Adjuvant effects on spray deposition and efficacy of diquat and glufosinate against Euphorbia heterophylla and Digitaria insularis

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Abstract

Agricultural adjuvants are among the most critical factors influencing spray deposition and herbicide efficacy against weeds. This study evaluated spray deposition parameters by spraying different non-ionic adjuvants on *Euphorbia heterophylla* and *Digitaria insularis* and their effects on the efficacy of diquat against *E. heterophylla* and glufosinate against *D. insularis*. Spray deposition treatments involved mixing the herbicides with five adjuvant classes (alkylphenol ethoxylated - AE, nonylphenol polyethanol - NP, trisiloxane ethoxylate - TE, mineral oil - MO, and alkyl ester phosphoric acid - AEPA) and analyzing both the quantity and quality of spray deposition. Two greenhouse dose-response experiments were conducted separately to identify suitable adjuvants for enhancing diquat and glufosinate efficacy in reducing the aboveground biomass of *E. heterophylla* and *D. insularis*. Spray deposition on *E. heterophylla* and *D. insularis* generally improved, varying according to the adjuvant class. All tested adjuvants enhanced diquat efficacy against *E. heterophylla*, except for TE in the second experiment. Among the adjuvants, AE exhibited the highest performance. However, incorporating AE, NP, TE, or MO into the glufosinate spray solution did not enhance its efficacy against *D. insularis*. Additionally, AEPA demonstrated an antagonistic effect on glufosinate performance.

Introduction

Applying herbicides is an indispensable tool in today’s agriculture, significantly reducing yield losses and helping improve crop quality. Adjuvants are substances commonly used in mixtures with post-emergent herbicides to optimize their control efficacy against weeds when applied appropriately (Mohassel et al. 2011; Polli et al. 2022; Brankoc et al. 2024; Xu et al., 2024). The increase in the herbicide's biological efficacy through the addition of adjuvants/surfactants may be related to several factors, such as reducing the surface tension of the spray solution, reducing the percentage of very fine droplets, minimizing the ricochet of droplets after impact with the leaves, allowing a smaller contact angle between the droplet and the leaf surface, increasing the spread and contact area of the droplet with the leaf surface (Ma et al. 2021; Xu et al. 2024) and finally, providing an increase in the concentration of the active ingredient retained and uptake by the plant (Gitsopoulos et al. 2018; Gao et al. 2022; Xu et al., 2024). However, adjuvants may not enhance the efficacy of certain herbicides on specific weed species and, in some cases, may even exhibit an antagonistic effect (Polli et al. 2022). Another important factor influencing leaf retention is the morphological characteristics of the target, including leaf type, orientation, trichomes, and cuticle wax. Vertical targets, such as grasses, offer a reduced surface area for droplet deposition and retention compared to horizontal targets (Massinon et al. 2014; Dorr et al. 2016). In this sense, using adjuvants in the spray solution that reduce the droplet's surface tension can improve the quantity and quality of the pesticide's active ingredient deposited on the targets (Dorr et al. 2016; Oliveira et al. 2021).

Ineffective weed control resulting from inadequate herbicide application techniques is one of the factors contributing to low yields in various crops in Brazil and globally. Sourgrass (*Digitaria insularis*) and Wild poinsettia (*Euphorbia heterophylla*) are considered some of the most important weeds competing with several annual and perennial crops across all agricultural areas in Brazil (Trezzi et al. 2021; Gonçalves-

Neto et al. 2021) and in many other countries (Chachalis, 2015). For example, improper management of *Digitaria insularis* and *E. heterophylla* can lead to yield reductions of 80% and 35% in soybean, respectively (Núñez et al. 2018; Braz et al. 2021), highlighting the importance of adopting optimal herbicide application techniques (Gao et al. 2022). In Brazil, with the discontinuation of paraquat, there are few options for non-selective contact herbicides as substitutes that offer equivalent control efficacy. Among the available options, the herbicides diquat and ammonium glufosinate are notable (Cinelli et al. 2025). The damage caused by glufosinate is linked to the accumulation of ammonia, destruction of chloroplasts, reduced photosynthetic activity, and decreased amino acid production, ultimately inhibiting photosynthesis and leading to cell death (Takano et al. 2020). Diquat, a bipyridylium inhibitor of photosystem I, drastically reduces green biomass's water content and is rapidly absorbed by plants (Zhang et al. 2023).

