vanden (1970) Foliar penetration of picloram and 2,4-D in aspen and balsam poplar. Weed Sci 18:57–63

Skelton JJ (2015) Uptake, translocation, and metabolism 2,4-D in enlist crops and control of drought-stressed waterhemp (*Amaranthus tuberculatus*) with 2,4-D and glyphosate. University of Illinois at Urbana-Champaign

Solomon CB, Bradley K (2014) Influence of application timings and sublethal rates of synthetic auxin herbicides on soybean. Weed Technol 28:454–464

Soltani N, Brown L, Sikkema PH (2018) Control of glyphosate-resistant common ragweed in corn with preemergence herbicides. Can J Plant Sci 98:959–962

Soltani N, Nurse RE, Sikkema PH (2016) Response of glyphosate-resistant soybean to

dicamba spray tank contamination during vegetative and reproductive growth stages. Can J Plant Sci 96:160–164

Steckel L, Thompson A (2005) Cleaning plant growth regulator (PGR) herbicides out of field sprayers. UT Extension

Sutton OG (1953) Micrometeorology. Q J R Meteorol Soc:333–335

Szabo SS, Buchholtz KP (1961) Penetration of living and non-living surfaces by 2 ,4-D as influenced by ionic additives. Weeds 9:177–184

Tedeschi LO (2006) Assessment of the adequacy of mathematical models. Agric Syst 89:225–247

Thelen KD, Jackson EP, Penner D (2020) The basis for the hard-water antagonism of glyphosate activity 43:541–548

Tromas A, Paponov I, Perrot-Rechenmann C (2010) Auxin binding protein 1: functional and evolutionary aspects. Trends Plant Sci 15:436–446

Tukey HB (1970) The leaching of substances from plants. Annu Rev Plant Physiol 21:305–324

U.S. FDA (2019) Pesticide residue monitoring program fiscal year 2017 pesticide report:48

United States Department of Agriculture (1967) Suggested guide for weed control

USDA National Organic Program, USDA Science and Technology Programs (2012) Pilot study pesticide residue testing of organic produce. 34 p

Vogel S (1970) Convective cooling at low airspeeds and the shapes of broad leaves. J Exp Bot 21:91–101

Waldecker MA, Wyse DL (1985) Soil moisture effects on glyphosate absorption and

rtanslocation in common milkweed (*Asclepias syriaca*). Weed Sci

Wax LM, Knuth LA, Slife FW (1969) Response of soybeans to 2,4-D, dicamba, and picloram. Weed Sci 17:388–393

Wechsler SJ, Smith D, Mcfadden J, Dodson L, Williamson S (2019) The use of genetically engineered dicamba-tolerant soybean seeds has increased quickly, benefting adopters but damaging crops in some fields. https://www.ers.usda.gov/amber-waves/2019/october/the-use-of-genetically-engineered-dicamba-tolerant-soybean-seeds-has-increased-quickly-benefiting-adopters-but-damaging-crops-in-some-fields/. Accessed April 9, 2020

Weidenhamer JD, Triplett GB, Sobotka FE (1989) Dicamba injury to soybean. Agron J 81:637–643

Whisenant SG, Bouse LF, Crane RA, Bovey RW (1993) Droplet size and spray volume effects on honey mesquite mortality with clopyralid. J Range Manag 46:257

Wolf S, Hématy K, Höfte H (2012) Growth control and cell wall signaling in plants. Annu Rev Plant Biol 63:381–407

Woodward AW, Bartel B (2005) Auxin: regulation, action, and interaction. Ann Bot 95:707–735

Xu Y, Zhu H, Tang J, Lin Y (2015) Chemical compositions of dew and scavenging of particles in Changchun, China. Adv Meteorol:1–11

Young BG (2019) Changes in herbicide use patterns and production practices resulting from glyphosate-resistant crops. Weed Technol 20:301–307

Young BG, Hart SE (1998) Optimizing foliar activity of isoxaflutole on giant foxtail (*Setaria faberi*) with various adjuvants. Weed Sci 46:397–402

Van de Zande JC, Stallinga H, Michielsen JMGP, van Velde P (2004) Effect of sprayer speed on spray drift. Annu Rev Agric Engeneering 4:11

Zimdahl R (2013) Fundamentals of Weed Science. 4th ed. Fort Collins, Colorado: Elsevier. 378–381 p

Table 2.1. Mean ± standard error of soybean apical meristem growth reduction (%) compared to untreated control plots. Data were averaged over developmental stages. Experiments were carried out at two locations in both 2018 and 2019 in central Missouri. Means with the same letter within rating timing (DAT= days after treatment) are not significantly different when separated by LS means at p≤0.05 and standard errors were noted (SE= standard error).

Dicamba (ppm)	**Apical meristem reduction (% control)**														
	0 DAT			**7 DAT**			**14 DAT**			**21 DAT**			**28 DAT**		
0	0	±3.7	bc	0	±4.2	a	0	±4.6	a	0	±4.3	a	0	±4.1	a
10	0	±3.7	bc	7	±4.2	b	9	±4.6	b	10	±4.3	b	13	±4.1	b
25	-1	±3.7	abc	13	±4.2	c	21	±4.6	c	23	±4.3	c	22	±4.1	c
50	-1	±3.7	abc	18	±4.2	cd	30	±4.6	d	34	±4.3	d	36	±4.1	d
100	-2	±3.7	abc	22	±4.2	e	38	±4.6	e	43	±4.3	e	45	±4.1	e
150	-3	±3.7	a	23	±4.2	ef	41	±4.6	ef	46	±4.3	ef	49	±4.1	ef
200	-2	±3.7	ab	22	±4.2	de	42	±4.6	ef	50	±4.3	fg	51	±4.1	f
250	1	±3.7	c	28	±4.2	fg	42	±4.6	ef	50	±4.3	fg	55	±4.1	fg
300	0	±3.7	bc	28	±4.2	g	43	±4.6	f	54	±4.3	g	59	±4.1	fg

Table 2.2. Mean ± standard error of soybean injury (0= no injury, 100= plant death) in response to dicamba (ppm=parts per million) exposure. Data were averaged over developmental stages (V3 or R1). Experiments were carried out at two locations in both 2018 and 2019 in central Missouri. Means with the same letter within rating timing (DAT= days after treatment) are not significantly different when separated by LS means at p≤0.05 and standard errors were noted (SE= standard error).

Dicamba (ppm)	**Visual injury (0-100)**			
	7 DAT	**14 DAT**	**21 DAT**	**28 DAT**
0	0 ±0.9 a	0 ±1.2 a	0 ±1.4 a	0 ±1.4 a
10	14 ±0.9 b	16 ±1.2 b	15 ±1.4 b	13 ±1.4 b
25	19 ±0.9 c	22 ±1.2 c	21 ±1.4 c	18 ±1.4 c
50	21 ±0.9 d	23 ±1.2 c	23 ±1.4 d	20 ±1.4 d
100	25 ±0.9 e	28 ±1.2 d	29 ±1.4 e	27 ±1.4 e
150	27 ±0.9 f	31 ±1.2 e	31 ±1.4 f	29 ±1.4 f
200	33 ±0.9 g	39 ±1.2 f	38 ±1.4 g	35 ±1.4 g
250	38 ±0.9 h	42 ±1.2 g	42 ±1.4 h	39 ±1.4 h
300	44 ±0.9 i	48 ±1.2 h	47 ±1.4 i	43 ±1.4 i

Table 2.3. Mean ± standard error of soybean injury (0=no injury, 100=plant death) in response to dicamba exposure Data were averaged over dicamba treatments (0 to 300 parts per million dicamba). Experiments were carried out at two locations in both 2018 and 2019 in central Missouri. Means with the same letter within rating timing (DAT= days after treatment) are not significantly different when separated by LS means at p≤0.05 and standard errors were noted (SE= standard error).

Timing	**Visual Injury (0-100)**											
	7 DAT			**14 DAT**			**21 DAT**			**28 DAT**		
V3	25	±0.7	a	28	±0.7	a	27	±1.1		24	±1.2	
R1	24	±0.7	b	27	±0.7	b	28	±1.1		26	±1.2	

Table 2.4. Mean ± standard error of soybean yield (kg ha^{-1}) in response to dicamba. Experiments were carried out at two locations in both 2018 and 2019 in central Missouri. Means with the same letter within timing, year, and location are not significantly different when separated by LS means at $p \leq 0.05$.

Timing	**Dicamba (ppm)**	**2018**						**2019**					
		Bradford kg ha^{-1}			Boonville kg ha^{-1}			Bradford kg ha^{-1}			Williamsburg kg ha^{-1}		
V3	0	3542	±198	a	4128	±203	a	4017	±188	ab	4262	±177	a
	10	3487	±183	a	3939	±203	ab	4188	±188	a	3769	±177	ab
	25	3536	±183	a	3490	±203	bc	3832	±188	ab	3662	±177	bc
	50	2846	±183	bc	3169	±203	cd	3620	±188	bc	3020	±177	de
	100	3046	±183	ab	2791	±203	de	3550	±188	bc	3416	±177	bcd
	150	2610	±183	bcd	2709	±203	de	3303	±188	cd	2849	±217	ef
	200	2315	±183	ed	2429	±203	ef	2927	±205	de	2849	±177	ef
	250	2412	±183	cde	2217	±203	f	2581	±188	e	3214	±177	cde
	300	2109	±183	e	1967	±203	f	2377	±188	e	2508	±177	f
R1	0	3271	±148	a	4398	±165	a	4465	±239	a	4575	±209	a
	10	3233	±148	a	4070	±165	ab	4297	±239	a	4168	±209	ab
	25	2959	±148	a	3745	±165	bc	4327	±239	a	3816	±233	bc
	50	2486	±148	b	3573	±197	cd	3283	±239	bc	3269	±209	cd
	100	1972	±148	c	3163	±165	d	3565	±239	b	3061	±209	d
	150	1673	±162	cd	2664	±165	e	2990	±239	bc	3271	±191	cd
	200	1383	±148	d	2398	±165	ef	2750	±239	c	3039	±191	d
	250	1446	±148	d	2199	±165	f	2700	±239	c	3111	±191	d
	300	1494	±148	d	1985	±165	f	2014	±239	d	2472	±191	e

Table 2.5. Mean ± standard error of residual dicamba concentrations in harvested soybean in response to dicamba exposure (0,150,300 ppm) (ppm=parts per million). Experiments were carried out at two locations in both 2018 and 2019 in central Missouri. Dicamba concentrations were selected as a representative subset of all treatment concentrations applied. Means with the same letter are not significantly different when separated by Scheffe protected LSD at p≤0.05.

Dicamba treatment (ppm)	**Residual dicamba (mg kg^{-1})**		
0	0	±0.07	a
150	0.72	±0.06	b
300	0.81	±0.06	b

Table 2.6. Mean ± standard error of residual dicamba concentrations in harvested soybean in response to dicamba exposure at two growth stages (V3 and R1). Experiments were conducted over three sites and with three treatments (0,150,300 ppm) (ppm=parts per million) over two years. Means with the same letter are not significantly different when separated by Scheffe protected LSD at p≤0.05.

Timing	**Residual dicamba (mg kg^{-1})**	
V3	0.50	±0.49
R1	0.57	±0.06

Table 2.7. Mean ± standard error of residual dicamba concentrations in harvested soybean in response to dicamba exposure at three sites averaged over three treatments (0,150,300 ppm) (ppm=parts per million) over two years. Means with the same letter are not significantly different when separated by Scheffe protected LSD at $p \leq 0.05$.

Site	**Residual dicamba ($mg\ kg^{-1}$)**		
Bradford (2018)	0.70	±0.76	a
Boonville (2018)	0.35	±0.79	b
Bradford (2019)	0.54	±0.76	ab

Table 2.8. Weekly rainfall (cm) following R1 dicamba application (WAA= weeks after application) at three field sites.

WAA	**Rainfall (cm)**		
	Bradford (2018)	Boonville (2018)	Bradford (2019)
1	4.0	0.0	4.1
2	0.4	0.1	2.9
3	0.0	2.2	0.3
4	0.1	1.5	2.7
5	2.1	0.0	0.3
6	1.4	0.5	4.1
7	5.7	3.8	3.9
8	1.7	1.0	1.9
9	0.0	4.5	0.0
10	0.3	9.9	1.2
11	0.3	0.0	2.0
12	8.4	0.5	0.4
13	4.4	0.8	3.5

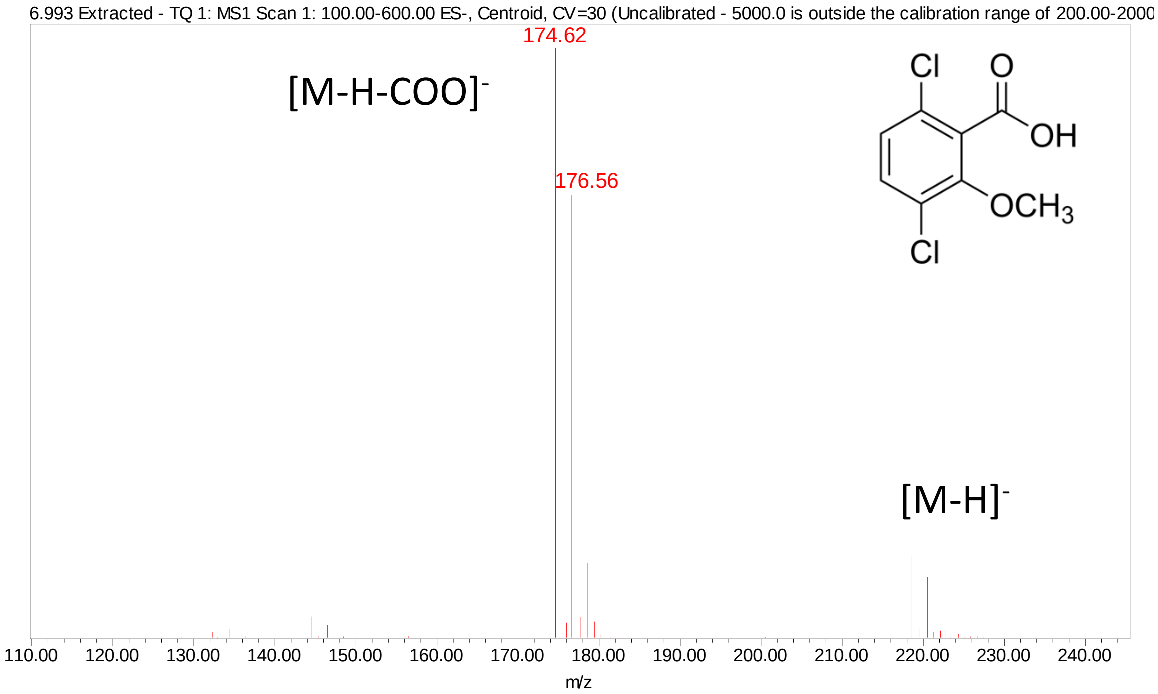

Figure 2.1. Full scan mass spectra of dicamba.

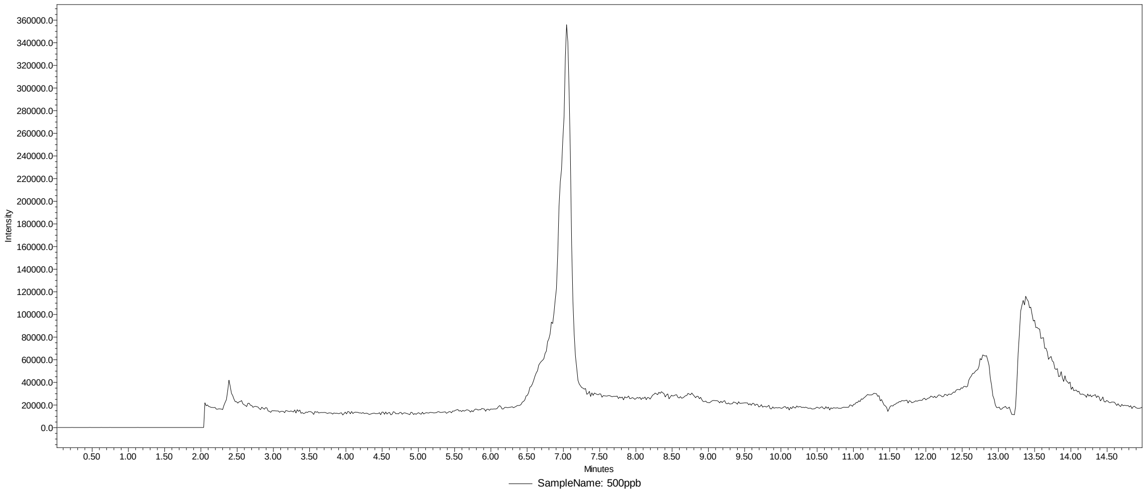

Figure 2.2. Ion chromatogram of dicamba m/z 174.72 [M-H-COO]$^-$.

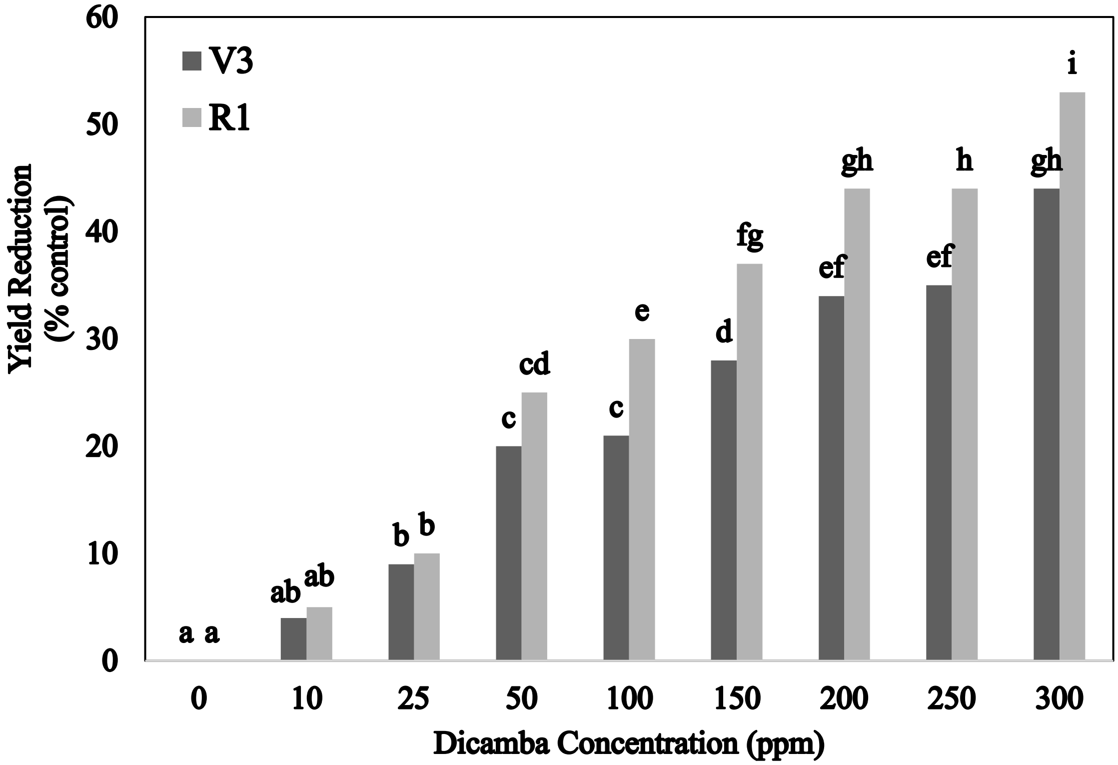

Figure 2.3. Mean soybean yield reductions (%) in response to dicamba (ppm=parts per million) exposure. Experiments were carried out at two locations in both 2018 and 2019 in central Missouri. Means with the same letter were not significantly different when separated by LS means when p≤0.05.

