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# The influence of adjuvants on physical properties, droplet-size, and efficacy of glufosinate and dicamba plus glyphosate solutions

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# THE INFLUENCE OF ADJUVANTS ON PHYSICAL PROPERTIES, DROPLET-SIZE, AND EFFICACY OF GLUFOSINATE AND DICAMBA PLUS GLYPHOSATE SOLUTIONS

by

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# THE INFLUENCE OF ADJUVANTS ON PHYSICAL PROPERTIES, DROPLET-SIZE, AND EFFICACY OF GLUFOSINATE AND DICAMBA PLUS GLYPHOSATE SOLUTIONS

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University of Nebraska, 2021

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Adjuvants are used in agriculture to improve herbicide activity or application performance. The addition of adjuvants to herbicide solution can enhance its penetration, wettability, and evaporation rates by altering density, viscosity, contact angle between the droplet and plant surface, and droplet surface tension. Furthermore, those alterations in the physical properties of the herbicide solution can result in changes in the droplet-size distribution that directly impact herbicide efficacy. The adoption of glufosinate-based herbicide programs has increased with the widespread occurrence of glyphosate-resistance (GR) weeds in recent years. Also, tank mixture of dicamba and glyphosate has been largely adopted for broad-spectrum weed control since the release of dicamba/glyphosate-tolerant soybeans in 2017. Therefore, it is essential to understand the influence of adjuvants on the performance of those commonly used herbicides. The objectives of this research were: (1) determine the physical properties (density, viscosity, dynamic surface tension, static contact angle, and droplet evaporation rate), and droplet size distribution of glufosinate, and dicamba plus glyphosate solutions in tank-mixture with adjuvants and (2) evaluate the response of weed species to glufosinate, and dicamba plus glyphosate solutions in tank-mixture with adjuvants under greenhouse and field conditions.

Key-words: glufosinate, glyphosate, synthetic auxin, adjuvant, droplet evaporation, weed species

# Dedication

I dedicate this thesis to my family whose believed in my potential and supported my choice to move to another country to pursue my dream. I also dedicate this thesis to my beloved fiancée Jose Henrique who never left my side and always encouraged me throughout the process. I could not have done this without them!

*"As much as talent counts, effort counts twice"*

*Angela Duckworth*

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# CHAPTER 1

## Literature Review

### Adjuvants

Adjuvants are commonly used in agriculture to improve the performance of herbicides. Curran et al. (1999) defined adjuvant as any substance in an herbicide formulation or added to the spray tank to improve herbicidal activity or application characteristics. However, in some circumstances, the addition of adjuvants will not improve herbicide performance (Pacanoski, 2010; Bunting et al., 2004). Sometimes adjuvants can result in negative effects, such as decrease of herbicide effectiveness, increase of herbicide spread and unwanted residual time in the environment, and increase harmful effects to non-target plants and animals (Kammler et al., 2010; Pacanoski, 2010; Frihauf et al., 2005; Kucharski, 2004; Swarcewicz et al., 1998). There is no universal adjuvant that can improve the performance of all herbicides, against all weeds, or under all environmental conditions (Tu and Randal, 2001). Adjuvants can be separated into two groups according to their function: activator and utility adjuvants.

Activator adjuvants are commonly used to enhance postemergence herbicides performance (Curran and Lingenfelter, 2009). Weed species may have different foliar surface characteristics (e.g., cuticle, number of stomata and trichomes, leaf position and angle and leaf age) that impose barriers to herbicide deposition (Koch et al. 2008; Kraemer et al. 2009; Hess 1985; Hull et al. 1982). Activators can act by reducing the spray solution surface tension and contact angle between the droplet and plant surface, solubilizing the leaf cuticle, prolonging the spray solution drying time, serving as an emulsifier and forming micelles, increasing spray retention on plant foliage, maintaining herbicide in the spray solution form for a long period, improving rainfastness, increasing solubility of the herbicide in the cuticle, and enhancing the movement of the herbicide on the surface of the plant to areas of greater absorption (Penner, 2010). This group includes surfactants, crop oil concentrates, and nitrogen fertilizers (Tu and Randal, 2001). Activator adjuvants can be classified by charge: nonionic, cationic, anionic, and amphoteric. Accordingly to Jordan et al. (2010), anionic and cationic surfactants form electrical charges in water (negative and positive, respectively), nonionic do not form an overall charge and amphoteric may or may not form a charge depending on the acidity of the spray solution. Nonionic surfactants are the most widely recommended and used adjuvant (Tu and Randal, 2001).

Utility adjuvants, also called spray modifiers, alter the physical or chemical characteristics of the spray mixture to improve its application performance, ability to remain on the plant surface rather than rolling off, and persistence in the environment (McWhorter 1982). Accordingly to McMullan (2010), utility adjuvants do not directly affect herbicide performance, they improve herbicide efficacy by reducing or minimizing any negative effects on application. Utility adjuvants include wetting agents, drift reducing agents, water conditioners, dye, stickers, compatibility agents, pH buffers, humectants, defoaming and antifoam agents, and UV absorbents (McMullan, 2010, Tu and Randal, 2001). Moreover, adjuvants can contain various combinations of utility adjuvants and/or activator adjuvants (e.g., NIS + AMS; drift reducing agent + water conditioner + spreader). Those blended adjuvants have become popular because multiple ingredients are included in an single jug (Curran and Lingenfelter, 2009) which makes the tank mixing process easier since one product works by serving multiple functions.

## Glufosinate and adjuvants

Glufosinate, ammonium (2RS)-2-amino-4-(methylphosphinato) butyric acid, is a postemergence (POST) herbicide that controls a broad spectrum of grass and broadleaf weed species. Adoption of this herbicide has increased with the development of genetically modified glufosinate-resistant crops (LibertyLink®) available in cotton (*Gossypium hirsutum* L.), corn (*Zea mays* L.), canola (*Brassica napus* L.), and soybean (*Glycine max* (L.) *Merr).* In 2004, when LibertyLink® was released in the market, the use of glufosinate per year was estimated at 2 million pounds, compared to 14 million pounds in 2017 (USGS,2020). Further, new technologies such as EnlistTM® cotton (tolerant to 2,4-D choline, and glufosinate) Enlist E3TM® soybean crops (tolerant to 2,4-D choline, glyphosate, and glufosinate), and Xtendflex® soybean crop (tolerant to dicamba, glyphosate, and glufosinate) will potentially boost glufosinate use in agriculture. Another factor that has contributed to the adoption of glufosinate-based herbicide programs is that there is only one report of a glufosinate-resistance weed in agricultural systems in the United States (Heap, 2021). Thus, this glufosinate can be used to manage weeds with resistance to other herbicides.

Glufosinate works by inhibiting glutamine synthetase (Logusch et al. 1991; Wild et al. 1987), the enzyme that catalyzes the conversion of glutamic acid and ammonia into glutamine (Steckel et al. 1997), which results in rapid accumulation of toxic ammonium and the concomitant depletion of glutamine and several other amino acids (Bellinder et al. 1987; Wild et al. 1987). Phytotoxic symptoms include membrane disruption and inhibition of photosynthesis and consequently plant death. Previous studies show that glufosinate efficacy is variable among weed species and under certain environmental conditions (Everman et. al 2009; Petersen and Hurle 2001; Anderson 1993).

Ammonium-sulfate (AMS) is the only adjuvant in the USA recommended to enhance glufosinate activity (Anonymous, 2019). However, the interaction of glufosinate and AMS on weed control efficacy is strongly species-specific (Zollinger et al. 2010; Maschoff et al. 2000; Pline et al. 1999). The mixture of AMS and surfactant(s) is often a beneficial combination that increases the efficacy of herbicides, especially for weak acid herbicides, such as glufosinate (Wosnika, 2003). Although commercial glufosinate formulations commonly contain surfactants in their composition (Baur et al. 2017), the amount may be insufficient to optimize herbicide efficacy. Additionally, under low humidity conditions, surfactants alone may not keep the herbicide droplets moist long enough for effective uptake (Ramsey et al. 2005).

### Tank mixture of dicamba and glyphosate, and adjuvants

One of the most effective tactics to prevent, delay, or manage herbicide-resistant weeds is the use of herbicides with different modes of action (Norsworthy et al. 2012). The release of dicamba-tolerant (DT) crops to the market in 2017, which are also tolerant to glyphosate, has provided an alternative mode of action to manage herbicide-resistant weeds by allowing POST applications of those two herbicides.

Dicamba, 3,6-dichloro-2-methoxybenzoic acid, was first registered as an herbicide in the United States in 1962 (Hartzler, 2017). This herbicide is a synthetic auxin that mimics the natural plant hormone indole-3-acetic acid (Grossmann, 2007) causing leaf cupping, malformation, and stem epinasty (Ahrens 1994) and necrosis of terminal meristematic tissues followed by reduced root and shoot growth (Tehranchian et al. 2017; Grabińska-Sota et al. 2003), and consequently, plant death. Auxin herbicides have long been used to control many dicotyledonous weed species in grain crops such as wheat (*Triticum aestivum* L.), corn, and grain sorghum [*Sorghum bicolor* (L.) Moench] and also to burndown applications before crop planting (Mithila et al. 2011).

Glyphosate, N-(phosphonomethyl) glycine, was first registered as an herbicide in the U.S in 1974 (Duke and Powles, 2008). This herbicide inhibits 5-enolpyruvylshikimate-3-phosphate (EPSP) enzyme leading to depletion of phenylalanine, tyrosine, and tryptophan (Herrmann and Weaver 1999; Steinrücken and Amrhein 1980) that results in inhibition of the plant growth, chlorosis, and necrosis and, eventually, death of plants (Yao et al. 2012). For the first 20 years after glyphosate was released to the market, its use was restricted to broad-spectrum weed control before crop planting (Duke and Powels, 2008). However, with the introduction of glyphosate-resistance (GR) crops in 1996, adoption of glyphosate has largely increased in the United States. Currently, glyphosate is the most widely used herbicide in the U.S. (EPA, 2019). Nevertheless, as a consequence of the overuse of this herbicide for a prolonged period of time, high occurrence of GR weed populations has been reported across the country. Currently, there are 17 GR weed species reported in the United States (Heap, 2020).

Ammonium sulfate (AMS) is commonly used as a water conditioner to overcome salt antagonism of weak acids in hard water and to enhance phytotoxicity of several herbicides, such as glyphosate (Thelen et al., 1995). However, the use of AMS is not recommended for dicamba herbicides since it increases the formation of volatile dicamba acid by acidifying the solution (Muller and Steckel, 2019; Anonymous, 2020a; Anonymous, 2020b). Non-AMS water conditioner (WC) adjuvants are an alternative to improve dicamba and glyphosate tank mixture's efficacy without increasing dicamba volatility potential. Previous research demonstrated that environmental periods with high evaporation rates, such as high temperature and low humidity, increase dicamba volatility potential (Behrens and Lueschen 1979; Egan and Mortensen 2012). Complementary to non-AMS WC, the use of other adjuvants (e.g., surfactant, humectant) could lead to a decrease in dicamba volatility while enhancing herbicide efficacy. Moreover, due to the many complaints received about dicamba symptomology on non-DT crops in the past few years, actions to mitigate off-target movement have become crucial. As physical drift is another way of off-target movement, the use of drift reducing agent (DRA) is recommended when spraying dicamba. (Anonymous, 2020b). DRA adjuvants alter the viscoelastic properties of the spray solution, increase droplet size, and weight, and minimize the number of easily windborne droplets (Hewitt 1998).

## Objectives

The adoption of glufosinate-based herbicide programs has increased with the widespread occurrence of herbicide resistant weeds in recent years. Also, tank mixture of dicamba and glyphosate has been largely adopted for broad-spectrum weed control since the release of dicamba/glyphosate-tolerant soybeans in 2017. Therefore, it is essential to understand the influence of adjuvants on the performance of those commonly used herbicides. The objective of this research were: (1) conduct laboratory studies to determine the physical properties and droplet spectrum of glufosinate, and dicamba plus glyphosate solutions in tank-mixture with adjuvants and (2) perform greenhouse and field studies to evaluate the response of weed species to glufosinate, and dicamba plus glyphosate solutions in tank-mixture with adjuvants.

## Literature Cited

Anderson, D., Swanton, C., Hall, J., & Mersey, B. (2006, July 28). The influence of temperature and relative humidity on the efficacy of glufosinate-ammonium. Retrieved March 10, 2021, from https://onlinelibrary.wiley.com/doi/abs/10.1111/j.1365-3180.1993.tb01927.x

Ahrens WH, ed (1994) Dicamba. In *Herbicide Handbook, 7th edn* (pp. 430). Champaign, IL: Weed Science Society of America.

Anonymous (2020a) Engenia® herbicide product label. EPA Reg. No. 7969-345. Research Triangle Park, NC: BASF Corporation, 16.

Anonymous (2020b) XtendiMax® with Vaporgrip technology herbicide product label. EPA Reg. No. 524-617. Research Triangle Park, NC: Bayer Crop Protection, Inc,2.

Anonymous (2019) *Liberty herbicide product label EPA Reg. No. 7969-448* (pp. 10-12) Research Triangle Park, NC: Bayer Crop Protection, 10-12.

Behrens, R., &; Lueschen, W. E. (1979). Dicamba volatility. Weed Science, 27(5), 486-493. doi:10.1017/s004317450004445.

Bellinder, R. R., Lyons, R. E., Scheckler, S. E., & Wilson, H. P. (1987). Cellular alterations resulting from foliar applications of hoe-39866. Weed Science, 35(1), 27-35. doi:10.1017/s0043174500026746

Bunting, J. A., Sprague, C. L., & Riechers, D. E. (2004). Absorption and activity of foramsulfuron in giant foxtail (Setaria faberi) and woolly cupgrass (Eriochloa villosa) with various adjuvants. Weed Science, 52(4), 513-517. doi:10.1614/ws-03-135r

Curran, W. (1999). Adjuvants for enhancing herbicide performance. Retrieved March 11, 2021, from https://extension.psu.edu/adjuvants-for-enhancing-herbicide-performance

Curran, W., & Lingenfelter, D. (2009). Adjuvants for enhancing herbicide performance. *In Agronomy Facts 37*. University Park, PA: Pennsylvania State University.

Curran, W., McGlamery, M., Liebl, R., & Lingenfelter, D. (1999). Adjuvants for enhancing herbicide performance. *In Agronomy Facts 37*. University Park, PA: Pennsylvania State University.

Duke, S. O., & Powles, S. B. (2008). Glyphosate: A once-in-a-century herbicide. *Pest Management Science*, *64*(4), 319-325. doi:10.1002/ps.1518

Egan, J. F., & Mortensen, D. A. (2012). Quantifying vapor drift of dicamba herbicides applied to soybean. Environmental Toxicology and Chemistry, 31(5), 1023-1031. doi:10.1002/etc.1778

[EPA] United States Environmental Protection Agency (2019). Glyphosate: Response to Comments, Usage, and Benefits. Retrieved March 22, 2021, from https://www.epa.gov/sites/production/files/2019-04/documents/glyphosate-response-comments-usage-benefits-final.pdf

Everman, W. J., Mayhew, C. R., Burton, J. D., York, A. C., & Wilcut, J. W. (2009). Absorption, Translocation, and Metabolism of 14C-glufosinate in glufosinate-resistant corn, goosegrass (Eleusine indica), large crabgrass (Digitaria sanguinalis), and Sicklepod (Senna obtusifolia). *Weed Science, 57*(1), 1-5. doi:10.1614/ws-08-089.1

Frihauf, J. C., Miller, S. D., & Alford, C. M. (2005). Imazamox rates, timings, and adjuvants affect imidazolinone-tolerant winter wheat cultivars. Weed Technology, 19(3), 599-607. doi:10.1614/wt-04-148r1.1

Grabińska-Sota, E., Wiśniowska, E., & Kalka, J. (2003). Toxicity of selected synthetic auxines—2,4-D and MCPA derivatives to broad-leaved and cereal plants. Crop Protection, 22(2), 355-360. doi:10.1016/s0261-2194(02)00178-3

Grossmann, K. (2007). Auxin herbicide action. *Plant Signaling & Behavior, 2*(5), 421-423. doi:10.4161/psb.2.5.4417

Hartzler, B. (2017). A historical perspective on dicamba [Web log post]. Retrieved from https://crops.extension.iastate.edu/blog/bob-hartzler/historical-perspective-dicamba

Heap, I. The International Herbicide-Resistant Weed Database. Online. Monday, October 26, 2020 .Available www.weedscience.org Copyright © 1993- 2020 WeedScience.org All rights reserved. Fair use of this material is encouraged. Proper citation is requested.

Herrmann, K. M., & Weaver, L. M. (1999). The shikimate pathway. Annual Review of Plant Physiology and Plant Molecular Biology, 50(1), 473-503. doi:10.1146/annurev.arplant.50.1.473

Hess, F. D., Bayer, D. E., & Falk, R. H. (1974). Herbicide dispersal patterns: I. as a function of leaf surface. *Weed Science*, *22*(4), 394-401. doi:10.1017/s0043174500037516

Hewitt, A.J. (1998) The effect of tank mix and adjuvants on spray drift. In: McMullan PM, editor. Adjuvants for agrochemicals: challenges and opportunities. *Proceedings of the Fifth International Symposium on Adjuvants for Agrochemicals, Chemical Producers Distributors Association*, Memphis, TN, 451–62.

https://doi.org/10.1520/STP161920180130

Hull, H. M., Davis, D. G., & Stolzenberg, G. E. (1982). Action of adjuvants on plant surfaces. *Adjuvants for Herbicides. Weed Science Society of America.*, 26-67.

Jordan, T., Johnson, B., & Nice, G. (2011, September). Adjuvants Used With Herbicides: Factors to Consider. Retrieved March 22, 2021, from https://ag.purdue.edu/btny/weedscience/documents/adjuvants%20-%2011.pdf

Kammler, K. J., Walters, S. A., & Young, B. G. (2010). Effects of adjuvants, halosulfuron, and grass herbicides on Cucurbita spp. injury and grass control. *Weed Technology, 24*(2), 147-152. doi:10.1614/wt-d-09-00015.1

Koch, K., Bhushan, B., & Barthlott, W. (2008). Diversity of structure, morphology and wetting of plant surfaces. *Soft Matter, 4*(10), 1943. doi:10.1039/b804854a

Kraemer, T., Hunsche, M., & Noga, G. (2009). Surfactant-induced deposit structures in relation to the biological efficacy of glyphosate on easy- and difficult-to-wet weed species. *Pest Management Science, 65*(8), 844-850. doi:10.1002/ps.1759

Kucharski, M. (n.d.). Degradation of phenmedipham in soil under laboratory conditions. Vegetable Crops Research Bulletin, 60, 63-70.

Logusch, E., Walker, D., McDonald, J., & Franz, J. (1991). Inhibition of plant glutamine synthetases by Substituted phosphinothricins. Plant Physiology, 95(4), 1057-1062. doi:10.1104/pp.95.4.1057

Maschhoff, J. R., Hart, S. E., & Baldwin, J. L. (2000). Effect of ammonium sulfate on the efficacy, absorption, and translocation of glufosinate. *Weed Science, 48*(1), 2-6. doi:10.1614/0043-1745(2000)048[0002:eoasot]2.0.co;2

McMullan, P. M. (2010). Utility adjuvants. Weed Technology, 14(4), 792-797. doi:10.1614/0890-037x(2000)014[0792:ua]2.0.co;2

McWhorter, C. G. (1982). The use of adjuvants. In Adjuvants for herbicides (pp. 10-21). Champaign, IL: Weed Science Society of America.

Mithila, J., Hall, J. C., Johnson, W. G., Kelley, K. B., & Riechers, D. E. (2011). Evolution of resistance to auxinic herbicides: Historical perspectives, mechanisms of resistance, and implications for broadleaf weed management in agronomic crops. Weed Science, 59(4), 445-457. doi:10.1614/ws-d-11-00062.1

Mueller, T. C., & Steckel, L. E. (2019). Spray mixture pH as affected by dicamba, glyphosate, and spray additives. Weed Technology, 33(4), 547-554. doi:10.1017/wet.2019.40

Norsworthy, J. K., Ward, S. M., Shaw, D. R., Llewellyn, R. S., Nichols, R. L., Webster, T. M., . . . Barrett, M. (2012). Reducing the risks of herbicide resistance: Best management practices and recommendations. Weed Science, 60(SP1), 31-62. doi:10.1614/ws-d-11-00155.1

Pacanoski, Z. (2010). Role of Adjuvants on herbicide behavior: A review of different experiences. Herbologia, 11(2), 67-79.

