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Influence of surfactant-humectant adjuvants on physical properties, droplet size, and efficacy of glufosinate formulations

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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 while decreasing evaporation rate (ER). However, there is a lack of information in the literature about the interaction of surfactant-humectants adjuvants with glufosinate. 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 at the Pesticide Application Technology Laboratory of the University of Nebraska-Lincoln. Treatment design was a 2 × 5 factorial with two glufosinate formulations combined with five adjuvant treatments plus an untreated control. Density and viscosity of glufosinate solutions mostly increased with the addition of adjuvants. However, the influence of the adjuvants on dynamic surface tension (dST), static contact angle (sCA), and evaporation rate (ER) varied by glufosinate formulation, adjuvant, and relative humidity (RH). Under greenhouse conditions, an improvement in efficacy by adding adjuvants was mainly observed for Interline solutions. The addition of adjuvants to Interline solutions increased biomass reduction up to 19 and 35% for common lambsquarters (*Chenopodium album* L.) and kochia [*Bassia scoparia* (L.) A. J. Scott], respectively. Also, some of the adjuvants presented null or antagonistic influence on herbicide efficacy. No increase in control, biomass reduction, and mortality of horseweed (*Erigeron canadensis* L.) and Palmer amaranth (*Amaranthus palmeri* S. Watson) was observed with the use of adjuvants under field conditions. Herbicide-adjuvant-plant-environment interaction is complex. Thus, the use of surfactant-humectant adjuvants may not increase herbicide efficacy.

Abbreviations: BR, biomass reduction; CA, contact angle; DAA, days after application; dST, dynamic surface tension; Dv, droplet diameter; EA, experimental adjuvant; ER, evaporation rate; GT, glyphosate-tolerant; M, mortality; NIS, non-ionic surfactant; PF, percentage of fines; RH, relative humidity; RS, relative span; sCA, static contact angle; VEC, visual estimation of control; WC, water conditioner.

1 | 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 pre-plant burndown in no-till systems and noncrop areas and as a POST on glufosinate-tolerant crops (Devkota & Johnson, 2016). Widespread occurrence of glyphosate-resistance (GR) weeds in recent years has increase the adoption of glufosinate-based herbicide programs (Chahal & Johnson, 2012; Craigmyle et al., 2013; Kaur et al., 2014) since glufosinate is the only nonselective 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 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 demonstrated that glufosinate efficacy is variable among weed species and under certain environmental conditions (Anderson et al., 1993; Everman et al., 2009; Petersen & Hurle, 2001).

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 United States recommended to enhance glufosinate activity (Anonymous, 2019a). Ammonium-sulfate is added to a 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 (Maschoff et al., 2000; Pline et al., 1999; Zollinger et al., 2010). 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 (Woznica et al., 2003).

Steckel, Hart, et al. (1997) demonstrated that absorption of glufosinate 24 h 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 (Hess et al., 1974 Hull et al., 1982; Koch et al., 2008; Kraemer et al., 2009). Surfactants minimize the effect of those barriers by decreasing the contact angle (CA) between the droplet and the surface tension which enhance wettability and herbicide penetration through the leaf cuticle (Tu et al., 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 slows or completely ceases leaf uptake (Cook & Ducan, 1978; Pricer, 1983; Tu et al., 2001). Coetzer et al. (2001) reported that glufosinate efficacy was greater in Palmer amaranth (*Amaranthus palmeri* S. Watson), redroot pigweed (*A. retroflexus* L.), and common waterhemp [*A. tuberculatus* (Moq.) J. D. Sauer.] grown at 90% relative humidity (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 (Babiker & Duncan, 1975; Cook et al., 1977). Adding surfactant-humectant adjuvants into the tank mixture may improve consistency of glufosinate efficacy among weed species under unfavorable environmental conditions. However, there is a lack of information in the literature about the interaction of surfactant-humectant adjuvants with glufosinate.