Selecting an appropriate spray adjuvant for post-emergence herbicides is difficult even for experts but essential because the herbicide efficacy against weeds is usually dependent on the herbicide type, herbicide formulation, weed species, weed development stage, environmental conditions, and others (Gitsoupolus et al. 2014; Polli et al. 2022; Zhang et al. 2022).

Adding adjuvants to the herbicide solution can consistently increase the efficacy of herbicides against various weed species (Sobiech et al. 2020; Polli et al. 2022; Zhang et al. 2022; Xu et al. 2024). However, the correct choice of adjuvant for a specified herbicide and weed is crucial to achieve optimal synergistic interaction and consequent improvements in the herbicide's performance. For instance, Polli et al. (2022) demonstrated that although adjuvants alter the physical properties of spray solutions (*e.g.*, enhancing herbicide penetration, wettability, and droplet drying time), these changes do not necessarily lead to improved weed control. Therefore, investigating the most suitable adjuvant tank mix for diquat and glufosinate could significantly contribute to the effective herbicide management of *E. heterophylla* and *D. insularis.*

This study hypothesizes that adding the proper agricultural spray adjuvant can improve the spray deposition parameters on *E. heterophylla* and *D. insularis* and the biological efficacy of the herbicide diquat against *E. heterophylla* and glufosinate against *D. insularis*. The objectives of the present study were (a) to investigate the quantity and quality of spray deposition resulting from the addition of different non-ionic adjuvants into diquat and glufosinate solutions on *E. heterophylla* and *D. insularis* weeds and (b) to evaluate the performance of diquat against *E. heterophylla* and glufosinate *D. insularis* when mixed with adjuvants.

Materials and Methods

Weed sowing and growth

The experiments were conducted in greenhouse conditions from January 2021 to April 2021. The greenhouse is located at latitude 21º27" S, longitude 51º33" W, and an altitude of 373 m above sea level. Panicles of *D. insularis* were collected from an area with no history of herbicide applications. These panicles were then agitated over 0.8 L plastic pots, each measuring 8 cm × 8 cm × 14 cm. The pots were filled with sandy loam soil (76% sand, 7% silt, and 17% clay; pH 6.5) and Carolina Soil® substrate in a 3:1 ratio (w/w). Approximately 20 seeds were evenly distributed and sown on the soil surface of each pot. Eight days after emergence (DAE), the seedlings were thinned to leave only one uniformly sized plant per pot. For the *E. heterophylla* weed, 5 to 8 seeds were sown in each cell of a 288-cell plastic tray filled with Carolina Soil® substrate. After plant emergence, only one seedling was retained per cell. Around 14 DAE, the seedlings were transplanted into 0.8 L plastic pots using the same substrate mixture mentioned earlier. After sowing, automatic micro-sprinkler irrigation was carried out daily to meet the plant's water needs. At 14 DAE, *D. insularis* plants received a nutritional supplement of 0.2 g per pot of a formulated mineral fertilizer (04-14-08). Subsequently, 4–5 leaves of *E. heterophylla* and one tiller of *D. insularis* were subjected to spray treatments.