Penner, D. (2000). Activator adjuvants. Weed Technology, 14(4), 785-791. doi:https://doi.org/10.1614/0890-037X(2000)014[0785:AA]2.0.CO;2

Petersen, J., & Hurle, K. (2001). Influence of climatic conditions and plant physiology on glufosinate-ammonium efficacy. *Weed Research*, *41*(1), 31-39. doi:10.1046/j.1365-3180.2001.00214.x

Pline, W. A., Wu, J., & Hatzios, K. K. (1999). Absorption, translocation, and metabolism of glufosinate in five weed species as influenced by ammonium sulfate and pelargonic acid. *Weed Science, 47*(6), 636-643. doi:10.1017/s0043174500091268

Ramsey, R., Stephenson, G., & Hall, J. (2005). A review of the effects of humidity, humectants, and surfactant composition on the absorption and efficacy of highly water-soluble herbicides. *Pesticide Biochemistry and Physiology, 82*(2), 162-175. doi:10.1016/j.pestbp.2005.02.005

Steckel, G. J., Wax, L. M., Simmons, F. W., & Phillips, W. H. (1997). Glufosinate efficacy on annual weeds is influenced by rate and growth stage. Weed Technology, 11(3), 484-488. doi:10.1017/s0890037x00045292

Steinrücken, H., & Amrhein, N. (1980). The herbicide glyphosate is a potent inhibitor of 5-enolpyruvylshikimic acid-3-phosphate synthase. Biochemical and Biophysical Research Communications, 94(4), 1207-1212. doi:10.1016/0006-291x(80)90547-1

Swarcewicz, M. (1996). Influence of oil adjuvants on trifluralin persistence in light soil. Zeszyty Naukowe AR Szczecin, Rolnictwo, 63, 211-217.

Tehranchian, P., Norsworthy, J. K., Powles, S., Bararpour, M. T., Bagavathiannan, M. V., Barber, T., & Scott, R. C. (2017). Recurrent sublethal-dose selection for reduced susceptibility of Palmer amaranth (Amaranthus palmeri) to dicamba. Weed Science, 65(2), 206-212. doi:10.1017/wsc.2016.27

Thelen, K. D., Jackson, E. P., & Penner, D. (1995). The basis for the hard-water antagonism of glyphosate activity. Weed Science, 43(4), 541-548. doi:10.1017/s0043174500081613

Tu, M., Hurd, C., & Randall, J. M. (2001). Adjuvants. In *Weed VEC methods handbook: Tools and techniques for use in natural areas* (pp.171-190). Davis, CA: Wildland Invasive Species Team, the Nature Conservancy. doi:https://www.invasive.org/gist/products/handbook/methods-handbook.pdf

[USGS] U.S Geological Survey (2020).Estimated Annual Agricultural Pesticide Use. Retrieved March 22, 2021, from https://water.usgs.gov/nawqa/pnsp/usage/maps/show_map.php?year=2017&map=GLUFOSINATE&hilo=L&disp=Glufosinate

Wild, A., Sauer, H., & Rühle, W. (1987). The effect of phosphinothricin (glufosinate) on photosynthesis. I. Inhibition of photosynthesis and accumulation of ammonia. Zeitschrift Für Naturforschung C, 42(3), 263-269. doi:10.1515/znc-1987-0316

Woznica, W. J. (2003). *U.S. Patent No. WO2003092373A2*. Washington, DC: U.S. Patent and Trademark Office.

Yao, H., Huang, Y., Hruska, Z., Thomson, S. J., & Reddy, K. N. (2012). Using vegetation index and modified derivative for early detection of soybean plant injury from glyphosate. Computers and Electronics in Agriculture, 89, 145-157.

Zollinger, R. K., Nalewaja, J. D., Peterson, D. E., & Young, B. G. (2010). Effect of hard water and ammonium sulfate on weak acid herbicide activity. *30th Symposium on Pesticide Formulations and Delivery Systems: Regulations and Innovation*. doi:10.1520/stp49228s

# CHAPTER 2

# INFLUENCE OF SURFACTANT-HUMECTANT ADJUVANTS ON PHYSICAL PROPERTIES, DROPLET-SIZE, AND EFFICACY OF GLUFOSINATE FORMULATIONS

## Abstract

Glufosinate efficacy is inconsistent among weed species and under environmental conditions that favor rapid droplet-drying. Surfactant-humectant adjuvants could maximize glufosinate efficacy by increasing wetting and penetration into the leaf surface and droplet-drying time. However, there is a lack of information in the literature about the interaction of those two classes of adjuvants with glufosinate. Therefore, the objective of this study was to investigate the influence of surfactant-humectant adjuvants on the physical properties, droplet-size, and efficacy of two glufosinate formulations. Laboratory, greenhouse, and field studies were conducted in 2019 and 2020. Treatment design was a 2 x 5 factorial where 2 represented the glufosinate formulations combined with 5 adjuvant treatments plus an untreated control where no herbicide or adjuvants were applied. Density and viscosity of glufosinate solutions mostly increased with the addition of adjuvants. However, the influence of the adjuvants on surface tension, contact angle, and evaporation highly varied among glufosinate formulations and RHs. With the addition of adjuvants to formulation 2 solution, biomass reduction was 20% to 35% and 2% to 19% greater for kochia and common lambsquarters under greenhouse conditions, respectively. Moreover, barnyardgrass biomass reduction was 5% greater by formulation 1 than formulation 2. No increase in control, biomass reduction or mortality were observed with the use of adjuvants under field conditions.

Key-words: surface tension, contact angle, density, viscosity, droplet evaporation, weed species

## Introduction

Glufosinate is a contact postemergence (POST) herbicide widely used to control a broad spectrum of grass and broadleaf weed species. This herbicide is applied as a preplant burndown in no-till systems and non-crop areas and as a POST on glufosinate-resistant crops (Devkota and Johnson, 2016). Widespread occurrence of glyphosate-resistance (GR) weeds in recent years has increase the adoption of glufosinate-based herbicides programs (Kaur et al. 2014; Craigmyle et al. 2013; Chahal and Johnson, 2012) since glufosinate is the only non-selective herbicide with low number of weed-resistance reports in agricultural systems (Heap, 2020).

Glufosinate is an anionic herbicide that kills the weeds by inhibiting the glutamine synthetase enzyme and thereby causing rapid accumulation of ammonia and glyoxylate within the plant which leads to damage the chloroplast structures and eventual termination of photosynthetic activity ultimately resulting in necrosis of the tissue (Devine et al. 1993; Hinchee et al.1993). Previous studies proved that glufosinate efficacy is variable among weed species and under certain environmental conditions (Everman et. al 2009; Petersen and Hurle 2001; Anderson 1993).

Adjuvants are commonly used in agriculture to improve the performance of herbicides. Curran et al. (1999) defined adjuvant as any substance in an herbicide formulation or added to the spray tank to improve herbicidal activity or application characteristics. Ammonium-sulfate (AMS) is the only adjuvant in the USA recommended to enhance glufosinate activity (Anonymous, 2020). AMS is added to glufosinate tank mixture mainly as a water conditioner to overcome salt antagonism in hard water (e.g. $Ca^{2+}$ and $Mg^{2+}$) and enhance herbicidal phytotoxicity (Thelen et al., 1995). However, the interaction of glufosinate and AMS is strongly species-specific (Zollinger et al. 2010; Maschoff et al. 2000; Pline et al. 1999). The mixture of AMS and surfactant(s) is often a beneficial combination that increases efficacy of herbicides, especially for weak acid herbicides, such as glufosinate (Wosnika, 2003).

Steckel et. al (1997a) demonstrated that absorption of glufosinate 24 hours after treatments for giant foxtail (*Setaria faberi Herrm.)*, barnyardgrass (*Echinochloa crus-galli (L.) P. Beauv.)*, velvetleaf (*Abutilon theophrasti Medik.)*, and common lambsquarters (*Chenopodium album L.)* was 67%, 53%, 42%, and 16% of applied amount, respectively. Weed species may have different foliar surface characteristics (e.g. cuticle, number of stomata and trichomes, leaf position and angle and leaf age) that impose barriers to herbicide deposition (Koch et al. 2008; Kraemer et al. 2009; Hess 1985; Hull et al. 1982). Surfactants minimize the effect of those barriers by decreasing the contact angle between the droplet and the surface tension which enhance wettability and herbicide penetration through leaf cuticle (Tu and Randall 2001). Although commercial glufosinate formulations commonly contain surfactants in its composition (Baur et al. 2017), the amount may be insufficient to optimize herbicide efficacy. Additionally, under low humidity conditions, surfactants alone may not keep the herbicide droplets moist long enough for effective uptake (Ramsey et al. 2005)

Under warm and dry conditions, the spray droplet evaporates rapid and the herbicide becomes a crystalline residue which slow or ceases completely leaf uptake (Tu and Randall 2001; Pricer, 1983; Cook and Ducan, 1978). Coetzer et al. (2001) reported that glufosinate control was greater in Palmer amaranth (*Amaranthus palmeri* S. Watson), redroot pigweed

(*Amaranthus retroflexus* L.), and common waterhemp (*Amaranthus tuberculatus* (Moq.) J. D. Sauer.) grown at 90% RH than in those grown at 35% RH. Humectants increase the drying-droplet time which allows the active ingredient to be available in solution for a longer period. Previous studies demonstrated that humectants and surfactants work better in the presence of each other (Cook et al. 1977; Babiker and Duncan, 1975). Adding surfactant-humectant adjuvants into the tank mixture may improve consistency of glufosinate efficacy among weed species and under unfavorable environmental conditions. However, there is a lack of information in the literature about the interaction of those two classes of adjuvants with glufosinate.

Besides surfactant-humectant adjuvants alter penetration, wetting and drying-time of the spray droplet, their influence on the physical properties of the solution can also result in changes on the droplet-size distribution (Spanoghe et al. 2007; Spanoghe et al. 2002). Each type of application requires a specific droplet size for optimum biological activity (Knoche, 1994). Therefore, the objectives of this research were to: (1) determine the physical properties (density, viscosity, dynamic surface tension, static contact angle, and droplet evaporation rate) and droplet size distribution of glufosinate solutions in tank-mixture with surfactant-humectant adjuvants and (2) evaluate the response of weed species to glufosinate solutions in tank-mixture with surfactant-humectant adjuvants under greenhouse and field conditions.

## Materials and Methods

Studies were conducted at the Pesticide Application Technology Laboratory of the University of Nebraska-Lincoln located at the West Central Research, Extension and Education Center (WCREEC) in North Platte, NE.

Treatment solutions were arranged in a factorial 2 x 5 where 2 consisted of the two formulations, Liberty® (formulation 1, Bayer CropScience, Research Triangle Park, NC, USA) and Interline® (formulation 2, UPL NA Inc., King of Prussia, PA, USA), at 656 g ai $ha^{-1}$ combined with 4 four experimental surfactant-humectant adjuvants (EA) individually plus each formulation solution with no adjuvant and an untreated control where no herbicide or adjuvants were applied. The EA1 was used at rate of 0.125% v $v^{-1}$, whereas the rates of ER2, ER3, and ER4 were 0.5% v $v^{-1}$. Analyzes of the water used in the solutions indicated presence of 188 mg $L^{-1}$ of $CaCO_3$ which categorizes this water as very hard (USGS 2020). An ammonium-based water conditioner adjuvant (Zippsol®, Martin Resources, Kilgore, TX, USA) was added to all solutions at 0.125% v $v^{-1}$ to overcome the antagonistic effects of cationic salts in the water. Solutions were prepared simulating a 140 L $ha^{-1}$ carrier volume.

## Physical properties Study

The density and dynamic viscosity of the solutions were measured at 20°C by a density meter (DMA™ 4500 M, Anton Paar USA Inc., Ashland, VA, USA) and microviscometer (Lovis 2000 M/ME, Anton Paar USA Inc., Ashland, VA, USA), respectively. Dynamic surface tension (dST), static contact angle (sCA), and evaporation rate (ER) analyses were conducted using a video-based optical contact angle measuring instrument (OCA 15EC, DataPhysics Instruments

GmbH, Filderstadt, Germany). This instrument is composed of a video measuring system with a USB camera of high performance linked to sCA software (SCA 20, V.4.1.11 build 1018) that collects, asses, and evaluates the measured data. A liquid circulator (Julabo USA Inc, Allentown, PA, USA) and a humidity generator and controller - HCG (DataPhysics Instruments GmbH, Filderstadt, Germany) were used to keep the temperature at 25 ± 1°C and the relative humidity at 20, 40, 60, and 80 ± 1%. For each treatment solution, density, viscosity, dST, sCA, and ER were replicated three times for each humidity. Moraes et al. (2019) provided detailed information regarding use and operation of the density meter, microviscometer, and OCA 15EC for dST and sCA measurements. Also, Fritz et al. (2017) described the ER measurement procedure using the OCA 15EC. In this present study, ER measurements were performed using an initial droplet volume of 0.15 µL and evaporation maximum time interval of 120 seconds. ER was calculated according to Equation (1):

$$ER = \left(\frac{Vi - Vf*}{Tf}\right) \qquad (1)$$

Where Vi is the initial volume of the droplet (µL) at 0 s, Vf is the final volume of the droplet at Tf which is the maximum time interval (120 s) or the time interval (s) in which the droplet completely evaporated before 120 s.

## Droplet-size Study

Solutions previously mentioned in the physical properties study were sprayed through TT 110015 nozzles (TeeJet Technologies Spraying Systems Co., Glendale Heights, IL, USA). The droplet-size distribution for each solution was measured using a HELOS-VARIO/KR laser diffraction system with the R7 lens (Sympatec Inc., Clausthal, Germany), as described with more details by Fritz et al. (2014) and Butts et al. (2019). For each treatment, the spray plume traversed through the measurement zone three times. Each complete traverse was considered a repetition for statistical analysis. The distance from the nozzle tip to the laser was 0.3 m. Nozzles operated at 276 kPa with a constant airspeed of 6.7 m $s^{-1}$.

The $Dv_{0.1}$, $Dv_{0.5}$, and $Dv_{0.9}$ (droplet diameters for which 10, 50, and 90% of the total spray volume is contained in droplets of lesser diameter, respectively), volume percentage of droplets smaller than 150 μm - percentage of fines (PF) and the relative span (RS) were measured for each treatment solution. RS is a dimensionless parameter that indicates uniformity of droplet-size distribution, calculated using Equation 2 (ASABE, 2016), while $V_{150}$ is an indicator of the potential risk of drift.

$$RS = \left(\frac{DV0.9 - D.V0.1}{DV0.5}\right) \qquad (2)$$

## Greenhouse Study

The study was conducted in a complete randomized block design with a 2 x 5 factorial arrangement, four replications and two runs. Same solution combinations and adjuvants rates as previously mentioned were used. However, glufosinate rates were reduced to 328 g ai $ha^{-1}$ to avoid complete weed control and enable treatment comparisons. Barnyardgrass (*Echinochloa crus-galli (L.) P. Beauv.*), common lambsquarters (*Chenopodium album L.)*, horseweed (*Erigeron canadensis* L.), kochia (*Bassia scoparia* (L.) A. J. Scott), velvetleaf (*Abutilon theophrasti Medik.*), and common waterhemp (*Amaranthus tuberculatus (Moq.) J. D. Sauer)* were grown in 10 cm cone-tainers (Stuewe and Sons Inc., Corvallis, OR, USA) using Pro-Mix BX5 (Premier Tech Horticulture Ltd, Riviere-du-Loup, Canada). Greenhouse temperature was maintained between 18 and 28°C and 60% ±10% RH. Supplemental LED lighting of 520 µmol $s^{-1}$ (Philips Lighting, Somerset, NJ, USA) was provided to extend daylight period to 16 hours. Plants were watered daily using a commercial liquid fertilizer (UNL 5-1-4, Wilbur-Ellis Agribusiness, Aurora, CO, USA) and treated weakly with *Bacillus thuringiniensis* (Gnatrol WDG®, Valent U.S.A., Walnut Creek, CA, USA) to avoid loopers (*Trichoplusia* spp.) and other insects. Once plants were 15 cm tall and horseweed was 10 cm in diameter, applications were made using a three-nozzle spray chamber (Generation III Research Track Sprayer DeVries Manufacturing, Hollandale, MN, USA) calibrated to deliver 140 L $ha^{-1}$ through TT 110015 nozzles (TeeJet Technologies Spraying Systems Co., Glendale Heights, IL, USA) at 276 kPa operating pressure. Nozzles spacing and boom height was 51 cm and application speed was 1.3 m $s^{-1}$.

At 28 days after application (DAA), visual estimations of control (VEC) were recorded, and surviving plants aboveground biomass were harvested and over-dried at 65°C until constant dry weight. Dry biomass data was recorded and converted into percentage of biomass reduction as compared with the untreated control according to the Equation 3:

$$\mathrm{BR} = 100 - \frac{(X*100)}{\mathrm{Y}} \qquad (3)$$

Where BR is the biomass reduction (%), X is the biomass (g) of an individual experimental unit after being treated and Y is the mean biomass (g) of the untreated control replicates.

## Field Study

Two trials of horseweed were conducted during the growing season of 2019 and 2020 in North Platte-NE and Paxton-NE, respectively, and one trial of Palmer amaranth (*Amaranthus palmeri* S. Watson) was conducted during the growing season of 2020 in North Platte-NE. Trials were randomized in complete block experimental designs with a 2 x 5 factorial arrangement of treatments with four replications. Individual plots were 3 m wide by 10 m long. Spray solution combinations and product rates were the same used in the physical proprieties and droplet-size study. Late-season horseweed plants (50 cm tall) and Palmer amaranth plants (40 cm tall) were sprayed using a six-nozzle handheld $CO_2$ pressurized backpack sprayer (Bellspray Inc., Opelousas, LA, USA) calibrated to deliver 140 L $ha^{-1}$ through TT110015 nozzles (TeeJet Technologies Spraying Systems Co., Glendale Heights, IL, USA) at 276 kPa. Nozzles spacing and boom height was 51 cm and application speed was 1.3 m $s^{-1}$. Tall plants were used so treatments could be differentiated using glufosinate rate commonly applied in the field (656 g ai $ha^{-1}$). Temperature and relative humidity during applications in 2019 and 2020 are described in Table 1.

VEC were recorded at 28 DAA for entire plots. In addition, 10 random plants per plot were marked with orange spray paint before application. At 28 DAA, marked plants were individually evaluated for mortality (dead or alive) and converted into percent of mortality reduction using Equation 4 (Butts et al. 2018):

$$\mathrm{M} = 100 * \left(\frac{D}{10}\right) \qquad (4)$$

Where M is mortality (%), and D is the number of dead plants per plot after being treated.

Those ten plants used for mortality evaluation were clipped at the soil surface, harvested, and oven-dried at 65°C until constant weight. Dry biomass was recorded and converted into percentage of biomass reduction as compared with the untreated control according to the Equation 3.

### Statistical Analyzes

Data were subjected to analysis of variance using the base package in R Statistical Software, version 3.3.1 (R Core Team 2019). Replications were treated as a random effect and year, formulation, and adjuvant as fixed effects. However, for Palmer amaranth, year effect was not included as a fixed effect because of availability of only one-year data. Treatments were compared to each other using Tukey's least significant at $\alpha = 0.05$.

## Results and Discussion

### Physical properties Study

A significant interaction formulation versus adjuvant was demonstrated by the ANOVA table for density, viscosity, sCA, dST, and ER ($p < 0.001$).

### Density and Viscosity

Solutions containing adjuvants had greater density than solutions without adjuvants for both glufosinate formulations (Table 2.1). The addition of adjuvants increased density from $2\ 10^{-4}$ to $4\ 10^{-4}$ g cm$^3$ (0.02% to 0.04%) for formulation 1 (F1) and from $1\ 10^{-4}$ to $5\ 10^{-4}$ g cm$^3$ (0.01% to 0.05%) for formulation 2 (F2), when compared to F1 (1.0089 g cm$^3$) and F2 (1.0084 g cm$^3$)

alone, respectively. Similar results were reported by Moraes et al. (2018) in which lactofen plus non-ionic surfactant (NIS) had density 0.02% greater than lactofen alone. Furthermore, in presence of adjuvants, F1 solutions had higher densities than F2 solutions. For example, F1 plus EA1 resulted in 1.0091 g $cm^3$ compared to 1.0085 g $cm^3$ when EA1 was mixed with F2.

Compared to F1 alone, the addition of adjuvants increased the viscosity of F1 solutions. For F2, only EA1 and EA3 increased viscosity compared to F2 without adjuvant. For example, when adjuvants were not used, the viscosity was 1.0623 mPa $s^{-1}$ for F1 and 1.0730 mPa.$s^{-1}$ for F2, with the addition of EA3 the viscosities increased by 1.2 $10^{-2}$ mPa $s^{-1}$ (0.9%) and 5.6 $10^{-2}$ mPa $s^{-1}$ (11.9%) for those respective herbicides. Assuncao et al. 2019 reported that addition of a synthetic adjuvant to glyphosate solution increased viscosity by 4.1% when compared to glyphosate alone. However, the addition of EA2 and EA4 to F2 solutions reduced the viscosity, which can be explained by the different NIS composition present in those formulations in relation to EA1 and EA3. Although the effect of surfactants usually increases the viscosity of formulated herbicides (Behrens, 1964), the nature of the adjuvant and other components in the herbicide formulation may result in adverse effects on the viscosity of the spray solution.

Normally, changes in density and viscosity are small because the recommended adjuvant concentration is low in relation to the total amount of water needed to prepare the spray solution (Cunha and Alves, 2009). However, minimal changes in density and viscosity may influence the droplet size and droplet spectrum (Assuncao et. al 2019) which can directly impact herbicide performance and spray application quality.