Besides surfactant-humectant adjuvants altering penetration, wetting and drying time of the spray droplet, their influence on the physical properties of the solution can also result in changes of the droplet size distribution (Spanoghe et al., 2006). Each type of application requires a specific droplet size for optimum biological activity (Knoche, 1994). Therefore, the objectives of this research were to: (a) determine the physical properties (density, viscosity, dynamic surface tension, static CA [sCA], and droplet evaporation rate [ER]), and droplet size distribution of glufosinate solutions in tank

Core Ideas

- The influence of adjuvants on physical properties varies by air relative humidity.
- Viscosity and dynamic surface tension are correlated to droplet-size distribution.
- Density and dynamic surface tension impact glufosinate evaporation rate.
- Weed control may not increase when physical properties and droplet-size change.
- Adjuvants can have null or antagonistic effect on glufosinate efficacy.

mixture with surfactant-humectant adjuvants and (b) evaluate the response of weed species to glufosinate solutions in tank mixture with surfactant-humectant adjuvants under greenhouse and field conditions.

2 | MATERIALS AND METHODS

Studies were conducted at the Pesticide Application Technology Laboratory (PAT Lab) 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 2 × 5 factorial with glufosinate formulations, Liberty (formulation 1, Bayer CropScience) and Interline (formulation 2, UPL NA Inc.), at 656 g a.i. ha^{-1} combined with four experimental surfactant-humectant adjuvants (noted as EA1 through EA4) individually plus each formulation solution with no adjuvant and an untreated control where no herbicide or adjuvants were applied. The EA1 was used at a rate of 0.125% v v^{-1}, whereas the rates of ER2, ER3, and ER4 were 0.5% v v^{-1}. All EAs were provided by Exacto Inc. Analysis of the water used in the solutions indicated the presence of 188 mg L^{-1} of $CaCO_3$ which categorizes this water as very hard (USGS, n.d.). An ammonium-based water conditioner adjuvant (Zippsol, Martin Resources) 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.

2.1 | Physical properties study

The density and viscosity of the solutions were measured at 20 °C by a density meter (DMA 4500 M, Anton Paar USA Inc.) and microviscometer (Lovis 2000 M/ME, Anton Paar USA Inc.). Dynamic surface tension (dST), sCA, and ER analyses were conducted using a video-based optical CA measuring instrument (OCA 15EC, DataPhysics Instruments GmbH). 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, assesses, and evaluates the measured data. A liquid circulator (Julabo USA Inc.) and a humidity generator and controller - HCG (DataPhysics Instruments GmbH) were used to keep the temperature at 25 ± 1 °C and the RH 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. (2018) 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 s. The ER was calculated according to Equation 1:

$$\mathrm{ER} = \left(V_i - V_f\right) / T_f \tag{1}$$

where V_i is the initial volume of the droplet (μl) at 0 s, V_f is the final volume of the droplet at T_f which is the maximum time interval (120 s) or the time interval (s) in which the droplet completely evaporated before 120 s.

2.2 | Droplet-size study

Solutions previously mentioned in the physical properties study were sprayed through TT110015 nozzles (TeeJet Technologies Spraying Systems Co.). The droplet-size distribution for each solution was measured using a HELOS-VARIO/KR laser diffraction system with the R7 lens (Sympatec Inc.), 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 determined for each treatment solution. The 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.

$$\mathrm{RS} = \left(\mathrm{Dv}_{0.9} - \mathrm{Dv}_{0.1}\right) / \mathrm{Dv}_{0.5} \tag{2}$$

2.3 | Greenhouse study

The study was conducted in a complete randomized block design with a 2 × 5 factorial arrangement, four replications and two independent runs. Solution combinations and adjuvants rates were the same as previously mentioned were used. However, glufosinate rates were reduced to 328 g a.i. 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.)