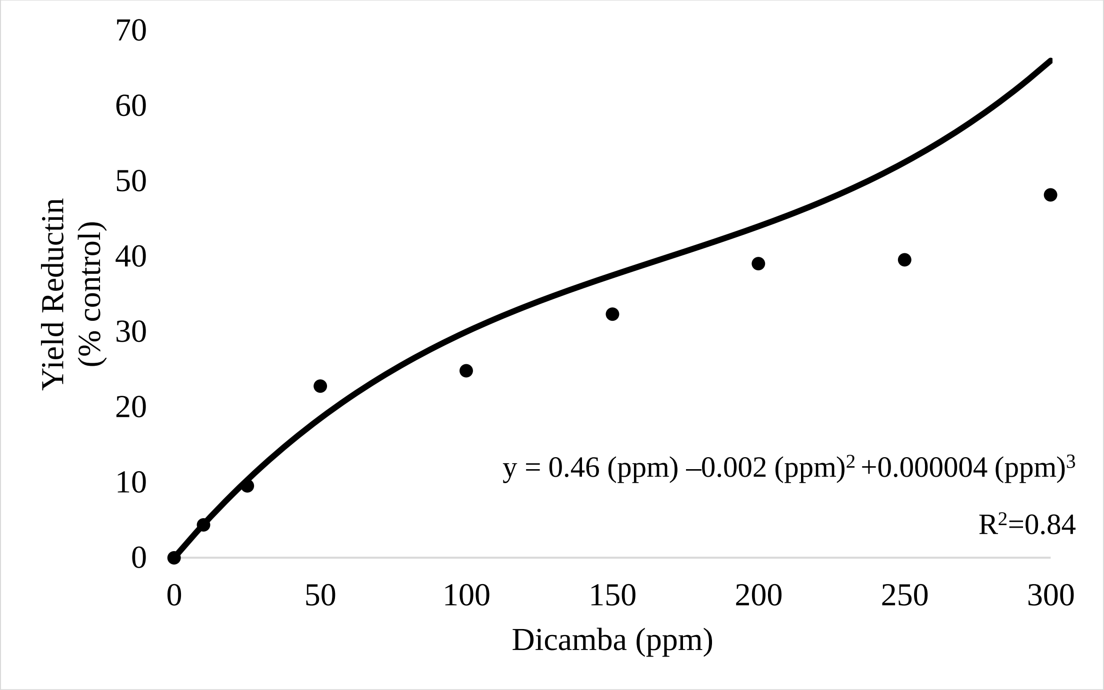

Figure 2.4. Soybean yield reduction curve (% based on untreated control) in response to dicamba concentrations (ppm=parts per million) averaged over all developmental growth stages.

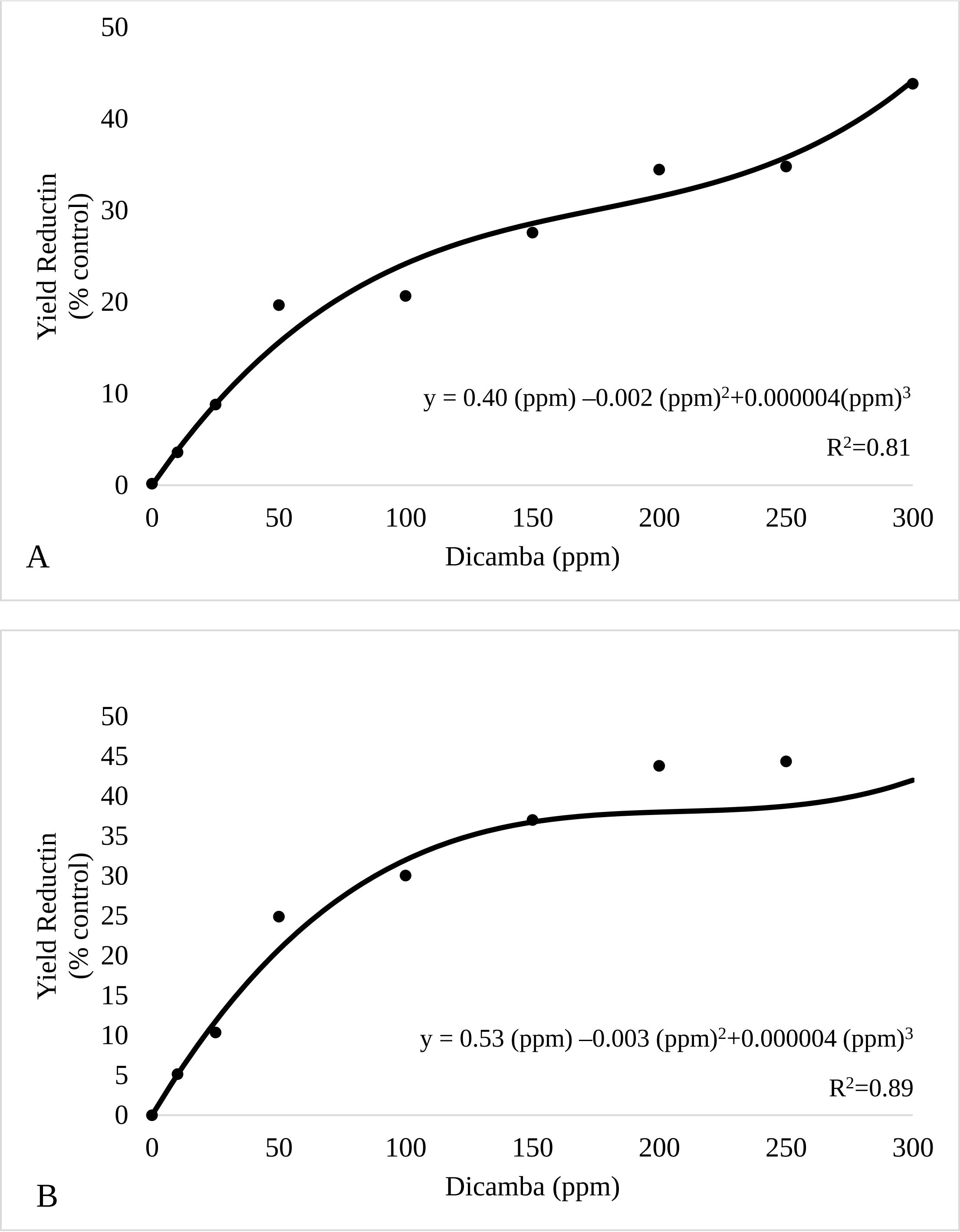

Figure 2.5. Soybean yield reduction curve (% based on untreated control) in response to dicamba concentrations (ppm=parts per million) for soybeans exposed at V3 (A) and R1 (B).

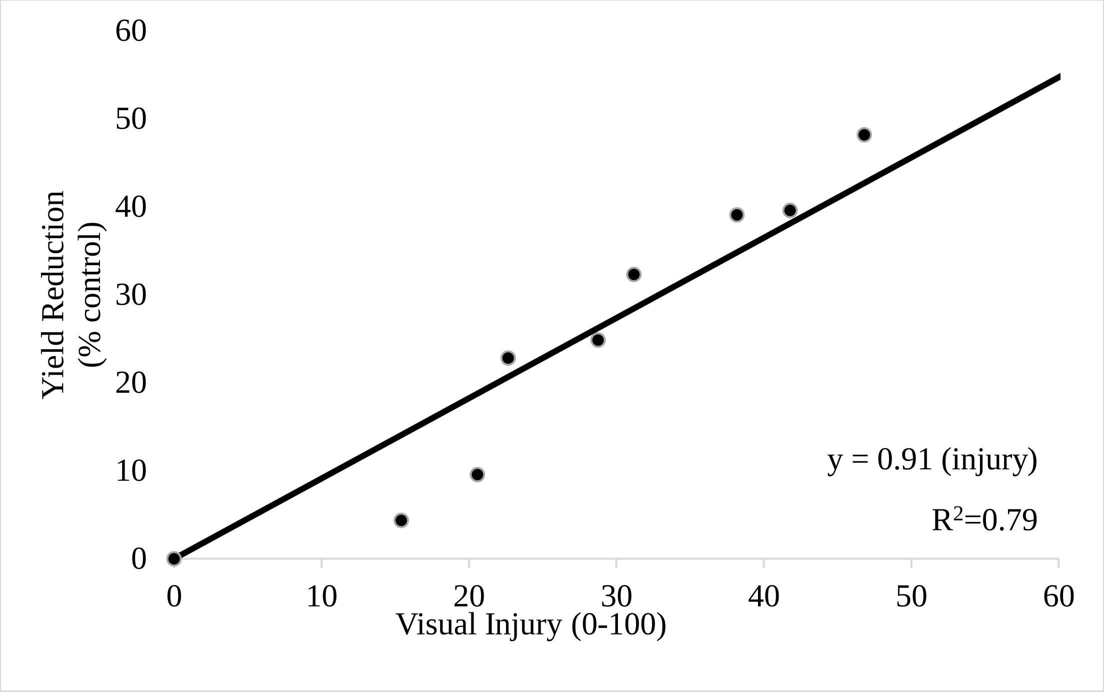

Figure 2.6. Soybean yield reduction curve (% based on untreated control) in relation to visual injury ratings (0= no injury; 100= plant death) averaged over all developmental growth stages.

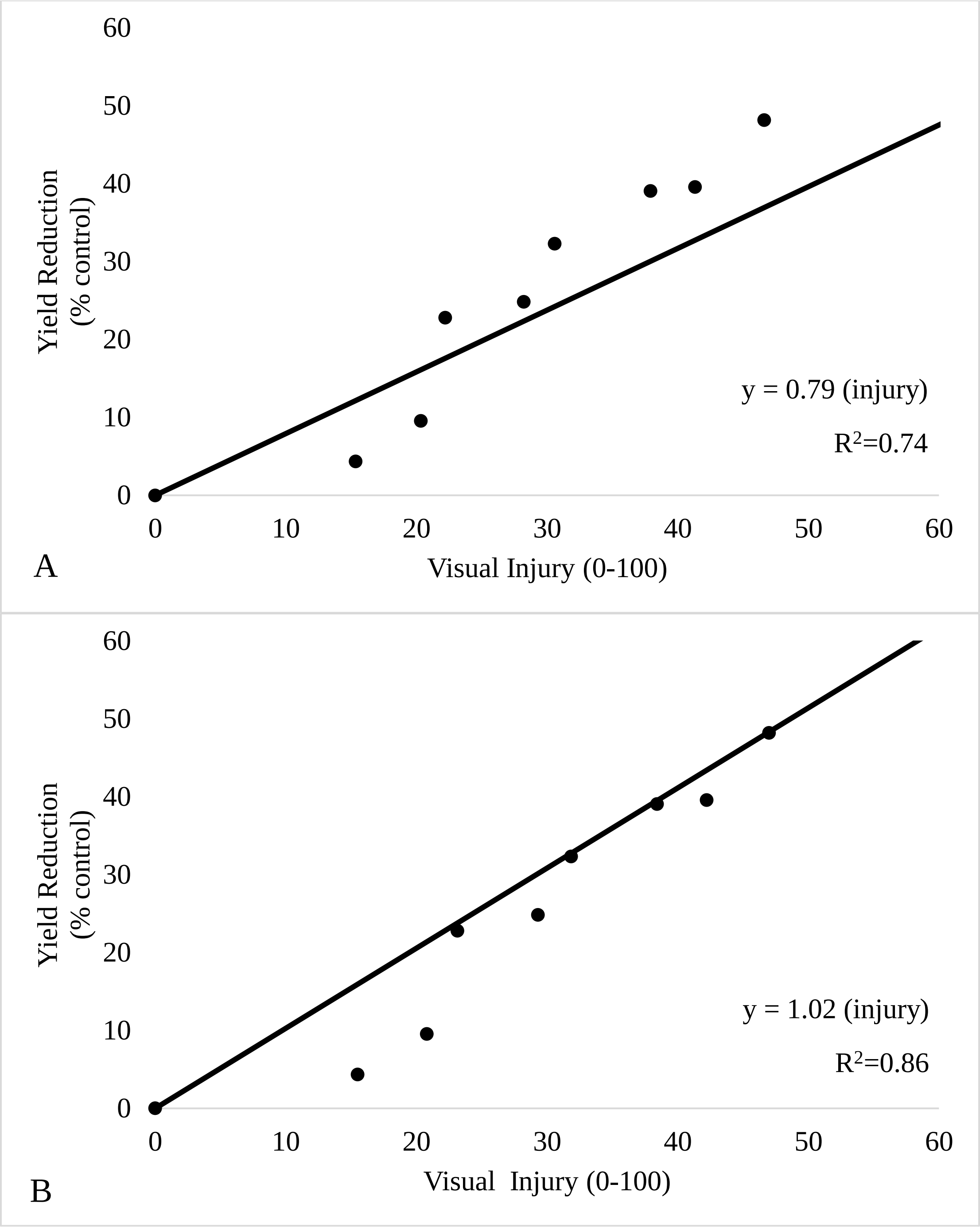

Figure 2.7. Soybean yield reduction curve (% based on untreated control) in relation to visual injury ratings (0= no injury; 100= plant death) for soybeans exposed at V3 (A) and R1 (B).

Chapter 3: Dew Increases Volatility of Dicamba from Soybean Leaves

Abstract

Widespread use of dicamba on tolerant soybeans (*Glycine max* L.) since 2017 has resulted in reports of off-target movement. The underlying cause in some cases has been attributed to weather related phenomena such as temperature inversions. However, inversions often accompany dew formation, and the potential role of dew in facilitating dicamba movement has not been reported. The objective of this controlled environment study was to determine if dew formed on dicamba treated soybeans increased volatility. Soybeans were treated with dicamba and herbicide solutions were allowed to dry. Some soybean plants were then placed directly into an air-tight polyethylene box connected to an air sampler and associated PUF tubes. For other soybean plants, dew was formed under humid conditions and plants were then moved to a sealed box. Volatiles were collected for 48 hr after treatment (HAT), replacing the polyurethane foam (PUF) tube every 24 hr. Dicamba was extracted using methanol and quantified by high-performance liquid chromatography with tandem mass spectrometry (HPLC-MS/MS). Dicamba concentrations found in air samples averaged 20% higher for soybeans with than without dew. The 20% greater dicamba volatilization occurred up to 48 HAT. Formation and evaporation of dew following a dicamba application may play an important role in increased dicamba volatility from soybean leaves.

Keywords: Environment**,** *Glycine max.* dew, volatility, off-target movement

Introduction

Since 1996, heavy reliance on glyphosate for weed management in glyphosate-tolerant (GT) crops has contributed to the selection of glyphosate-resistant (GR) weed species (Heap 2020). Management of 27 known GR weed species has increased herbicide costs up to $86.50 per hectare (Nandula 2010). With over 85% of soybean fields being planted in GT varieties (Dill 2005, Perry et al. 2016), soybean producers have limited herbicide options to control GR weeds. Release of dicamba-tolerant (DT) soybeans [*Glycine Max* (L.) Merr.] in 2016 provided an effective management tool for combating GR weeds.

Upon introduction, adoption of DT-soybeans was rapid and widespread, with up to 43% of U.S. soybean production areas planted with tolerant varieties by 2018 (Wechsler et al. 2019). Many DT varieties were often located in fields adjacent to sensitive soybean varieties as well as other sensitive crops. Although dicamba was first commercially developed in the 1950's, new formulations (XtendiMax™ with VaporGrip, Engenia®, FeXapan™) were approved strictly for use on DT soybeans. DT technologies proved to be an effective tool for controlling GR weed species, so DT soybeans and the use of dicamba POST were rapidly adopted.

Increased applications of dicamba brought concerns about potential damage to adjacent, sensitive crops. Dicamba is lethal to broadleaf plants, such as soybeans and cotton (*Gossypium hirsutum* L.), by mimicking the functions of the hormone indole acetic acid (IAA) (Christoffoleti et al. 2015, Do-Thanh et al. 2016, Grossmann 2010). In the first year of using the DT technology, Bradley (2017) reported in excess of 2,700 cases of off-target movement (Bradley 2017), affecting over 1.45 million hectares nation-wide.

Several factors contribute to off-target movement of dicamba. This includes sprayer tank contamination (Cundiff et al. 2017, Luke et al. 2017, Soltani et al. 2016, Steckel and Thompson 2005), spray drift (Guilherme et al. 2017, Hanks 1995, Wolf et al. 2012), and vapor drift (Behrens and Lueschen 1979, Mueller et al. 2013).

Spray drift is a function of both droplet size and wind. Dicamba drift is reduced with the use of appropriate nozzles, such as air induction nozzles, which decrease incidences of small droplets (Bird et al. 1996). Coarse droplets are effective at mitigating drift (Celen 2010). Guilherme et al. (2017) showed that generation of larger droplets reduced drift of dicamba up to 24-fold compared to traditional nozzle tips.

Dicamba is a volatile compound (4.5×10^{-3} mm Hg), and new formulations for DT crops were developed to address volatility. Using field conditions, Mueller et al. (2013) found that older formulations of dicamba, including the DMA salt (Banvel®) and diglycolamine (DGA) salt (Clarity®) were 2-fold more volatile than newer formulations. Under lab conditions, dicamba volatility with a new formulation (Xtendimax with VaproGrip) was reduced by 5505 and 97% compared to older formulations, Banvel and Clarity, respectively (Gavlick et al. 2016).Vapor drift of dicamba is strongly affected by environmental factors such as air temperature. Numerous studies have documented higher vapor concentrations of dicamba with increased air temperatures (Miller and Tuck 2005, Mueller and Steckel 2019a, Ouse et al. 2018). Burnside and Lavy (1966) found that soybeans yielded up to 50% of the dry weight of untreated soybeans when exposed to 1/8 ppm dicamba at 32˚C ambient temperature, as compared to 75% of the dry weight of untreated soybeans when exposed to 1/8 ppm dicamba at 21 C. Mueller and Steckel (2019) quantified <5% dicamba volatiles when applications were made at 15 C compared to 30 C. Both Mortensen et al. (2012) as well as Behrens and Lueschen (1979) reported reduced dicamba vapors at lower air temperatures. Additionally, Behrens and Lueschen (1979) noted reduced dicamba vapors at higher relative humidity. Therefore, current recommendations for reducing vapor drift include avoiding application during periods of high temperature and low relative humidity(Burnside and Lavy 1966, Mortensen et al. 2012, Ouse et al. 2018).