## Dynamic Surface Tension

The addition of adjuvants resulted in a decrease of dST for both glufosinate formulations. However, different trends were observed for the relative humidities tested (Table 2.2). At 20% RH, compared to F1 alone (30.1 mN $m^{-1}$), the addition of EA1 and EA3 to F1 solutions decreased dST in 0.7 mN $m^{-1}$ and 0.6 mN $m^{-1}$, respectively, and EA4 increased in 0.7 mN $m^{-1}$. For F2 solutions, the addition of adjuvants decreased dST from 0.4 to 3.7 mN m-1 compared to F2 alone (30.8 mN m-1). At 40% RH, dST of F1 solutions did not change with the addition of adjuvants. However, when adjuvants were added to F2 solutions, dST decreased in a range of 0.6 to 2.2 mN $m^{-1}$, compared to F2 alone (30.1 mN m-1). At 60% RH, the influence of adjuvants on dST varied for both formulations. Compared to F1 alone (29.9 mN $m^{-1}$), while the addition of EA1 to F1 solution decreased dST in 2.3 mN $m^{-1}$, EA2 and EA4 increased in 0.4 mN $m^{-1}$ and 0.3 mN $m^{-1}$, respectively. Moreover, for F2 solutions, the addition of EA1 and EA3 decreased dST in 0.6 mN $m^{-1}$ and 1.7 mN $m^{-1}$ and EA2 and EA4 increased in 1.0 mN $m^{-1}$ and 0.8 mN $m^{-1}$, respectively, both compared to F2 alone (29.1 mN $m^{-1}$). At 80% RH, compared to F1 alone (29.6 mN $m^{-1}$), dST decreased in 0.6 mN $m^{-1}$ when EA4 was added to F1 solution. However, the addition of EA1, EA2 and EA3 to F2 solutions decreased dST from 0.9 to 2.6 mN $m^{-1}$, compared to F2 alone (29.9 mN $m^{-1}$). It is well reported in the literature that surfactants reduce the surface tension of herbicide solutions (Ogino et al. 1990; Ferri and Stebe, 2000; Curran et al. 2009; Moraes 2018). Sobiech et al. (2020) reported that compared to sulcotrione alone, the addition of NIS to sulcotrione solutions reduced the dST by 20.8 mN. m-1. Surfactants typically reduce the surface tension of a solution between 30 and 50 mN. m-1 (Curran et al. 1999). However, surfactant nature and concentration, presence of other adjuvants (Qazi, 2020), herbicide formulation (Castro el at. 2018), and RH (Torrecila et al. 2008) can also affect surface tension.

Moreover, ammonium sulfate salt increases the surface tension of water (Pegram and Record, 2007) which may explain the higher surface tension observed for some of the treatment solutions.

## Static Contact Angle

At 20% RH, the addition of EA1, EA3, and EA4 decreased sCA from 7.3 to 10.0° for F1 and from 1.9 to 10.7° for F2, compared to those respective formulations alone. At 40% RH, compared to F1 alone (34.7°), when EA1 and EA2 were added to F1 solutions sCA decreased in 5.9° and 2.9°, respectively. Contrarily, for F2, sCA decrease only with the addition of EA3. At 60%, compared to F1 alone (32.5°), the addition of EA3 to F1 solution increased sCA in 4.3° However, for F2, the addition of EA1 and EA3 decreased sCA in 5.9° and 8.1°, respectively, compared to F2 alone (38.4°). No decrease in sCA was observed when adjuvants were added to both formulations at 80% RH. Sobiech et. at (2020) reported that at 60% RH CA of sulcotrione solutions containing NIS was 20.2° smaller than sulcotrione alone. Although sCA is directly related to the dST, some of the adjuvant solutions that had lower dST in relation to formulations alone did not necessarily had lower sCA. The CA is affected by the ST of the liquid, surrounding vapor (Kraemer et al. 2009), and adjuvant nature and concentration (Singh et al. 1984) ,which may explain the variable influence of adjuvants on the contact angles of the spray solutions at different relative humidities observed in this study. Therefore, herbicide formulation-adjuvant-humidity is a complex interaction.

## Evaporation rate

The use of adjuvants had variable ER responses for each glufosinate formulation and RH (Table 2.4). At 20% RH, the ER of F1 without adjuvants was 6.0 $10^{-4}$ µL $s^{-1}$. With the addition of adjuvants, the ER increased from 4.0 $10^{-4}$ to 1.2 $10^{-3}$ µL.$s^{-1}$ which is equivalent to 67 % to 200%. The ER of F2 with adjuvants reduced from 5.0 $10^{-4}$ to 1.7 $10^{-3}$ µL.$s^{-1}$ (22% to 74%) in comparison to F2 alone (2.3 $10^{-3}$ µL.$s^{-1}$). At 40% RH, where the addition of EA1, EA2, and ER4 decreased the ER for F1 solutions and increased for F2 solutions. At 60% RH, the influence of adjuvants was similar to 20% RH considering the F2 solutions, where ER was reduced from 7.0 $10^{-4}$ to 2.0 $10^{-3}$ µL.$s^{-1}$ (35% to 100%) with the addition of adjuvants, compared to F2 alone (2.7 $10^{-3}$ µL.$s^{-1}$). At 80% RH, when compared to F1 alone (0.9 $10^{-3}$ µL.$s^{-1}$), the addition of EA1, EA2, and EA3 increased ER in a range of 7 $10^{-4}$ to 1.8 $10^{-3}$ µL.$s^{-1}$ (78% to 200%) for F1. Also, compared to F2 alone (1.2 $10^{-3}$ µL.$s^{-1}$), ER increased in 9 $10^{-4}$ µL.$s^{-1}$ when EA2, EA3, and EA4 (75%) were added to F2 solutions. Literature about the influence of surfactant-humectant on droplet evaporation rate is limited. However, Cook and Ducan (1978) reported that aminotriazole penetration into bean leaves maintained at 50 ± 10% RH and 30C increased 71% when a surfactant-humectant (polysorbate-glycerol) was added to the solution, compared to herbicide solution containing just surfactant. One possible interpretation of this data is that solution containing only surfactant did not keep the herbicide droplets moist long enough for effective uptake (Ramsey et al. 2005), but with the addition of a humectant, evaporation rate decreased and, consequently herbicide stayed in solution available for uptake for a longer period. According to Li et al. (2019), the high concentration of the surfactants could shorten the evaporation duration of the droplet since in some cases the adjuvant reduces the spray solution surface tension that would accelerate the spreading and evaporation. Further, surfactants that reduce contact angle can result in a 10-fold increase in surface area available for evaporation (Price, 1983). Wang et al. (2020) demonstrated that the evaporation ratio of NIS solutions raised with temperature increasing and humidity decreasing. However, the evaporation ratio of two NIS investigated in this same study differed at the same temperature and humidity.

## Droplet-Size Study

The ANOVA table demonstrated a significant formulation versus adjuvant interaction for Dv0.1, Dv0.5, Dv0.9, PF and RS ($p < 0.001$). In general, the addition of EA to F1 and F2 solutions decreased and increased the volumetric diameters, respectively (Table 3). Consequently, the PF was increased and decreased when EAs were used in comparison to F1 and F2 alone, respectively.

The solutions with EA2 and EA3 produced similar Dv0.5 when tank mixed with F1 (420-425 µm). However, EA3 produced 15 µm coarser Dv0.5 than EA2 when tank mixed with F2. F1 solutions containing EA presented 2 to 3-fold higher PF than F1 alone. Contrarily, compared to F2 alone, PF of F2 lowered 1-fold when adjuvants were added to F2 solutions. The response of RS to the addition of adjuvants was similar to PF. When adjuvants were added to the solutions, RS increased by 0.06 to 0.14 for F1 and decreased by 0.02 to 0.05 for F2 when compared to those respective formulations alone.

Mueller and Womac (1997) demonstrated that droplet size spectrum differed between three glyphosate formulations. The Spray Drift Task Force defined physical properties as one of the primary factors affecting droplet size spectrum (Hewitt, 2001). Cunha and Alves (2009) concluded that viscosity and surface tension were the most affected physical properties by the addition of adjuvants. Despite the use of EA has decreased the surface tension for both glufosinate solutions, viscosity values of F2 solutions were greater than F1 solutions when using the EA1 and EA3, which may explain that F2 produced coarser droplets in comparison to F1.

## Greenhouse study

The ANOVA table demonstrated a significant formulation versus adjuvant interaction for BR and VEC for c. lambsquarters and kochia ($p < 0.05$). For barnyardgrass, the main effect formulation was significant for VEC and BR and the main effect adjuvant was only significant for BR ($p < 0.05$). Regarding velvetleaf, both main effects were significant for the abovementioned parameters ($p < 0.05$). No significant interaction between formulation and adjuvant and main effects were observed for VEC and BR for horseweed and c. waterhemp (data not shown).

The addition of EA to F1 solution did not improve VEC and BR of c. lambsquarters, which ranged from 31% to 36% for VEC and 44% to 49% for BR. The EA4 was the only adjuvant added to F2 solution that increased the VEC (26%) compared to formulations alone (7%) In contrast, all adjuvants improved BR of c. lambsquarters compared to F2 alone (12%). Common lambsquarters has a high wax content per unit of leaf area (Sanyal et al 2006). Chachalis et al. 2001 demonstrated that wax content and the spread area of herbicide droplet are inversely related, which explains the poor control of this specie for both glufosinate formulations, especially F2. Steckel et. al (1997b) showed that the absorption of glufosinate (140 g ai ha$^{-1}$) was low for c. lambsquarters, even tank mixed with a NIS.

For kochia, the addition of adjuvants did not change VEC for F1 which was above 93% for all solutions tested. Kumar and Jha (2015) reported that kochia control by F1 (590 g ai ha$^{-1}$) at 28 DAA was 95%. VEC of F2 tank mixed with adjuvants ranged from 92% to 100% compared to 56% from F2 alone. No differences in BR was observed with the use of adjuvants for F1. In general, F1 provided above 89% biomass reduction for kochia. However, compared to F2 alone (62%), the use of adjuvants increased biomass reduction by 27 to 35 percentage points.

Regardless of adjuvant, F1 resulted in greater VEC and BR of barnyardgrass and velvetleaf in comparison to F2 (Table 4.2). Among adjuvants, few differences were observed. Adjuvant treatments resulted in VEC from 82% to 92% on barnyardgrass and from 74% to 86% on velvetleaf. Among adjuvants, EA1 presented barnyardgrass VEC 10% lower than EA4. Moreover, EA3 decreased velvetleaf VEC in 10 percentage points compared to solutions without adjuvants (84%). For BR, solutions containing EA3 and EA4 presented 6% and 7% greater barnyardgrass BR than solutions without adjuvant (90%), respectively. However, for velvetleaf, among adjuvants EA2 presented greater BR than the other EAs.

Control and biomass reduction of horseweed and common waterhemp by F1 and F2 was above 98% (data not shown) which made treatments comparisons unfeasible. Takano and Dayan (2020) demonstrated that horseweed is very susceptible to glufosinate, achieving 50% BR with 26 g ai ha$^{-1}$. Beyers et at (2002) reported 99% or greater control of common waterhemp with glufosinate (230 g ai ha$^{-1}$) at 28 DAA.

The variable influence of the adjuvants on the glufosinate efficacy observed throughout this study may occurred due to differences on the formulation composition. Commercial glufosinate formulations contain surfactants in its composition (Baur et al. 2017), and the addition of other adjuvants in tank mixtures may not provide additional effect on efficacy or may cause antagonistic effect, as observed for F1.

### Field Study

Field results show no interaction between formulation and adjuvant. Formulations produced similar VEC, BR, and mortality of both horseweed and Palmer amaranth (Table 5). BR ranged from 66 to 69% for horseweed and from 69 to 72% for Palmer amaranth. No differences were observed in BR and mortality between adjuvants and the addition of EA did not provide increments of efficacy on both weed species. Eubank et al.(2013), demonstrated that by 28 DAT, the level of horseweed control with saflufenacil plus NIS at 0.25 v $v^{-1}$ and 0.5 v $v^{-1}$ was similar to saflufenacil alone under field conditions. Furthermore, VanGessel (2001) reported that were no difference in control of horseweed by two different glyphosate formulations. Nandula et al. (2018) reported that control of Palmer amaranth did not increased with the addition of NIS at 3 weeks after treatment.

## Literature Cited

Anderson, D., Swanton, C., Hall, J., & Mersey, B. (2006, July 28). The influence of temperature and relative humidity on the efficacy of glufosinate-ammonium. Retrieved March 10, 2021, from https://onlinelibrary.wiley.com/doi/abs/10.1111/j.1365-3180.1993.tb01927.x

Anonymous (2019) *Liberty herbicide product label EPA Reg. No. 7969-448* (pp. 10-12) Research Triangle Park, NC: Bayer Crop Protection, 10-12.

*ASABE Standards. S327.4: Terminology and definitions for applications of crop or forestry production and protective agents.* (2016). St. Joseph, MI: ASABE.

Assuncao, H. H., Campos, S. F., Sousa, L. A., Lemes, E. M., Zandonadi, C. H., & Cunha, J. P. (2019). Adjuvants plus phytosanitary products and the effects on the physical-chemical properties of the spray liquids. *Bioscience Journal, 35*(6), 1878-1885.

Babiker, A. G., & Duncan, H. J. (1975). Penetration of bean leaves by asulam as influenced by adjuvants and humidity. *Pesticide Science, 6*(6), 655-664. doi:10.1002/ps.2780060613

Baur, P., Bauer, M., Schweinitzer, G., & Wolf, S. (2017). *U.S. Patent No. US 20170265477A.* Washington, DC: U.S. Patent and Trademark Office.

Behrens, R. W. (1964). The physical and chemical properties of surfactants and their effects on formulated herbicides. *Weeds, 12*(4), 255. doi:10.2307/4040747

Beyers, J. T., Smeda, R. J., & Johnson, W. G. (2002). Weed management programs in glufosinate-resistant soybean (Glycine max)1. *Weed Technology, 16*(2), 267-273. doi:10.1614/0890-037x(2002)016[0267:wmpigr]2.0.co;2

Butts, T. R., Butts, L. E., Luck, J. D., Fritz, B. K., Hoffmann, W. C., & Kruger, G. R. (2019). Droplet size and nozzle tip pressure from a pulse-width modulation sprayer. *Biosystems Engineering, 178*, 52-69. doi:10.1016/j.biosystemseng.2018.11.004

Butts, T. R., Samples, C. A., Franca, L. X., Dodds, D. M., Reynolds, D. B., Adams, J. W., . . . Kruger, G. R. (2018). Spray droplet size and carrier volume effect on dicamba and glufosinate efficacy. *Pest Management Science, 74*(9), 2020-2029. doi:10.1002/ps.4913

Castro, E., Carbonari, C., Velini, E., Gomes, G., & Belapart, D. (2018). Influence of adjuvants on the surface tension, deposition and effectiveness of herbicides on fleabane plants. *Planta Daninha, 36*(0). doi:10.1590/s0100-83582018360100067

Chachalis, D., Reddy, K. N., Elmore, C. D., & Steele, M. L. (2001). Herbicide efficacy, leaf structure, and spray droplet contact angle among Iomoea species and smallflower morningglory. *Weed Science, 49*(5), 628-634. doi:10.1614/0043-1745(2001)049[0628:helsas]2.0.co;2

Chahal, G. S., & Johnson, W. G. (2012). Influence of glyphosate or glufosinate combinations with growth regulator herbicides and other agrochemicals in controlling glyphosate-resistant weeds. *Weed Technology, 26*(4), 638-643. doi:10.1614/wt-d-12-00058.1

Coetzer, E., Al-Khatib, K., & Loughin, T. M. (2001). Glufosinate efficacy, absorption, and translocation in Amaranth as affected by relative humidity and temperature. *Weed Science, 49*(1), 8-13. doi:10.1614/0043-1745(2001)049[0008:geaati]2.0.co;2

Cook, G. T., & Duncan, H. J. (1978). Uptake of aminotriazole from humectant-surfactant combinations and the influence of humidity. *Pesticide Science, 9*(6), 535-544. doi:10.1002/ps.2780090609

Cook, G. T., & Duncan, H. J. (1978). Uptake of aminotriazole from humectant-surfactant combinations and the influence of humidity. *Pesticide Science, 9*(6), 535-544. doi:10.1002/ps.2780090609

Corbett, J. L., Askew, S. D., Thomas, W. E., & Wilcut, J. W. (2004). Weed efficacy evaluations for bromoxynil, glufosinate, glyphosate, pyrithiobac, and sulfosate. *Weed Technology, 18*(2), 443-453. doi:10.1614/wt-03-139r

Craigmyle, B. D., Ellis, J. M., & Bradley, K. W. (2013). Influence of herbicide programs on weed management in soybean with resistance to glufosinate and 2,4-d. *Weed Technology, 27*(1), 78-84. doi:10.1614/wt-d-12-00099.1

Creech, C. F., Henry, R. S., Fritz, B. K., & Kruger, G. R. (2015). Influence of Herbicide active Ingredient, Nozzle Type, Orifice Size, Spray pressure, and Carrier Volume rate on spray droplet Size characteristics. *Weed Technology, 29*(2), 298-310. doi:10.1614/wt-d-14-00049.1

Cunha, J., & Alves, G. (2009). Características físico-químicas de soluções aquosas com adjuvantes de uso agrícola. *Interciencia, 34*(9), 655-659.

Curran, W., McGlamery, M., Liebl, R., & Lingenfelter, D. (1999). Adjuvants for enhancing herbicide performance. *In Agronomy Facts 37*. University Park, PA: Pennsylvania State University.

Devine, M. D., Duke, S. O., & Fedke, C. (1993). Inhibition of amino acid biosynthesis. In *Physiology of Herbicide Action* (pp. 274-275). Englewood Cliffs, NJ: Prentice Hall.

Devkota, P., & Johnson, W. G. (2016). Glufosinate efficacy as influenced by carrier water pH, hardness, foliar fertilizer, and ammonium sulfate. *Weed Technology, 30*(4), 848-859. doi:10.1614/wt-d-16-00053.1

Eubank, T. W., Nandula, V. K., Reddy, K. N., Poston, D. H., & Shaw, D. R. (2013). Saflufenacil efficacy on horseweed and its interaction with glyphosate. *Weed Biology and Management, 13*(4), 135-143. doi:10.1111/wbm.12022

Everman, W. J., Mayhew, C. R., Burton, J. D., York, A. C., & Wilcut, J. W. (2009). Absorption, Translocation, and Metabolism of 14C-glufosinate in glufosinate-resistant corn, goosegrass (Eleusine indica), large crabgrass (Digitaria sanguinalis), and Sicklepod (Senna obtusifolia). *Weed Science, 57*(1), 1-5. doi:10.1614/ws-08-089.1

Eytcheson, A. N. (2015). *Antagonism of barnyargrass (Echinochloa crus-galli) control with graminicides by glufosinate in LibertyLink soybeans (Glycine max)* (Unpublished doctoral dissertation). Mississippi State University.

Ferri, J. K., & Stebe, K. J. (2000). Which surfactants reduce surface tension faster? A scaling argument for diffusion-controlled adsorption. *Advances in Colloid and Interface Science, 85*(1), 61-97. doi:10.1016/s0001-8686(99)00027-5

Fritz, B. K., Hoffmann, W. C., Gizotti-de-Moraes, J., Guerrerio, M., Golus, J., & Kruger, G. R. (2018). The impact of spray adjuvants on solution physical properties and spray droplet size. *Pesticide Formulation and Delivery Systems: 37th Volume, Formulations with Ingredients on the EPA's List of Minimal Concern,* 22-32. doi:10.1520/stp160220160134

Fritz, B. K., Hoffmann, W. C., Kruger, G. R., Henry, R. S., Hewitt, A., & Czaczyk, Z. (2014). Comparison of drop size data from ground and aerial application nozzles at three testing laboratories. *Atomization and Sprays, 24*(2), 181-192. doi:10.1615/atomizspr.2013009668

Grayson, B. T., Webb, J. D., Pack, S. E., & Edwards, D. (1991). Development and assessment of a mathematical model to predict foliar spray deposition under laboratory track spraying conditions. *Pesticide Science, 33*(3), 281-304. doi:10.1002/ps.2780330304

Henry, R. S., Kruger, G. R., Fritz, B. K., Hoffmann, W. C., & Bagley, W. E. (2014). Measuring the effect of spray plume angle on the accuracy of droplet size data. *Pesticide Formulation and Delivery Systems "Sustainability: Contributions from Formulation Technology", 33,* 129-138. doi:10.1520/stp156920120130

Hess, F. D., Bayer, D. E., & Falk, R. H. (1974). Herbicide dispersal patterns: I. as a function of leaf surface. *Weed Science, 22*(4), 394-401. doi:10.1017/s0043174500037516

Hewitt, A., (2001). Spray Drift Task Force, Science Peer Review Report. Macon, Missouri: Stewart Agricultural Research Services, Unpublished Report. Retrieved from AG_DRIFT_TankMixNozzleEffectDropSize.pdf (wisc.edu)

Hinchee, M. A., Padgette, S. R., Kishore, G. M., Delannay, X., & Fraley, R. T. (1993). Herbicide-tolerant crops. *Transgenic Plants,* 243-263. doi:10.1016/b978-0-12-428781-5.50037-5

Holloway, P. J. (1994). Physicochemical factors influencing the adjuvant-enhanced spray deposition and coverage of foliage-applied agrochemicals. *Interactions Between Adjuvants, Agrochemicals and Target Organisms,* 83-106. doi:10.1007/978-3-662-02988-6_4

Hull, H. M., Davis, D. G., & Stolzenberg, G. E. (1982). Action of adjuvants on plant surfaces. *Adjuvants for Herbicides. Weed Science Society of America.,* 26-67.