using Pro-Mix BX5 (Premier Tech Horticulture Ltd.). Greenhouse temperature was maintained between 18 and 28 ˚C and 60 ± 10% RH. Supplemental LED lighting of 520 μmol s^{-1} (Philips Lighting) was provided to extend the daylight period to 16 h. Plants were watered daily using a commercial liquid fertilizer (UNL 5-1-4, Wilbur-Ellis Agribusiness) and treated weakly with *Bacillus thuringiniensis* (Gnatrol WDG, Valent U.S.A.) 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) calibrated to deliver 140 L ha^{-1} through TT110015 nozzles (TeeJet Technologies Spraying Systems Co.) at 276 kPa operating pressure. Nozzle 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 oven-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:

$$\mathrm{BR} = 100 - (100x/y) \tag{3}$$

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

2.4 | Field study

Two trials evaluating horseweed control were conducted during the summer growing season of 2019 and 2020 in North Platte, NE, and Paxton, NE, respectively, and one trial evaluating Palmer amaranth was conducted during the summer growing season of 2020 in North Platte, NE. Trials were randomized in complete randomized block designs with a 2 × 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 properties 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.) calibrated to deliver 140 L ha^{-1} through TT110015 nozzles (TeeJet Technologies Spraying Systems Co.) 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 rates commonly applied in the field (656 g a.i. ha^{-1}). Temperature and RH during applications in 2019 and 2020 are described in Table 1.

TABLE 1 Average temperature and relative humidity (RH) during applications at the field sites of horseweed and Palmer amaranth in 2019 and 2020 growing seasons

	Horseweed		Palmer amaranth	
Year	Temperature	RH	Temperature	RH
	˚C	%	˚C	%
2019	17	75	–	–
2020	37	25	33	43

Visual estimation of control was 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 percentage of mortality reduction using Equation 4 (Butts et al., 2018):

$$\mathrm{M} = 100\,(D/10) \tag{4}$$

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

Those 10 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 compared to the untreated control according to the Equation 3.

2.5 | Statistical analyses

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 was not included as a fixed effect because of availability of only 1-yr data. Treatments were compared to each other using Tukey's least significant at α = .05. In addition, Pearson's correlation coefficients analysis (PROC CORR procedure) was conducted in SAS, version 9.4, (SAS Institute, Inc.), to identify significant relationships (α = .05) between physical properties, droplet size, and RH.

3 | RESULTS AND DISCUSSION

3.1 | Physical properties study

Analysis of variance indicated a significant interaction between formulation and adjuvant for density, viscosity, sCA, dST, and ER ($p < .001$).

TABLE 2 Density and viscosity of glufosinate formulations alone and tank mixed with four surfactant-humectant adjuvants at 20 ˚C

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

Note. Means followed by the same letter in the column do not differ using Tukey's test at α = .05.
[a]F1-Liberty (Bayer CropScience) and F2-Interline (UPL NA Inc.) at 656 g a.i. ha^{-1}.
[b]EA1 at 0.125 v v^{-1} and EA2, EA3, and EA4 at 0.5 v v^{-1}.
***$p \leq .001$.

3.1.1 | Density and viscosity

Solutions containing adjuvants had greater density than solutions without adjuvants for both glufosinate formulations (Table 2).

The addition of adjuvants increased density from 2 10^{-4} to 4 10^{-4} g cm^{3} (0.02–0.04%) for formulation 1 (F1) and from 1 10^{-4} to 5 10^{-4} g cm^{3} (0.01–0.05%) 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. (2019) 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 an adjuvant. For example, when adjuvants were not used, the viscosity was 1.0623 mPa s for F1 and 1.0730 mPa s for F2, with the addition of EA3 the viscosities increased by 1.2 10^{-2} mPa s (0.9%) and 5.6 10^{-2} mPa s (11.9%) for those respective herbicides. Assuncao et al. (2019) reported that the 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 & 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.

3.1.2 | Dynamic surface tension

The addition of adjuvants resulted in a decrease of dST for both glufosinate formulations. However, different trends were observed for the RHs tested (Table 3).