Because air temperatures and wind are frequently lower around sunrise and sunset, growers avoid herbicide applications in the middle of the day. However, environmental conditions known to increase dicamba volatility can occur early and late in the day, often due to the formation of temperature inversions. A temperature inversion is a naturally occurring phenomenon, characterized by stable air masses, cooler air near the earth’s surface and a layer of warmer air trapped above (Enz et al. 2017). Inversions are often formed close to sunset and sunrise, and are typically characterized by the presence of dew (Bish and Bradley 2017). The air stability caused by inversions poses an increased risk for the suspension of fine particles in the air as applicators apply agrochemicals. As the temperature inversion dissipates, fine particles freely flow with the wind and descend. While the dissipation of a temperature inversion may facilitate the movement of fine particles, the environmental conditions present during an inversion influence the conversion of dicamba to a gaseous form, enabling vapor drift (Enz et al. 2017).

The link of increased dicamba volatility with temperature inversions under field conditions was made by Farrell et al. (2018). Using air samplers, they measured airborne dicamba particles as long as 16 to 24 HAT, under conditions when temperature inversions were present. This confirmed previous research suggesting environmental conditions present during a temperature inversion could exacerbate volatilization of dicamba (Foster 2018). An increase in volatilization in an inversion can create a concentration of fine, gaseous dicamba particles that will be moved off-target when the temperature inversion dissipates.

Dew is an indicator for temperature inversions (Bish and Bradley 2017, Enz et al. 2017, Farrell et al. 2018); however, the formation and persistence of dew has yet to be studied as it relates to dicamba volatility. Dew forms on a surface when the temperature drops below the dew-point (Agam and Berliner 2006), and is dictated by the leaf microclimate boundary layer (Sutton 1953). This boundary layer for soybean differs from other plants; having a broad leaf area, heavily ridged surfaces, and adaxial trichomes that are optimum for dew formation (Vogel 1970). Therefore, soybean leaf characteristics escalate diurnal radiative cooling and dew formation when exposed to the cool, humid air masses present during a temperature inversion.

Currently, environmental factors contribute to dicamba volatility, but the specific underlying cause remains unknown. Dew formation and dissipation is a frequent and naturally occurring event, and likely acts as a humectant on the plant leaf surface. We question the impact dew may be having on dicamba present on a soybean leaf after application. The objective of this research was to determine if the formation and evaporation of dew on dicamba treated DT soybeans can influence the volatilization of dicamba.

Materials and Methods

Soybeans tolerant to both dicamba and glyphosate were grown in 15 cm pots in a Promix™: sand mixture (80:20 by wt), in greenhouse conditions and watered, as needed, up to the V3 growth stage. Pots were thinned to 4 soybean plants per pot and sprayed with 0.54 kg ai ha^{-1} dicamba (XtendiMax™ with VaporGrip Technology) using an air driven greenhouse sprayer coupled with a single TeeJet 8001EVS (TeeJet Technologies, Springfield, IL, USA) nozzle tip (56.775 L ha$^{-1)}$. Soybean leaves were allowed to air dry and transported to a separate location to prevent contamination from small aerosol particles. In a controlled environment chamber, two 0.66 m^3 plexiglass boxes with removable front panels were used to simulate a microclimate that could mimic typical field conditions during the soybean growing season. Two holes (2.2 cm) were cut into the opposite sides of the plexiglass boxes; one for air intake and one for insertion of a glass air sampling tube (22 by 100mm) (SKC Inc., Eighty-Four, PA, USA). The air intake hole was covered with a 3M (60926) multi-gas, vapor cartridge, filter, P100 (3M Science, St. Paul, MN, USA) to prevent vapor contamination between boxes. The boxes were situated inside a growth chamber (GC1) and programmed for a 16:8 day: night cycle (06:00-22:00), low (approximately 200 µmol m^{-2} s^{-1}) light intensity, and 29 and 23.9 C day and nighttime temperatures, respectively

One set of four pots was placed inside one plexiglass box and sealed air tight The glass air sampling tube, containing one polyurethane foam (PUF) sorbent tube (SKC Inc., Cleveland, OH, USA), was inserted in one hole of the plexiglass box and connected to a previously calibrated SKC AirChek TOUCH (SKC Inc., Cleveland, OH, USA) set to pump 2 L per minute for 48 hr via flexible airline tubing (SKC Inc.) covered with gray insulation tubing. An additional four pots were placed in a separate Plexiglas box, without front panel, located in a separate growth chamber (GC2). GC2 was programmed to approximately 98% relative humidity, and 28 C with plants in darkness. Prior to closing GC2, a light spray of deionized water (~5 mL) was applied as a mist to the soybean plants. Previous research had determined this method facilitated the formation of dew on leaf surfaces. Pots were left in GC2 for 3 hr, then were moved directly to a separate plexiglass box in GC1 and treated as previously described.

The PUF tubes were changed every 24 hr, up to 48 hr, from each box based on the time SKC pumps were started. The PUF tubes were stored in a freezer until extraction. HPLC grade methanol (20 mL) was used to extract dicamba from PUF tubes following methods as described in Gavlick et al. (2016). Aliquots of sample solution (1.5 mL) were filtered through Whatman Anotop 0.2 µM membranous filters. Technical replications (3) were taken from each PUF tube extraction and mean dicamba concentrations were generated.

Dicamba concentrations, in solution, were quantified with a Waters Alliance 2695 High Performance Liquid Chromatography (HPLC) system coupled with Waters Acquity TQ triple quadrupole mass spectrometer (MS/MS). Dicamba standards were dissolved in HPLC grade methanol (Sigma-Aldrich, Merck, Darmstadt, Germany). Standard dicamba concentrations were 10, 50, 100, 500, 1000, 1000, and 2,5000 parts per billion were purchased (Sigma-Aldrich, Merck, Darmstadt, Germany) and used to generate standard curves and calibration equations for the quantification of dicamba. The compounds were chromatographically separated by a Phenomenex (Torrance, CA, USA) Kinetex C18 (100 mm by 4.6 mm; 2.6 µm particle size) reverse-phase analytical column. The mobile phase consisted of 10 mM ammonium acetate and 0.1% formic acid in water (A) and 100% acetonitrile (B). The gradient conditions were 0 to 0.5 min, 2% B; 0.5 to 7.0 min, 2 to 80% B; 7.0 – 9.0 min, 80 to 98% B; 9.0 to 10.0 min, 2% B; 10.0 to 15.0 min, 2% B at a flow rate of 0.5 mL/min. The system was operated with electrospray ionization (ESI) in the negative ion mode with capillary voltage of 1.5 kV. The ionization source was programmed at 150°C and the desolvation temperature was programmed at 450°C. The MS/MS system was operated in the single ion recording (SIR) mode, and the full spectrum of the deprotonated molecular ion [M - H]- and the spectrum of fragmented product ions were determined by injecting 20 µL of a standard solution containing 1000 µg L^{-1} of the analytical standards ionized by electrospray ionization in negative ion mode (ES^-, Figures 3.1 and 3.2). The ionization energy, SIR transition ions, capillary and cone voltage, desolvation gas flow and collision energy were optimized by Waters IntelliStart™ optimization software package. Analytical data were processed using Waters Empower 3 software (Waters, CA, USA). The ions m/z 174.72 $[M\text{-}H\text{-}COO]^-$ and 177.62 $[Md3\text{-}H\text{-}COO]^-$ were used for the quantification of dicamba and dicamba-d3 PESTANAL®, respectively (Figure 3.3). Experimental methods and extraction techniques were validated using dicamba-d3 PESTANAL isotopic standards and methods as described above. Spike solutions (0.5 mL of 50 ppm v/v stock solution) were added to a new, clean PUF tube, subjected to 24-hr air sampling methods, stored, extracted, and quantified as previously described.

This experiment was conducted using a split-plot design, with treatment and time being the main and sub-plot, respectively. Dew and timing treatments were considered fixed variables, whereas replications within treatments were considered random.

Experimental replicates (5) were conducted across time, on November 8 and 15, 2017, January 25 and 31, 2018, and February 1 and 13, 2018. A general linear mixed model (GLIMMIX) was used to test for statistical significance of treatments as well as interaction between dew and timing treatment in SAS version 9.4 (SAS Inc., Cary, North Carolina, USA). Means were separated with p|diff lines when $p \leq 0.05$.

Results and Discussion

Dicamba d-3 PESTANAL was used to determine the extraction efficiency of the experimental methods. Analysis of spiked PUF tubes (dicamba d-3 PESTANAL) indicated a 94% extraction efficiency (data not shown). Recovery rates fell within the accepted range from 88 to 106% of the dicamba applied (Mueller et al. 2013); therefore, data were not adjusted for extraction efficiencies.

In the initial 24 h period following placement of dicamba-treated soybeans in plexiglass boxes, dicamba volatility increased by 20% ($p>0.0178$) for soybeans with dew formed versus dry leaves (Figure 3.4). Dicamba concentrations in air samples, due to volatility, averaged 840.0 and 669.5 ng 24 hr^{-1}. Volatility of dicamba continued at the same rate for both dew-covered and dry leaves ($p>0.6331$) (Figure 3.5); however, dicamba volatility continued at a 20% higher rate for the soybeans with dew formed versus dry leaves up to 48 hr. These findings support previous work where dew acts as a natural humectant (Marth et al. 1945) and dew rewets the soybean leaf, lengthens the dry time of the dicamba deposit (Marth et al. 2018, Ramsey et al. 2005), and leads to an increase in dicamba volatility.

There was no interaction between the main and sub plot factors, formation of dew and the passage of time since dew formation ($p>0.6224$) (Figure 3.6). Therefore, dew formation and the passage of time are independent factors and changes in volatility are exclusively linked to those factors and not an interaction.

Reports of dicamba volatility under controlled and field conditions are not new (Behrens and Lueschen 1979, Burnside and Lavy 1966, Long 2017, Mueller et al. 2013, Mueller and Steckel 2019a, 2019b, Sciumbato et al. 2004, Solomon and Bradley 2014).

Recent studies (Bish et al. 2019, Cundiff et al. 2017, Ester et al. 2010, Long 2017, Mueller and Steckel 2019b) have focused on identify potential sources of off-target dicamba. These studies found that formulation type, ambient temperature, humidity, solution pH, and tank mix additives can influence dicamba volatility.

In this study, dicamba volatility differed based upon the presence or absence of dew and dicamba concentrations quantified over a 24 hr period were like those reported by Long (2017). However, soybeans with dew formed did not have decreased dicamba volatility after the first 24 hr like the dry soybeans did nor field studies from Behrens and Lueschen (1979), Mueller et al. (2013), Farrell et al (2018), but volatility remained consistent between 24 and 48 hr, after the formation of dew. Furthermore, this study would suggest that dew extends the time of greatest dicamba volatility from soybean leaves following a dicamba application.

While the present research was conducted in a controlled setting, dew is relevant to soybeans in a field setting. The frequency of dew occurrences varies upon location (Gałek et al. 2015, Kabela et al. 2009, Madeira et al. 2002), however, Kabela et al. (2009) reported dew presence in soybean fields in Iowa approximately 80% of the observed days in the growing season (Kabela et al. 2009).

Dew may influence dicamba volatility by increasing the time dicamba is suspended in a solution on the leaf surface. Dew is a natural humectant (Marth et al. 2018) that increases the time herbicides are available for plant uptake (Rice 1948). Humectants can be added to herbicide solutions to increase efficacy (Babiker and Duncan 1975, Holly 1956, Hughes 1968), promote cuticular penetration (Holly 1956, Hughes and Freed 1961, Sargent 1965), and lengthen herbicide dry time. Herbicide penetration across the leaf cuticle ceases once the carrier droplet has dried (Holly 1956, Knoche and Petracek 2014, Sharma and Born 1970), but in the presence of dew auxin herbicides, like dicamba, are suspended in a solution longer. Dew forms more than 50% of the time in soybeans throughout the growing season (Kabela et al. 2009) causing the leaves to be repeatedly rewetted, thus increasing the mobility of the residual herbicide on the leaf for penetration (Knoche and Petracek 2014, Sharma and Born 1970), but also subjecting the herbicide to interactions between the leaf surface and adverse environmental conditions for a longer period of time (Marth et al. 2018, Ramsey et al. 2005). Additionally, dew contains many mineral cations that can alter the absorption or penetration of an herbicide into a plant leaf. The chemical composition and concentration of cations in deposited dew varies depending on geographical location (Beysens et al. 2019, Gałek et al. 2015, Jiries 2001, Lekouch et al. 2010, Nath and Yadav 2018, Xu et al. 2015), but consistently contain concentrations of Ca^{2+}, Na^{+}, NH_4^{+}, K^{+}, $Mg^{2+,}$ and H^{+}; as well as trace mineral concentrations of Fe and Cu (Beysens et al. 2019, Lakhani et al. 2012). Both Ca^{2+} and Fe^{3+} appear antagonistic to the penetration of other herbicides, such as glyphosate (Buhler and Burnside 1983, Gauvrit 2003, Hall et al. 2000, Thelen et al. 2020); whereas, Fe^{3+} and Cu^{2+} can completely inhibit leaf penetration of auxin herbicides (Szabo and Buchholtz 1961). In addition, dew stimulates leaching of mineral nutrients from within the plant tissue (Hall et al. 2000, Morgan and Tukey Jr. 1964, Tukey 1970), including Ca and Fe, increasing the concentration of minerals on the leaf surface. This would suggest that mineral concentrations found in naturally forming dew could be antagonistic to the absorption of dicamba into soybean leaves. Because the deposition of dew from the atmosphere and leaching of minerals stimulated by dew both deposit ions Fe and Cu onto the leaf surface, the increasing concentrations of these minerals could further inhibit dicamba penetrations across the leaf cuticle and residual dicamba on the leaf surface would remain exposed to the environment.

Conditions that favor dew formation are also known indicators of temperature inversions. Calm winds, cooling temperatures, and clear skies are well-known indicators of dew and temperature inversion. Additionally, dew is noted to be a tell-tale indicator that a temperature inversion is present (Bish and Bradley 2017, Enz et al. 2017). Interestingly, Farrell et al. (2018) noted that the time of day with the greatest dicamba volatility was during a temperature inversion and observed the highest concentrations of dicamba volatiles (17.834 ng dicamba m^{-3}) were lost during the time frame of the greatest dew accumulation (Kabela et al. 2009). While inversions may suspend small droplets containing dicamba, the rewetting of the plant surface and evaporation of dew contributes to the increase in dicamba volatility. Therefore, this would suggest that dew is the main contributor to increased volatilization of dicamba, whereas temperature inversions are the mechanism of dicamba volatile disbursement.

The reason for increase volatilization due to dicamba interactions with dew is still not understood. This study found that dew can be a contributor to volatility of dicamba, but because dew can occur on consecutive days, rewetting event may contribute to several periods for volatility in the days following dicamba applications. This research is the first report of dew formation and dissipation as a contributing factor to dicamba volatilization. It was surprising that greater volatilization extended beyond the drying period of dew. Additional research is needed to examine the influence of dew on dicamba lying on the plant leaf surface as well as mineral ions that may be leached from leaves and interact with dicamba.

Literature Cited

Agam N, Berliner PR (2006) Dew formation and water vapor adsorption in semi-arid environments - A review. J Arid Environ 65:572–590

AGCO (2020) Weed control efficacy. https://www.croplife.com/iron/sprayers/sprayer-setup-best-practices-maximize-weed-control-efficacy/

Ahmadi MS, Haderlie LC, Wicks GA (1980) Effect of growth stage and water stress on barnyardgrass (*Echinochloa crus-galli*) control and on glyphosate absorption and translocation. Weed Sci 28:277–282

Akey WC, Morrison IN (1983) Effect of moisture stress on wild oat (*Avena fatua*) response to diclofop. Weed Sci 31:247–253

Anastassiades M, Lehotay SJ, Stajnbaher D, Schenck FJ (2003) Fast and easy multiresidue method employing acetonitrile extraction/partitioning and “dispersive solid-phase extraction” for the determination of pesticide residues in produce. J AOAC Int 86:412–431

Anonymous (2010) Clarity label. Research Triangle, NC: BASF Corporation

Anonymous (2019a) Engenia herbicide product label. Research Triangle, NC: BASF Corporation

Anonymous (2019b) XtendiMax with vaporgrip technology herbicide product label. St. Louis, MO: Bayer

Anonymous (2020) FeXapan plus vaporgrip technology herbicide product label. Indianapolis, IN

Auch DE, Arnold WE (1978) Dicamba use and injury on soybeans (*Glycine max*) in South Dakota. Weed Sci 26:471–475

Babiker AGT, Duncan HJ (1975) Penetration of bean leaves by asulam as influenced by adjuvants and humidity. Pestic Sci 6:655–664

Basler E, Todd GW, Meyer RE (1961) Effects of moisture stress on absorption, translocation, & distribution of 2,4-dichlorophenoxyacetic acid in bean plants. Plant Physiol 36:573–576

Behrens MR, Mutlu N, Chakraborty S, Dumitru R, Jiang WZ, Lavallee BJ, Herman PL, Clemente TE, Weeks DP (2007) Dicamba resistance: enlarging and preserving biotechnology-based weed management strategies. Science (80-) 316:1185–1189

Behrens R, Lueschen WE (1979) Dicamba volatility. Weed Sci 27:486–493

Benbrook CM (2016) Trends in glyphosate herbicide use in the United States and globally. Environ Sci Eur 28:1–15

Beysens D, Lekouch I, Mileta M, Milimouk I, Muselli M (2019) Dew and rain collection in South Croatia. Int J Civ Environ Eng 1:64–70

Bird SL, Esterly DM, Perry SG (1996) Off-target deposition of pesticides from agricultural aerial spray applications. J Agric Food Chem 14:585–588

Bish M, Bradley K (2017) Knowing when to spray: monitoring the weather. https://weedscience.missouri.edu/Missouri Weather Analysis_2017.pdf

Bish MD, Farrell ST, Lerch RN, Bradley KW (2019) Dicamba losses to air after applications to soybean under stable and nonstable atmospheric conditions. J Environ Qual 48:1675–1682

Boerboom C (2004) Field case studies of dicamba movement to soybeans. Page *in* Wisconsin Crop Management Conference