Kaur, S., Sandell, L. D., Lindquist, J. L., & Jhala, A. J. (2014). Glyphosate-resistant giant ragweed (Ambrosia trifida) control in glufosinate-resistant soybean. *Weed Technology, 28*(4), 569-577. doi:10.1614/wt-d-14-00009.1

Knoche, M. (1994). Effect of droplet size and carrier volume on performance of foliage-applied herbicides. *Crop Protection, 13*(3), 163-178. doi:10.1016/0261-2194(94)90075-2

Koch, K., Bhushan, B., & Barthlott, W. (2008). Diversity of structure, morphology and wetting of plant surfaces. *Soft Matter, 4*(10), 1943. doi:10.1039/b804854a

Kraemer, T., Hunsche, M., & Noga, G. (2009). Surfactant-induced deposit structures in relation to the biological efficacy of glyphosate on easy- and difficult-to-wet weed species. *Pest Management Science, 65*(8), 844-850. doi:10.1002/ps.1759

Kumar, V., & Jha, P. (2015). Influence of herbicides applied postharvest in wheat stubble on control, fecundity, and progeny fitness of Kochia scoparia in the US Great Plains. *Crop Protection, 71*, 144-149. doi:10.1016/j.cropro.2015.02.016

Li, Travlos, Qi, Kanatas, & Wang. (2019). Optimization of herbicide use: Study on spreading and evaporation characteristics of glyphosate-organic silicone mixture droplets on weed leaves. *Agronomy, 9*(9), 547. doi:10.3390/agronomy9090547

Maschhoff, J. R., Hart, S. E., & Baldwin, J. L. (2000). Effect of ammonium sulfate on the efficacy, absorption, and translocation of glufosinate. *Weed Science, 48*(1), 2-6. doi:10.1614/0043-1745(2000)048[0002:eoasot]2.0.co;2

Miller, P., & Westra, P. (1998). How surfactants work. Retrieved March 11, 2021, from http://thanyagroup.com/research/download/25530111_2.pdf

Colorado State University Cooperative Extension, Crop Fact no. 0.564

Moraes, J. G., Luck, J. D., Antuniassi, U. R., Hoffmann, W. C., & Kruger, G. R. (2019). Effect of adjuvants on physical properties of glyphosate and PPO-Inhibiting Herbicide Spray Mixtures. *Pesticide Formulation and Delivery Systems: Innovative Formulation, Application and Adjuvant Technologies for Agriculture, 39,* 64-74. doi:10.1520/stp161920180130

Mueller, T. C., & Womac, A. R. (1997). Effect of formulation and nozzle type on droplet size with isopropylamine and trimesium salts of glyphosate. *Weed Technology, 11*(4), 639-643. doi:10.1017/s0890037x00043177

Nalewaja, J. D., & Matysiak, R. (1993). Spray carrier salts affect herbicide toxicity to kochia (Kochia Scoparia). *Weed Technology, 7*(1), 154-158. doi:10.1017/s0890037x00037040

Nandula, V. K., Molin, W. T., & Bond, J. A. (2018). Influence of water Quality, formulation, adjuvant, rainfastness, and nozzle type on efficacy of fomesafen on Palmer amaranth (Amaranthus palmeri) control. *American Journal of Plant Sciences, 09*(08), 1660-1676. doi:10.4236/ajps.2018.98120

Ogino, K., Onoe, Y., Abe, M., Ono, H., & Bessho, K. (1990). Reduction of surface tension by novel polymer surfactants. *Langmuir, 6*(7), 1330-1330. doi:10.1021/la00097a025

Oliveira, R. B., Antuniassi, U. R., Mota, A. A., & Chechetto, R. G. (2013). Potential of adjuvants to reduce drift in agricultural spraying. *Engenharia Agrícola, 33*(5), 986-992. doi:10.1590/s0100-69162013000500010

Pegram, L. M., & Record, M. T. (2007). Hofmeister salt effects on surface tension arise from partitioning of anions and cations between bulk water and the air−water interface. *The Journal of Physical Chemistry B, 111*(19), 5411-5417. doi:10.1021/jp070245z

Petersen, J., & Hurle, K. (2001). Influence of climatic conditions and plant physiology on glufosinate-ammonium efficacy. *Weed Research, 41*(1), 31-39. doi:10.1046/j.1365-3180.2001.00214.x

Pline, W. A., Wu, J., & Hatzios, K. K. (1999). Absorption, translocation, and metabolism of glufosinate in five weed species as influenced by ammonium sulfate and pelargonic acid. *Weed Science, 47*(6), 636-643. doi:10.1017/s0043174500091268

Pricer, C. E. (1983). The effect of environment on foliage uptake and translocation of herbicides. *A.o.A. Biologists (Ed.), Aspects of Applied Biology 4: Influence of Environmental Factors on Herbicide Performance and Crop and Weed Biology, 4*, 157-169.

Qazi, M. J., Schlegel, S. J., Backus, E. H., Bonn, M., Bonn, D., & Shahidzadeh, N. (2020). Dynamic surface tension of surfactants in the presence of high salt concentrations. *Langmuir, 36*(27), 7956-7964. doi:10.1021/acs.langmuir.0c01211

R Core Team (2019) R: A language and environment for statistical computing. Vienna, Austria: R Foundation for Statistical Computing. https://www.R-project.org/. Accessed: November 9, 2020

Ramsey, R., Stephenson, G., & Hall, J. (2005). A review of the effects of humidity, humectants, and surfactant composition on the absorption and efficacy of highly water-soluble herbicides. *Pesticide Biochemistry and Physiology, 82*(2), 162-175. doi:10.1016/j.pestbp.2005.02.005

Sanyal, D., Bhowmik, P. C., & Reddy, K. N. (2006). Leaf characteristics and surfactants affect primisulfuron droplet spread in three broadleaf weeds. *Weed Science, 54*(1), 16-22. doi:10.1614/ws-05-019r.1

Singh, M., Orsenigo, J. R., & Shah, D. O. (1984). Surface tension and contact angle of herbicide solutions affected by surfactants. *Journal of the American Oil Chemists' Society, 61*(3), 596-600. doi:10.1007/bf02677040

Sobiech, L., Grzanka, M., Skrzypczak, G., Idziak, R., Włodarczak, S., & Ochowiak, M. (2020). Effect of adjuvants and ph adjuster on the efficacy of sulcotrione herbicide. *Agronomy, 10*(4), 530. doi:10.3390/agronomy10040530

Spanoche, P., Van Eeckhout, H., Steurbaut, W., & Van der Meeren, P. (2002). The effect of static and dynamic surface tension on atomization of agricultural nozzles. *Mededelingen (Rijksuniversiteit Te Gent. Fakulteit Van De Landbouwkundige En Toegepaste Biologische Wetenschappen), 67*(2), 37-45.

Spanoghe, P., De Schampheleire, M., Van der Meeren, P., & Steurbaut, W. (2006). Influence of agricultural adjuvants on droplet spectra. *Pest Management Science, 63*(1), 4-16. doi:10.1002/ps.1321

Steckel, G. J., Hart, S. E., & Wax, L. M. (1997). Absorption and translocation of glufosinate on four weed species. *Weed Science, 45*(3), 378-381. doi:10.1017/s0043174500093012

Steckel, G. J., Wax, L. M., Simmons, F. W., & Phillips, W. H. (1997). Glufosinate efficacy on annual weeds is influenced by rate and growth stage. *Weed Technology, 11*(3), 484-488. doi:10.1017/s0890037x00045292

Takano, H. K., & Dayan, F. E. (2020). Glufosinate-ammonium: A review of the current state of knowledge. *Pest Management Science, 76*(12), 3911-3925. doi:10.1002/ps.5965

Thelen, K. D., Jackson, E. P., & Penner, D. (1995). The basis for the hard-water antagonism of glyphosate activity. *Weed Science, 43*(4), 541-548. doi:10.1017/s0043174500081613

Torrecilla, J. S., Rafione, T., García, J., & Rodríguez, F. (2008). Effect of relative humidity of air on density, Apparent Molar Volume, viscosity, surface tension, and water content of 1-ethyl-3-methylimidazolium ethylsulfate ionic liquid. *Journal of Chemical & Engineering Data, 53*(4), 923-928. doi:10.1021/je700523b

Tu, M., Hurd, C., & Randall, J. M. (2001). Adjuvants. In *Weed control methods handbook: Tools and techniques for use in natural areas* (pp. 171-190). Davis, CA: Wildland Invasive Species Team, the Nature Conservancy. doi:https://www.invasive.org/gist/products/handbook/methods-handbook.pdf

VanGessel, M. J. (2001). Glyphosate-resistant horseweed from Delaware. *Weed Science, 49*(6), 703-705. doi:10.1614/0043-1745(2001)049[0703:rprhfd]2.0.co;2

Wang, Z., Lan, L., He, X., & Herbst, A. (2020). Dynamic evaporation of droplet with adjuvants under different environment conditions. *International Journal of Agricultural and Biological Engineering, 13*(2), 1-6. doi:10.25165/j.ijabe.20201302.5353

Wang, Z., Lan, L., He, X., & Herbst, A. (2020). Dynamic evaporation of droplet with adjuvants under different environment conditions. *International Journal of Agricultural and Biological Engineering, 13*(2), 1-6. doi:10.25165/j.ijabe.20201302.5353

Woznica, W. J. (2003). *U.S. Patent No. WO2003092373A2*. Washington, DC: U.S. Patent and Trademark Office.

Yu, Y., Zhu, H., Frantz, J., Reding, M., Chan, K., & Ozkan, H. (2009). Evaporation and coverage area of pesticide droplets on hairy and waxy leaves. *Biosystems Engineering, 104*(3), 324-334. doi:10.1016/j.biosystemseng.2009.08.006

Zollinger, R. K., Nalewaja, J. D., Peterson, D. E., & Young, B. G. (2010). Effect of hard water and ammonium sulfate on weak acid herbicide activity. *30th Symposium on Pesticide Formulations and Delivery Systems: Regulations and Innovation*. doi:10.1520/stp49228s

**Table 1**. Mean temperature and relative humidity (RH) during applications in the field sites of horseweed and Palmer amaranth in 2019 and 2020 growing seasons.

| | Horseweed | | Palmer amaranth | |
|---|---|---|---|---|
| Year | Temperature (°C) | RH (%) | Temperature (°C) | RH (%) |
| 2019 | 17 | 75 | - | - |
| 2020 | 37 | 25 | 33 | 43 |

**Table 2.1.** Density and dynamic viscosity of glufosinate formulations tank mixed with four surfactant-humectant adjuvants at 20°C.

| Formulation [a] | Adjuvant [b] | Density | Viscosity |
|---|---|---|---|
| | | g cm$^{-3}$ | mPa s$^{-1}$ |
| F1 | none | 1.0089 c | 1.0623 h |
| F1 | EA1 | 1.0091 b | 1.0713 e |
| F1 | EA2 | 1.0092 b | 1.0738 d |
| F1 | EA3 | 1.0093 a | 1.0723 de |
| F1 | EA4 | 1.0093 a | 1.0783 c |
| F2 | none | 1.0084 e | 1.0730 de |
| F2 | EA1 | 1.0085 d | 1.1343 b |
| F2 | EA2 | 1.0088 c | 1.0658 g |
| F2 | EA3 | 1.0088 c | 1.2003 a |
| F2 | EA4 | 1.0089 c | 1.0685 f |
| | | *** | *** |

[a] Abbreviation: F1-Liberty® (Bayer CropScience, Research Triangle Park, NC, USA) and F2-Interline® (UPL NA Inc., King of Prussia, PA, USA) at 656 g ai ha$^{-1}$.

[b] EA1 at 0.125 v v$^{-1}$ and EA2, EA3, and EA4 at 0.5 v v$^{-1}$.

Means followed by the same letter in the column do not differ using Tukey's test at $\alpha = 0.05$.

Significance levels: ***$p \leq 0.001$.

**Table 2.2.** Dynamic surface tension of glufosinate formulations tank mixed with four surfactant-humectant adjuvants at 25°C.

| Formulation [a] | Adjuvant [b] | 20% RH | | 40% RH | | 60% RH | | 80% RH | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | mN $m^{-1}$ | | | | |
| F1 | none | 30.1 | b | 29.9 | abc | 29.9 | bc | 29.6 | bc |
| F1 | EA1 | 29.4 | c | 29.7 | bc | 27.6 | f | 29.8 | abc |
| F1 | EA2 | 30.2 | b | 30.4 | a | 30.3 | a | 29.9 | ab |
| F1 | EA3 | 29.5 | c | 29.7 | bc | 29.6 | c | 29.4 | bc |
| F1 | EA4 | 30.8 | a | 30.3 | a | 30.2 | a | 30.1 | a |
| F2 | none | 30.8 | a | 30.1 | ab | 29.1 | d | 29.9 | abc |
| F2 | EA1 | 28.9 | d | 28.5 | d | 28.5 | e | 28.2 | e |
| F2 | EA2 | 30.4 | b | 29.5 | c | 30.1 | ab | 29.0 | d |
| F2 | EA3 | 27.1 | e | 27.9 | e | 27.4 | f | 27.3 | f |
| F2 | EA4 | 28.6 | d | 29.5 | c | 29.9 | bc | 29.5 | c |
| | | *** | | *** | | *** | | *** | |

[a] Abbreviation: F1-Liberty® (Bayer CropScience, Research Triangle Park, NC, USA) and F2-Interline® (UPL NA Inc., King of Prussia, PA, USA) at 656 g ai $ha^{-1}$.

[b] EA1 at 0.125 v $v^{-1}$ and EA2, EA3, and EA4 at 0.5 v $v^{-1}$.

Means followed by the same letter in the column do not differ using Tukey's test at $\alpha = 0.05$.

Significance levels: ***$p \leq 0.001$.

**Table 2.3.** Static contact angle of glufosinate formulations tank mixed with four surfactant-humectant adjuvants at 25°C.

| Formulation [a] | Adjuvant [b] | 20% RH | 40% RH | 60% RH | 80% RH |
|---|---|---|---|---|---|
| | | angle (°) | | | |
| F1 | none | 34.7 bc | 35.3 ab | 32.5 cd | 32.3 cd |
| F1 | EA1 | 27.4 d | 29.4 e | 31.6 cd | 33.4 bc |
| F1 | EA2 | 34.5 c | 32.4 cd | 36.8 b | 34.1 abc |
| F1 | EA3 | 24.7 e | 34.4 bc | 33.0 c | 36.0 a |
| F1 | EA4 | 27.4 d | 37.4 a | 32.7 c | 32.4 cd |
| F2 | none | 39.7 a | 35.0 ab | 38.4 ab | 31.3 d |
| F2 | EA1 | 34.1 c | 35.1 ab | 32.5 cd | 32.6 cd |
| F2 | EA2 | 37.3 ab | 37.1 a | 39.7 a | 32.5 cd |
| F2 | EA3 | 29.0 d | 30.1 de | 30.3 d | 30.7 d |
| F2 | EA4 | 37.8 a | 36.8 ab | 38.9 ab | 34.9 ab |
| | | *** | *** | *** | *** |

[a] Abbreviation: F1-Liberty® (Bayer CropScience, Research Triangle Park, NC, USA) and F2-Interline® (UPL NA Inc., King of Prussia, PA, USA) at 656 g ai $ha^{-1}$.

[b] EA1 at 0.125 v $v^{-1}$ and EA2, EA3, and EA4 at 0.5 v $v^{-1}$.

Means followed by the same letter in the column do not differ using Tukey's test at $\alpha = 0.05$.

Significance levels: ***$p \leq 0.001$.

**Table 2.4.** Evaporation of glufosinate formulations tank mixed with four surfactant-humectant adjuvants at 25°C.

| Formulation [a] | Adjuvant [b] | 20% RH | | 40% RH | | 60% RH | | 80% RH | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | $\mu$ml $s^{-1}$ | | | | |
| F1 | none | $6.0\ 10^{-4}$ | e | $1.7\ 10^{-3}$ | ab | $1.0\ 10^{-3}$ | e | $9.0\ 10^{-4}$ | d |
| F1 | EA1 | $1.1\ 10^{-3}$ | d | $1.2\ 10^{-3}$ | de | $1.6\ 10^{-3}$ | cd | $2.7\ 10^{-3}$ | a |
| F1 | EA2 | $1.8\ 10^{-3}$ | b | $4.0\ 10^{-4}$ | f | $8.0\ 10^{-4}$ | ef | $2.2\ 10^{-3}$ | b |
| F1 | EA3 | $1.2\ 10^{-3}$ | cd | $1.5\ 10^{-3}$ | bc | $4.0\ 10^{-4}$ | f | $1.6\ 10^{-3}$ | c |
| F1 | EA4 | $1.0\ 10^{-3}$ | d | $1.2\ 10^{-3}$ | cd | $3.5\ 10^{-3}$ | a | $1.3\ 10^{-3}$ | cd |
| F2 | none | $2.3\ 10^{-3}$ | a | $5.0\ 10^{-4}$ | f | $2.7\ 10^{-3}$ | b | $1.2\ 10^{-3}$ | d |
| F2 | EA1 | $1.8\ 10^{-3}$ | b | $1.2\ 10^{-3}$ | de | $2.0\ 10^{-3}$ | c | $4.0\ 10^{-4}$ | e |
| F2 | EA2 | $6.0\ 10^{-4}$ | e | $9.0\ 10^{-4}$ | e | $1.2\ 10^{-3}$ | de | $2.1\ 10^{-3}$ | b |
| F2 | EA3 | $1.6\ 10^{-3}$ | bc | $5.0\ 10^{-4}$ | f | $1.1\ 10^{-3}$ | de | $2.1\ 10^{-3}$ | b |
| F2 | EA4 | $1.8\ 10^{-3}$ | b | $1.8\ 10^{-3}$ | a | $0.7\ 10^{-3}$ | ef | $2.1\ 10^{-3}$ | b |
| | | | *** | | *** | | *** | | *** |

[a] Abbreviation: F1-Liberty® (Bayer CropScience, Research Triangle Park, NC, USA) and F2-Interline® (UPL NA Inc., King of Prussia, PA, USA) at 656 g ai $ha^{-1}$.

[b] EA1 at 0.125 v $v^{-1}$ and EA2, EA3, and EA4 at 0.5 v $v^{-1}$.

Means followed by the same letter in the column do not differ using Tukey's test at $\alpha = 0.05$.

Significance levels: ***$p \leq 0.001$.

**Table 3.** Dv0.1, Dv0.5, and Dv0.9 (droplet diameters for which 10, 50, and 90% of the total spray volume is contained in droplets of lesser diameter, respectively), volume percentage of droplets smaller than 150 µm (V150), and relative span (RS) of glufosinate formulations tank mixed with four surfactant-humectant adjuvants sprayed at 246 kPa through TT 110015 nozzle.

| Formulation [a] | Adjuvant [b] | Dv0.1 | Dv0.5 | Dv0.9 | PF | RS |
|---|---|---|---|---|---|---|
| | | -------------------- | %-------------------- | --------------------- | % | dimensionless |
| F1 | none | 274 a | 530 a | 784 a | 1.4 g | 0.96 f |
| F1 | EA1 | 224 e | 448 f | 687 e | 3.0 c | 1.03 c |
| F1 | EA2 | 207 f | 425 g | 670 f | 3.9 b | 1.09 a |
| F1 | EA3 | 203 f | 420 g | 665 f | 4.3 a | 1.10 a |
| F1 | EA4 | 228 e | 461 e | 715 d | 2.7 d | 1.06 b |
| F2 | none | 240 d | 488 d | 744 c | 2.5 d | 1.03 c |
| F2 | EA1 | 256 c | 511 c | 765 b | 2.0 ef | 0.99 de |
| F2 | EA2 | 252 c | 504 c | 745 c | 2.1 e | 0.98 ef |
| F2 | EA3 | 262 b | 519 b | 785 a | 1.8 f | 1.01 d |
| F2 | EA4 | 253 c | 511 c | 758 b | 2.1 e | 0.99 de |
| | | *** | *** | *** | *** | *** |

[a] Abbreviation: F1-Liberty® (Bayer CropScience, Research Triangle Park, NC, USA) and F2-Interline® (UPL NA Inc., King of Prussia, PA, USA) at 656 g ai ha$^{-1}$.

[b] EA1 at 0.125 v v $^{-1}$ and EA2, EA3, and EA4 at 0.5 v v$^{-1}$.

Means followed by the same letter in the column do not differ using Tukey's test at α = 0.05.

Significance levels: ***p ≤ 0.001.