Spray deposition study

The spray deposition experiments were analyzed using a completely randomized design, with six treatments and 40 replicates for each treatment, represented by the pots of each weed plant species. The experiment was repeated twice for both weed species. The treatments used to quantify spray deposits on *E. heterophylla* e *D. insularis* plants were: T1- distilled water (DW) + herbicide (H) + Blue dye (BD) + nonylphenol ethoxylated; T2- DW + H + BD + polyethoxylated nonylphenol; T3- DW + H + BD + trisiloxane ethoxylate; T4- DW + H + BD + mineral oil; T5- DW + H + BD + alkyl ester phosphate; and T6- DW + H + BD (Control). In all treatments, the diquat dose for *E. heterophylla* and the glufosinate dose for *D. insularis* were 2.0 L ha^{-1} (the recommended dose), with a Brilliant Blue dye FCF concentration of 2.0 g L^{-1}. Table 1 provides the doses and characteristics of the adjuvants.

Table 1
Agricultural adjuvants description used in the spray deposition and weed dose-response experiments.

Active ingredient (ai)	Trade name	Concentration of a.i. L^{-1}	Adjuvant class	Label dose
alkylphenol ethoxylated	Fixade	900 g	Spreader-sticker	200 mL 100 L^{-1}
nonylphenol polyethanol	Agral	200 g	Spreader-sticker	50 mL 100 L^{-1}
trisiloxane ethoxylate	Silwet L-77	1000 g	Super spreader	100 mL 100 L^{-1}
mineral oil	Nimbus	428 g	Adjuvant	750 mL 100 L^{-1}
alkyl ester phosphoric acid	Ochima	752 g	Adjuvant	250 mL ha^{-1}

The absorbance of the spray solution of all treatments with the adjuvants was determined and did not show a significant difference from the solution with only the dye. Cerqueira et al. (2012) reported the appropriate suitability of Brilliant Blue dye, particularly on natural targets, with an extraction coefficient of

93%. Herbicide was mixed with the spray solution to simulate a real field application and for the possible spray solution physicochemical modification provided by the herbicide, which could influence spray deposition (Prado et al. 2024).

Treatments were sprayed in a track room (3.6 m wide and 10 m long) by a rail-mounted four-nozzle spray boom driven by an electric motor spaced 0.50 m apart, traveling at 5.0 km h^{-1}, which delivered a spray volume of 156 L ha^{-1} at 200 kPa. The plants were arranged on the ground above the spray boom in four rows, with ten plants in each row, spaced at 0.2 meters between rows and plants (Prado et al., 2024). The flat fan nozzles Teejet® XR 11002 sprayed fine droplet class were placed 0.5 m above the plants. Meteorological data of temperature and air relative humidity were recorded during all the application scenarios by a digital thermo-hygrometer (SH-122).

After applying the treatments and drying the solution (approximately 7 min), plants of *E. heterophylla* and *D. insularis* were cut 1 cm above the ground, placed in plastic bags, and washed with 68 mL of deionized water to remove the dye. The dye solution was placed in 70 mL plastic containers and stored in the dark until absorbance determination. After washing, the plants were placed in paper bags and oven-dried at 65 ± 5°C for 96 h, and the dry weight (DW) was determined using an analytical balance (Marten, model AY220).

The amount of dye deposited on the plants was quantified using a spectrophotometer (Biospectrum, model SP 220) at a wavelength of 630 nm (Godinho Jr. 2020; Prado et al. 2024). A linear equation was established using the previously known dye concentrations of 15, 7.5, 3.75, 1.875, 0.938, 0.469, and 0.234 mg L^{-1}, which allowed for the transformation of the absorbance values into dye concentrations in mg L^{-1} (Table 2).

Equation (1) established the volume retained on the target using the dye concentration values in the spray solution, dye concentration detected by the spectrophotometer, and sample dilution volume.

$$V1 = \frac{C2 \times V2}{C1}$$

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Where: *V1* = volume retained on the plants (mL), *C2* = concentration detected by the spectrophotometer (mg L^{-1}), *V2* = sample dilution volume (mL), *C1* = initial dye concentration in the spray solution (mg L^{-1}). The volume retained on each plant was transformed into microliters and divided by its respective DW to obtain the volume in μL g^{-1} DW.

Bioefficacy study (dup: abstract ?)