Boydston R (1990) Soil water content affects the activity of four herbicides on green

foxtail (*Setaria viridis*). Weed Res 38:578–582

Bradley K (2017) Integrated pest 2017. 1–2 p

Bradley K (2018) July 15 dicamba injury update. different year, same questions:1–2

Broadhurst NA, Montgomery ML, Freed VH (1966) Metabolism of 2-methoxy-3,6-dichlorobenzoic acid (dicamba) by wheat and bluegrass plants. J Agric Food Chem 14:585–588

Browne FB, Li X, Price KJ, Wang J, Wang Y, Kruger GR, Golus J, De Castro Macedo G, Vieira BC, Sandlin T (2020) Dicamba retention in commercial sprayers following triple rinse cleanout procedures, and soybean response to contamination concentrations. Agronomy 10:1–15

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

Burnside OC, Lavy TL (1966) Dissipation of dicamba. Weeds 14:211–214

Celen IH (2010) The effect of spray mix adjuvants on spray drift. Bulg J Agric Sci 16:105–110

Cenkci S, Yildiz M, Ciĝerci IH, Bozdaĝ A, Terzi H, Terzi ESA (2010) Evaluation of 2,4-D and dicamba genotoxicity in bean seedlings using comet and RAPD assays. Ecotoxicol Environ Saf 73:1558–1564

Chang FY, Vanden Born WH (1968) Translocation of dicamba in Canada thistle. Weed Sci 16:176–181

Chang FY, Vanden Born WH (1971) Dicamba uptake, translocation, metabolism, and selectivity. Weed Sci 19:113–117

Christoffoleti PJ, Figueiredo MRA de, Peres LEP, Nissen S, Gaines T (2015) Auxinic

herbicides, mechanisms of action, and weed resistance: a look into recent plant science advances. Sci Agric 72:356–362

Creech CF, Henry RS, Fritz BK, Kruger GR (2014) Influence of herbicide active ingredient, nozzle type, orifice size, spray pressure, and carrier volume rate on spray droplet size characteristics. Weed Sci 62:193–206

Cundiff GT, Reynolds DB, Mueller TC (2017) Evaluation of dicamba persistence among various agricultural hose types and cleanout procedures using soybean (*Glycine max*) as a bio-indicator. Weed Sci 65:305–316

Davis FS, Merkle MG, Bovey RW (1968) Effect of moisture stress on the absorption and transport of herbicides in woody plants. Bot Gaz 129:183–189

Davis J, Barber T, Max C (2015) Tank clean-out recommendations for common herbicides. 1–2 p

Dickson RL, Andrews M, Field RJ, Dickson EL (1990) Effect of water stress, nitrogen, and gibberellic acid on fluazifop and glyphosate activity on oats (Avena sativa). Weed Sci 38:54–61

Dill GM (2005) Glyphosate-resistant crops : history , status and future †. Pest Manag Sci 224:219–224

Dintelmann BR, Warmund MR, Bish MD, Bradley KW (2019) Investigations of the sensitivity of ornamental, fruit, and nut plant species to driftable rates of 2,4-D and dicamba. Weed Technol:1–11

Do-Thanh CL, Vargas JJ, Thomas JW, Armel GR, Best MD (2016) Design, synthesis, and evaluation of novel auxin mimic herbicides. J Agric Food Chem 64:3533–3537

Duke SO (2018) The history and current status of glyphosate. Pest Manag Sci 74:1027–

1034

Duke SO, Powles SB (2008) Glyphosate: a once-in-a-century herbicide. Pest Manag Sci 63:1100–1106

Egan JF, Barlow KM, Mortensen DA (2014a) A meta-analysis on the effects of 2,4-D and dicamba on soybean and cotton. Weed Sci 62:193–206

Egan JF, Barlow KM, Mortensen DA (2014b) A meta-analysis on the effects of 2,4-D and dicamba drift on soybean and cotton. Weed Sci 62:193–206

Environmental Protection Agency (2005) Reregistration eligibility decision (RED) document for nitrapyrin. 1–38 p

Environmental Protection Agency (2018) EPA announces changes to dicamba registration. https://archive.epa.gov/epa/newsreleases/epa-announces-changes-dicamba-registration.html

Environmental Protection Agency (2019) Food and pesticides. https://www.epa.gov/safepestcontrol/food-and-pesticides. Accessed October 25, 2020

Environmental Protection Agency (2020) Dicamba training requirements. https://www.epa.gov/ingredients-used-pesticide-products/dicamba-training-requirements-frequently-asked-questions#components

Enz JW, Hofman V, Thostenson A (2017) Air temperature inversions causes, characteristics, and potential effects on pesticide spray drift. NDSU Ext 1705:1–16

EPA (2010) Index to pesticide chemical names, part 180 tolerance information, and food and feed commodities (by commodity). Environ Prot Agency:1–314

Ester A, Strachan SD, Casini MS, Heldreth KM, Scocas JA, Nissen SJ, Bukun B,

Lindenmayer RB, Shaner DL, Westra P, Ester A, Strachan SD, Casini MS, Heldreth KM, Scocas JA, Nissen SJ, Bukun B, Lindenmayer RB, Shaner DL, Westra P, Brunk G (2010) Vapor movement of synthetic auxin herbicides : Aminocyclopyrachlor-methyl ester, dicamba, and aminopyralid. Weed Sci 58:103–108

Farrell S, Lerch RN, Bish M (2018) Influence of formulations and application time of day on dicamba air concentrations following treatment. Page *in* Proceedings of the 73rd Annual Meeting of the North Central Weed Science Society

Foster MR (2018) Soybean response to dicamba : Associated injury criteria and development of a model to predict yield loss. Louisiana State University

Foster MR, Griffin JL, Copes JT, Blouin DC (2019) Development of a model to predict soybean yield loss from dicamba exposure. Weed Technol 33:287–295

Gałek G, Sobik M, Błaś M, Polkowska Z, Cichała-Kamrowska K, Wałaszek K (2015) Dew and hoarfrost frequency, formation efficiency and chemistry in Wroclaw, Poland. Atmos Res 151:120–129

Gauvrit C (2003) Glyphosate response to calcium, ethoxylated amine surfactant, and ammonium sulfate. Weed Technol 17:799–804

Gavlick WK, Wright DR, MacInnes A, Hemminghaus JW, Webb JK, Yermolenka VI, Su W (2016) A method to determine the relative volatility of auxin herbicide formulations.pdf. Pestic Formul Deliv Syst 35:24–32

Grafstrom LD, Nalewaja JD (1986) Uptake and translocation of fluazifop in green goxtail (*Setaria viridis*). Weed Sci 108:115–123

Griffin JL, Bauerle MJ, Stephenson DO, Miller DK, Boudreaux JM (2013) Soybean

response to dicamba applied at vegetative and reproductive growth stages. Weed Technol 27:696–703

Grossmann K (2010) Auxin herbicides: Current status of mechanism and mode of action. Pest Manag Sci 66:113–120

Guilherme A, Alves S, Kruger GR, Paulo J, Cunha AR, Denise G, Santana D, Pinto LAT (2017) Dicamba spray drift as influenced by wind speed and nozzle type dicamba spray drift as influenced by wind speed and nozzle type. Weed Technol 31:724–731

Hall GJ, Hart CA, Jones CA (2000) Plants as sources of cations antagonistic to glyphosate activity. Pest Manag Sci 56:351–358

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

Hartzler R (2017) Wind speed and herbicide application. https://crops.extension.iastate.edu/cropnews/2017/01/wind-speed-and-herbicide-application

Hartzler R, Hartzler R (2020) 2020 Herbicide guide for Iowa corn and soybean production. Page Iowa State University Extension and Outreach Integrated Crop Management

Hatterman-Valenti H, Owen MD, Christians NE (1995) Comparison of spray drift during postemergence herbicide applications to turfgrass. Weed Technol 9:321–325

Hauser EW (1955) Absorption of 2,4-dichlorophenoxyacetic acid by soybean and corn plants. Agron J 47:32

Heap I (2020) International herbicide-resistant weed database. http://weedscience.org/Home.aspx

Hertel R, Thomson KS, Russo VEA (1972) In-vitro auxin binding to particulate cell fractions from corn coleoptiles. Planta 107:325–340

Hewitt AJ (1993) Droplet size spectra produced by air-assisted atomizers. J Aerosol Sci 24:155–162

Holly K (1956) Penetration of chlorinated phenoxyacetic acid into leaves. Pages 195–199 *in* Annals of Applied Biology

Hughes EE (1968) Hygroscopic additives to phenoxy herbicides for control of saltcedar. Weed Sci 16:486–488

Hughes RE, Freed VH (1961) The role of surfactants in the foliar absorption of indole-3-acetic acid (IAA). Weeds 9:54–59

Hull HM, Davis DG, Stolzenberg GE (1982) Action of adjuvants on plant surfaces. Pages 26–67 *in* Adjuvants for Herbicides. Weed Science Society of America

Jhala A, Knezevic S, Klein RN (2017) Dicamba injury symptoms on sensitive crops

Jiries A (2001) Chemical composition of dew in Amman, Jordan. Atmos Res 57:261–268

Johnson WG, Casady B, Peterson D, Kuhlman D (1997) Cleaning field sprayers to avoid crop injury. MU Extension, Univ Missouri-Columbia

Johnson WG, Hallett SG, Legleiter TR, Whitford F, Weller SC, Bordelon BP, Lerner BR (2012) 2,4-D and dicamba-tolerant crops- some facts to consider. Page Purdue Extension. 1–7 p

Jones GT (2018) Evaluation of dicamba off-target movement and subsequent effects on soybean offspring. University of Arkansas

Jones GT, Norsworthy JK, Barber T, Gbur E, Kruger GR (2019) Off-target movement of DGA and BAPMA dicamba to sensitive soybean. Weed Technol 33:51–65

Kabela ED, Hornbuckle BK, Cosh MH, Anderson MC, Gleason ML (2009) Dew frequency, duration, amount, and distribution in corn and soybean during SMEX05. Agric For Meteorol 149:11–24

Kelley KB, Wax LM, Hager AG, Riechers DE (2005) Soybean response to plant growth regulator herbicides is affected by other postemergence herbicides. Weed Sci 53:101–112

Kidder DW, Behrens R (1988) Plant responses to haloxyfop as influenced by water stress. Weed Sci

Klein RN, Schulze L, Ogg CL (2008) Factors affecting spray drift of pesticides. Crop Soils:19–23

Klevorn TB, Wyse DL (1984) Effect of soil temperature and moisture on glyphosate and photoassimilate distribution in quackgrass (*Agropyron repens*). Weed Sci 32:402–407

Kniss AR (2018a) Genetically engineered herbicide-resistant crops and herbicide-resistant weed evolution in the United States. Weed Sci 66:260–273

Kniss AR (2018b) Soybean response to dicamba: a meta-analysis. Weed Technol 32:507–512

Knoche M, Petracek PD (2014) Foliar uptake of PGRs: barriers, mechanisms, model systems, and factors. Acta Hortic 1042:125–141

Kroin J (2009) Auxins and the pathways for foliar application. 53–59 p

Lakhani A, Parmar RS, Prakash S (2012) Chemical composition of dew resulting from radiative cooling at a semi-arid site in Agra, India. Pure Appl Geophys 169:859–871

Lauridson TC, Wilson RG, Haderlie LC (1983) Effect of moisture stress on Canada

thistle (*Cirsium arvense*) control. Weed Sci 31:674–680

Lehotay SJ, Son KA, Kwon H, Koesukwiwat U, Fu W, Mastovska K, Hoh E, Leepipatpiboon N (2010) Comparison of QuEChERS sample preparation methods for the analysis of pesticide residues in fruits and vegetables. J Chromatogr 1217:2548–2560

Lekouch I, Mileta M, Muselli M, Milimouk-Melnytchouk I, Šojat V, Kabbachi B, Beysens D (2010) Comparative chemical analysis of dew and rain water. Atmos Res 95:224–234

Lin LI-K (1989) A concordance correlation coefficient to evaluate reproducibility. Biometrics 45:255–268

Long J (2017) Infuence of application factors on dicamba volatility. Purdue. 98 p

Long J, Basler E (1973) Some factors regulating auxin translocation in intact bean seedlings. Plant Physiol 51:128–135

Luke AJ, Weirich JW, Smeda RJ (2017) Dicamba residues in spray equipment reduces soybean (*Glycine max*) growth and yield. University of Missouri

Madeira AC, Kim KS, Taylor SE, Gleason ML (2002) A simple cloud-based energy balance model to estimate dew. Agric For Meteorol 111:55–63

Marth PC, Davis FF, Mitchell JW (2018) Herbicidal properties of 2,4-dichlorophenoxyacetic acid applied in dusts containing hygroscopic agents. Bot Gaz 107:129–136

Maybank J, Yoshida K, Grover R (1978) Spray drift from agricultural pesticide applications. J Air Pollut Control Assoc 28:1009–1014

McMullan PM (2000) Utility adjuvants. Weed Technol 14:792–797

McWhorter CG, Jordan TN, Wills GD (1980) Translocation of 14 C-glyphosate in soybeans (Glycine max) and johnsongrass (*Sorghum halepense*). Weed Sci 28:113–118

McWorter CG (1982) The use of adjuvants. Pages 10–25 *in* Adjuvants for Herbicides. Weed Science Society of America

Merkle MG, Davis FS (1967) Effect of moisture stress on absorption and movement of picloram and 2,4,5-T in beans. Weeds 15:10–12

Miller A, Donnie K, Robert G, Roger B, Merritt E, Steve T, Miller DK, Downer RG, Leonard BR, Kelly ST (2003) Response of non-glufosinate-resistant cotton to reduced rates of glufosinate. Weed Sci 51:781–785

Miller PCH, Butler Ellis MC (2000) Effects of formulation on spray nozzle performance for applications from ground-based boom sprayers. Page *in* Crop Protection

Miller PCH, Tuck CR (2005) Factors influencing the performance of spray delivery systems: A review of recent developments. J ASTM Int 2:1–13

Mills MS, Thurman EM (1994) Reduction of nonpoint source contamination of surface water and groundwater by starch encapsulation of herbicides. Environ Sci Technol 28:73–79

Monshausen GB, Gilroy S (2009) Feeling green: mechanosensing in plants. Trends Cell Biol 19:228–235

Morgan J V, Tukey Jr. HB (1964) Characterization of leachate from plant foliage. Plant Physiol 39:590–593

Morrison RG, Lownds NK, Sterling TM (1995) Picloram uptake, translocation, and efficacy in relation to water status of Russian knapweed (*Acroptilon repens*). Weed

Sci 43:34–39

Mortensen DA, Egan JF, Maxwell BD, Ryan MR, Smith RG (2012) Navigating a critical juncture for sustainable weed management. Bioscience 6:75–84

Mueller TC, Steckel LE (2019a) Dicamba volatility in humidomes as affected by temperature and herbicide treatment. Weed Technol 33:1–6

Mueller TC, Steckel LE (2019b) Spray mixture pH as affected by dicamba, glyphosate, and spray additives. Weed Technol 33:547–554

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

Mueller TC, Wright DR, Remund KM (2013) Effect of formulation and application time of day on detecting dicamba in the air under field conditions. Weed Sci 61:586–593

Nandula VK (2010) Glyphosate resistance in crops and weeds: History, development, and management. Page Glyphosate Resistance in Crops and Weeds: History, Development, and Management. 1–33 p

Nath S, Yadav S (2018) A comparative study on fog and dew water chemistry at New Delhi, India. Aerosol Air Qual Res 18:26–36

National Center for Biotechnology Information (2020) PubChem compound summary for CID 3030, dicamba. https://pubchem.ncbi.nlm.nih.gov/compound/Dicamba. Accessed December 11, 2020

Natural Resources Conservation Services (n.d.) Official soil series descriptions. https://soilseries.sc.egov.usda.gov/osdname.aspx. Accessed April 9, 2020

Nordby A, Skuterud R (1974) The effects of boom height, working pressure and wind speed on spray drift. Weed Res 14:385–395

Nuyttens D, Schampheleire M, Steurbaut W, Baetens K (2006) Experimental study of factors influencing the risk of drift from field sprayers, part 2: spray application technique. Asp Appl Biol 77:1–9

Osborne PP, Xu Z, Swanson KD, Walker T, Farmer DK (2015) Dicamba and 2,4-D residues following applicator cleanout: a potential point source to the environment and worker exposure. J Air Waste Manag Assoc 65:1153–1158

Ouse DG, Gifford JM, Schleier J, Simpson DD, Tank HH, Jennings CJ, Annangudi SP, Valverde-Garcia P, Masters RA (2018) A new approach to quantify herbicide volatility. Weed Technol 32:691–697

Pallas, JE, Williams GG (1962) Foliar absorption and translocation of P32 and 2,4-dichlorophenoxyacetic acid as affected by soil-moisture tension. Bot Gaz 123:175–180

Peachey E (2009) Tank cleaners: why and when they work

Peregoy R, Kitchen L, Jordan P, Griffin JL (1990) Moisture stress effects on the absorption, translocation, and metabolism of haloxyfop in johnsongrass (*Sorghum halepense*) and large crabgrass (*Digitaria sanguinalis*). Weed Sci 38:331–337

Perry ED, Ciliberto F, Hennessy DA, Moschini GC (2016) Genetically engineered crops and pesticide use in U.S. maize and soybeans. Sci Adv 2:1–8

Petersen PJ, Haderlie LC, Hoefer RH, McAllister RS (1985) Dicamba absorption and translocation as influenced by formulation and surfactant. Weed Sci 33:717–720

Ramsey RJL, Stephenson GR, Hall JC (2005) A review of the effects of humidity, humectants, and surfactant composition on the absorption and efficacy of highly water-soluble herbicides. Pestic Biochem Physiol 82:162–175

Rayle DL, Cleland R (1970) Enhancement of wall loosening and elongation by acid solutions. Plant Physiol 46:250–253

Rice EL (1948) Absorption and translocation of ammonium 2,4-dichlorophenoxyacetate by bean plants. Bot Gaz 109:301–314

Ross MA, Lembi CA (1999) Applied Weed Science. 3rd ed. Minneapolis, Minnesota: Burgess Pub Co

Sargent JA (1965) The penetration of growth regulators into leaves. Annu Rev Plant Physiol 16:1–12

Sciumbato AS, Chandler JM, Senseman SA, Bovey RW, Smith KL (2004) Determining exposure to auxin-like herbicides. I. quantifying injury to cotton and soybean. Weed Technol 18:1125–1134

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

Sharma MP, Born WH Vanden (1970) Foliar penetration of picloram and 2,4-D in aspen and balsam poplar. Weed Sci 18:57–63

Skelton JJ (2015) Uptake, translocation, and metabolism 2,4-D in enlist crops and control of drought-stressed waterhemp (*Amaranthus tuberculatus*) with 2,4-D and glyphosate. University of Illinois at Urbana-Champaign

Solomon CB, Bradley K (2014) Influence of application timings and sublethal rates of synthetic auxin herbicides on soybean. Weed Technol 28:454–464