At 20% RH, compared to F1 alone (30.1 mN m^{-1}), the addition of EA1 and EA3 to F1 solutions decreased dST by 0.7 mN m^{-1} and 0.6 mN m^{-1}, respectively, and EA4 increased by 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 by 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 by 2.3 mN m^{-1}, EA2 and EA4 increased by 0.4 mN m^{-1} and 0.3 mN m^{-1}, respectively. Moreover, for F2 solutions, the addition of EA1 and EA3 decreased dST by 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 by 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 (Curran et al., 2009; Ferri & Stebe, 2000; Moraes, 2019; Ogino et al., 1990). Sobiech et al. (2020) demonstrated that the addition of NIS to sulcotrione solutions reduced dST by 20.8 mN m^{-1} compared to sulcotrione alone. 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 et al., 2020), herbicide formulation (Castro et al., 2018), and RH (Torrecila et al., 2008) can also affect surface tension. Moreover, AMS salt increases the surface tension of water (Pegram & Record, 2007) which may explain the higher surface tension observed for some of the treatment solutions.

TABLE 3 Dynamic surface tension of glufosinate formulations alone and tank mixed with four surfactant-humectant adjuvants at 25 °C and different relative humidities (RHs)

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

Note. Means followed by the same letter in the column do not differ using Tukey's test at α = .05.
[a]F1-Liberty (Bayer CropScience) and F2-Interline (UPL NA Inc.) at 656 g a.i. ha^{-1}.
[b]EA1 at 0.125 v v^{-1} and EA2, EA3, and EA4 at 0.5 v v^{-1}.
***$p \leq .001$.

TABLE 4 Static contact angle of glufosinate formulations alone and tank mixed with four surfactant-humectant adjuvants at 25 °C and different relative humidities (RHs)

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

Note. Means followed by the same letter in the column do not differ using Tukey's test at α = .05.
[a]F1-Liberty (Bayer CropScience) and F2-Interline (UPL NA Inc.) at 656 g a.i. ha^{-1}.
[b]EA1 at 0.125 v v^{-1} and EA2, EA3, and EA4 at 0.5 v v^{-1}.
***$p \leq .001$.

3.1.3 | sCA

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 (Table 4).

At 40% RH, compared to F1 alone (34.7°), when EA1 and EA2 were added to F1 solutions sCA decreased by 5.9° and 2.9°, respectively. Contrarily, for F2, sCA decreased only with the addition of EA3. At 60%, compared to F1 alone (32.5°), the addition of EA3 to F1 solution increased sCA by 4.3° However, for F2, the addition of EA1 and EA3 decreased sCA by 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 al. (2020) reported that at 60% RH CA of sulcotrione solutions containing NIS was 20.2° smaller than sulcotrione alone. Although sCA is

TABLE 5 Evaporation of glufosinate formulations alone and tank mixed with four surfactant-humectant adjuvants at 25 ˚C and different relative humidities (RHs)

Formulation[a]	Adjuvant[b]	20% RH	40% RH	60% RH	80% RH
		μml 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
		***	***	***	***

Note. Means followed by the same letter in the column do not differ using Tukey's test at α = .05.
[a]F1-Liberty (Bayer CropScience) and F2-Interline (UPL NA Inc.) at 656 g a.i. ha^{-1}.
[b]EA1 at 0.125 v v^{-1} and EA2, EA3, and EA4 at 0.5 v v^{-1}.
***$p \leq .001$.

directly related to dST, some of the adjuvant solutions that presented lower dST in relation to formulations alone did not necessarily present lower sCA. The CA is affected by the dST 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 CAs of the spray solutions at different RHs observed in this study. Therefore, herbicide formulation-adjuvant-humidity is a complex interaction.

3.1.4 | Evaporation rate

The use of adjuvants had variable ER impacts for each glufosinate formulation and RH combination (Table 5).