**Table 4.1.** Biomass reduction (BR) and visual estimation of control (VEC) of common lambsquarters and kochia for glufosinate formulations tank mixed with four surfactant-humectant adjuvants in greenhouse condition.

| Formulation [a] | Adjuvant [b] | Common lambsquarters | | Kochia | |
|---|---|---|---|---|---|
| | | VEC | BR | VEC | BR |
| | | | % | | |
| F1 | none | 49 a | 64 a | 93 a | 89 a |
| F1 | EA1 | 31 bc | 47 c | 100 a | 97 a |
| F1 | EA2 | 36 ab | 48 bc | 100 a | 93 a |
| F1 | EA3 | 36 ab | 44 d | 99 a | 97 a |
| F1 | EA4 | 34 ab | 49 b | 100 a | 97 a |
| F2 | none | 7 e | 12 i | 56 b | 62 b |
| F2 | EA1 | 16 cde | 20 g | 96 a | 95 a |
| F2 | EA2 | 13 de | 26 f | 92 a | 92 a |
| F2 | EA3 | 6 e | 14 h | 93 a | 89 a |
| F2 | EA4 | 26 bcd | 31 e | 100 a | 97 a |
| | | * | * | *** | ** |

[a] Abbreviation: F1-Liberty® (Bayer CropScience, Research Triangle Park, NC, USA) and F2-Interline® (UPL NA Inc., King of Prussia, PA, USA) at 328 g ai ha$^{-1}$.

[b] EA1 at 0.125 v v $^{-1}$ and EA2, EA3, and EA4 at 0.5 v v$^{-1}$.

Means followed by the same letter in the column do not differ using Tukey's test at α = 0.05.

Significance levels: -, nonsignificant at α = 0.05; *p ≤ 0.05; **p ≤ 0.01; ***p ≤ 0.001.

**Table 4.2.** Biomass reduction (BR) and visual estimation of control (VEC) of barnyardgrass and velvetleaf for glufosinate formulations tank mixed with four surfactant-humectant adjuvants in greenhouse condition.

| Formulation [a] | Barnyardgrass | | Velvetleaf | |
|---|---|---|---|---|
| | VEC | BR | VEC | BR |
| | % | | | |
| F1 | 93 A | 96 A | 88 A | 96 A |
| F2 | 84 B | 91 B | 75 B | 89 B |
| | ** | ** | *** | *** |
| Adjuvant [b] | | | | |
| none | 90 ab | 90 b | 84 a | 95 ab |
| EA1 | 82 b | 92 ab | 77 ab | 89 b |
| EA2 | 88 ab | 94 ab | 86 a | 96 a |
| EA3 | 91 ab | 96 a | 74 b | 89 b |
| EA4 | 92 a | 97 a | 86 a | 94 b |
| | * | * | ** | * |

[a] Abbreviation: F1-Liberty® (Bayer CropScience, Research Triangle Park, NC, USA) and F2-Interline® (UPL NA Inc., King of Prussia, PA, USA) at 328 g ai ha$^{-1}$.

[b] EA1 at 0.125 v v $^{-1}$ and EA2, EA3, and EA4 at 0.5 v v$^{-1}$.

Means followed by the same letter in the column do not differ using Tukey's test at $\alpha = 0.05$.

Significance levels: -, nonsignificant at $\alpha = 0.05$; *$p \leq 0.05$; **$p \leq 0.01$; ***$p \leq 0.001$.

**Table 5.** Biomass reduction (BR), visual estimation of control (VEC), and mortality (M) of horseweed for glufosinate formulations tank mixed with four surfactant-humectant adjuvants in field conditions.

| | Horseweed | | | Palmer amaranth | | |
|---|---|---|---|---|---|---|
| Formulation [a] | VEC | BR | M | VC | BR | M |
| | | | % | | | |
| F1 | 85 A | 66 A | 49 A | 85 A | 69 A | 32 A |
| F2 | 87 A | 69 A | 56 A | 81 A | 72 A | 34 A |
| | - | - | - | - | - | - |
| Adjuvant [b] | | | | | | |
| none | 84 a | 65 a | 50 a | 83 ab | 67 a | 25 a |
| EA1 | 85 a | 66 a | 50 a | 84 a | 71 a | 35 a |
| EA2 | 87 a | 65 a | 55 a | 78 b | 73 a | 30 a |
| EA3 | 87 a | 70 a | 50 a | 84 a | 69 a | 41 a |
| EA4 | 85 a | 70 a | 58 a | 79 b | 72 a | 34 a |
| | - | - | - | * | - | - |

[a] Abbreviation: F1-Liberty® (Bayer CropScience, Research Triangle Park, NC, USA) and F2-Interline® (UPL NA Inc., King of Prussia, PA, USA) at 656 g ai $ha^{-1}$.

[b] EA1 at 0.125 $v\ v^{-1}$ and EA2, EA3, and EA4 at 0.5 $v\ v^{-1}$.

Means followed by the same letter in the column do not differ using Tukey's test at $\alpha = 0.05$.

Significance levels: -, nonsignificant at $\alpha = 0.05$; $^{*}p \leq 0.05$.

# CHAPTER 3

# PHYSICAL-CHEMICAL PROPERTIES, DROPLET-SIZE, AND EFFICACY OF DICAMBA PLUS GLYPHOSATE TANK MIXTURE INFLUENCED BY ADJUVANTS

## Abstract

Dicamba and glyphosate tank mixtures have been largely adopted for postemergence weed control mainly after the development of dicamba-tolerant crops. Ammonium sulfate (AMS) is commonly used as water conditioner in order to increase glyphosate efficacy. However, the use of AMS is restricted for dicamba herbicides due to the increase in formation of volatile dicamba acid. New adjuvant approaches containing non-AMS water conditioner (WC) and other adjuvants could be a solution to optimize efficacy of this tank mixture while mitigating herbicide off-target movement. The objective of this study was to determine the physical-chemical properties, evaporation rate, and droplet size distribution of dicamba and glyphosate solutions without and with non-AMS WC alone or tank mixed with DRA, humectant, and surfactant adjuvants and evaluate the response of weed species to these solutions under greenhouse and field conditions. Laboratory, greenhouse, and field studies were conducted in 2019 and 2020. Treatment design was a 2 x 11 factorial where 2 consisted of presence or not of WC combined with 11 adjuvant treatments plus an untreated control where no herbicide or adjuvants were applied. Under greenhouse conditions, biomass reduction was 29% to 47% and 15% to 33% greater for velvetleaf and waterhemp, respectively, when adjuvants where added to solutions without WC. No increase in control were observed for horseweed and Palmer amaranth with the addition of adjuvants under field conditions.

**Key-words:** synthetic auxin, droplet evaporation, static contact angle, weed species

## Introduction

The introduction of glyphosate-resistant (GR) crops in 1996 has largely contributed to the adoption of glyphosate in the United States. In 1996, the estimated used amount of this herbicide was 25 million pounds compared to 300 million pounds in 2016 (USGS,2020a). Currently, glyphosate is the most widely used herbicide in the country (EPA, 2019). However, as a consequence of the overuse of this herbicide for a prolonged period of time, high occurrence of glyphosate-resistance (GR) weed populations has been reported across the country. Currently, there are 17 GR weed species reported in the United States (Heap, 2020). USDA (2015) estimated a reduction in financial returns of 66% and 14% to corn and soybean growers affected by GR weed infestation, respectively.

One of the most effective tactics to prevent, delay, or manage herbicide-resistant weeds is the use of herbicides with different modes of action (Norsworthy et al. 2012). In 2017, the release of dicamba-tolerant (DT) crops in the marked which are also tolerant to glyphosate has provided an alternative mode of action to manage herbicide-resistant weeds by allowing POST applications of those two herbicides. At the same year, use of dicamba increased 225% compared with previous year (USGS,2020b). Glyphosate is an herbicide that inhibits 5-enolpyruvylshikimate-3-phosphate (EPSP) enzyme leading to depletion of phenylalanine, tyrosine, and tryptophan (Herrmann and Weaver 1999; Steinrücken and Amrhein 1980), whereas dicamba is a synthetic auxin that mimics the natural plant hormone indole-3-acetic acid causing an epinastic response (Grossmann, 2007).

Other important tool to manage herbicide-resistant weeds is the use of adjuvants. Adjuvants are commonly added to the spray tank to improve herbicidal activity or application characteristics (Curran et al., 1999). Ammonium sulfate (AMS) is commonly used as a water conditioner to overcome salt antagonism of weak acids in hard water and to enhance phytotoxicity of several herbicides, such as glyphosate (Thelen et al., 1995). Pratt et al. (2003) demonstrated that when using tap water  (500 ppm of CaCO3), glyphosate solution containing AMS at 2% v.v $^{-1}$ provided velvetleaf control 53% greater than glyphosate solution alone. Thelen et al. (1995) reported that glyphosate molecule reacts with $Ca^{2+}$ and other cations present in the water to form a less absorbed glyphosate-Ca salt. Further, in the presence of AMS, sulfate ion from the AMS effectively binds with $Ca^{2+}$ from solution by forming $CaSO_4$ which prevents the formation of glyphosate-Ca salt and allows $NH_4^+$ to form the readily absorbed glyphosate-$NH_4$ salt.

Although dicamba is also a weak acid that has its efficacy increased with addition of AMS in the solution (Roskamp et al. 2013), this adjuvant is restricted for dicamba herbicides since it increases the formation of volatile dicamba acid by acidifying the solution (Muller and Steckel, 2019; Anonymous, 2020a; Anonymous, 2020b). Volatility can result in losses up to 90% of an applied herbicide (Long, 2017, Taylor and Spencer 1990) and can cause severe injury to sensitive species nearby. Non-AMS water conditioner (WC) adjuvants are an alternative to improve dicamba and glyphosate tank mixture's efficacy without increasing dicamba volatility potential. Zollinger et al. (2018) observed that 10 non-AMS WC adjuvants increased glyphosate and dicamba activity in hard water compared with treatment with no WC.

Complementary to non-AMS WC, use of surfactant and humectant adjuvants could lead to a decrease in dicamba volatility while enhancing herbicide efficacy. Long (2017) suggested that an increase in the amount of dicamba penetrating through the leaf cuticle should reduce the amount of the herbicide available on the leaf surface to volatilize. Surfactants are known for significantly accelerate the penetration of herbicides in plant cuticles (Schonherr and Baur, 1994; Bukovac and Petracek, 1993, Kirkwood, 1993). Harbors et al. (2013) reported that glyphosate and 2,4-D penetration on kochia (*Bassia scoparia* (L.) A. J. Scott) increased by 14% and 47%, respectively, when applied with surfactants compared to the herbicides alone. Surfactants reduce surface tension of spray droplets which increases the contact angle between the droplet and leaf which increases wettability and penetration (Tu and Randall, 2003).

Previous research demonstrated that environmental periods with high evaporation rates, such as high temperature and low humidity, increase dicamba volatility potential (Behrens and Lueschen 1979; Egan and Mortensen 2012). Even though high temperatures increase foliar absorption of auxin herbicides, that does not necessarily mean a decrease in volatility because the rate of evaporation exceeds the herbicide uptake rate (Long, 201, Sharma and Vanden Born 1970). As humectants slow droplet evaporation rates (Ramsey et al. 2005), herbicide stays in the liquid form for a longer period of time which may reduce the formation of dicamba vapor. Further, the herbicide uptake by the plant increases since this process just occurs as long as the spray deposit remains moist (Hess, 1999; Hazen, 2000) which reduces the amount of dicamba available on the leaf to evaporate and consequently, form dicamba vapor.

Due to the many complaints received about dicamba symptomology on non-DT crops in the past few years, actions to mitigate off-target movement have become crucial. Besides vapor drift, physical drift is another way of off-target movement. Spray droplet size is one of the most important factors affecting physical drift (Hofman and Solseng, 2017). Finer droplets are carried away from the target area by the wind (Downer et al. 1998). Drift-reducing agent (DRA) adjuvants alter the viscoelastic properties of the spray solution, increase droplet size, and weight, and minimize the number of easily-windborne droplets (Hewitt, 1998). The combined action of non-AMS WC with surfactant, humectant, and DRA adjuvants could favor DG tank mixture efficacy as well as mitigate herbicides off-target movement. However, there is a lack of information in the literature about the combination of those adjuvants with dicamba and glyphosate herbicides.

Changes in physical properties of solution caused by these adjuvants can result in undesirable droplet formation and size distribution (Spanoghe et al. 2007; Spanoghe et al. 2002), which reduce the effectiveness of the application (Knoche 1994). Therefore, the objectives of this research were to: (1) determine the physical properties (density, viscosity, surface tension, contact angle, and droplet evaporation rate) and droplet size distribution of dicamba and glyphosate solutions without and with non-AMS WC alone or tank mixed with DRA, humectant, and surfactant adjuvants and (2) evaluate the response of weed species to these solutions under greenhouse and field conditions.

## Materials and Methods

Studies were conducted at the Pesticide Application Technology Laboratory of the University of Nebraska-Lincoln located at the West Central Research, Extension and Education Center (WCREEC) in North Platte, NE, and in Paxton-NE.

Dicamba (Xtendimax ® with Vapor Grip®, Monsanto Company, St. Louis, MO, USA) plus glyphosate (Roundup PowerMax®, Monsanto Company, St. Louis, MO, USA) solutions at full dose, 559 and 1541 g ae. ha$^{-1}$, respectively, were arranged in a factorial 2 x 11 treatment design, where 2 consisted of presence or not of a non-AMS WC at 0.5 % v $v^{-1}$ combined with 10 adjuvants plus an herbicide solution with no adjuvant and an untreated control where no herbicide or adjuvants were applied . Adjuvant types and rates are described in Table 6. All the adjuvants used in this study were experimental. Analyzes of the water used in the solutions indicated presence of 188 mg $L^{-1}$ of CaCO3 which categorizes this water as very hard (USGS 2020). Spray solutions were prepared simulating a 140 L $ha^{-1}$ carrier volume.

## Physical Properties Study

The density and dynamic viscosity of the solutions and water were measured at 20°C by a density meter (DMA$^{TM}$ 4500 M, Anton Paar USA Inc., Ashland, VA, USA) and microviscometer (Lovis 2000 M/ME, Anton Paar USA Inc., Ashland, VA, USA), respectively. A video-based optical contact angle measuring instrument (OCA 15EC, DataPhysics Instruments GmbH, Filderstadt, Germany) was used to measure dynamic surface tension (dST), static contact angle (sCA), and evaporation rate (ER). A liquid circulator (Julabo USA Inc, Allentown, PA 18109) and a humidity generator and controller - HCG (DataPhysics Instruments GmbH, Filderstadt, Germany) were used to maintain the temperature at 25 ± 1°C and relative humidity at 20, 40, 60, and 80 ± 1%, respectively. For each treatment solution, physical properties were measured three times for each humidity. Moraes et al. (2019) provided detailed information regarding use and operation of the density meter, microviscometer, and OCA 15EC for dST and sCA measurements. Also, Fritz et al. (2017) described the ER measurement procedure using the OCA 15EC. In this present study, ER measurements were performed using an initial droplet volume of 0.15 µL and evaporation maximum time interval of 120 seconds. ER was calculated according to Equation (1):

$$ER = \left(\frac{Vi - Vf*}{Tfinal}\right) \qquad (1)$$

Where Vi is the initial volume of the droplet (µL) at 0s, Vf is the final volume of the droplet at 120s or in the case of the droplet completely evaporated before the 120s Vf is equal 0 µL, and Tf is the maximum time interval of 120s or the time interval (s) in which the droplet completely evaporated before 120s.

### pH

pH measurements were performed using a pH meter (200 Series Benchtop pH/Cond. Meter, Cole-Parmer Instruments ,Vernon Hills, IL). Each treatment solutions was measured one time. A plastic cup was filled with the treatment solution and electrode was placed into the cup until pH reached equilibrium. Between treatments, electrode was cleaned with distilled water and dried with paper and plastic cup was discarded and replaced for a new one.

### Droplet Size Distribution Study

Droplet diameters for which 10%, 50%, and 90% of the total spray volume is contained in droplets of lesser diameter ($Dv_{0.1}$, $Dv_{0.5}$, and $Dv_{0.9}$, respectively), volume percentage of droplets smaller than 150 µm - percentage of fines (PF) and the relative span (RS) were measured for each solution using a laser diffraction system (HELOS-VARIO/KR, Sympatec Inc., Clausthal, Germany) with the R7 lens, following methodology described by Fritz et al. (2014) and Butts et al. (2019). $V_{150}$ is an indicator of the potential risk of drift and RS is a dimensionless parameter that indicates uniformity of droplet size distribution, calculated using Equation 2 (ASABE, 2016). Solutions were sprayed through TTI110015 nozzles (Spraying Systems Co., Glendale Heights, IL, USA) operating at 276 kPa with a constant airspeed of 6.7 m $s^{-1}$. Each solution was replicated three times.

$$RS = \left(\frac{DV0.9 - D.V0.1}{DV0.5}\right) \qquad (2)$$

## Efficacy Study in Greenhouse

The study was conducted in a complete randomized block design with four replications, and two experimental runs. Dicamba and glyphosate rates were applied at reduced rates, 279 g ae $ha^{-1}$ and 385 g ae $ha^{-1}$, respectively, to avoid complete weed control. Solutions were sprayed on barnyardgrass (*Echinochloa crus-galli* (L.) P. Beauv.), common lambsquarters (*Chenopodium album* L.), horseweed (*Erigeron canadensis* L.), kochia (*Bassia scoparia* (L.) A. J. Scott), velvetleaf (*Abutilon theophrasti* Medik.), and common waterhemp (*Amaranthus tuberculatus* (Moq.) J. D. Sauer), grown in 10 cm cone-tainers (Stuewe and Sons Inc., Corvallis, OR, USA) using Pro-Mix BX5 (Premier Tech Horticulture Ltd, Riviere-du-Loup, Canada). Greenhouse temperature was maintained between 18 and 28°C and 60% ±10% RH. Supplemental LED lighting of 520 µmol $s^{-1}$ (Philips Lighting, Somerset, NJ, USA) was provided to extend daylight period to 16 hours. Plants were watered daily using a commercial liquid fertilizer (UNL 5-1-4, Wilbur-Ellis Agribusiness, Aurora, CO, USA) and treated weakly with *Bacillus thuringiniensis* (Gnatrol WDG$^{®, \text{Valent}}$ U.S.A., Walnut Creek, CA, USA) to avoid loopers (*Trichoplusia* spp.) and other insects. Once plants were 15 cm tall and horseweed was 10 cm in diameter, they were sprayed using a three-nozzle spray chamber (Generation III Research Track Sprayer DeVries Manufacturing, Hollandale, MN, USA) calibrated to deliver 140 L $ha^{-1}$ through TTI110015 nozzles (Spraying Systems Co., Glendale Heights, IL, USA) at 1.3 m $s^{-1}$ travel speed and 276 kPa operating pressure. Nozzle spacing and boom height from the top of plants were 51 cm.

At 28 days after application (DAA), visual estimations of injury were recorded, and aboveground biomass of surviving plants were harvested and oven-dried at 65°C until reaching constant dry weight. Dry biomass data was recorded and converted into percentage of biomass reduction as compared with the untreated control according to Equation 3:

$$\mathrm{BR} = 100 - \frac{(X*100)}{\mathrm{Y}} \qquad (3)$$

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

## Efficacy Study in Field

Two trials on horseweed control were conducted during the growing season of 2019 and 2020 in North Platte-NE and Paxton-NE, respectively, and one trial on Palmer amaranth (*Amaranthus palmeri S. Watson*) control was conducted during the growing season of 2020 in North Platte-NE. Trials were conducted in a randomized complete block design with four replications. Each plot was 3 m wide by 10 m long. Spray solutions combination and product rates were the same as used in physical properties and droplet size distribution studies. Late-season horseweed (50 cm tall) and Palmer amaranth (40 cm tall) plants were sprayed using a six-nozzle handheld $CO_2$ pressurized backpack sprayer (Bellspray Inc., Opelousas, LA, USA) calibrated to deliver 140 L $ha^{-1}$ through TTI110015 nozzles (Spraying Systems Co., Glendale Heights, IL, USA) at 1.3 m $s^{-1}$ walking speed and 276 kPa operating pressure. Nozzle spacing and boom height from plants were 51 cm. Plants over recommended application size were used in order to enable treatment comparisons using full herbicides rates. Temperature and relative humidity during applications in 2019 and 2020 are described in Table 1.

Visual estimations of injury were recorded at 28 DAA. In addition, 10 random plants per plot were marked with orange spray paint before application. At 28 DAA, marked plants were individually evaluated for mortality (dead or alive) and converted into percent of mortality reduction using Equation 4 (Butts et al. 2018):

$$\mathrm{M} = 100 * \left(\frac{D}{10}\right) \qquad (4)$$

Where M is mortality (%), and D is the number of dead plants per plot after being treated.

The ten plants used for mortality evaluation were clipped at the soil surface, harvested, and dried at 65°C until reaching constant weight. Dry biomass of those 10 plants were recorded and converted into percentage of biomass reduction and compared with the untreated control according to Equation 2.