Soltani N, Brown L, Sikkema PH (2018) Control of glyphosate-resistant common ragweed in corn with preemergence herbicides. Can J Plant Sci 98:959–962

Soltani N, Nurse RE, Sikkema PH (2016) Response of glyphosate-resistant soybean to

dicamba spray tank contamination during vegetative and reproductive growth stages. Can J Plant Sci 96:160–164

Steckel L, Thompson A (2005) Cleaning plant growth regulator (PGR) herbicides out of field sprayers. UT Extension

Sutton OG (1953) Micrometeorology. Q J R Meteorol Soc:333–335

Szabo SS, Buchholtz KP (1961) Penetration of living and non-living surfaces by 2 ,4-D as influenced by ionic additives. Weeds 9:177–184

Tedeschi LO (2006) Assessment of the adequacy of mathematical models. Agric Syst 89:225–247

Thelen KD, Jackson EP, Penner D (2020) The basis for the hard-water antagonism of glyphosate activity 43:541–548

Tromas A, Paponov I, Perrot-Rechenmann C (2010) Auxin binding protein 1: functional and evolutionary aspects. Trends Plant Sci 15:436–446

Tukey HB (1970) The leaching of substances from plants. Annu Rev Plant Physiol 21:305–324

U.S. FDA (2019) Pesticide residue monitoring program fiscal year 2017 pesticide report:48

United States Department of Agriculture (1967) Suggested guide for weed control

USDA National Organic Program, USDA Science and Technology Programs (2012) Pilot study pesticide residue testing of organic produce. 34 p

Vogel S (1970) Convective cooling at low airspeeds and the shapes of broad leaves. J Exp Bot 21:91–101

Waldecker MA, Wyse DL (1985) Soil moisture effects on glyphosate absorption and

rtanslocation in common milkweed (*Asclepias syriaca*). Weed Sci

Wax LM, Knuth LA, Slife FW (1969) Response of soybeans to 2,4-D, dicamba, and picloram. Weed Sci 17:388–393

Wechsler SJ, Smith D, Mcfadden J, Dodson L, Williamson S (2019) The use of genetically engineered dicamba-tolerant soybean seeds has increased quickly, benefting adopters but damaging crops in some fields. https://www.ers.usda.gov/amber-waves/2019/october/the-use-of-genetically-engineered-dicamba-tolerant-soybean-seeds-has-increased-quickly-benefiting-adopters-but-damaging-crops-in-some-fields/. Accessed April 9, 2020

Weidenhamer JD, Triplett GB, Sobotka FE (1989) Dicamba injury to soybean. Agron J 81:637–643

Whisenant SG, Bouse LF, Crane RA, Bovey RW (1993) Droplet size and spray volume effects on honey mesquite mortality with clopyralid. J Range Manag 46:257

Wolf S, Hématy K, Höfte H (2012) Growth control and cell wall signaling in plants. Annu Rev Plant Biol 63:381–407

Woodward AW, Bartel B (2005) Auxin: regulation, action, and interaction. Ann Bot 95:707–735

Xu Y, Zhu H, Tang J, Lin Y (2015) Chemical compositions of dew and scavenging of particles in Changchun, China. Adv Meteorol:1–11

Young BG (2019) Changes in herbicide use patterns and production practices resulting from glyphosate-resistant crops. Weed Technol 20:301–307

Young BG, Hart SE (1998) Optimizing foliar activity of isoxaflutole on giant foxtail (*Setaria faberi*) with various adjuvants. Weed Sci 46:397–402

Van de Zande JC, Stallinga H, Michielsen JMGP, van Velde P (2004) Effect of sprayer speed on spray drift. Annu Rev Agric Engeneering 4:11

Zimdahl R (2013) Fundamentals of Weed Science. 4th ed. Fort Collins, Colorado: Elsevier. 378–381 p

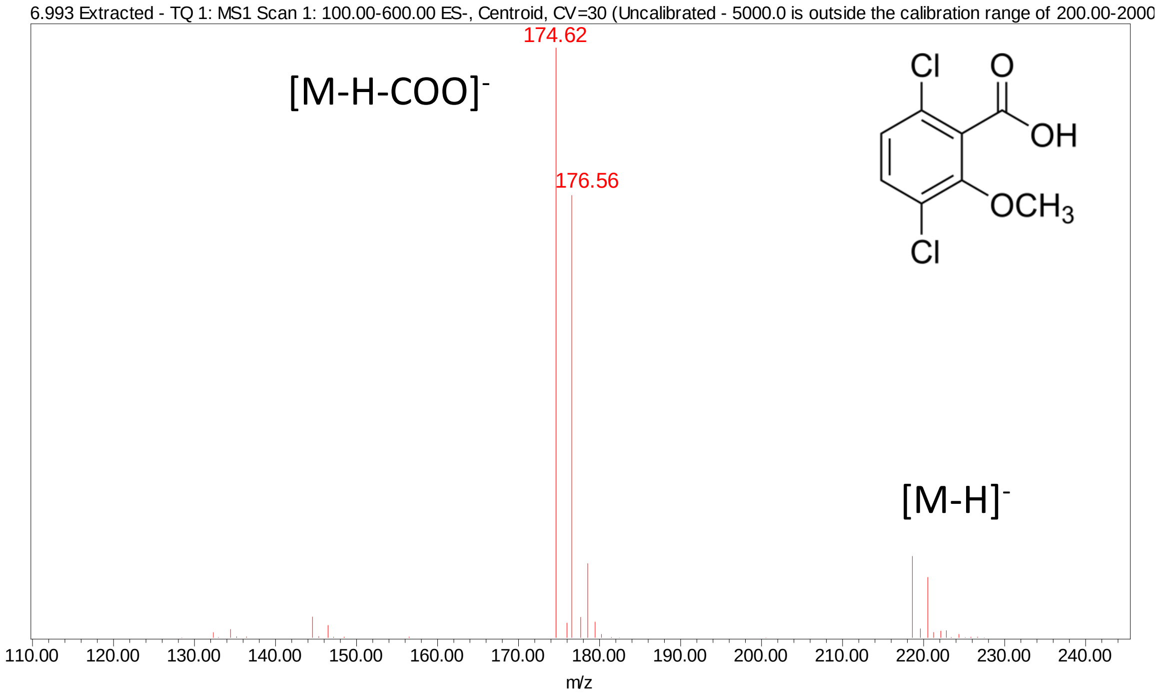

Figure 3.1. Full scan mass spectra of the dicamba.

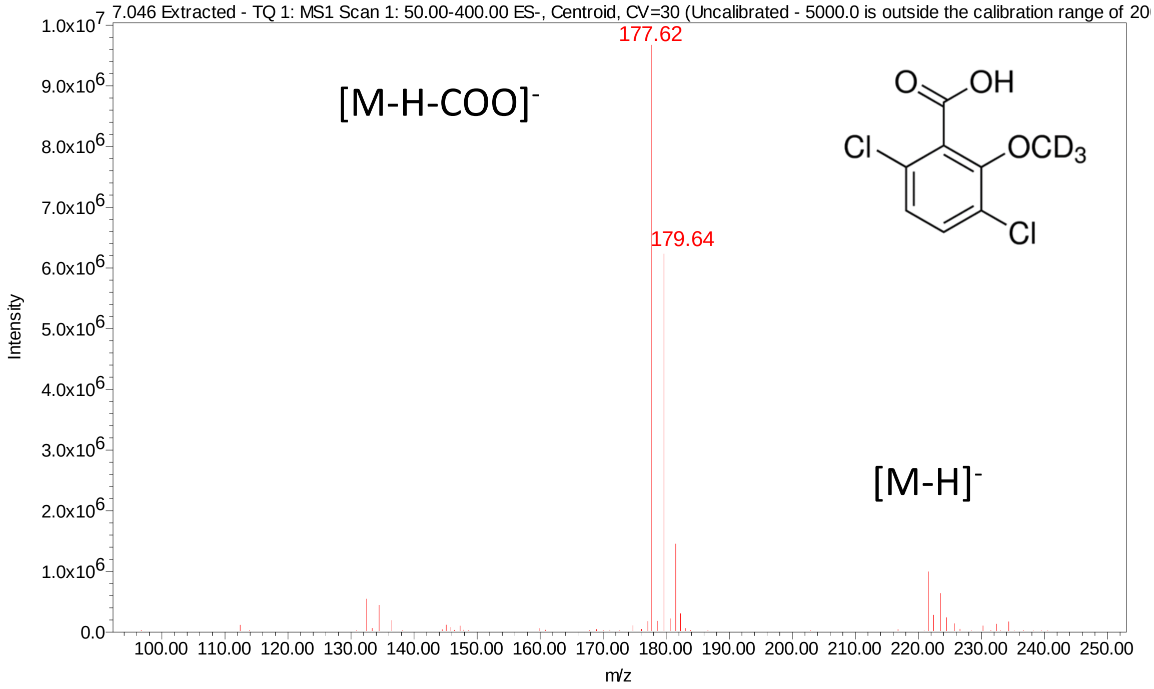

Figure 3.2. Full scan mass spectra of the internal isotopic standard dicamba-d3.

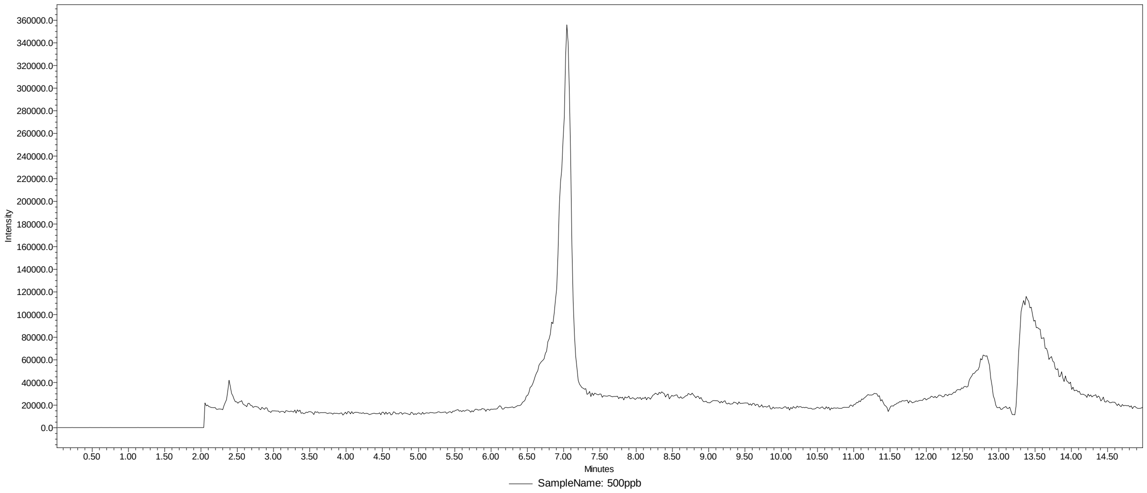

Figure 3.3. Ion chromatogram of the dicamba m/z 174.72 $[M\text{-}H\text{-}COO]^-$.

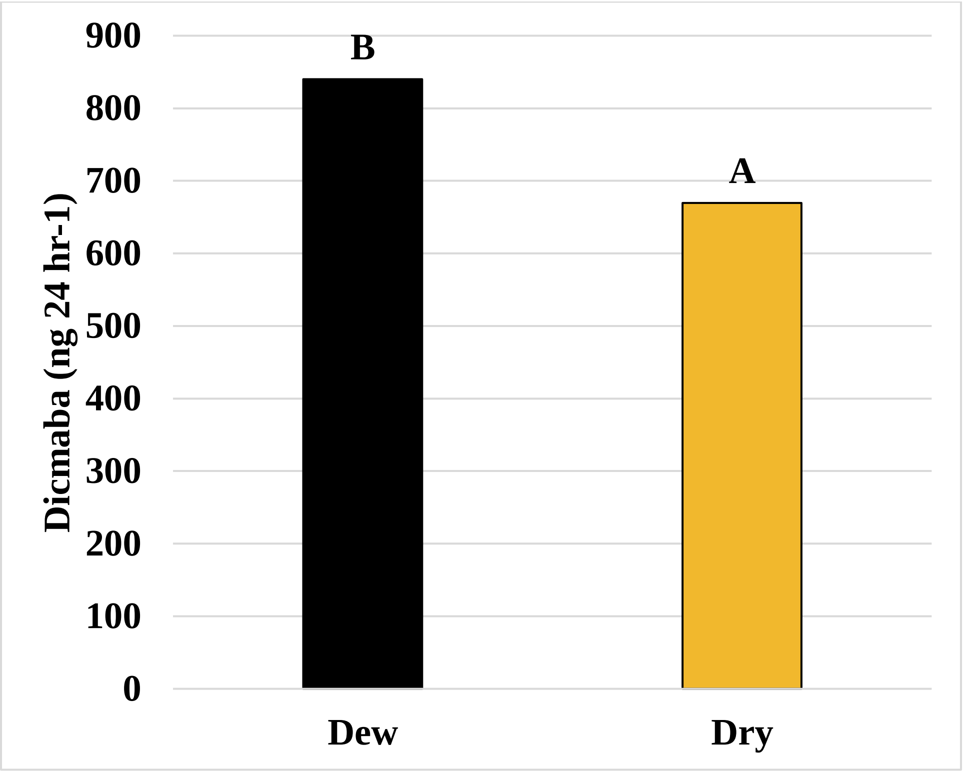

Figure 3.4. Mean mass of volatilized dicamba (ng), applied as XtendiMax with VaporGrip, over 24 hr when treated (540 g ae ha^{-1}) soybean leaves were dry or covered with dew. Means not followed by the same letter are considered significantly different ($p<0.05$).

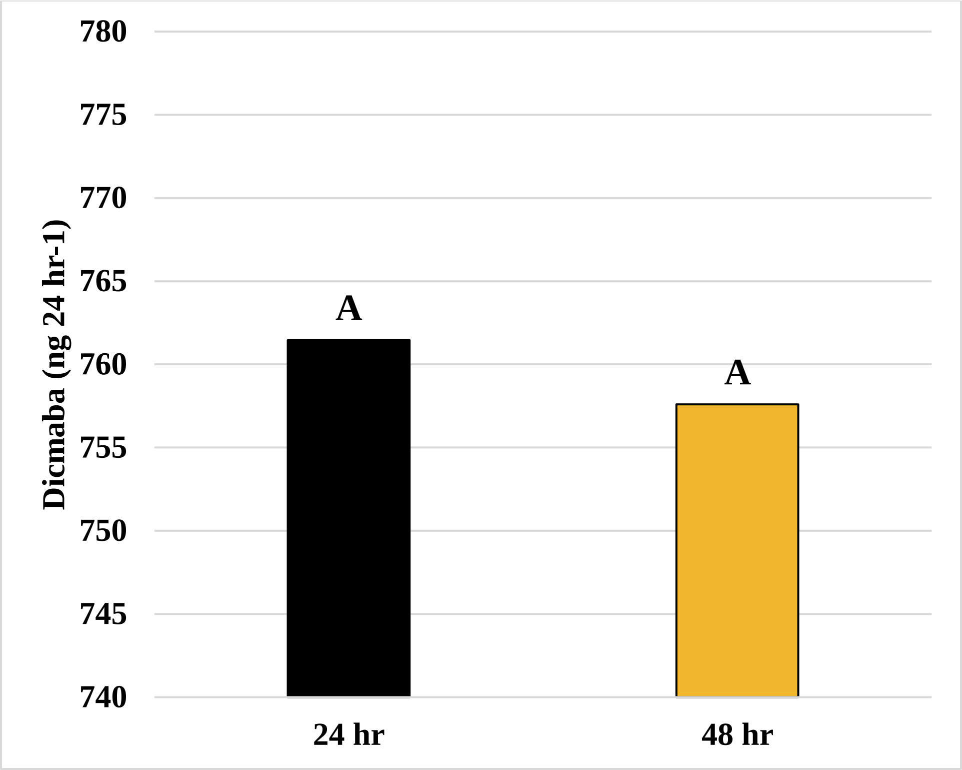

Figure 3.5. Across treatments, mean mass of volatilized dicamba (ng 24 hr^{-1}) from soybean leaves treated with XtendiMax with VaporGrip (540 g ae ha^{-1}) over the first and second 24 hr sampling periods. Means not followed by the same letter are considered significantly different ($p<0.05$).

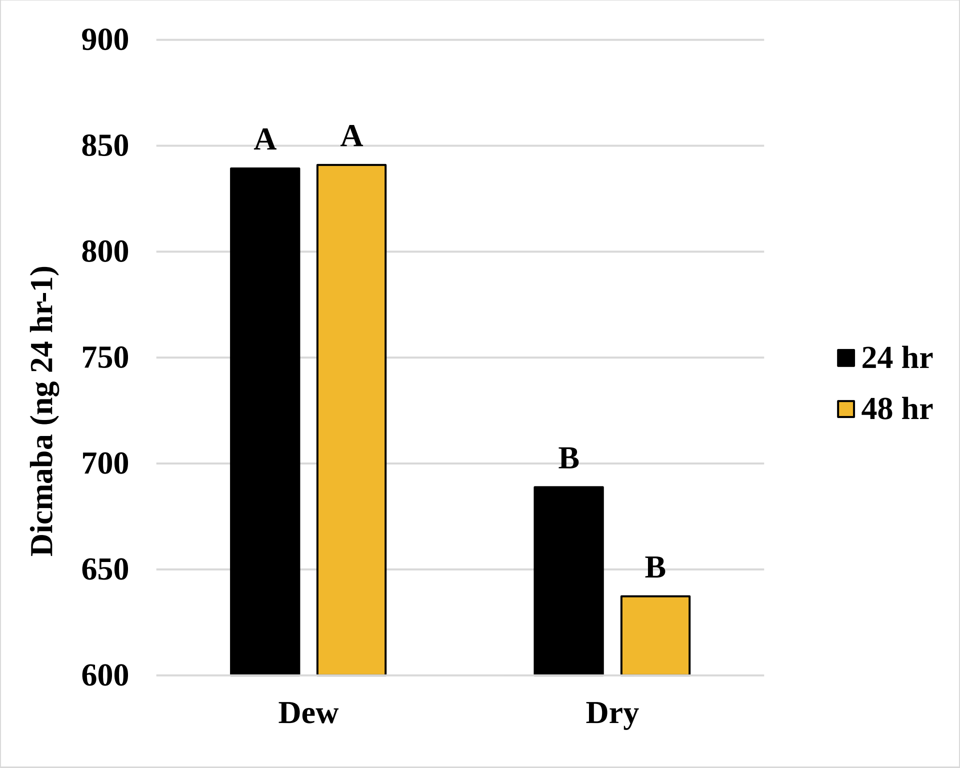

Figure 3.6. Mean mass of volatilized dicamba from soybean leaves treated with XtendiMax with VaporGrip (540 g ae ha^{-1}) over 24 hr, separated by 24 hr sampling periods, when soybean leaves were dry or covered with dew. Means not followed by the same letter are considered significantly different ($p<0.05$).