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 67–200%. The ER of F2 with adjuvants reduced from 5.0 10^{-4} to 1.7 10^{-3} μl s^{-1} (22–74%) in comparison to F2 alone (2.3 10^{-3} μl s^{-1}). At 40% RH, the addition of EA1, EA2, and ER4 decreased the ER for F1 solutions and increased the ER 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} (35–100%) 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 by a range of 7 10^{-4} to 1.8 10^{-3} μl s^{-1} (78–200%) for F1. Also, compared to F2 alone (1.2 10^{-3} μl s^{-1}), ER increased by 9 10^{-4} μl s^{-1} when EA2, EA3, and EA4 (75%) were added to F2 solutions.

Literature is limited about the influence of surfactant-humectant on droplet evaporation rate. However, Cook and Duncan (1978) reported that aminotriazole penetration into bean leaves maintained at 50 ± 10% RH and 30 ˚C 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 the solution containing only surfactant did not keep the herbicide droplets moist long enough for effective uptake (Ransey et al., 2005), but with the addition of a humectant, the evaporation rate decreased and, consequently the 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 CA can result in a 10-fold increase in surface area available for evaporation (Pricer, 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 formulations investigated in this same study differed at the same temperature and humidity.

3.2 | Droplet-size study

A significant interaction between formulation and adjuvant was observed in the analysis of variance for $Dv_{0.1}$, $Dv_{0.5}$, $Dv_{0.9}$, PF, and RS ($p < .001$). In general, the addition of EA to F1 and F2 solutions decreased and increased the volumetric

TABLE 6 $Dv_{0.1}$, $Dv_{0.5}$, 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 relative span (RS) of glufosinate formulations alone and tank mixed with four surfactant-humectant adjuvants sprayed at 246 kPa through TT110015 nozzle.

Formulation[a]	Adjuvant[b]	$Dv_{0.1}$	$Dv_{0.5}$	$Dv_{0.9}$	PF	RS
		µm			%	
F1	none	274a	530a	784a	1.4g	0.96f
F1	EA1	224e	448f	687e	3.0c	1.03c
F1	EA2	207f	425g	670f	3.9b	1.09a
F1	EA3	203f	420g	665f	4.3a	1.10a
F1	EA4	228e	461e	715d	2.7d	1.06b
F2	none	240d	488d	744c	2.5d	1.03c
F2	EA1	256c	511c	765b	2.0ef	0.99de
F2	EA2	252c	504c	745c	2.1e	0.98ef
F2	EA3	262b	519b	785a	1.8f	1.01d
F2	EA4	253c	511c	758b	2.1e	0.99de
		***	***	***	***	***

Note. Means followed by the same letter in the column do not differ using Tukey's test at $\alpha = .05$.
[a]F1-Liberty (Bayer CropScience) and F2-Interline (UPL NA Inc.) at 656 g a.i. ha^{-1}.
[b]EA1 at 0.125 v v^{-1} and EA2, EA3, and EA4 at 0.5 v v^{-1}.
$^{***}p \leq .001$.

diameters, respectively (Table 6). 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 $Dv_{0.5}$ when tank mixed with F1 (420–425 µm). However, EA3 produced 15-µm coarser $Dv_{0.5}$ than EA2 when tank mixed with F2. The F1 solutions containing EA presented two- to threefold higher PF than F1 alone. Contrarily, compared to F2 alone, PF of F2 lowered onefold 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 6–15% for F1 and decreased by 2–5% for F2 when compared to those respective formulations alone.

In a study conducted by Mueller and Womac (1997), it was 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 (ST) 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.