## Statistical Analyzes

Data were subjected to analysis of variance using the base package in R Statistical Software, version 3.3.1 (R Core Team 2019). Replications were treated as a random effect and year, water conditioner, and other adjuvants as fixed effects. However, for Palmer amaranth, year effect was not included as a fixed effect because of availability of only one-year data. Treatments were compared to each other using Tukey's least significant at $\alpha = 0.05$.

## Results

### Physical-chemical Properties Study

The ANOVA table demonstrated a water conditioner versus other adjuvants interaction for density, viscosity, sCA, dST, and ER ($p<0.001$).

### Density

The addition of most adjuvants slightly increased density of DpG solutions independently of the presence or not of WC (Table 7.1). For example, in the absence of WC, DpG solutions containing adjuvants NIS1, NIS-DRA2, NISH4, NISH5, and NISH6 presented density of 1.0070 g cm$^3$ compared to 1.0060 g cm$^3$ for DpG alone which corresponds to 0.1%. Furthermore, in the presence of WC, compared to DpG solution with only WC (1.0070 g cm$^3$), addition of adjuvants, except for NISH1 and NISH2, increased density in a range of 0.0008 to 0.0018 g cm$^3$ (0.08% to 0.18%).

Similar do density, DpG solutions containing adjuvants presented greater viscosity than solutions without adjuvant, independently of presence or not of WC. In the absence of WC, addition of adjuvant to DpG solutions increased viscosity from 0.01 up to 0.09 mPa s$^{-1}$ , which is equivalent to 1 to 9%, compared to DpG solution alone (1.0400 mPa s$^{-1}$). Equally, in the presence of WC, compared to DpG solution with only WC (1.0400 mPa s$^{-1}$), addition of adjuvants increased viscosity in a range of 0.01 to 0.09 mPa s$^{-1}$. The highest density was observed with addition of NIS-DRA2, independently of presence or not of WC, but the majority of treatment solutions containing WC presented higher density than solutions without WC.

### Static Contact Angle

At 20% RH, the addition of NIS1, NIS2, NIS-DRA 1, NISH3, NISH5, and NISH 6 to DpG solutions without WC decreased CA by 2 to 11° compared to DpG alone (38°) (Table 7.2). Also, compared to DpG with only WC (39°), the addition of adjuvants , except for NISH2 and NISH 5, to DpG solution with WC decreased sCA by 2 to 9°. Similarly, at 40% and 60% RH, sCA decreased when the majority of adjuvants were added to DpG solutions. However, at 40% RH, NISH2 and NISH 4 increased sCA when added to DpG solution without and with WC, respectively. At 80% RH, in the absence of WC, compared to DpG alone (36°), the addition of NIS1 and NIS2 decreased CA in 4° and NISH2, NISH3, NISH4, NISH5 and NISH6 increased sCA in a range of 3 to 6°. Also, compared to DpG only with WC, in the presence of WC, NIS1, NIS2, NIS-DRA1, NIS-DRA2, NISH1, NISH5, and NISH6 decreased sCA by 4 to 6° and NISH2 and NISH4 increased by 3° and 10°.

### Dynamic Surface Tension

The influence of adjuvants on the dST of DpG solutions without and with WC was the same at 20%, 40%, and 60% RH (Table 7.3). For example, in the absence of WC, compared to DpG alone (37 mN m$^{-1}$), the addition of adjuvants decreased dST in a range of 1 to 6 mN m$^{-1}$. Furthermore, in the presence of WC, the addition of all adjuvants, but adjuvant NISH2, decreased dST from 1 to 5 mN m$^{-1}$ compared to DpG with only WC (36 mN m$^{-1}$). At 80% RH, in the absence of WC, the addition of NIS1, NIS2, NIS-DRA1, NIS-DRA2, NISH3, NISH5, and NISH6 decreased ST from 2 to 5 mN m$^{-1}$ and NISH2 and NISH4 increased dST by 1 mN.m$^{-1}$, compared to DpG with only WC (35 mN m$^{-1}$). Moreover, in the presence of WC, compared to solution with only WC (32 mN m$^{-1}$), NIS2 and NISH6 decreased dST in 2 and 1 mN m$^{-1}$, respectively, and NIS-DRA1, NISH1, NISH2, NISH3, and NISH4 increased dST by 3 to 6 mN $m^{-1}$.

## Evaporation time

At 20% RH, in the absence of WC, the use of NIS2, NIS-DRA2, NISH1, NISH2, NISH4, NISH5, and NISH6 increased ER from 0.6 to 3 µL $s^{-1}$ (75% to 375%) compared to DpG alone (0.8 µL $s^{-1}$) (Table 7.4). However, in the presence of WC, DpG solutions with adjuvants presented lower ER in a range of 0.9 to 3.3 µL $s^{-1}$ (25% to 96%) than DpG with only WC (3.6 µL $s^{-1}$). At 40% RH, the influence of adjuvants on DpG solutions without and with WC was opposite. In the absence of WC the use of adjuvants, except for NIS-DRA2 and NISH6, decreased ER in a range of 0.3 to 1.0 µL $s^{-1}$ (21% to 77%) compared to DpG alone (1.4 µL $s^{-1}$). However, in the presence of WC, the use of all adjuvants increase ER in a range of 0.2 to 1.4 µL $s^{-1}$ (66% to 467%), compared to DpG with only WC (0.3 µL $s^{-1}$). At 60% RH, DpG solutions with adjuvants presented greater ER than solutions without adjuvant, independently of the presence or not of WC. In the absence of WC, compared to DpG alone (0.4 µL $s^{-1}$), ER increased in a range of 0.3 to 1.2 µL $s^{-1}$ (75% to 300%) when adjuvants were added. Also, in the presence of WC, with the addition of adjuvants ER increased from 0.2 to 0.5 µL.$s^{-1}$ (25% to 250%) compared to DpG with only WC (0.8 µL $s^{-1}$). At 80% RH, the addition of most adjuvants to DpG solutions without WC did not change ER, compared to DpG alone (0.9 µL $s^{-1}$). However, in the presence of WC, the addition of NIS2, NIS-DRA2, NISH2, and NISH6 decreased ER decreased from 0.7 up to 0.8 µL $s^{-1}$ (50% up to 57%) and adjuvants NISH3 and NISH5 increased by 0.3 µL.$s^{-1}$ (21%) and 1.1 µL $s^{-1}$ (79%) respectively, compared to DpG with only WC (1.4 µL $s^{-1}$).

## pH

In the absence of WC, the addition of most adjuvants did not change pH for DpG solutions compared to DpG alone, but there were some exceptions (Table 7.5). Compared to DpG alone (4.9), the use of adjuvants NIS1 and NISH6 decreased pH to 4.5 and 4.7, respectively, and adjuvant NISH4 increased to 5.0. Similarly, in the presence of WC, most adjuvants did not change pH compared to DpG solution with only WC (5.1). However, adjuvants NIS1 and NISH6 decreased pH to 4.9 and 5.0, respectively, and adjuvants NIS2, NIS-DRA1, NISH2, and NISH5 increased pH to 5.2. Overall pH for solutions without WC was 4.9 and for solution with WC was 5.1.

## Droplet Size Study

The ANOVA table demonstrated a water conditioner versus other adjuvants interaction for Dv0.1, Dv0.5, Dv0.9, PF, and RS ($p<0.001$). Addition of adjuvants to DpG solutions without and with non-AMS water conditioner (WC) resulted in variable response on volumetric diameters, and consequently, on PF (Table 8). Compared to DpG alone, in the absence of WC, the addition of NIS1, NIS2, NISH3, and NISH6 presented finer Dv0.5 and NIS-DRA1, NIS-DRA2, NISH2, NISH4, and NISH5 coarser Dv0.5. However, in the presence of WC, DpG solutions containing adjuvants, except for NIS-DRA2, presented finer Dv0.5 than DpG with only WC. As expected, in the absence of WC, with the addition of NIS2, NISH3, and NISH6 PF was 3% to 28% lower than DpG alone (0.46%). However, when NIS-DRA2 and NISH6 were added to the solution PF was 5% to 17% greater than DpG alone. Moreover, in the presence of WC, compared to DpG solution with only WC (0.41%), PF was 3% to 22% higher when adjuvants, except NIS-DRA2 and NISH5, were added to solution. The addition of NIS-DRA2 decreased PF to 0.18%. Regarding RS, the addition of NIS1, NIS2, NIS-DRA1, NIS-DRA2, NISH2, NISH4, and NISH5 to DpG solution without WC decreased RS compared to DpG alone. In the presence of WC, compared to DpG with only WC, while NIS2, NIS-DRA1, NIS-DRA2 increased RS, NIS1, NISH3, and NISH6 decreased.

**Greenhouse study**

A significant interaction water conditioner versus other adjuvants was demonstrated by the ANOVA table for visual estimation of control at 28 DAA (VEC) and biomass reduction (BR) for barnyardgrass, kochia, velvetleaf, and waterhemp ($p<0.001$). For common lambsquarters, its high control by reduced doses of DpG unable comparisons between treatments. Therefore, no significant interaction water conditioner versus other adjuvants and main effects were detected for any of the abovementioned parameters. Overall, VEC and BR for this weed species were ≥ 99% and 95%, respectively (data not shown).

**Barnyardgrass**

The addition of mostly adjuvants did not change VEC for DpG solutions, independently of the presence or not of WC (Table 9.1). However, there were a few exceptions. Compared to DpG alone (61%), in the absence of WC, adjuvant NIS2 decreased VEC by 25% and adjuvant NISH6 increased by 28%. Furthermore, in the presence of WC, addition of adjuvant NIS2 and NISH6 decreased VEC by 16% and 14%, respectively, compared to DpG with only WC (69%).

Similar to VEC, BR did not change with the use of most adjuvants. However, in the absence of WC, the use of adjuvant NIS2 decreased BR by 22%, compared to DpG alone (78%).

Moreover, when adjuvant NISH1 was added to solution with WC, BR decreased by 18%, compared do DpG with WC only (80%).

### Horseweed

VEC of horseweed by DpG solutions without and with WC was 97% and 98%, respectively. No differences were observed with the addition of adjuvants to DpG solutions, independently of presence or not of WC.  However, the addition of adjuvants NIS-DRA1 and NISH5 decreased BR by 4% and 5% and by 3% and 4% for treatment solutions without and with WC, compared to DpG alone (93%) and DpG with only WC (91%), respectively.

### Kochia

In the absence of WC, the use of adjuvants NIS1,NISH2, NISH3, NISH5, and NISH6 increased VEC in a range of 7 to 16 % compared to DpG alone (79%). DpG plus adjuvant NISH6 presented a VEC of 95%. Further, for DpG solutions in the presence of WC, adjuvants NISH5, NISH4, NISH6 increased VEC in a range of 7 to 9% compared to DpG only with WC (85%).

When WC was not added to the solution, BR was also greater for DpG solutions containing adjuvants NISH2 (85%) and NISH6 (88%) than to DpG alone (76%). However, with addition of adjuvant NIS-DRA1, BR was 13% lower than DpG alone. For DpG solutions with WC, addition of adjuvant NISH1 and NISH6 increased BR by 10% and 11%, respectively, and adjuvant NIS2 reduced by 9%, both compared to DpG with only WC (77%).

### Velvetleaf

The addition of adjuvants to DpG solutions without WC increased VEC in a range of 32 to 40% compared to DpG Alone (41%) (Table 9.2). The highest VEC (81%) was observed with addition of adjuvant NISH6. In the presence of WC, solution with adjuvant NISH4 was the only that presented greater VEC (82%) than DpG with only WC (77%).

The influence of adjuvants on BR for solution without and with WC was similar to VEC. In absence of WC, solutions containing adjuvants presented greater BR in a range of 29 to 47% compared to DpG alone (41%). Also, DpG plus adjuvant NISH6 presented the highest BR (75%). Furthermore, in the presence of WC, DpG plus adjuvant NISH4 was again the only solution that had greater BR (78%) than DpG with only WC (71%).

### Common waterhemp

The influence of adjuvants on DpG solutions VEC was very similar as for velvetleaf in the absence of WC. The use of adjuvants increased VEC from 27% to 44% compared to DpG alone (52%). The highest VEC was achieved with addition of adjuvant NIS-DRA1 and NISH3. However, in the presence of WC, the addition of adjuvants NIS2, NISH2, and NISH5 reduced VEC in 15%, 19%, and 13%, respectively, compared to DpG solution with only WC (96%).

The BR raised from 15% to 32% with addition of adjuvants to DpG solutions without WC, compared to DpG alone (58%). DpG plus adjuvant NIS-DRA1 provided the highest BR (91%). However, in the presence of WC, adjuvant NISH2 and NISH5 decreased BR by 22% and 16%, compared to solution with only WC (93%).

### Field Study

The ANOVA table demonstrated no significant interaction water conditioner versus other adjuvants for VEC, BR and M for horseweed. However, main effect adjuvant was significant for VEC ($p<0.01$). For Palmer amaranth, no water conditioner versus other adjuvants and main effects were detected for any of the parameters aforementioned.

### Horseweed

The average VEC by DpG solutions without WC was 91 % and with WC was 90 % (Table 10). Among adjuvants treatments, VEC by DpG plus adjuvant NIS-DRA1 and by DpG plus adjuvant NISH4 were 3 % lower than DpG plus NIS-DRA2 (92 %). The overall biomass reduction and mortality were 65% and 59% for DpG solutions without WC and 64% and 60% for DpG solutions with WC. Further, the average biomass reduction and mortality among adjuvants treatments were 64% and 59%, respectively.

### Palmer amaranth

Overall VEC was 59% and 60% by DpG solutions without WC and with WC, respectively. Also, the average VEC among adjuvants treatments was 60%. DpG solutions without WC provided a biomass reduction and mortality of 49% and 18% compared to 46% and 17% for DpG solutions with WC. Moreover, the average biomass reduction and mortality was 49% and 17% among adjuvants treatments, respectively.

### Discussion

Previous studies reported that density, viscosity, surface tension, contact angle, droplet-size, and droplet evaporation of the spray solution can change with the addition of adjuvants in the spray solution (Cunha and Alves, 2019; Xu et al. 2010; Spanoghe et al. 2007; Prokop and

Kejklice et. al 2002; Bouse et al.1990). Results confirmed that density and viscosity of solutions containing NIS, NIS-DRA, and NIS-surfactant were greater than herbicide alone, independently of the presence of water conditioner. Similar results were found by Assuncao et al. (2019) in which glyphosate solution containing a synthetic adjuvant presented density 2.2% higher than glyphosate alone. Furthermore, Moraes et al. (2018) demonstrated that Lactofen containing COC (crop oil concentrate), NIS, MSO (methylated soybean oil) and COC-DRA increased viscosity by 4.3%, 2.6%, 3.6%, and 5.7%, respectively, compared to Lactofen alone. As expected, the highest viscosity observed in this present study were also by solutions containing DRA, since this type of adjuvants work by changing the viscoelastic properties of the spray solution, yielding a coarser spray with greater mean droplet sizes and weights, and minimizing the number of small, easily-windborne droplets (Hewitt 1998).

Furthermore, results showed that majority of solutions containing adjuvants presented lower CA and ST.  All adjuvants used in this study contained NIS and the primary purpose of a surfactant is to reduce the surface tension and contact angle between the spray droplet and the plant surface which increases wettability and herbicide penetration into the leaf (Curran and Lingenfelter, 2009). However, surfactant nature and concentration, presence of other adjuvants herbicide formulation and surrounding vapor can also affect surface tension and contact angle (Qazi, 2020; Castro el at. 2018; Kraemer et al. 2009, Torrecila et al. 2008; Singh et al. 1984) which may explain some of the adjuvants did not work as expect by maintaining or increasing ST and CA. Those uncommon results were observed mainly at 80% RH which indicates that adjuvants effects are less likely to occur at high humidities.

Besides penetration and wettability, CA and ST directly impact evaporation rate of the droplet. According to Li et al. (2019), surfactant could shorten the evaporation duration of the droplet, since in some cases the adjuvant reduces the spray solution surface tension that would accelerate the spreading and evaporation. Also, surfactants that reduce contact angle can result in a 10-fold increase in surface area available for evaporation (Pricer, 1983). Although some of the adjuvants in this study contained a humectant in their formulation, it was not enough to decrease evaporation rate in all scenarios, especially at high humidities, 60% and 80% RH, were droplet evaporation is naturally slower. Other factor affecting evaporation rate is the droplet size (Xu et al. 2010). Larger droplets will take a longer time to evaporate which may explain the fact that solutions containing NIS-DRA2 presented greater DMV among adjuvants and also consistently decreased evaporation rate in the absence of WC. However, in the presence of WC, decreased was not consistent throughout all the RHs which indicates that droplet evaporation rate is dependable of multiples factors.

The droplet spectrum has been recognized as the most important variable to be controlled to reduce spray drift (Oliveira et al. 2015). The Spray Drift Task Force defined physical properties as one of the primary factors affecting droplet size spectrum. Cunha and Alves (2019) concluded that viscosity and surface tension were the most affected physical properties by the addition of adjuvants. While a decrease in surface tension causes a decrease in droplet size, an increase in density result in formation of larger droplets (Kooji et al. 2018, Ellis et al. 2001) which explain the variable influence of adjuvant on droplet spectra in this study. However, solutions containing NIS-DRA2 presented the highest DMV and lowest PF which indicates that density was more important to determine droplet spectrum in this case.

One of the most important factors to consider when applying tank mixture of dicamba and glyphosate is the pH of the spray solution. At pH bellow 5.0 dicamba will convert to the acid form when pH has very high vapor potential (Anonymous, 2020b). Results obtained from this study showed that in the absence of WC only NISH4 would be adequate since all the other treatments solutions including DpG alone presented pH <5. However, in the presence of WC, expect for DpG plus NIS1, all treatment solutions presented ≥ 5 which indicates that WC has in its compositions elements that increase pH. Moreover, considering the initial pH of the water was 7.5, all DpG solutions acidified the water which agrees with results found by Mueller and Steckel (2019).

Greenhouse studies demonstrated that the influence of adjuvants on herbicide effectiveness in the absence of WC was species specific. Although for barnyardgrass, horseweed, and kochia most adjuvant treatments performed similarly to DpG alone, for velvetleaf and waterhemp, all adjuvants tested improved herbicide effectiveness. Weed species have different foliar surface characteristics (e.g. cuticle, number of stomata and trichomes, leaf position and angle and leaf age) that impose barriers to herbicide deposition (Koch et al. 2008; Kraemer et al. 2009; Hess 1985; Hull et al. 1982). However, in the presence of WC most adjuvants treatments were statistically comparable to DpG solution with only WC, independently of the weed species. Also, under field conditions, compared to DpG alone or DpG with WC only, the addition of adjuvants did not increase DpG solutions efficacy for both horseweed and Palmer amaranth. Eubank et al.(2013) demonstrated that at 28 DAA, the level of horseweed VEC with saflufenacil plus NIS at 0.25 v $v^{-1}$ and 0.5 v $v^{-1}$ was similar to saflufenacil alone. Furthermore, except for velvetleaf, reduced herbicide efficacy was noticed with the addition of some adjuvants to DpG solutions with and without WC.  One possible explication for the null or antagonistic response to adjuvants is that NIS contained in all adjuvants decreased the dST and sCA, but adjuvants also increased VMD, especially NIS-DRAs. Thus, as each type of application requires a specific droplet size for optimum biological activity (Knoche, 1994), the improvement in wettability and herbicide penetration may not be enough to overcome the unsatisfactory herbicide coverage by the larger droplets. Also, these larger spray droplets are less likely to adhere to a leaf surface which may result in roll or fall-off of those spray droplets, and consequently in a reduction of herbicide efficacy (Tu and Randall, 2001). Regarding the humectants, although the humidity under greenhouse conditions may be enough to prevent rapid droplet drying regardless of surfactant humectancy, in 2020 horseweed and Palmer amaranth fields were sprayed under hot and dry weather conditions. Therefore, the humectant composition or concentration may be not adequate for DpG solutions. Overall, results demonstrated that adjuvants will not always increase efficacy of herbicides.

## Literature Cited

Anonymous (2020a) Engenia® herbicide product label. EPA Reg. No. 7969-345. Research Triangle Park, NC: BASF Corporation, 16.

Anonymous (2020) XtendiMax® with Vaporgrip technology herbicide product label. EPA Reg. No. 524-617. Research Triangle Park, NC: Bayer Crop Protection, Inc,2.

*ASABE Standards. S327.4: Terminology and definitions for applications of crop or forestry production and protective agents.* (2016). St. Joseph, MI: ASABE.