Chapter 4: A Survey of Dicamba Residues in Commercial Spray Equipment Following an Application of Dicamba

Abstract

Cleansing spray equipment following dicamba applications is important before subsequent applications on sensitive plants. Since soybeans (*Glycine max*) are extremely sensitive to dicamba the need for thorough cleansing of sprayers cannot be overstressed. This study was conducted to quantify dicamba concentrations in rinsate samples during the cleaning of commercial spray systems, in conjunction with a survey of the spray application and cleanout process. Rinsate samples were collected from MO (n=32), NE (n=3), and IL (n=6) from 2017 to 2020. Results show that cleanout procedures between 2017 and 2020 removed 98 to 100% of applied dicamba. However, the concentration of residual dicamba ranged from 0 to 77 parts per million (ppm) and may be sufficient to damage sensitive crops. Sprayer systems with polyethylene tanks and/or plastic and rubber lines contained more dicamba than spray systems with a stainless steel tank and/or stainless steel and rubber lines. However, the pump system, the number of tank rinses following initial rinsing, and the chemical subsequently added had no measurable impact on the concentration of dicamba in rinsate samples. As part of good stewardship practices, greater consistency of cleaning spray equipment following the dicamba application is needed for sprayers used to treat both dicamba-tolerant and -sensitive soybeans.

Keywords: *Glycine max*, tank contamination, dicamba, off-target movement, sprayer tank cleaning, survey

Introduction

Improper cleaning of spray equipment, or tank contamination, is an important but often overlooked source for chemical trespassing. Poor cleaning of spray equipment following the use of herbicides like atrazine, glyphosate, dicamba, clopyralid, glufosinate, 2,4-D, , and others can result in end of season yield losses (AGCO 2020, Kelley et al. 2005, Miller et al. 2003, Mills and Thurman 1994). Contaminations as low as 1% of the labelled rate of dicamba (560 kg ae ha^{-1}) can lead to 5% yield losses in soybeans (Soltani et al. 2016). Due to the effectiveness of dicamba at minute concentrations, it is critical to remove residual herbicides from the spray equipment before use in applying herbicides onto subsequent, sensitive crops.

Recommended removal of dicamba from commercial spray equipment often follows a triple-rinse cleansing procedure with the use of a commercial cleaning agent or ammonia (Davis et al. 2015, Johnson et al. 1997, Osborne et al. 2015). Cleaning agents or ammonia are added to the first rinse of the spray tank followed by two rinses of water alone; however Osborne et al. (2015) found that only 95% of dicamba was removed from commercial sprayers (n=46) after using a triple water rinse procedure. Luke et al. (2017) found that the use of a commercial tank cleaner, Erase® (Precision Laboratories, Waukegan, IL, USA) or Cleanse® (Universal Crop Protection Alliance, Eagan, MN, USA), removed significantly more dicamba residue from spray equipment than a triple water rinse alone. Luke et al. (2017) suggested that commercial cleaners should be used in spray tanks after dicamba applications have been performed, as triple rinses with water or ammonia left dicamba concentrations adequate to reduce yields in the tank. These data suggest that the recommended triple rinse may not be adequate to eliminate the risk of damage due to residual dicamba.

Commercial tank cleansers are typically chosen based on the herbicide used and can remove both water and oil soluble herbicides (Johnson et al. 1997). Cleaning agents solubilize or deactivate the herbicide in the spray tank (Peachey 2009), while others alter the pH thereby rendering the herbicide more water soluble. Deactivation cleaning agents prevent further damage by oxidizing pesticide particles and decomposition of herbicide molecules into inactive compounds (Peachey 2009). Interestingly, addition of herbicides like glyphosate have been found to facilitate the removal of dicamba from contaminated spray equipment (Steckel and Thompson 2005).

Efficient cleaning of commercial spray equipment can be challenging because application equipment systems are made up of an extensive network of hoses, fittings, and nozzles. For each part, micropores can be present and harbor minute amounts of dicamba (Cundiff et al. 2017). Extension professionals from the University of Arkansas, the University of Missouri, and the University of Tennessee have emphasized the importance of taking extra precautions when cleaning out commercial spray equipment after dicamba applications; including the use of detergent cleaning agents, prolong agitation and soaking time, and repeated rinsing procedures (Davis et al. 2015, Johnson et al. 1997, Steckel and Thompson 2005).

Minute amounts of dicamba can result in significant injury to sensitive soybeans. As low as 0.01% of the labeled rate (560 g ae ha^{-1}) reduced soybean yields by 10% (Weidenhamer et al. 1989). The extent of damage also depends on the soybean growth stage. Auch and Arnold (1978) found soybeans exposed to 11 g ae ha^{-1} dicamba had yield reductions ranging from 2% higher to 9% lower when exposed at V3 and R1 growth stages, respectively. Griffin et al. (2013) noted yield reductions of 4 to 15% for V3 soybeans exposed to 4.4 to 17.5 g ae ha^{-1} dicamba, respectively, but noted a 10 to 36% yield reduction when R1 soybeans were exposed to similar rates. Similarly, Solomon and Bradley (2014) reported yield losses ranging from 2 to 67% when soybeans were exposed at R2 but had no significant yield loss when soybeans were exposed to similar rates at V3. These studies concluded that soybeans exposed to dicamba in the reproductive growth stage were injured more than soybeans exposed to similar concentrations at a vegetative growth stage. Therefore, the off-target movement of dicamba, even at sublethal concentrations, can have significant economic repercussions.

The introduction of dicamba-tolerant (DT) crops in 2017 brought significant changes in the use of dicamba. Prior to 2017, dicamba products such as Banvel® and Clarity® were used to control broadleaf weeds in lawns, cereal grains, grazing lands, and other monocot crops (United States Department of Agriculture 1967). However, applications were restricted to pre-plant conditions in broadleaf crops (Anonymous 2010). Following the introduction of DT crops and the approval of postemergence (POST) applications of dicamba, commercial applicators used spray equipment to apply dicamba onto DT soybeans and subsequently used the same equipment to apply other POST herbicides to non-DT soybeans.

This study was initiated to assess the effectiveness of spray tank cleanout procedures in Missouri in 2017 and was expanded to include Nebraska and

Illinois in 2019. The objective of this study was to quantify dicamba concentrations in rinsate from commercial spray equipment following dicamba applications. Additionally, survey information was collected from commercial applicators regarding the sprayer equipment to determine if potential rinsate samples of dicamba correlated with spray tank components or subsequent herbicides applied.

Materials and Methods

Rinsate samples were collected from commercial spray systems from 2017 to 2020 (n=49). Samples were collected from Missouri only in 2017 (n=7) and 2018 (n=12), from Missouri (n=13), Nebraska (n=9), and Illinois (n=4) in 2019, and from Missouri (n=2) and Illinois (n=2) in 2020. The spray applications that rinsate samples were collected from were made by 18 unique applicators at 20 different locations. Only samples coming from the final tank rinse and the new load were included for dicamba residue analysis.

Commercial spray applicators were asked to clean out their spray tank equipment following procedures as recommended by their organization. Prior to the disposal of the final rinsate, participants collected approximately 50 mL of solution by discharging rinsate solution from the boom. Samples were taken from nozzles at one end of the fully extended boom. Once participants had loaded a new herbicide mix (new load) into the spray tank, samples (referred to as new load samples) were collected. After approximately 76 L of the new load solution was discharged from the end of the spray boom, another 50 mL sample was collected. Samples were initially refrigerated and then stored <0 ^{o}C beginning the day of collection.

All participants contributing samples were asked to fill out a short survey (Figure 4.1) to obtain details about the herbicide application and the spray system used. The survey collected data on the spray system, dicamba application, cleanout procedure, and herbicides used following dicamba cleanout. Spray system information collected included sprayer type, tank size and composition, composition of the boom line, herbicides, surfactants, and modifiers used, and acres treated at the time of application. Cleanout procedure information was also collected including the use of a commercial tank cleaner, number of tank rinses, and duration of the entire cleanout process. Additional information included herbicide, surfactants, and drift reducing agents used in the new herbicide load.

Samples were analyzed to determine dicamba concentrations in the rinsate solutions. Samples were diluted with methanol (5:95) and filtered through Whatman® Anotop® 0.2 µM membranous filter (Millipore Sigma, Burlington, MA, USA) to remove all particulates. Dicamba concentrations, in solution, were determined using a Waters Alliance 2695 High Performance Liquid Chromatography (HPLC) system coupled with Waters Acquity TQ triple quadrupole mass spectrometer (MS/MS). Dicamba standards were dissolved in HPLC grade methanol (Sigma-Aldrich, Merck, Darmstadt, Germany). Standard dicamba concentrations of 10, 50, 100, 500, 1,000, 10,000, and 25,000 parts per billion were purchased (Sigma-Aldrich, Merck, Darmstadt, Germany) and used to generate the standard curve to quantify dicamba concentrations in solution. The compounds were chromatographically separated by a Phenomenex (Torrance, CA, USA) Kinetex C18 (100 mm by 4.6 mm; 2.6 µm particle size) reverse-phase analytical column. The mobile phase consisted of 10 mM ammonium acetate and 0.1% formic acid in water (A) and 100% acetonitrile (B). The gradient conditions were 0 to 0.5 minutes, 2% B; 0.5 to 7.0 minutes, 2 to 80% B; 7.0 to 9.0 minutes, 80 to 98% B; 9.0 to 10.0 minutes, 2% B; 10 to 15 minutes, 2% B at a flow rate of 0.5 mL per minute. The system was operated with electrospray ionization (ESI) in the negative ion mode with a capillary voltage of 1.5 kV. The ionization source was programmed at 150°C and the desolvation temperature was programmed at 450°C. The MS/MS system was operated in the single ion recording

(SIR) mode, and the spectrum of fragmented product ions was determined by injecting 30 μL of a standard solution containing 1000 μg L^{-1} of the analytical standards ionized by electrospray ionization in negative ion mode (ES^{-}). Analytical data were processed using Waters Empower 3 software (Waters, CA, USA). Analytical data were processed using Waters Empower 3 software (Waters, CA, USA). The ion m/z 174.72 $[M\text{-}H\text{-}COO]^{-}$ was used for the quantification of dicamba.

Surveys and dicamba concentration data were subjected to ANOVA using PROC GLM in SAS 9.4. Year, tank and line material, the use of a direct inject system, boom length, rinse, and active ingredient were considered fixed effects and analyzed individually. All possible pairs of means were compared using Scheffe’s procedure and considered significant when $p \leq 0.05$.

Results and Discussion

Dicamba concentrations found in rinsate samples collected between 2017 and 2020 ranged from 0 to 77 ppm (parts per million) (n=41) (Table 4.1) and averaged 14 ppm. The labeled rate of dicamba is approximately 4,000 ppm, therefore, cleanout procedures used in this study removed 98 to 100% of dicamba in the tank. Concentrations up to 77 ppm may be sufficient to cause significant yield losses in sensitive soybeans (Kelley et al. 2005, Kniss 2018b, Luke et al. 2017, Solomon and Bradley 2014).

The time of sampling (2017 – 2020) was not important, as unacceptable levels of dicamba were detected each year. Mean dicamba concentrations quantified each year were 22, 2, 21, and >1 ppm dicamba in 2017 (n=7), 2018 (n=12), 2019 (n=18), and 2020 (n=4), respectively. Although all applicators were required to take mandatory dicamba training beginning in 2018, which included spray rig cleanout training (Environmental Protection Agency 2020), cleanout regiments varied.

Spray equipment is comprised of materials and small spaces that sequester or trap dicamba. Spray systems with a stainless-steel tank resulted in lower dicamba concentrations in rinsate samples than spray systems with a polyethylene tank (p=0.014) (Table 4.1). However, the tank pump system, direct inject or other, did not affect residual dicamba concentrations in rinsate samples (p=0.25) (Table 4.1). This finding was surprising as the common belief is that dicamba does not enter the spray tank in a direct inject system so dicamba concentrations would be lower; however, that was not the case in this study. Additionally, spray systems with spray lines of steel and rubber have significantly less dicamba in rinsate samples than spray systems composed of rubber and plastic (p=0.021) (Table 4.1). Cundiff et al. (2017) noted that synthetic rubber hoses sequester more dicamba than polyvinyl chloride (PVV), low density polyethylene blend hoses; sequestering concentrations sufficient to cause significant yield losses to sensitive soybeans. Rubber and plastic pieces have greater potential for compositional breakdown than steel (Cundiff et al. 2017). Breakdown of sprayer components creates pockets or cracks that increase the likelihood of sequestered dicamba. Additionally, dicamba more effectively binds to rubber than stainless steel based on its log Kow of 2.21 (National Center for Biotechnology Information 2020). Dicamba is more greatly partitioned in octanol compounds, like rubber, than water, hence dicamba has a greater affinity to bind to rubber hoses than the water used during sprayer tank cleaning.

Of the samples collected for this study, the applicators used a triple or four-rinse procedure. Participants reported using detergent tank cleaners in 81.5% of the tanks cleaned out, while others used water, ammonia, or glyphosate as a tank cleaner (Figure 4.1). Unlike the results of the sprayer tank cleanout study conducted by Luke et al. (2017) that found greater cleanout efficiency with the use of a detergent tank cleaner, this study was not conducted in a controlled setting and the use of detergent tank cleaners had no effect on dicamba concentrations in final rinsate samples (p=0.1). However, dicamba concentrations decreased with every additional rinse, while not significantly different between rinses 2 through 4 (Table 4.1). Rinses 2 through 4 contained similar dicamba concentrations, however, the concentration in rinses 2, 3, and 4 (95, 18, and 6 ppm dicamba, respectively) is likely to cause yield losses in sensitive soybeans. Soltani et al. (2016) found that dicamba tank contamination of as little as 1.1 g ae ha^{-1}, or 19 ppm, can cause a significant yield loss in sensitive soybeans. Similarly, Luke et al. (2017) and

Kniss (2018) found 13 and 12 ppm dicamba, respectively, were the lowest concentrations that resulted in a measurable yield loss for sensitive soybeans. Rinsate samples from this study in some cases contained sufficient dicamba to damage sensitive crops in the subsequent application using that spray equipment.

In new load rinsate samples, the herbicide in the new load had no effect releasing additional dicamba from sprayer components (Table 4.3). Steckel and Thompson (2005) suggested that glyphosate can be used as an effective tank cleaner and Browne et al. (2020) found that using glyphosate as a tank cleaner is as affective as using ammonia as a cleaning agent. In this study, neither glyphosate nor the other herbicides used in the new load, including s-metolachlor, acetochlor, glufosinate, clethodim, mesotrione, and atrazine, released significant dicamba from the spray equipment (p=0.9664) (Table 4.3).

Results from this study further differ from those of Browne et al. (2020) that demonstrated a cleanout efficiency of 99.996% with the use of a triple rinse with water alone. In the rinsate samples collected, Browne et. al (2020) quantified > 1 ppm (ug mL$^{-1)}$ dicamba after four rinses of the spray system, whereas this survey found an average of 14 ppm dicamba. The concentrations quantified in Browne et. al (2020) (>1 ppm dicamba) caused visual injury but did not result in significant yield losses, whereas the samples from this study (14 ppm dicamba) were sufficient to cause visual injury as well as yield losses in senstive soybeans.

This survey would suggest that cleanout procedures in use from 2017 through 2020 were inconsistent for adequate removal of dicamba, resulting in the potential for off-target damage to subsequent, sensitive crops. The triple rinse procedure has been recommended for many years when cleaning commercial spray systems (Davis et al. 2015, Johnson et al. 1997, Steckel and Thompson 2005) but this process may not be always adequate for plant growth regulating (PGR) herbicides, like dicamba. PGR herbicides can bind to porous sprayer components, making water rinses less effective desprite dicamba being a water soluble herbicide (Cundiff et al. 2017). Also, PGR herbicides are highly effective at minute concentrations, with varying sensitivity among many crop species, making tank cleaning imperitive before applying additional herbicides. If not, the next load applied may result in damage, with the potential for damage likely decreasing with additional tank refills, further diluting dicamba concentrations. Therefore, each applicator should take precautions to understand the composition and materials in their spray systems as damage caused by tank contamination is considered the applicators' liability.

This study stresses the importance of proper dicamba stewardship to avoid unintended damages to sensitive crops. Concerns of off-target movement of dicamba are likely to continue as long as DT crops are commercially used and will become a greater concern with greater adoption of 2,4-D tolerant crops. More research is needed to understand how sprayer design, tank materials, hose materials, and plumbing sequester dicamba, despite the use of proper cleanout procedures. In addition, consideration should be given as to whether a single method to rinse spray equipment in sufficient, given the variability in spray equipment as well as differences in plant sensitivity to herbicides.