3.3 | Correlation physical properties and droplet size

Pearson's correlation coefficients analysis indicated that density, viscosity, and ST are strongly correlated to droplet-size distribution (Table 7). While density is negative correlated to $Dv_{0.1}$, $Dv_{0.5}$, and $Dv_{0.9}$, and positive correlated to PF, viscosity and dST are positively correlated to $Dv_{0.1}$, $Dv_{0.5}$, and $Dv_{0.9}$, and negative correlated to PF. Thus, as the density of glufosinate solutions increase, a finer droplet-size distribution is expected. Contrarily, a coarser droplet-size distribution is expected as viscosity and dST of glufosinate solutions increase. Furthermore, density and dST are strongly positive and negatively correlated to ER, respectively, which indicates the higher the viscosity and the lower the dST of glufosinate solutions, the slower is the droplet evaporation. Dynamic ST and sCA also demonstrated a strong positive correlation which means that glufosinate solutions presenting high dST are less likely to spread on the leaf surface.

Relative humidity and ER are strongly negative correlated (Table 8). As the RH decreases, the air gets dryer and the ER increases. However, as the RH increases, the air gets closer to its saturation point, and the ER decreases. Moreover, similar to previous results observed at 40% RH, dST and sCA presented a strong positive correlation.

TABLE 7 Pearson's correlation coefficients analysis between density, viscosity, dynamic surface tension (dST), static contact angle (sCA), evaporation rate (ER), $Dv_{0.1}$, $Dv_{0.5}$, $Dv_{0.9}$ (droplet diameters for which 10, 50, and 90% of the total spray volume is contained in droplets of lesser diameter), volume percentage of droplets smaller than 150 µm – percentage of fines (PF) analyzed

Coefficients	Density	Viscosity	dST[a]	sCA[b]	ER[c]	$Dv_{0.1}$	$Dv_{0.5}$	$Dv_{0.9}$	PF
Density	1.00								
Viscosity	−0.25	1.00							
dST	−0.70***	0.38*	1.00						
sCA	−0.14	−0.13	0.47**	1.00					
ER	0.57***	−0.30	−0.79***	−0.31	1.00				
$Dv_{0.1}$	−0.51**	0.34*	0.51**	0.30	−0.61***	1.00			
$Dv_{0.5}$	−0.58***	0.36*	0.60***	0.35*	−0.67***	0.99***	1.00		
$Dv_{0.9}$	−0.56***	0.45**	0.57***	0.30	−0.64***	0.96***	0.98***	1.00	
PF	0.51**	−0.32*	−0.54***	−0.27	0.65***	−0.97***	−0.96***	−0.94***	1.00

[a, b, c] dST, sCA, and ER were measured at 40% relative humidity (RH), respectively.
*$p \leq .05$. ** $p \leq .01$. ***$p \leq .001$.

TABLE 8 Pearson's correlation coefficients analysis for relative humidity (RH), dynamic surface tension (dST), static contact angle (sCA), evaporation rate (ER) at 25 °C

Coefficients	RH[a]	sCA	dST	ER
RH	1.00			
sCA	−0.15	1.00		
dST	−0.04	0.30***	1.00	
ER	−0.77***	−0.16	−0.18*	1.00

[a]RHs analyzed: 20, 40, 60, and 80%.
*$p \leq .05$. ***$p \leq .001$.

3.4 | Greenhouse study

Analysis of variance demonstrated a significant interaction between formulation and adjuvant for BR and VEC for common lambsquarters and kochia ($p < .05$). For barnyardgrass, the main effect formulation was significant for VEC and BR, and the main effect adjuvant was only significant for BR ($p < .05$). Regarding velvetleaf, both main effects were significant for the abovementioned parameters ($p < .05$). No significant interaction between formulation and adjuvant and main effects were observed for VEC and BR for horseweed and common waterhemp (data not shown).

The addition of EA to F1 solution did not improve VEC and BR of common lambsquarters, which ranged from 31 to 36% for VEC and 44 to 49% for BR (Table 9).