Behrens, M. R., Mutlu, N., Chakraborty, S., Dumitru, R., Jiang, W. Z., LaVallee, B. J., . . . Weeks, D. P. (2007). Dicamba resistance: Enlarging and preserving biotechnology-based weed management strategies. Science, 316(5828), 1185-1188. doi:10.1126/science.1141596

Behrens, R., &; Lueschen, W. E. (1979). Dicamba volatility. Weed Science, 27(5), 486-493. doi:10.1017/s0043174500044453

Bouse, L., Kirk, I., & Bode, L. (1990). Effect of spray mixture on droplet size. Transactions of the ASAE, 33(3), 0783-0788. doi:10.13031/2013.31401

Bukovac, M. J., &; Petracek, P. D. (1993). Characterizing pesticide and surfactant penetration with isolated plant cuticles. Pesticide Science, 37(2), 179-194. doi:10.1002/ps.2780370212

Butler Ellis, M., Tuck, C., & Miller, P. (2001). How surface tension of surfactant solutions influences the characteristics of sprays produced by hydraulic nozzles used for pesticide application. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 180(3), 267-276. doi:10.1016/s0927-7757(00)00776-7

Butts, T. R., Samples, C. A., Franca, L. X., Dodds, D. M., Reynolds, D. B., Adams, J. W., . . . Kruger, G. R. (2018). Spray droplet size and carrier volume effect on dicamba and glufosinate efficacy. Pest Management Science, 74(9), 2020-2029. doi:10.1002/ps.4913

Castro, E., Carbonari, C., Velini, E., Gomes, G., & Belapart, D. (2018). Influence of adjuvants on the surface tension, deposition and effectiveness of herbicides on fleabane plants. Planta Daninha, *36*(0). doi:10.1590/s0100-83582018360100067

Coret, J., Gambonnet, B., Brabet, F., & Chamel, A. R. (1993). Diffusion of three ethoxylated octylphenols across isolated plant cuticles. Pesticide Science, 38(2-3), 201-209. doi:10.1002/ps.2780380215

Cunha, J., & Alves, G. (2009). Características físico-químicas de soluções aquosas com adjuvantes de uso agrícola. *Interciencia*, *34*(9), 655-659.

Curran, W., McGlamery, M., Liebl, R., & Lingenfelter, D. (1999). Adjuvants for enhancing herbicide performance. *In Agronomy Facts 37*. University Park, PA: Pennsylvania State University.

Curran, W., & Lingenfelter, D. (2009). Adjuvants for enhancing herbicide performance. *In Agronomy Facts 37*. University Park, PA: Pennsylvania State University.

Downer, R. A., Underwood, A. K., Hall, F. R., & Mack, R. E. (1998). Roundup Ultra with drift management adjuvants. In *Fifth International Symposium on Adjuvants for Agrochemicals*. Memphis, TN: Memphis: ISAA.

Egan, J. F., & Mortensen, D. A. (2012). Quantifying vapor drift of dicamba herbicides applied to soybean. Environmental Toxicology and Chemistry, 31(5), 1023-1031. doi:10.1002/etc.1778

[EPA] United States Environmental Protection Agency (2019). Glyphosate: Response to Comments, Usage, and Benefits. Retrieved March 22, 2021, from https://www.epa.gov/sites/production/files/2019-04/documents/glyphosate-response-comments-usage-benefits-final.pdf

Eubank, T. W., Nandula, V. K., Reddy, K. N., Poston, D. H., & Shaw, D. R. (2013). Saflufenacil efficacy on horseweed and its interaction with glyphosate. *Weed Biology and Management, 13*(4), 135-143. doi:10.1111/wbm.12022

Fritz, B. K., Hoffmann, W. C., Gizotti-de-Moraes, J., Guerrerio, M., Golus, J., & Kruger, G. R. (2018). The impact of spray adjuvants on solution physical properties and spray droplet size. *Pesticide Formulation and Delivery Systems: 37th Volume, Formulations with Ingredients on the EPA's List of Minimal Concern*, 22-32. doi:10.1520/stp160220160134

Fritz, B. K., Hoffmann, W. C., Kruger, G. R., Henry, R. S., Hewitt, A., & Czaczyk, Z. (2014). Comparison of drop size data from ground and aerial application nozzles at three testing laboratories. Atomization and Sprays, 24(2), 181-192. doi:10.1615/atomizspr.2013009668

Grossmann, K. (2007). Auxin herbicide action. *Plant Signaling & Behavior*, *2*(5), 421-423. doi:10.4161/psb.2.5.4417

Harbour, J. D., Messersmith, C. G., & Ramsdale, B. K. (2003). Surfactants affect herbicides on kochia (Kochia scoparia) and Russian thistle (Salsola iberica). Weed Science, 51(3), 430-434. doi:10.1614/0043-1745(2003)051[0430:sahokk]2.0.co;2

Hazen, J. L. (2000). Adjuvants - terminology, classification and chemistry. *Weed Technology, 14*(4), 773-784. doi:https://doi.org/10.1614/0890-037X(2000)014[0773:ATCAC]2.0.CO;2

Heap, I. The International Herbicide-Resistant Weed Database. Online. Monday, October 26, 2020 .Available www.weedscience.org Copyright © 1993- 2020 WeedScience.org All rights reserved. Fair use of this material is encouraged. Proper citation is requested. https://doi.org/10.1520/STP161920180130

Herrmann, K. M., & Weaver, L. M. (1999). The shikimate pathway. Annual Review of Plant Physiology and Plant Molecular Biology, 50(1), 473-503. doi:10.1146/annurev.arplant.50.1.473

Hess, F. D., Bayer, D. E., & Falk, R. H. (1974). Herbicide dispersal patterns: I. as a function of leaf surface. *Weed Science, 22*(4), 394-401. doi:10.1017/s0043174500037516

Hewitt, A.J. (1998) The effect of tank mix and adjuvants on spray drift. In: McMullan PM, editor. Adjuvants for agrochemicals: challenges and opportunities. *Proceedings of the Fifth International Symposium on Adjuvants for Agrochemicals, Chemical Producers Distributors Association,* Memphis, TN, 451–62.

Hofman, V., & Solseng, E. (2017, June/July). Reducing Spray Drift. Agricultural and Biosystems Engineering, North Dakota State University. Retrieved February 18, 2021, from https://www.ag.ndsu.edu/publications/crops/reducing-spray-drift/ae1210.pdf

Hull, H. M., Davis, D. G., & Stolzenberg, G. E. (1982). Action of adjuvants on plant surfaces. *Adjuvants for Herbicides. Weed Science Society of America.,* 26-67.

Koch, K., Bhushan, B., & Barthlott, W. (2008). Diversity of structure, morphology and wetting of plant surfaces. *Soft Matter, 4*(10), 1943. doi:10.1039/b804854a

Kirkwood, R. C. (1993). Use and mode of action of adjuvants for herbicides: A review of some current work. Pesticide Science, 38(2-3), 93-102. doi:10.1002/ps.2780380205

Kirkwood, R. C. (1999). Recent developments in our understanding of the plant cuticle as a barrier to the foliar uptake of pesticides†. Pesticide Science, 55(1), 69-77. doi:10.1002/(sici)1096-9063(199901)55:13.0.co;2-h

Knoche, M. (1994). Effect of droplet size and carrier volume on performance of foliage-applied herbicides. *Crop Protection, 13*(3), 163-178. doi:10.1016/0261-2194(94)90075-2

Kooij, S., Sijs, R., Denn, M. M., Villermaux, E., & Bonn, D. (2018). What determines the drop size in sprays? Physical Review X, 8(3). doi:10.1103/physrevx.8.031019

Kraemer, T., Hunsche, M., & Noga, G. (2009). Surfactant-induced deposit structures in relation to the biological efficacy of glyphosate on easy- and difficult-to-wet weed species. *Pest Management Science, 65*(8), 844-850. doi:10.1002/ps.1759

Long, J. L. (2017). Influence of application factors on dicamba volatility (Doctoral dissertation, Purdue University, 2017). Ann Arbor: ProQuest Dissertations & Theses.

Moraes, J. G., Luck, J. D., Antuniassi, U. R., Hoffmann, W. C., & Kruger, G. R. (2019). Effect of adjuvants on physical properties of glyphosate and PPO-Inhibiting Herbicide Spray Mixtures. *Pesticide Formulation and Delivery Systems: Innovative Formulation, Application and Adjuvant Technologies for Agriculture, 39*, 64-74. doi:10.1520/stp161920180130

Mueller, T. C., & Steckel, L. E. (2019). Spray mixture pH as affected by dicamba, glyphosate, and spray additives. Weed Technology, 33(4), 547-554. doi:10.1017/wet.2019.40

Norsworthy, J. K., Ward, S. M., Shaw, D. R., Llewellyn, R. S., Nichols, R. L., Webster, T. M., . . . Barrett, M. (2012). Reducing the risks of herbicide resistance: Best management practices and recommendations. Weed Science, 60(SP1), 31-62. doi:10.1614/ws-d-11-00155.1

Oliveira, R. B., Antuniassi, U. R., & Gandolfo, M. A. (2015). Spray adjuvant characteristics affecting agricultural spraying drift. Engenharia Agrícola, 35(1), 109-116. doi:10.1590/1809-4430-eng.agric.v35n1p109-116/2015

Pratt, D., Kells, J. J., & Penner, D. (2003). Substitutes for ammonium Sulfate as additives with glyphosate and glufosinate. Weed Technology, 17(3), 576-581. doi:10.1614/0890-037x(2003)017[0576:sfasaa]2.0.co;2

Pricer, C. E. (1983). The effect of environment on foliage uptake and translocation of herbicides. *A.o.A. Biologists (Ed.), Aspects of Applied Biology 4: Influence of Environmental Factors on Herbicide Performance and Crop and Weed Biology, 4*, 157-169.

Qazi, M. J., Schlegel, S. J., Backus, E. H., Bonn, M., Bonn, D., & Shahidzadeh, N. (2020). Dynamic surface tension of surfactants in the presence of high salt concentrations. *Langmuir, 36*(27), 7956-7964. doi:10.1021/acs.langmuir.0c01211

R Core Team (2019) R: A language and environment for statistical computing. Vienna, Austria: R Foundation for Statistical Computing. https://www.R-project.org/. Accessed: November 9, 2020

Ramsey, R., Stephenson, G., & Hall, J. (2005). A review of the effects of humidity, humectants, and surfactant composition on the absorption and efficacy of highly water-soluble herbicides. *Pesticide Biochemistry and Physiology, 82*(2), 162-175. doi:10.1016/j.pestbp.2005.02.005

Roskamp, J. M., Chahal, G. S., & Johnson, W. G. (2013). The effect of cations and ammonium sulfate on the efficacy of Dicamba and 2,4-D. Weed Technology, 27(1), 72-77. doi:10.1614/wt-d-12-00106.1

Schönherr, J., & Baur, P. (1994). Modelling penetration of plant cuticles by crop protection agents and effects of adjuvants on their rates of penetration. Pesticide Science, 42(3), 185-208. doi:10.1002/ps.2780420308

Sharma, M. P., & Born, W. H. (1970). Foliar penetration of picloram and 2,4-D in Aspen and balsam poplar. Weed Science, 18(1), 57-63. doi:10.1017/s0043174500077341

Singh, M., Orsenigo, J. R., & Shah, D. O. (1984). Surface tension and contact angle of herbicide solutions affected by surfactants. *Journal of the American Oil Chemists' Society, 61*(3), 596-600. doi:10.1007/bf02677040

Sobiech, Ł, Grzanka, M., Skrzypczak, G., Idziak, R., Włodarczak, S., & Ochowiak, M. (2020). Effect of adjuvants and pH adjuster on the efficacy of sulcotrione herbicide. *Agronomy, 10*(4), 530. doi:10.3390/agronomy10040530

Schönherr, J., & Baur, P. (1994). Modelling penetration of plant cuticles by crop protection agents and effects of adjuvants on their rates of penetration. Pesticide Science, 42, 185-208. doi:https://doi.org/10.1002/ps.2780420308

Spanoghe, P., De Schampheleire, M., Van der Meeren, P., & Steurbaut, W. (2006). Influence of agricultural adjuvants on droplet spectra. Pest Management Science, 63(1), 4-16. doi:10.1002/ps.1321

Spanoche, P., Van Eeckhout, H., Steurbaut, W., & Van der Meeren, P. (2002). The effect of static and dynamic surface tension on atomization of agricultural nozzles. Mededelingen (Rijksuniversiteit Te Gent. Fakulteit Van De Landbouwkundige En Toegepaste Biologische Wetenschappen), 67(2), 37-45.

Steinrücken, H., & Amrhein, N. (1980). The herbicide glyphosate is a potent inhibitor of 5-enolpyruvylshikimic acid-3-phosphate synthase. Biochemical and Biophysical Research Communications, 94(4), 1207-1212. doi:10.1016/0006-291x(80)90547-1

Subramanian, M. V., Tuckey, J., Patel, B., & Jensen, P. J. (1997). Engineering dicamba selectivity in crops: A search for appropriate degradative enzyme(s). Journal of Industrial Microbiology and Biotechnology, 19(5-6), 344-349. doi:10.1038/sj.jim.2900441

Taylor, A. W., & Spencer, W. F. (2018). Volatilization and vapor transport processes. Pesticides in the Soil Environment: Processes, Impacts and Modeling, 213-269. doi:10.2136/sssabookser2.c7

Thelen, K. D., Jackson, E. P., & Penner, D. (1995). The basis for the hard-water antagonism of glyphosate activity. Weed Science, 43(4), 541-548. doi:10.1017/s0043174500081613

Torrecilla, J. S., Rafione, T., García, J., & Rodríguez, F. (2008). Effect of relative humidity of air on density, Apparent Molar Volume, viscosity, surface tension, and water content of 1-ethyl-3-methylimidazolium ethylsulfate ionic liquid. *Journal of Chemical & Engineering Data, 53*(4), 923-928. doi:10.1021/je700523b

Tu, M., Hurd, C., & Randall, J. M. (2001). Adjuvants. In *Weed VEC methods handbook: Tools and techniques for use in natural areas* (pp. 171-190). Davis, CA: Wildland Invasive Species Team, the Nature Conservancy. doi:https://www.invasive.org/gist/products/handbook/methods-handbook.pdf

[USGS] U.S Geological Survey (2020a).Estimated Annual Agricultural Pesticide Use. Retrieved March 22, 2021, from https://water.usgs.gov/nawqa/pnsp/usage/maps/show_map.php?year=2017&map=GLYPHOSATE&hilo=L&disp=Glyphosate

[USGS] U.S Geological Survey (2020b).Estimated Annual Agricultural Pesticide Use. Retrieved March 22, 2021, from https://water.usgs.gov/nawqa/pnsp/usage/maps/show_map.php?year=2017&map=DICAMBA&hilo=L&disp=Dicamba

Xu, L., Zhu, H., Ozkan, H., Bagley, W., Derksen, R. C., & Krause, C. R. (2010). Adjuvant effects on evaporation time and wetted area of droplets on waxy leaves. Transactions of the ASABE, 53(1), 13-20. doi:10.13031/2013.29495

Zollinger, R. K., Bernards, M. L., Young, B. G., Peterson, D. E., & Kruger, G. R. (2016). Efficacy of water-conditioning adjuvants for dicamba-tolerant soybean. Pesticide Formulation and Delivery Systems: 38th Volume, Innovative Application, Formulation, and Adjuvant Technologies, 89-97. doi:10.1520/stp161020170216

**Table 6.** Description of the herbicides and adjuvants evaluated.

| Herbicide | Trade name | Full rate | Reduced rate |
|---|---|---|---|
| | | g ae $ha^{-1}$ | |
| Dicamba | Xtendimax ® with Vapor Grip® | 559 | 279 |
| Glyphosate | Roundup PowerMax® | 1541 | 385 |
| Adjuvant | Adjuvant type | Rate | Abbreviation |
| | | % v $v^{-1}$ | |
| Water conditioner | non-AMS-water conditioner | 0.5 | WC |
| Adjuvant 1 | non-ionic surfactant | 0.25 | NIS1 |
| Adjuvant 2 | non-ionic surfactant | 0.25 | NIS2 |
| Adjuvant 3 | non-ionic surfactant-drift reducing agent | 0.25 | NIS-DRA1 |
| Adjuvant 4 | non-ionic surfactant-drift reducing agent | 0.75 | NIS-DRA2 |
| Adjuvant 5 | non-ionic surfactant-humectant | 0.5 | NISH1 |
| Adjuvant 6 | non-ionic surfactant-humectant | 0.5 | NISH2 |
| Adjuvant 7 | non-ionic surfactant-humectant | 0.5 | NISH3 |
| Adjuvant 8 | non-ionic surfactant-humectant | 0.5 | NISH4 |
| Adjuvant 9 | non-ionic surfactant-humectant | 0.5 | NISH5 |
| Adjuvant 10 | non-ionic surfactant-humectant | 0.5 | NISH6 |

**Table 7.1.** Density and viscosity for dicamba plus glyphosate solutions at 559 and 1541 g ae ha$^{-1}$, respectively, with no water conditioner and with non-AMS water conditioner alone or in combination with 10 adjuvants at 20°C.

| Water Conditioner | Other adjuvants | Density | | Viscosity | |
|---|---|---|---|---|---|
| | | g cm$^3$ | | mPa s$^{-1}$ | |
| none | none | 1.0060 | d | 1.0400 | j |
| none | NIS1 | 1.0070 | c | 1.0800 | e |
| none | NIS2 | 1.0060 | d | 1.0900 | d |
| none | NIS-DRA1 | 1.0070 | c | 1.0600 | f |
| none | NIS-DRA2 | 1.0060 | d | 1.1250 | b |
| none | NISH1 | 1.0060 | d | 1.0500 | i |
| none | NISH2 | 1.0060 | d | 1.0500 | i |
| none | NISH3 | 1.0060 | d | 1.0500 | i |
| none | NISH4 | 1.0070 | c | 1.0500 | i |
| none | NISH5 | 1.0070 | c | 1.0500 | i |
| none | NISH6 | 1.0068 | c | 1.0550 | h |
| non-AMS WC | none | 1.0070 | c | 1.0400 | j |
| non-AMS WC | NIS1 | 1.0080 | b | 1.0600 | f |
| non-AMS WC | NIS2 | 1.0080 | b | 1.1000 | c |
| non-AMS WC | NIS-DRA1 | 1.0088 | a | 1.0600 | f |
| non-AMS WC | NIS-DRA2 | 1.0078 | b | 1.1300 | a |
| non-AMS WC | NISH1 | 1.0070 | c | 1.0500 | i |
| non-AMS WC | NISH2 | 1.0070 | c | 1.0575 | g |
| non-AMS WC | NISH3 | 1.0080 | b | 1.0500 | i |
| non-AMS WC | NISH4 | 1.0080 | b | 1.0600 | f |
| non-AMS WC | NISH5 | 1.0080 | b | 1.0600 | f |
| non-AMS WC | NISH6 | 1.0078 | b | 1.0520 | i |
| | | *** | | *** | |

Means followed by the same letter in the column do not differ using Tukey's test at $\alpha = 0.05$.
Significance level: ***$p \leq 0.001$.

**Table 7.2.** Static contact angle for dicamba plus glyphosate solutions at 559 and 1541 g ae ha$^{-1}$, respectively, with no water conditioner and with non-AMS water conditioner alone or in combination with 10 adjuvants at 25°C.

| Water conditioner | Adjuvants | 20% RH | | 40% RH | | 60% RH | | 80%RH | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | angle | | | | | |
| none | none | 38 | bcd | 40 | c | 42 | a | 36 | fg |
| none | NIS1 | 32 | hi | 33 | gh | 31 | ij | 32 | j |
| none | NIS2 | 28 | k | 32 | gh | 32 | hi | 32 | j |
| none | NIS-DRA1 | 37 | cde | 37 | de | 36 | de | 35 | fg |
| none | NIS-DRA2 | 33 | ghi | 34 | fg | 35 | ef | 35 | g |
| none | NISH1 | 36 | ef | 33 | fg | 36 | def | 35 | fg |
| none | NISH2 | 40 | a | 45 | a | 40 | ab | 41 | bc |
| none | NISH3 | 33 | ghi | 34 | fg | 34 | efg | 39 | cde |
| none | NISH4 | 41 | a | 40 | c | 41 | ab | 42 | bc |
| none | NISH5 | 35 | fg | 39 | c | 39 | bc | 41 | bc |
| none | NISH6 | 27 | k | 27 | j | 26 | k | 28 | k |
| non-AMS WC | none | 39 | abc | 40 | c | 38 | cd | 38 | de |
| non-AMS WC | NIS1 | 34 | fgh | 34 | fg | 33 | ghi | 34 | gh |
| non-AMS WC | NIS2 | 30 | j | 31 | hi | 30 | j | 32 | hij |
| non-AMS WC | NIS-DRA1 | 33 | ghi | 34 | fg | 31 | ij | 32 | ij |
| non-AMS WC | NIS-DRA2 | 35 | fg | 35 | ef | 31 | ij | 32 | hij |
| non-AMS WC | NISH1 | 37 | de | 37 | de | 33 | ghi | 34 | ghi |
| non-AMS WC | NISH2 | 39 | ab | 40 | c | 40 | ab | 41 | bc |
| non-AMS WC | NISH3 | 32 | hi | 34 | fg | 34 | fgh | 40 | bcd |
| non-AMS WC | NISH4 | 37 | de | 43 | b | 40 | bc | 48 | a |
| non-AMS WC | NISH5 | 40 | ab | 39 | cd | 38 | cd | 37 | ef |
| non-AMS WC | NISH6 | 32 | i | 30 | i | 32 | ij | 32 | hij |
| | | *** | | *** | | *** | | *** | |

Means followed by the same letter in the column do not differ using Tukey's test at α = 0.05.
Significance level: ***$p \leq 0.001$.