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Literature Cited

Agam N, Berliner PR (2006) Dew formation and water vapor adsorption in semi-arid environments - A review. J Arid Environ 65:572–590

AGCO (2020) Weed control efficacy. https://www.croplife.com/iron/sprayers/sprayer-setup-best-practices-maximize-weed-control-efficacy/

Ahmadi MS, Haderlie LC, Wicks GA (1980) Effect of growth stage and water stress on barnyardgrass (*Echinochloa crus-galli*) control and on glyphosate absorption and translocation. Weed Sci 28:277–282

Akey WC, Morrison IN (1983) Effect of moisture stress on wild oat (*Avena fatua*) response to diclofop. Weed Sci 31:247–253

Anastassiades M, Lehotay SJ, Stajnbaher D, Schenck FJ (2003) Fast and easy multiresidue method employing acetonitrile extraction/partitioning and “dispersive solid-phase extraction” for the determination of pesticide residues in produce. J AOAC Int 86:412–431

Anonymous (2010) Clarity label. Research Triangle, NC: BASF Corporation

Anonymous (2019a) Engenia herbicide product label. Research Triangle, NC: BASF Corporation

Anonymous (2019b) XtendiMax with vaporgrip technology herbicide product label. St. Louis, MO: Bayer

Anonymous (2020) FeXapan plus vaporgrip technology herbicide product label. Indianapolis, IN

Auch DE, Arnold WE (1978) Dicamba use and injury on soybeans (*Glycine max*) in South Dakota. Weed Sci 26:471–475

Babiker AGT, Duncan HJ (1975) Penetration of bean leaves by asulam as influenced by adjuvants and humidity. Pestic Sci 6:655–664

Basler E, Todd GW, Meyer RE (1961) Effects of moisture stress on absorption, translocation, & distribution of 2,4-dichlorophenoxyacetic acid in bean plants. Plant Physiol 36:573–576

Behrens MR, Mutlu N, Chakraborty S, Dumitru R, Jiang WZ, Lavallee BJ, Herman PL, Clemente TE, Weeks DP (2007) Dicamba resistance: enlarging and preserving biotechnology-based weed management strategies. Science (80-) 316:1185–1189

Behrens R, Lueschen WE (1979) Dicamba volatility. Weed Sci 27:486–493

Benbrook CM (2016) Trends in glyphosate herbicide use in the United States and globally. Environ Sci Eur 28:1–15

Beysens D, Lekouch I, Mileta M, Milimouk I, Muselli M (2019) Dew and rain collection in South Croatia. Int J Civ Environ Eng 1:64–70

Bird SL, Esterly DM, Perry SG (1996) Off-target deposition of pesticides from agricultural aerial spray applications. J Agric Food Chem 14:585–588

Bish M, Bradley K (2017) Knowing when to spray: monitoring the weather. https://weedscience.missouri.edu/Missouri Weather Analysis_2017.pdf

Bish MD, Farrell ST, Lerch RN, Bradley KW (2019) Dicamba losses to air after applications to soybean under stable and nonstable atmospheric conditions. J Environ Qual 48:1675–1682

Boerboom C (2004) Field case studies of dicamba movement to soybeans. Page *in* Wisconsin Crop Management Conference

Boydston R (1990) Soil water content affects the activity of four herbicides on green

foxtail (*Setaria viridis*). Weed Res 38:578–582

Bradley K (2017) Integrated pest 2017. 1–2 p

Bradley K (2018) July 15 dicamba injury update. different year, same questions:1–2

Broadhurst NA, Montgomery ML, Freed VH (1966) Metabolism of 2-methoxy-3,6-dichlorobenzoic acid (dicamba) by wheat and bluegrass plants. J Agric Food Chem 14:585–588

Browne FB, Li X, Price KJ, Wang J, Wang Y, Kruger GR, Golus J, De Castro Macedo G, Vieira BC, Sandlin T (2020) Dicamba retention in commercial sprayers following triple rinse cleanout procedures, and soybean response to contamination concentrations. Agronomy 10:1–15

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

Burnside OC, Lavy TL (1966) Dissipation of dicamba. Weeds 14:211–214

Celen IH (2010) The effect of spray mix adjuvants on spray drift. Bulg J Agric Sci 16:105–110

Cenkci S, Yildiz M, Ciĝerci IH, Bozdaĝ A, Terzi H, Terzi ESA (2010) Evaluation of 2,4-D and dicamba genotoxicity in bean seedlings using comet and RAPD assays. Ecotoxicol Environ Saf 73:1558–1564

Chang FY, Vanden Born WH (1968) Translocation of dicamba in Canada thistle. Weed Sci 16:176–181

Chang FY, Vanden Born WH (1971) Dicamba uptake, translocation, metabolism, and selectivity. Weed Sci 19:113–117

Christoffoleti PJ, Figueiredo MRA de, Peres LEP, Nissen S, Gaines T (2015) Auxinic

herbicides, mechanisms of action, and weed resistance: a look into recent plant science advances. Sci Agric 72:356–362

Creech CF, Henry RS, Fritz BK, Kruger GR (2014) Influence of herbicide active ingredient, nozzle type, orifice size, spray pressure, and carrier volume rate on spray droplet size characteristics. Weed Sci 62:193–206

Cundiff GT, Reynolds DB, Mueller TC (2017) Evaluation of dicamba persistence among various agricultural hose types and cleanout procedures using soybean (*Glycine max*) as a bio-indicator. Weed Sci 65:305–316

Davis FS, Merkle MG, Bovey RW (1968) Effect of moisture stress on the absorption and transport of herbicides in woody plants. Bot Gaz 129:183–189

Davis J, Barber T, Max C (2015) Tank clean-out recommendations for common herbicides. 1–2 p

Dickson RL, Andrews M, Field RJ, Dickson EL (1990) Effect of water stress, nitrogen, and gibberellic acid on fluazifop and glyphosate activity on oats (Avena sativa). Weed Sci 38:54–61

Dill GM (2005) Glyphosate-resistant crops : history , status and future †. Pest Manag Sci 224:219–224

Dintelmann BR, Warmund MR, Bish MD, Bradley KW (2019) Investigations of the sensitivity of ornamental, fruit, and nut plant species to driftable rates of 2,4-D and dicamba. Weed Technol:1–11

Do-Thanh CL, Vargas JJ, Thomas JW, Armel GR, Best MD (2016) Design, synthesis, and evaluation of novel auxin mimic herbicides. J Agric Food Chem 64:3533–3537

Duke SO (2018) The history and current status of glyphosate. Pest Manag Sci 74:1027–

1034

Duke SO, Powles SB (2008) Glyphosate: a once-in-a-century herbicide. Pest Manag Sci 63:1100–1106

Egan JF, Barlow KM, Mortensen DA (2014a) A meta-analysis on the effects of 2,4-D and dicamba on soybean and cotton. Weed Sci 62:193–206

Egan JF, Barlow KM, Mortensen DA (2014b) A meta-analysis on the effects of 2,4-D and dicamba drift on soybean and cotton. Weed Sci 62:193–206

Environmental Protection Agency (2005) Reregistration eligibility decision (RED) document for nitrapyrin. 1–38 p

Environmental Protection Agency (2018) EPA announces changes to dicamba registration. https://archive.epa.gov/epa/newsreleases/epa-announces-changes-dicamba-registration.html

Environmental Protection Agency (2019) Food and pesticides. https://www.epa.gov/safepestcontrol/food-and-pesticides. Accessed October 25, 2020

Environmental Protection Agency (2020) Dicamba training requirements. https://www.epa.gov/ingredients-used-pesticide-products/dicamba-training-requirements-frequently-asked-questions#components

Enz JW, Hofman V, Thostenson A (2017) Air temperature inversions causes, characteristics, and potential effects on pesticide spray drift. NDSU Ext 1705:1–16

EPA (2010) Index to pesticide chemical names, part 180 tolerance information, and food and feed commodities (by commodity). Environ Prot Agency:1–314

Ester A, Strachan SD, Casini MS, Heldreth KM, Scocas JA, Nissen SJ, Bukun B,

Lindenmayer RB, Shaner DL, Westra P, Ester A, Strachan SD, Casini MS, Heldreth KM, Scocas JA, Nissen SJ, Bukun B, Lindenmayer RB, Shaner DL, Westra P, Brunk G (2010) Vapor movement of synthetic auxin herbicides : Aminocyclopyrachlor-methyl ester, dicamba, and aminopyralid. Weed Sci 58:103–108

Farrell S, Lerch RN, Bish M (2018) Influence of formulations and application time of day on dicamba air concentrations following treatment. Page *in* Proceedings of the 73rd Annual Meeting of the North Central Weed Science Society

Foster MR (2018) Soybean response to dicamba : Associated injury criteria and development of a model to predict yield loss. Louisiana State University

Foster MR, Griffin JL, Copes JT, Blouin DC (2019) Development of a model to predict soybean yield loss from dicamba exposure. Weed Technol 33:287–295

Gałek G, Sobik M, Błaś M, Polkowska Z, Cichała-Kamrowska K, Wałaszek K (2015) Dew and hoarfrost frequency, formation efficiency and chemistry in Wroclaw, Poland. Atmos Res 151:120–129

Gauvrit C (2003) Glyphosate response to calcium, ethoxylated amine surfactant, and ammonium sulfate. Weed Technol 17:799–804

Gavlick WK, Wright DR, MacInnes A, Hemminghaus JW, Webb JK, Yermolenka VI, Su W (2016) A method to determine the relative volatility of auxin herbicide formulations.pdf. Pestic Formul Deliv Syst 35:24–32

Grafstrom LD, Nalewaja JD (1986) Uptake and translocation of fluazifop in green goxtail (*Setaria viridis*). Weed Sci 108:115–123

Griffin JL, Bauerle MJ, Stephenson DO, Miller DK, Boudreaux JM (2013) Soybean

response to dicamba applied at vegetative and reproductive growth stages. Weed Technol 27:696–703

Grossmann K (2010) Auxin herbicides: Current status of mechanism and mode of action. Pest Manag Sci 66:113–120

Guilherme A, Alves S, Kruger GR, Paulo J, Cunha AR, Denise G, Santana D, Pinto LAT (2017) Dicamba spray drift as influenced by wind speed and nozzle type dicamba spray drift as influenced by wind speed and nozzle type. Weed Technol 31:724–731

Hall GJ, Hart CA, Jones CA (2000) Plants as sources of cations antagonistic to glyphosate activity. Pest Manag Sci 56:351–358

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

Hartzler R (2017) Wind speed and herbicide application. https://crops.extension.iastate.edu/cropnews/2017/01/wind-speed-and-herbicide-application

Hartzler R, Hartzler R (2020) 2020 Herbicide guide for Iowa corn and soybean production. Page Iowa State University Extension and Outreach Integrated Crop Management

Hatterman-Valenti H, Owen MD, Christians NE (1995) Comparison of spray drift during postemergence herbicide applications to turfgrass. Weed Technol 9:321–325

Hauser EW (1955) Absorption of 2,4-dichlorophenoxyacetic acid by soybean and corn plants. Agron J 47:32

Heap I (2020) International herbicide-resistant weed database. http://weedscience.org/Home.aspx

Hertel R, Thomson KS, Russo VEA (1972) In-vitro auxin binding to particulate cell fractions from corn coleoptiles. Planta 107:325–340

Hewitt AJ (1993) Droplet size spectra produced by air-assisted atomizers. J Aerosol Sci 24:155–162

Holly K (1956) Penetration of chlorinated phenoxyacetic acid into leaves. Pages 195–199 *in* Annals of Applied Biology

Hughes EE (1968) Hygroscopic additives to phenoxy herbicides for control of saltcedar. Weed Sci 16:486–488

Hughes RE, Freed VH (1961) The role of surfactants in the foliar absorption of indole-3-acetic acid (IAA). Weeds 9:54–59

Hull HM, Davis DG, Stolzenberg GE (1982) Action of adjuvants on plant surfaces. Pages 26–67 *in* Adjuvants for Herbicides. Weed Science Society of America

Jhala A, Knezevic S, Klein RN (2017) Dicamba injury symptoms on sensitive crops

Jiries A (2001) Chemical composition of dew in Amman, Jordan. Atmos Res 57:261–268

Johnson WG, Casady B, Peterson D, Kuhlman D (1997) Cleaning field sprayers to avoid crop injury. MU Extension, Univ Missouri-Columbia

Johnson WG, Hallett SG, Legleiter TR, Whitford F, Weller SC, Bordelon BP, Lerner BR (2012) 2,4-D and dicamba-tolerant crops- some facts to consider. Page Purdue Extension. 1–7 p

Jones GT (2018) Evaluation of dicamba off-target movement and subsequent effects on soybean offspring. University of Arkansas

Jones GT, Norsworthy JK, Barber T, Gbur E, Kruger GR (2019) Off-target movement of DGA and BAPMA dicamba to sensitive soybean. Weed Technol 33:51–65

Kabela ED, Hornbuckle BK, Cosh MH, Anderson MC, Gleason ML (2009) Dew frequency, duration, amount, and distribution in corn and soybean during SMEX05. Agric For Meteorol 149:11–24

Kelley KB, Wax LM, Hager AG, Riechers DE (2005) Soybean response to plant growth regulator herbicides is affected by other postemergence herbicides. Weed Sci 53:101–112

Kidder DW, Behrens R (1988) Plant responses to haloxyfop as influenced by water stress. Weed Sci

Klein RN, Schulze L, Ogg CL (2008) Factors affecting spray drift of pesticides. Crop Soils:19–23

Klevorn TB, Wyse DL (1984) Effect of soil temperature and moisture on glyphosate and photoassimilate distribution in quackgrass (*Agropyron repens*). Weed Sci 32:402–407

Kniss AR (2018a) Genetically engineered herbicide-resistant crops and herbicide-resistant weed evolution in the United States. Weed Sci 66:260–273

Kniss AR (2018b) Soybean response to dicamba: a meta-analysis. Weed Technol 32:507–512

Knoche M, Petracek PD (2014) Foliar uptake of PGRs: barriers, mechanisms, model systems, and factors. Acta Hortic 1042:125–141

Kroin J (2009) Auxins and the pathways for foliar application. 53–59 p

Lakhani A, Parmar RS, Prakash S (2012) Chemical composition of dew resulting from radiative cooling at a semi-arid site in Agra, India. Pure Appl Geophys 169:859–871

Lauridson TC, Wilson RG, Haderlie LC (1983) Effect of moisture stress on Canada

thistle (*Cirsium arvense*) control. Weed Sci 31:674–680

Lehotay SJ, Son KA, Kwon H, Koesukwiwat U, Fu W, Mastovska K, Hoh E, Leepipatpiboon N (2010) Comparison of QuEChERS sample preparation methods for the analysis of pesticide residues in fruits and vegetables. J Chromatogr 1217:2548–2560

Lekouch I, Mileta M, Muselli M, Milimouk-Melnytchouk I, Šojat V, Kabbachi B, Beysens D (2010) Comparative chemical analysis of dew and rain water. Atmos Res 95:224–234

Lin LI-K (1989) A concordance correlation coefficient to evaluate reproducibility. Biometrics 45:255–268

Long J (2017) Infuence of application factors on dicamba volatility. Purdue. 98 p

Long J, Basler E (1973) Some factors regulating auxin translocation in intact bean seedlings. Plant Physiol 51:128–135

Luke AJ, Weirich JW, Smeda RJ (2017) Dicamba residues in spray equipment reduces soybean (*Glycine max*) growth and yield. University of Missouri

Madeira AC, Kim KS, Taylor SE, Gleason ML (2002) A simple cloud-based energy balance model to estimate dew. Agric For Meteorol 111:55–63

Marth PC, Davis FF, Mitchell JW (2018) Herbicidal properties of 2,4-dichlorophenoxyacetic acid applied in dusts containing hygroscopic agents. Bot Gaz 107:129–136

Maybank J, Yoshida K, Grover R (1978) Spray drift from agricultural pesticide applications. J Air Pollut Control Assoc 28:1009–1014

McMullan PM (2000) Utility adjuvants. Weed Technol 14:792–797

McWhorter CG, Jordan TN, Wills GD (1980) Translocation of 14 C-glyphosate in soybeans (Glycine max) and johnsongrass (*Sorghum halepense*). Weed Sci 28:113–118

McWorter CG (1982) The use of adjuvants. Pages 10–25 *in* Adjuvants for Herbicides. Weed Science Society of America

Merkle MG, Davis FS (1967) Effect of moisture stress on absorption and movement of picloram and 2,4,5-T in beans. Weeds 15:10–12

Miller A, Donnie K, Robert G, Roger B, Merritt E, Steve T, Miller DK, Downer RG, Leonard BR, Kelly ST (2003) Response of non-glufosinate-resistant cotton to reduced rates of glufosinate. Weed Sci 51:781–785

Miller PCH, Butler Ellis MC (2000) Effects of formulation on spray nozzle performance for applications from ground-based boom sprayers. Page *in* Crop Protection

Miller PCH, Tuck CR (2005) Factors influencing the performance of spray delivery systems: A review of recent developments. J ASTM Int 2:1–13

Mills MS, Thurman EM (1994) Reduction of nonpoint source contamination of surface water and groundwater by starch encapsulation of herbicides. Environ Sci Technol 28:73–79

Monshausen GB, Gilroy S (2009) Feeling green: mechanosensing in plants. Trends Cell Biol 19:228–235

Morgan J V, Tukey Jr. HB (1964) Characterization of leachate from plant foliage. Plant Physiol 39:590–593

Morrison RG, Lownds NK, Sterling TM (1995) Picloram uptake, translocation, and efficacy in relation to water status of Russian knapweed (*Acroptilon repens*). Weed

Sci 43:34–39

Mortensen DA, Egan JF, Maxwell BD, Ryan MR, Smith RG (2012) Navigating a critical juncture for sustainable weed management. Bioscience 6:75–84

Mueller TC, Steckel LE (2019a) Dicamba volatility in humidomes as affected by temperature and herbicide treatment. Weed Technol 33:1–6

Mueller TC, Steckel LE (2019b) Spray mixture pH as affected by dicamba, glyphosate, and spray additives. Weed Technol 33:547–554

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

Mueller TC, Wright DR, Remund KM (2013) Effect of formulation and application time of day on detecting dicamba in the air under field conditions. Weed Sci 61:586–593

Nandula VK (2010) Glyphosate resistance in crops and weeds: History, development, and management. Page Glyphosate Resistance in Crops and Weeds: History, Development, and Management. 1–33 p

Nath S, Yadav S (2018) A comparative study on fog and dew water chemistry at New Delhi, India. Aerosol Air Qual Res 18:26–36

National Center for Biotechnology Information (2020) PubChem compound summary for CID 3030, dicamba. https://pubchem.ncbi.nlm.nih.gov/compound/Dicamba. Accessed December 11, 2020

Natural Resources Conservation Services (n.d.) Official soil series descriptions. https://soilseries.sc.egov.usda.gov/osdname.aspx. Accessed April 9, 2020

Nordby A, Skuterud R (1974) The effects of boom height, working pressure and wind speed on spray drift. Weed Res 14:385–395

Nuyttens D, Schampheleire M, Steurbaut W, Baetens K (2006) Experimental study of factors influencing the risk of drift from field sprayers, part 2: spray application technique. Asp Appl Biol 77:1–9

Osborne PP, Xu Z, Swanson KD, Walker T, Farmer DK (2015) Dicamba and 2,4-D residues following applicator cleanout: a potential point source to the environment and worker exposure. J Air Waste Manag Assoc 65:1153–1158

Ouse DG, Gifford JM, Schleier J, Simpson DD, Tank HH, Jennings CJ, Annangudi SP, Valverde-Garcia P, Masters RA (2018) A new approach to quantify herbicide volatility. Weed Technol 32:691–697

Pallas, JE, Williams GG (1962) Foliar absorption and translocation of P32 and 2,4-dichlorophenoxyacetic acid as affected by soil-moisture tension. Bot Gaz 123:175–180

Peachey E (2009) Tank cleaners: why and when they work

Peregoy R, Kitchen L, Jordan P, Griffin JL (1990) Moisture stress effects on the absorption, translocation, and metabolism of haloxyfop in johnsongrass (*Sorghum halepense*) and large crabgrass (*Digitaria sanguinalis*). Weed Sci 38:331–337

Perry ED, Ciliberto F, Hennessy DA, Moschini GC (2016) Genetically engineered crops and pesticide use in U.S. maize and soybeans. Sci Adv 2:1–8

Petersen PJ, Haderlie LC, Hoefer RH, McAllister RS (1985) Dicamba absorption and translocation as influenced by formulation and surfactant. Weed Sci 33:717–720

Ramsey RJL, Stephenson GR, Hall JC (2005) A review of the effects of humidity, humectants, and surfactant composition on the absorption and efficacy of highly water-soluble herbicides. Pestic Biochem Physiol 82:162–175