The EA4 was the only adjuvant added to the F2 solution that increased the VEC (26%) compared to this formulation alone (7%). In contrast, all adjuvants improved BR of common 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 species for both glufosinate formulations, especially F2. Steckel, Wax, et al. (1997) observed that the absorption of glufosinate (140 g a.i. ha^{-1}) was low for common lambsquarters, even when 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 a.i. ha^{-1}) at 28 DAA was 95%. Visual estimations of control of F2 tank mixed with adjuvants ranged from 92 to 100% compared to 56% from F2 alone. No differences in BR were 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 27–35%. Regardless of adjuvant, F1 resulted in greater VEC and BR of barnyardgrass and velvetleaf in comparison to F2 (Table 10).

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 an 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 treatment comparisons unfeasible. Takano and Dayan (2020) demonstrated that horseweed is very susceptible to glufosinate, achieving 50% BR with 26 g a.i. ha^{-1}. Beyers et al. (2002) reported 99% or greater control of common waterhemp with glufosinate (230 g a.i. ha^{-1}) at 28 DAA.

The variable influence of the adjuvants on glufosinate efficacy observed throughout this study potentially occurred due

TABLE 9 Biomass reduction (BR) and visual estimation of control (VEC) of common lambsquarters and kochia for glufosinate formulations alone and tank mixed with four surfactant-humectant adjuvants at 28 days after application (DAA) under greenhouse condition

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

Note. Means followed by the same letter in the column do not differ using Tukey's test at $\alpha = .05$.
[a]F1-Liberty (Bayer CropScience) and F2-Interline (UPL NA Inc.) at 328 g a.i. ha^{-1}.
[b]EA1 at 0.125 v v^{-1} and EA2, EA3, and EA4 at 0.5 v v^{-1}.
*$p \leq .05$. **$p \leq .01$. ***$p \leq .001$.

TABLE 10 Biomass reduction (BR) and visual estimation of control (VEC) of barnyardgrass and velvetleaf for glufosinate formulations alone and tank mixed with four surfactant-humectant adjuvants at 28 days after application (DAA) under greenhouse conditions.

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

Note. Means followed by the same letter in the column do not differ using Tukey's test at $\alpha = .05$.
[a]F1-Liberty (Bayer CropScience) and F2-Interline (UPL NA Inc.) at 328 g a.i. ha^{-1}.
[b]EA1 at 0.125 v v^{-1} and EA2, EA3, and EA4 at 0.5 v v^{-1}.
*$p \leq .05$. **$p \leq .01$. ***$p \leq .001$.

to differences of 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 an additional effect on efficacy or may cause antagonistic effect, as observed for F1.

3.5 | Field study

No significant differences in VEC, BR, and M were observed across years for horseweed trials, even though weather conditions at the application time varied in 2019 and 2020. In a field study conducted by Martison et al. (2005), temperature and RH ranked in second and sixth place of the most powerful factors influencing annual weed species control by glufosinate, respectively. The authors demonstrated a positive relation between temperature and weed control of glufosinate, whereas RH varying from 41 to 100% did not have a significant effect on the percentage of weed control for this herbicide. Contrarily, Anderson et al. (1993) reported that RH had a higher influence on glufosinate ammonium efficacy than temperature on barley foxtail (*Hordeum jubatum* L) and green foxtail [*Setaria viridis* (L.) P. Beauv.] control. In this study, barley and green foxtail plants that were grown at a day/night temperature regime of 22/17 ˚C and sprayed at 800 and 100 g a.i. ha^{-1} of glufosinate, respectively, survived to applications at 40% RH, but were completely controlled at 95% RH. The applications for this present study were performed under mild temperatures and high RH in 2019 and under high temperatures and low RH in 2020. The herbicides manufactures' labels suggest applying glufosinate at warm temperatures and high humidities for best results (Anonymous, 2017; Anonymous, 2019b). With these studies, the weather conditions

TABLE 11 Biomass reduction (BR), visual estimation of control (VEC), and mortality (M) of horseweed across years (2019 and 2020) and Palmer amaranth single year (2020) for glufosinate formulations alone or tank mixed with four surfactant-humectant adjuvants at 28 DAA (days after application) under field conditions