**Table 7.3.** Dynamic surface tension for dicamba plus glyphosate solutions at 559 and 1541 g ae $ha^{-1}$, respectively, with no water conditioner and with non-AMS water conditioner alone or in combination with 10 adjuvants at 25°C.

| Water conditioner | Adjuvants | 20% RH | 40% RH | 60% RH | 80%RH |
|---|---|---|---|---|---|
| | | | mN $m^{-1}$ | | |
| none | none | 37 a | 37 a | 37 a | 35 b |
| none | NIS1 | 32 f | 32 f | 32 f | 31 g |
| none | NIS2 | 31 g | 31 g | 31 g | 30 h |
| none | NIS-DRA1 | 35 c | 35 c | 35 c | 34 d |
| none | NIS-DRA2 | 33 e | 33 e | 33 e | 32 f |
| none | NISH1 | 35 c | 35 c | 35 c | 35 b |
| none | NISH2 | 36 b | 36 b | 36 b | 36 a |
| none | NISH3 | 34 d | 34 d | 34 d | 33 e |
| none | NISH4 | 36 b | 36 b | 36 b | 36 a |
| none | NISH5 | 35 c | 35 c | 35 c | 32 f |
| none | NISH6 | 31 g | 31 g | 31 g | 30 h |
| non-AMS WC | none | 36 b | 36 b | 36 b | 32 f |
| non-AMS WC | NIS1 | 33 e | 33 e | 33 e | 32 f |
| non-AMS WC | NIS2 | 31 g | 31 g | 31 g | 30 h |
| non-AMS WC | NIS-DRA1 | 34 d | 34 d | 34 d | 33 e |
| non-AMS WC | NIS-DRA2 | 33 e | 33 e | 33 e | 32 f |
| non-AMS WC | NISH1 | 35 c | 35 c | 35 c | 35 c |
| non-AMS WC | NISH2 | 36 b | 36 b | 36 b | 36 a |
| non-AMS WC | NISH3 | 34 d | 34 d | 34 d | 34 d |
| non-AMS WC | NISH4 | 35 c | 35 c | 35 c | 35 b |
| non-AMS WC | NISH5 | 35 c | 35 c | 35 c | 32 f |
| non-AMS WC | NISH6 | 32 f | 32 f | 32 f | 31 g |
| | | *** | *** | *** | *** |

Means followed by the same letter in the column do not differ using Tukey's test at $\alpha = 0.05$.
Significance level: ***$p \leq 0.001$.

**Table 7.4.** Evaporation rate for dicamba plus glyphosate solutions at 559 and 1541 g ae ha$^{-1}$, respectively, with no water conditioner and with non-AMS water conditioner alone or in combination with 10 adjuvants at 25°C.

| Water conditioner | Adjuvants | 20% RH | | 40% RH | | 60% RH | | 80%RH | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | μL s$^{-1}$ | | | | |
| none | none | $8.0\ 10^{-4}$ | i-m | $1.4\ 10^{-3}$ | b | $4.0\ 10^{-4}$ | j | $9.0\ 10^{-4}$ | gh |
| none | NIS1 | $6.0\ 10^{-4}$ | klm | $1.0\ 10^{-3}$ | def | $1.4\ 10^{-3}$ | ab | $9.0\ 10^{-4}$ | fgh |
| none | NIS2 | $1.4\ 10^{-3}$ | f-j | $6.0\ 10^{-4}$ | ij | $7.0\ 10^{-4}$ | i | $1.1\ 10^{-3}$ | efg |
| none | NIS-DRA1 | $7.0\ 10^{-4}$ | j-m | $7.0\ 10^{-4}$ | hi | $1.1\ 10^{-3}$ | def | $1.1\ 10^{-3}$ | efg |
| none | NIS-DRA2 | $2.6\ 10^{-3}$ | cde | $1.7\ 10^{-3}$ | a | $8.0\ 10^{-4}$ | hi | $1.3\ 10^{-3}$ | de |
| none | NISH1 | $1.6\ 10^{-3}$ | fgh | $1.1\ 10^{-3}$ | de | $1.4\ 10^{-3}$ | abc | $7.0\ 10^{-4}$ | h |
| none | NISH2 | $2.0\ 10^{-3}$ | def | $5.0\ 10^{-4}$ | jk | $8.0\ 10^{-4}$ | hi | $1.1\ 10^{-3}$ | efg |
| none | NISH3 | $1.1\ 10^{-3}$ | h-l | $1.1\ 10^{-3}$ | d | $1.5\ 10^{-3}$ | ab | $6.0\ 10^{-4}$ | h |
| none | NISH4 | $3.8\ 10^{-3}$ | a | $4.0\ 10^{-4}$ | kl | $8.0\ 10^{-4}$ | hi | $2.0\ 10^{-3}$ | b |
| none | NISH5 | $1.9\ 10^{-3}$ | efg | $9.0\ 10^{-4}$ | fg | $1.5\ 10^{-3}$ | a | $1.1\ 10^{-3}$ | efg |
| none | NISH6 | $3.0\ 10^{-3}$ | bc | $1.4\ 10^{-3}$ | b | $9.0\ 10^{-4}$ | gh | $1.1\ 10^{-3}$ | efg |
| non-AMS WC | none | $3.6\ 10^{-3}$ | ab | $3.0\ 10^{-4}$ | l | $8.0\ 10^{-4}$ | hi | $1.4\ 10^{-3}$ | de |
| non-AMS WC | NIS1 | $4.0\ 10^{-4}$ | lm | $9.0\ 10^{-4}$ | fg | $1.2\ 10^{-3}$ | cde | $1.3\ 10^{-3}$ | de |
| non-AMS WC | NIS2 | $1.3\ 10^{-3}$ | g-k | $5.0\ 10^{-4}$ | jk | $1.1\ 10^{-3}$ | def | $7.0\ 10^{-4}$ | h |
| non-AMS WC | NIS-DRA1 | $3.0\ 10^{-4}$ | m | $1.3\ 10^{-3}$ | bc | $1.3\ 10^{-3}$ | bcd | $1.6\ 10^{-3}$ | cd |
| non-AMS WC | NIS-DRA2 | $2.7\ 10^{-3}$ | cd | $1.3\ 10^{-3}$ | b | $1.0\ 10^{-3}$ | fgh | $6.0\ 10^{-4}$ | h |
| non-AMS WC | NISH1 | $1.4\ 10^{-3}$ | f-j | $9.0\ 10^{-4}$ | fg | $1.1\ 10^{-3}$ | efg | $1.4\ 10^{-3}$ | cde |
| non-AMS WC | NISH2 | $1.6\ 10^{-3}$ | f-i | $1.7\ 10^{-3}$ | a | $1.1\ 10^{-3}$ | efg | $7.0\ 10^{-4}$ | h |
| non-AMS WC | NISH3 | $8.0\ 10^{-4}$ | j-m | $9.0\ 10^{-4}$ | efg | $1.2\ 10^{-3}$ | cde | $2.5\ 10^{-3}$ | a |
| non-AMS WC | NISH4 | $2.7\ 10^{-3}$ | cd | $1.7\ 10^{-3}$ | a | $1.1\ 10^{-3}$ | efg | $1.3\ 10^{-3}$ | def |
| non-AMS WC | NISH5 | $1.0\ 10^{-3}$ | h-m | $8.0\ 10^{-4}$ | gh | $1.1\ 10^{-3}$ | efg | $1.7\ 10^{-3}$ | bc |
| non-AMS WC | NISH6 | $1.6\ 10^{-3}$ | fgh | $1.1\ 10^{-3}$ | cd | $1.4\ 10^{-3}$ | ab | $6.0\ 10^{-4}$ | h |
| | | *** | | *** | | *** | | *** | |

Means followed by the same letter in the column do not differ using Tukey's test at α = 0.05.
Significance level: ***$p \leq 0.001$.

**Table 7.5.** pH for dicamba plus glyphosate solutions at 559 and 1541g ae $ha^{-1}$, respectively, with no water conditioner and with non-AMS water conditioner alone or in combination with 10 adjuvants.

| Solution [a] | Water Conditioner | Other adjuvants | pH |
|---|---|---|---|
| Water | none | none | 7.5 |
| DpG | none | none | 4.9 |
| DpG | none | NIS1 | 4.5 |
| DpG | none | NIS2 | 4.9 |
| DpG | none | NIS-DRA1 | 4.9 |
| DpG | none | NIS-DRA2 | 4.9 |
| DpG | none | NISH1 | 4.9 |
| DpG | none | NISH2 | 4.9 |
| DpG | none | NISH3 | 4.9 |
| DpG | none | NISH4 | 5.0 |
| DpG | none | NISH5 | 4.9 |
| DpG | none | NISH6 | 4.7 |
| DpG | non-AMS WC | none | 5.1 |
| DpG | non-AMS WC | NIS1 | 4.9 |
| DpG | non-AMS WC | NIS2 | 5.2 |
| DpG | non-AMS WC | NIS-DRA1 | 5.2 |
| DpG | non-AMS WC | NIS-DRA2 | 5.1 |
| DpG | non-AMS WC | NISH1 | 5.1 |
| DpG | non-AMS WC | NISH2 | 5.2 |
| DpG | non-AMS WC | NISH3 | 5.1 |
| DpG | non-AMS WC | NISH4 | 5.1 |
| DpG | non-AMS WC | NISH5 | 5.2 |
| DpG | non-AMS WC | NISH6 | 5.0 |

[a] Abbreviation: DpG, dicamba (Xtendimax ® with Vapor Grip®, Monsanto Company, St. Louis, MO, USA) plus glyphosate (Roundup PowerMax®, Monsanto Company, St. Louis, MO, USA).

**Table 8.** Dv0.1, Dv0.5, and Dv0.9 (droplet diameters for which 10, 50, and 90% of the total spray volume is contained in droplets of lesser diameter, respectively), volume percentage of droplets smaller than 150 µm (PF) and relative span (RS) for dicamba plus glyphosate solutions at 559 and 1541 g ae ha$^{-1}$, respectively, with no water conditioner and with non-AMS water conditioner alone or in combination with 10 adjuvants at 246 kPa using TTI110015 nozzle.

| Water Conditioner | Other adjuvants | Parameters | | | | |
|---|---|---|---|---|---|---|
| | | Dv0.1 | Dv0.5 | Dv0.9 | PF | RS |
| | | | | µm | | |
| none | none | 371 c | 717 e | 1069 e | 0.46 c | 0.97 d |
| none | NIS1 | 369 c | 710 d | 1057 d | 0.47 c | 0.96 c |
| none | NIS2 | 349 a | 653 a | 964 a | 0.51 d | 0.94 b |
| none | NIS-DRA1 | 375 d | 724 a | 1073 e | 0.47 c | 0.96 c |
| none | NIS-DRA2 | 502 e | 941 g | 1350 f | 0.18 a | 0.9 a |
| none | NISH1 | 372 c | 718 e | 1068 e | 0.48 c | 0.97 d |
| none | NISH2 | 377 d | 729 f | 1078 e | 0.43 b | 0.96 c |
| none | NISH3 | 360 b | 702 c | 1046 c | 0.58 e | 0.97 d |
| none | NISH4 | 375 d | 727 f | 1075 e | 0.46 c | 0.96 c |
| none | NISH5 | 375 d | 727 f | 1075 e | 0.47 c | 0.96 c |
| none | NISH6 | 349 a | 684 b | 1026 b | 0.63 f | 0.98 d |
| non-AMS WC | none | 383 e | 736 f | 1083 e | 0.41 b | 0.95 c |
| non-AMS WC | NIS1 | 363 c | 709 c | 1060 d | 0.52 e | 0.98 d |
| non-AMS WC | NIS2 | 343 a | 645 a | 941 a | 0.53 e | 0.92 b |
| non-AMS WC | NIS-DRA1 | 377 d | 727 d | 1074 e | 0.45 c | 0.96 c |
| non-AMS WC | NIS-DRA2 | 509 f | 949 g | 1362 f | 0.14 a | 0.90 a |
| non-AMS WC | NISH1 | 373 d | 721 d | 1069 d | 0.48 d | 0.96 c |
| non-AMS WC | NISH2 | 381 e | 731 e | 1078 e | 0.42 b | 0.95 c |
| non-AMS WC | NISH3 | 362 c | 705 c | 1053 c | 0.56 f | 0.98 d |
| non-AMS WC | NISH4 | 377 d | 729 e | 1076 e | 0.44 c | 0.96 c |
| non-AMS WC | NISH5 | 375 d | 726 d | 1073 e | 0.47 d | 0.96 c |
| non-AMS WC | NISH6 | 350 b | 685 b | 1029 b | 0.63 g | 0.99 d |
| | | *** | *** | *** | *** | *** |

Means followed by the same letter in the column do not differ using Tukey's test at $\alpha = 0.05$.
Significance level: ***$p \leq 0.001$.

**Table 9.1.** Biomass reduction (BR) and visual estimation of control (VEC) of barnyardgrass, horseweed, and kochia at 28 days after application (28 DAA) for dicamba plus glyphosate solutions at 279 and 385 g ae ha$^{-1}$, respectively, with no water conditioner and with non-AMS water conditioner alone or in combination with 10 adjuvants in greenhouse experiments.

| Water Conditioner | Other adjuvants | Barnyardgrass | | Horseweed | | Kochia | |
|---|---|---|---|---|---|---|---|
| | | VEC | BR | VEC | BR | VEC | BR |
| | | | | % | | | |
| none | none | 61 efg | 78 a-e | 98 a | 93 a | 79 h | 76 def |
| none | NIS1 | 59 fg | 76 b-e | 99 a | 93 a | 88 c-f | 79 b-e |
| none | NIS2 | 36 h | 56 fg | 98 a | 92 abc | 85 d-h | 80 bcd |
| none | NIS-DRA1 | 54 g | 77 a-e | 94 a | 89 b-f | 81 gh | 66 g |
| none | NIS-DRA2 | 72 cde | 84 abc | 97 a | 90 a-f | 83 e-h | 71 efg |
| none | NISH1 | 61 efg | 82 abc | 98 a | 90 a-f | 81 f-h | 73 d-g |
| none | NISH2 | 52 g | 64 ef | 97 a | 91 a-e | 88 b-e | 85 abc |
| none | NISH3 | 70 def | 83 abc | 98 a | 92 abc | 86 c-g | 78 cde |
| none | NISH4 | 52 g | 66 de | 98 a | 90 a-f | 85 d-h | 75 def |
| none | NISH5 | 51 g | 73 cde | 97 a | 88 ef | 89 a-d | 81 a-d |
| none | NISH6 | 89 a | 94 a | 97 a | 89 b-f | 95 a | 88 a |
| non-AMS WC | none | 69 def | 80 a-d | 93 a | 91 a-d | 85 d-h | 77 cde |
| non-AMS WC | NIS1 | 71 def | 86 abc | 100 a | 92 ab | 85 d-h | 74 d-g |
| non-AMS WC | NIS2 | 53 g | 73 cde | 98 a | 92 abc | 79 f-h | 68 fg |
| non-AMS WC | NIS-DRA1 | 74 bcd | 86 abc | 98 a | 88 c-f | 81 fgh | 74 d-g |
| non-AMS WC | NIS-DRA2 | 83 abc | 91 ab | 98 a | 91 a-e | 84 d-h | 77 cde |
| non-AMS WC | NISH1 | 55 g | 62 g | 99 a | 92 ab | 89 a-d | 87 ab |
| non-AMS WC | NISH2 | 71 de | 82 abc | 99 a | 92 abc | 92 abc | 85 abc |
| non-AMS WC | NISH3 | 77 bcd | 87 abc | 98 a | 92 ab | 89 a-e | 86 abc |
| non-AMS WC | NISH4 | 76 bcd | 86 abc | 97 a | 88 def | 92 abc | 80 a-d |
| non-AMS WC | NISH5 | 71 de | 85 abc | 99 a | 87 f | 89 a-e | 78 b-e |
| non-AMS WC | NISH6 | 84 abc | 92 ab | 98 a | 90 a-f | 94 ab | 88 a |
| | | ** | *** | - | *** | *** | ** |

Means followed by the same letter in the column do not differ using Tukey's test at α = 0.05.

Significance levels: -, nonsignificant at α = 0.05; **$p \leq 0.01$; ***$p \leq 0.001$.

**Table 9.2.** Biomass reduction (BR) and visual estimation of control (VEC) of velvetleaf and common waterhemp at 28 days after application (28 DAA) for dicamba plus glyphosate solutions at 279 and 385 g ae ha$^{-1}$, respectively, with no water conditioner and with non-AMS water conditioner alone or in combination with 10 adjuvants in greenhouse experiments.

| Water Conditioner | Other adjuvants | Velvetleaf | | C. waterhemp | |
|---|---|---|---|---|---|
| | | VEC | BR | VEC | BR |
| | | % | | | |
| none | none | 41 d | 28 e | 52 g | 58 e |
| none | NIS1 | 74 abc | 69 a-d | 86 a-f | 85 a-d |
| none | NIS2 | 75 abc | 69 a-d | 90 a-e | 80 a-d |
| none | NIS-DRA1 | 74 abc | 65 a-d | 96 ab | 91 ab |
| none | NIS-DRA2 | 73 abc | 70 a-d | 79 ef | 73 cd |
| none | NISH1 | 73 abc | 65 a-d | 89 a-e | 84 a-d |
| none | NISH2 | 73 abc | 73 ab | 95 ab | 90 ab |
| none | NISH3 | 73 abc | 70 a-d | 96 ab | 90 ab |
| none | NISH4 | 76 abc | 66 a-d | 91 a-e | 87 abc |
| none | NISH5 | 74 abc | 57 d | 92 a-d | 88 abc |
| none | NISH6 | 81 a | 75 ab | 94 abc | 89 ab |
| non-AMS WC | none | 73 abc | 71 abc | 96 ab | 93 a |
| non-AMS WC | NIS1 | 73 abc | 67 a-d | 93 a-d | 89 ab |
| non-AMS WC | NIS2 | 71 abc | 69 a-d | 81 def | 82 a-d |
| non-AMS WC | NIS-DRA1 | 73 abc | 69 a-d | 86 a-f | 86 a-d |
| non-AMS WC | NIS-DRA2 | 76 abc | 68 a-d | 93 abc | 87 abc |
| non-AMS WC | NISH1 | 68 c | 58 cd | 94 abc | 92 ab |
| non-AMS WC | NISH2 | 71 c | 63 bcd | 77 f | 71 de |
| non-AMS WC | NISH3 | 75 abc | 71 abc | 85 b-f | 82 a-d |
| non-AMS WC | NISH4 | 82 a | 78 a | 88 a-f | 85 a-d |
| non-AMS WC | NISH5 | 74 abc | 67 a-d | 83 c-f | 77 bcd |
| non-AMS WC | NISH6 | 77 abc | 75 ab | 97 a | 93 a |
| | | *** | *** | *** | *** |

Means followed by the same letter in the column do not differ using Tukey's test at α = 0.05.
Significance levels: $**p \leq 0.01$; $***p \leq 0.001$.

**Table 10.** Biomass reduction (BR), visual estimation of control (VEC), and mortality (M) of horseweed and Palmer amaranth at 28 days after application (28 DAA) for dicamba plus glyphosate solutions at 559 and 1541 g ae ha$^{-1}$, respectively, with no water conditioner and with non-AMS water conditioner alone or in combination with 10 adjuvants in field experiments.

|  | Horseweed |  |  | Palmer amaranth |  |  |
|---|---|---|---|---|---|---|
|  | Parameter |  |  |  |  |  |
| Water conditioner | VEC | BR | M | VEC | BR | M |
|  | % |  |  |  |  |  |
| none | 91 A | 65 A | 59 A | 59 A | 49 A | 18 A |
| non-AMS WC | 90 A | 64 A | 59 A | 60 A | 46 A | 16 A |
|  | - | - | - | - | - | - |
| Other adjuvants |  |  |  |  |  |  |
| none | 91 ab | 62 a | 55 a | 57 a | 38 a | 22 a |
| NIS1 | 91 ab | 63 a | 66 a | 59 a | 51 a | 17 a |
| NIS2 | 90 ab | 65 a | 59 a | 61 a | 50 a | 17 a |
| NIS-DRA1 | 89 b | 65 a | 54 a | 58 a | 51 a | 21 a |
| NIS-DRA2 | 92 a | 64 a | 63 a | 59 a | 33 a | 15 a |
| NISH1 | 90 ab | 64 a | 60 a | 59 a | 60 a | 19 a |
| NISH2 | 91 ab | 62 a | 55 a | 59 a | 52 a | 25 a |
| NISH3 | 90 ab | 69 a | 57 a | 62 a | 48 a | 12 a |
| NISH4 | 89 b | 64 a | 60 a | 61 a | 53 a | 16 a |
| NISH5 | 91 ab | 67 a | 62 a | 62 a | 43 a | 20 a |
| NISH6 | 91 ab | 61 a | 60 a | 53 a | 46 a | 5 a |
|  | ** | - | - | - | - | - |

Means followed by the same letter in the column do not differ using Tukey's test at α = 0.05.
Significance levels: -; nonsignificant at α = 0.05; **$p \leq 0.01$.