Rayle DL, Cleland R (1970) Enhancement of wall loosening and elongation by acid solutions. Plant Physiol 46:250–253

Rice EL (1948) Absorption and translocation of ammonium 2,4-dichlorophenoxyacetate by bean plants. Bot Gaz 109:301–314

Ross MA, Lembi CA (1999) Applied Weed Science. 3rd ed. Minneapolis, Minnesota: Burgess Pub Co

Sargent JA (1965) The penetration of growth regulators into leaves. Annu Rev Plant Physiol 16:1–12

Sciumbato AS, Chandler JM, Senseman SA, Bovey RW, Smith KL (2004) Determining exposure to auxin-like herbicides. I. quantifying injury to cotton and soybean. Weed Technol 18:1125–1134

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

Sharma MP, Born WH Vanden (1970) Foliar penetration of picloram and 2,4-D in aspen and balsam poplar. Weed Sci 18:57–63

Skelton JJ (2015) Uptake, translocation, and metabolism 2,4-D in enlist crops and control of drought-stressed waterhemp (*Amaranthus tuberculatus*) with 2,4-D and glyphosate. University of Illinois at Urbana-Champaign

Solomon CB, Bradley K (2014) Influence of application timings and sublethal rates of synthetic auxin herbicides on soybean. Weed Technol 28:454–464

Soltani N, Brown L, Sikkema PH (2018) Control of glyphosate-resistant common ragweed in corn with preemergence herbicides. Can J Plant Sci 98:959–962

Soltani N, Nurse RE, Sikkema PH (2016) Response of glyphosate-resistant soybean to

dicamba spray tank contamination during vegetative and reproductive growth stages. Can J Plant Sci 96:160–164

Steckel L, Thompson A (2005) Cleaning plant growth regulator (PGR) herbicides out of field sprayers. UT Extension

Sutton OG (1953) Micrometeorology. Q J R Meteorol Soc:333–335

Szabo SS, Buchholtz KP (1961) Penetration of living and non-living surfaces by 2 ,4-D as influenced by ionic additives. Weeds 9:177–184

Tedeschi LO (2006) Assessment of the adequacy of mathematical models. Agric Syst 89:225–247

Thelen KD, Jackson EP, Penner D (2020) The basis for the hard-water antagonism of glyphosate activity 43:541–548

Tromas A, Paponov I, Perrot-Rechenmann C (2010) Auxin binding protein 1: functional and evolutionary aspects. Trends Plant Sci 15:436–446

Tukey HB (1970) The leaching of substances from plants. Annu Rev Plant Physiol 21:305–324

U.S. FDA (2019) Pesticide residue monitoring program fiscal year 2017 pesticide report:48

United States Department of Agriculture (1967) Suggested guide for weed control

USDA National Organic Program, USDA Science and Technology Programs (2012) Pilot study pesticide residue testing of organic produce. 34 p

Vogel S (1970) Convective cooling at low airspeeds and the shapes of broad leaves. J Exp Bot 21:91–101

Waldecker MA, Wyse DL (1985) Soil moisture effects on glyphosate absorption and

rtanslocation in common milkweed (*Asclepias syriaca*). Weed Sci

Wax LM, Knuth LA, Slife FW (1969) Response of soybeans to 2,4-D, dicamba, and picloram. Weed Sci 17:388–393

Wechsler SJ, Smith D, Mcfadden J, Dodson L, Williamson S (2019) The use of genetically engineered dicamba-tolerant soybean seeds has increased quickly, benefting adopters but damaging crops in some fields. https://www.ers.usda.gov/amber-waves/2019/october/the-use-of-genetically-engineered-dicamba-tolerant-soybean-seeds-has-increased-quickly-benefiting-adopters-but-damaging-crops-in-some-fields/. Accessed April 9, 2020

Weidenhamer JD, Triplett GB, Sobotka FE (1989) Dicamba injury to soybean. Agron J 81:637–643

Whisenant SG, Bouse LF, Crane RA, Bovey RW (1993) Droplet size and spray volume effects on honey mesquite mortality with clopyralid. J Range Manag 46:257

Wolf S, Hématy K, Höfte H (2012) Growth control and cell wall signaling in plants. Annu Rev Plant Biol 63:381–407

Woodward AW, Bartel B (2005) Auxin: regulation, action, and interaction. Ann Bot 95:707–735

Xu Y, Zhu H, Tang J, Lin Y (2015) Chemical compositions of dew and scavenging of particles in Changchun, China. Adv Meteorol:1–11

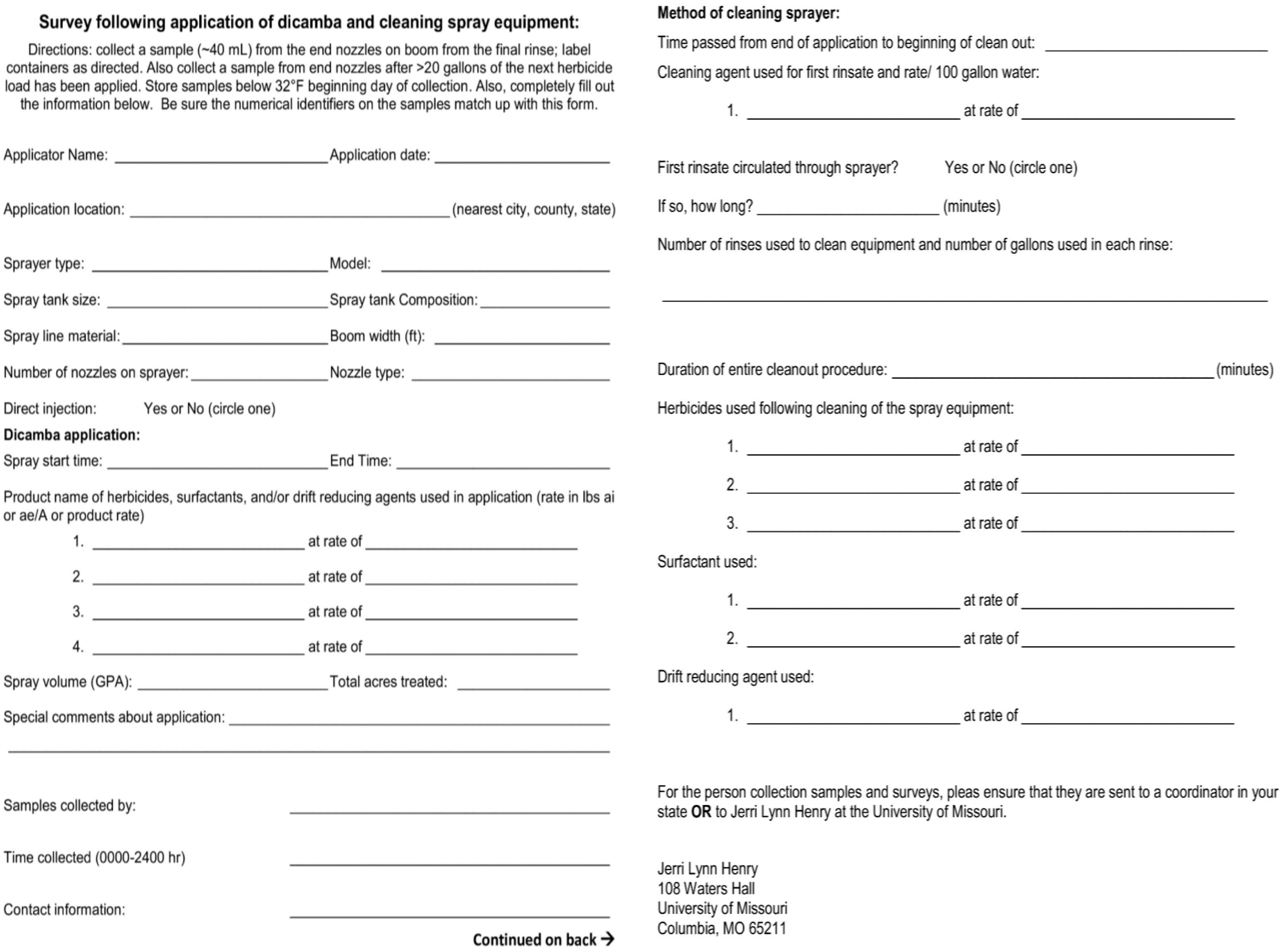
Young BG (2019) Changes in herbicide use patterns and production practices resulting from glyphosate-resistant crops. Weed Technol 20:301–307

Young BG, Hart SE (1998) Optimizing foliar activity of isoxaflutole on giant foxtail (*Setaria faberi*) with various adjuvants. Weed Sci 46:397–402

Van de Zande JC, Stallinga H, Michielsen JMGP, van Velde P (2004) Effect of sprayer speed on spray drift. Annu Rev Agric Engeneering 4:11

Zimdahl R (2013) Fundamentals of Weed Science. 4th ed. Fort Collins, Colorado: Elsevier. 378–381 p

Figure 4.1. Survey sent to participating commercial applicators collecting rinsate samples between 2017 and 2020.



Survey following application of dicamba and cleaning spray equipment:

Directions: collect a sample (~40 mL) from the end nozzles on boom from the final rinse; label containers as directed. Also collect a sample from end nozzles after >20 gallons of the next herbicide load has been applied. Store samples below 32°F beginning day of collection. Also, completely fill out the information below. Be sure the numerical identifiers on the samples match up with this form.

Applicator Name: ____________________ Application date: ________________

Application location: ______________________________ (nearest city, county, state)

Sprayer type: ____________________ Model: ____________________

Spray tank size: ____________________ Spray tank Composition: ____________

Spray line material: ____________________ Boom width (ft): ________________

Number of nozzles on sprayer: ____________ Nozzle type: ____________________

Direct injection: Yes or No (circle one)

Dicamba application:

Spray start time: ____________________ End Time: ____________________

Product name of herbicides, surfactants, and/or drift reducing agents used in application (rate in lbs ai or ae/A or product rate)

1. ____________________ at rate of ____________________
2. ____________________ at rate of ____________________
3. ____________________ at rate of ____________________
4. ____________________ at rate of ____________________

Spray volume (GPA): ________________ Total acres treated: ______________

Special comments about application: ____________________________________

____

Samples collected by: ______________________________

Time collected (0000-2400 hr) ______________________________

Contact information: ______________________________

Continued on back →

Method of cleaning sprayer:

Time passed from end of application to beginning of clean out: ____________________

Cleaning agent used for first rinsate and rate/ 100 gallon water:

1. ____________________ at rate of ____________________

First rinsate circulated through sprayer? Yes or No (circle one)

If so, how long? ________________ (minutes)

Number of rinses used to clean equipment and number of gallons used in each rinse:

____

Duration of entire cleanout procedure: ______________________________ (minutes)

Herbicides used following cleaning of the spray equipment:

1. ____________________ at rate of ____________________
2. ____________________ at rate of ____________________
3. ____________________ at rate of ____________________

Surfactant used:

1. ____________________ at rate of ____________________
2. ____________________ at rate of ____________________

Drift reducing agent used:

1. ____________________ at rate of ____________________

For the person collection samples and surveys, pleas ensure that they are sent to a coordinator in your state **OR** to Jerri Lynn Henry at the University of Missouri.

Jerri Lynn Henry
108 Waters Hall
University of Missouri
Columbia, MO 65211

Table 4.1. Survey results detailing sprayer system material composition (polyethylene or stainless steel; stainless steel+ rubber or plastic+ rubber; direct inject (yes or no)), cleaning agent (detergent used (yes or no)), date and location collected, the tank rinse the sample was collected from (3 or 4 (new load)), and the concentration of dicamba in rinsate samples (ppm= parts per million).

Year	**State**	**Tank Material**	**Line Material**	**Direct Inject**	**Detergent Used**	**Rinse Collected**	**Dicamba (ppm)**
2017	MO	Steel	Stainless steel and rubber	yes	yes	3	34.0
2017	MO	Poly	Plastic and rubber	no	yes	3	77.2
2017	MO	Steel	Stainless steel and rubber	yes	yes	3	22.2
2017	MO	Poly	Plastic and rubber	no	yes	3	7.7
2017	MO	Steel	Stainless steel and rubber	yes	yes	3	6.0
2017	MO	Steel	Plastic and rubber	no	yes	3	4.2
2017	MO	Steel	Plastic and rubber	no	yes	3	3.4
2018	MO	Steel	Stainless steel and rubber	no	no	3	0.7
2018	MO	Steel	Stainless steel and rubber	no	yes	3	0.7
2018	MO	Steel	Stainless steel and rubber	no	no	3	0.5
2018	MO	Steel	Stainless steel and rubber	no	yes	3	1.3
2018	MO	Steel	Stainless steel and rubber	yes	yes	3	15.8
2018	MO	Steel	Stainless steel and rubber	yes	no	3	0.6
2019	MO	Steel	Stainless steel and rubber	no	yes	3	0.3
2019	MO	Steel	Stainless steel and rubber	no	yes	3	0.1
2019	MO	Steel	Plastic and rubber	yes	yes	3	4.1
2019	MO	Steel	Stainless steel and rubber	yes	yes	3	0.9
2019	MO	Poly	Stainless steel and rubber	no	yes	3	0.2
2019	MO	Steel	Stainless steel and rubber	yes	yes	3	0.1
2019	IL	Poly	Plastic and rubber	no	yes	3	60.0
2019	IL	Poly	Plastic and rubber	no	no	3	59.0

2019	IL	Poly	Plastic and rubber	no	no	3	61.0
2019	NE	Steel	Stainless steel and rubber	no	no	3	57.0
2019	NE	Steel	Stainless steel and rubber	no	no	3	62.0
2019	NE	Steel	Stainless steel and rubber	no	no	3	1.6
2020	MO	Poly	Plastic and rubber	no	yes	3	0.9
2020	IL	Poly	Plastic and rubber	no	yes	3	0.7
2018	MO	Steel	Stainless steel and rubber	no	no	4	1.0
2018	MO	Steel	Stainless steel and rubber	no	yes	4	1.4
2018	MO	Steel	Stainless steel and rubber	no	no	4	0.7
2018	MO	Steel	Stainless steel and rubber	no	yes	4	1.0
2018	MO	Steel	Stainless steel and rubber	yes	yes	4	1.3
2018	MO	Steel	Stainless steel and rubber	yes	no	4	1.1
2019	MO	Steel	Stainless steel and rubber	no	yes	4	0.0
2019	MO	Steel	Plastic and rubber	yes	yes	4	0.9
2019	MO	Steel	Stainless steel and rubber	yes	yes	4	9.5
2019	MO	Poly	Stainless steel and rubber	no	yes	4	0.5
2019	MO	Steel	Stainless steel and rubber	yes	yes	4	0.0
2019	IL	Poly	Plastic and rubber	no	yes	4	59.0
2020	MO	Poly	Plastic and rubber	no	yes	4	1.7
2020	IL	Poly	Plastic and rubber	no	yes	4	0.2

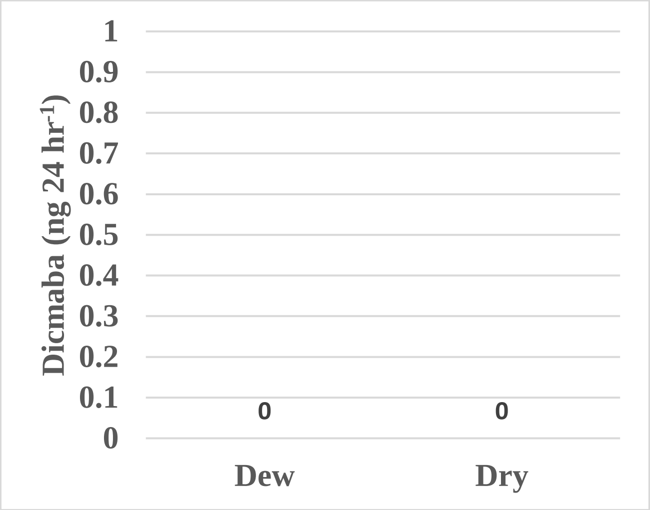
Table 4.2. Mean dicamba concentrations in rinsate samples, in parts per million (ppm) dicamba, for year of collection (2017-2020), tank material (polyethylene (poly) or stainless steel (steel)), line material (stainless steel+ rubber or plastic+ rubber), pump system (direct inject or other), and tank rinse (first, second, third, or new load). Means with the same letter within each column are not significantly different when separated by Scheffe protected LSD at p≤0.05.

Year	**Dicamba (ppm)**	**Tank Material**	**Dicamba (ppm)**	**Line Material**	**Dicamba (ppm)**	**Pump**	**Dicamba (ppm)**	**Tank Rinse**	**Dicamba (ppm)**
2017	22	Poly	27b	Stainless steel + Rubber	9a	Direct Inject	7	First	548b
2018	2	Steel	8a	Plastic + Rubber	28b	Other	17	Second	95a
2019	21	————		————		————		Third	18a
2020	>1	————		————		————		New load	6a

Table 4.3. Mean dicamba concentration in new herbicide load samples (n=14), in parts per million (ppm), from a sprayer rinsate previously used to apply dicamba and thoroughly cleansed. Herbicides (s-metolachlor, acetochlor, glyphosate, glufosinate, clethodim, mesotrione, and atrazine) were analyzed individually and not as mixes with other herbicides or adjuvants. All possible pairs of means were compared using Scheffe's procedure and considered significant when $p \leq 0.05$.

	S-metolachlor (n=1)	**Acetochlor (n=2)**	**Glyphosate (n=6)**	**Glufosinate (n=5)**	**Clethodim (n=4)**	**Mesotrione (n=2)**	**Atrazine (n=1)**
Dicamba (ppm)	0.9	1.2	10.4	2.4	3.1	0.8	0.8

APPENDIX



A.1. Mean mass of volatilized dicamba (ng) from Engenia® over 24 hr when treated (540 g ae ha^{-1}) soybean leaves were dry or covered with dew. All possible pairs of means were compared using Scheffe’s procedure and considered significant when $p \leq 0.05$.

VITA

Jerri Lynn Henry was born October 11, 1994 to Jerry and Kathy Henry. Jerri Lynn grew up on her family's beef cattle farm where she gained an appreciation for agriculture while checking cows with her family. In high school, Jerri Lynn became active in the local FFA chapter and was introduced to soil science. From there, her passion for soil science and agronomy became her future career path.

After high school, Jerri Lynn attended Missouri State University, where she received her B.S. in Environmental Plant Science. Jerri Lynn stayed at Missouri State University and pursued a master's degree in Plant Sciences, focusing on mineral nutrition and plant physiology under the direction of Dr. Melissa Remley Bledsoe. Her passion for plant physiology led her to pursue a doctoral degree focusing on environmental and human factors influencing the off-target movement of dicamba. After receiving her Ph.D., Jerri Lynn plans to relocate to North Carolina to begin a career in crop protection and environmental safety.