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

Note. Means followed by the same letter in the column do not differ using Tukey's test at $\alpha = .05$.
[a]F1-Liberty (Bayer CropScience) and F2-Interline (UPL NA Inc.) at 656 g a.i. ha^{-1}.
[b]EA1 at 0.125 v v^{-1} and EA2, EA3, and EA4 at 0.5 v v^{-1}.
*$p \leq .05$.

were not ideal which may explain the similarity in result across years despite the differences in temperature and RH. Moreover, there are other environmental factors not analyzed in this study such as ultraviolet (UV) light, application time (Kumaratilake & Preston, 2005; Martinson et al., 2005), and weed density that can influence glufosinate effectiveness.

Regarding the interaction between formulation and adjuvant, no significant differences were observed in VEC, BR, and M for both horseweed and Palmer amaranth (Table 11).

For horseweed, no differences were observed within the main effects of formulation and adjuvant for any of the three parameters analyzed. The VEC varied from 84 to 87%, BR from 65 to 70%, and M from 49 to 58%. For Palmer amaranth, only adjuvant main effect was significant for VEC, EA2 and EA4 presented 6% and 5% lower VEC, respectively, than EA1 and EA3 (84%). However, treatments with adjuvants were similar to those without an adjuvant. For BR and M, no differences were observed among formulation and adjuvant. Biomass reduction ranged from 67 to 73% and M from 25 to 41%. Therefore, the addition of EA did not increase glufosinate effectiveness. Results agree with research published by Eubank et al. (2013) who demonstrated that 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, O'Sullivan et al. (1981) reported that the addition of surfactants to the commercial formulation of glyphosate at 0.21 kg ha^{-1} did not enhance control of annual grass weeds under field conditions. Also, in a field study, Jordan (1999) showed that control of common cocklebur (*Xanthium strumarium* L.) and redroot pigweed by imazapic + NIS was similar to imazapic alone.

4 | CONCLUSION

This research demonstrated that the use of adjuvants increased the density of spray solutions regardless of glufosinate formulation used. Similarly, the viscosity of F1 solutions increased in presence of adjuvants. However, for F2 solutions, the influence of adjuvants varied by EA used. Furthermore, the influence of adjuvants on dST, sCA, and ST of the spray solutions depended on herbicide formulation, adjuvant nature, and environment RH. Although the primary function of a surfactant-humectant adjuvant is to reduce dST, sCA, and ER, in some cases the addition of EA to glufosinate solutions did not change those variables or even increased them. The droplet-size distribution was also altered by the addition of adjuvants to spray solutions. While F1 solutions produced finer droplets and greater PF, F2 solutions produced coarser droplets and lower PF. Regarding herbicide efficacy under greenhouse conditions, the influence of adjuvants varied by weed species, glufosinate formulation, and EA. Overall, an improvement in efficacy by adding adjuvants was mainly observed for F2 solutions, especially for common lambsquarters and kochia. Also, some of the adjuvants presented null or antagonistic influence on herbicide efficacy. Moreover, F1 solutions with and without adjuvants presented greater control of common lambsquarters, barnyardgrass, and velvetleaf than F2 solutions. Under field conditions, no differences were observed with the use of adjuvants on horseweed and Palmer amaranth despite unfavorable weather conditions on the application day in both years, especially in 2020. Herbicide-adjuvant-plant-environment is a complex interaction. There is no adjuvant that will increase glufosinate efficacy under all circumstances.

Therefore, it is essential to consider the herbicide formulation, target weed species, and weather conditions to decide the necessity of an adjuvant and best adjuvant options available.

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AUTHOR CONTRIBUTIONS

Estefania G. Polli: Data curation; Formal analysis; Investigation; Project administration; Writing – original draft. Guilherme S. Alves: Formal analysis; Writing – review & editing. Jesaelen Gizotti de Moraes: Data curation; Methodology; Writing – review & editing. Greg Robert Kruger: Conceptualization; Funding acquisition; Project administration; Resources; Supervision; Writing – review & editing.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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