The dose-response curve trials were conducted using a completely randomized experimental design, and each pot with a single plant was considered an experimental unit. The experiment followed 6 (same treatments described previously, excluding BD) × 8 herbicide concentrations for *E. heterophylla* experiments and 7 for *D. insularis* in a factorial scheme, replicated four times. The herbicides used in the study were glufosinate (Finale®) and diquat (Reglone®). The label dose for both herbicides for *E. heterophylla* and *D. insularis* is 400 g ha^{-1}. The eight doses of herbicides were 0, 4.9, 14.8, 44.4, 133.3, 400, 1,200, and 3,600 g ai ha^{-1} for *E. heterophylla* and 0, 14.8, 44.4, 133.3, 400, 1,200, and 3,600 g ai ha^{-1} for *D. insularis*. The concentration doses were chosen based on previous studies by Oliveira et al. (2021) and Prado et al. (2024). Spraying was carried out using the same equipment and operating conditions described in the spray deposition experiment, except for a spray boom featuring two nozzles spaced 0.5 m apart. The four plants were arranged in a row on the ground between the two nozzles. This setup allowed different herbicide concentrations to be applied to the weed plants in the pots. The experiment was repeated twice for both weed species. Meteorological data, including temperature and relative humidity, were recorded during the application using a digital thermo-hygrometer (SH-122). Following treatment application, the plants were placed in a greenhouse for 24 hours without irrigation. After this period, the plants were irrigated once a day using an automatic micro-sprinkler system, with the irrigation schedule based on the plants' needs. At 20 days after treatment (DAT), plants were clipped 1 cm above the soil surface, put into a paper bag, and placed in an oven-dried at 65 ± 5°C for 96 hours, and DW was recorded using an analytical balance (Marten, model AY220).

Data analysis

As mentioned before, the spray deposition experiments were carried out twice, and the data obtained from both experiments were analyzed separately due to the significant interaction (P > 0.05) observed between them. The dataset was then subjected to analysis of variance (ANOVA), and means were compared using the Scott-Knott test at a significant level of 5%.

The coefficient of variation (CV) was calculated as the index to analyze the spray deposition distribution's uniformity on weed plants in each treatment (40 replicates). CV is the ratio of the standard deviation to the overall average. The smaller the value, the better the data uniformity. The CV was calculated according to Eq. (2).

$$CV = \frac{SD}{\bar{x}} \times 100 \text{, with } SD = \sqrt{\frac{\sum_{i=1}^{n}(xi - \bar{x})^2}{n-1}} \qquad (2)$$

Where: *CV* is the coefficient of variation (%); S*D* is the standard deviation; *xi* is the spray deposition of each sample point; $\bar{x}$ is the average spray deposition, and *n* is the number of samples.

The dose-response data were utilized to evaluate the efficacy of herbicides against *E. heterophylla* and *D. insularis*. The DW reduction of *E. heterophylla* and *D. insularis* was determined by fitting the four-parameter logarithmic logistic response Eq. (3) (Seefeldt et al. 1995) using the *drc* package in R software (R Development Core Team 2016).

$$\varvec{y} = \frac{\varvec{d} - \varvec{c}}{1 + \mathbf{exp}\left\{\varvec{b}[\mathbf{log}\left(\varvec{x}\right) - \mathbf{log}\left(\varvec{E}\varvec{D}50\right)]\right\}} + \varvec{c}$$

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Where: *y*: corresponds to weed DW, *d*: curve upper limit, *c*: curve lower limit, *b*: relative slope around the inflection point *ED50*, *x*: independent variable (doses of diquat or glufosinate - g ai ha^{-1}), and *ED50* is the inflection point (effective dose to reduce 50% of DW). Any ED level can replace the ED50 parameter, so the selected model was used to estimate the dose of herbicides required to obtain a 90% DW reduction against each weed species (Pannaci 2016).

As in the spray deposition experiments, the trials were analyzed separately for the dose-response experiments. The ANOVA function was used to perform the lack-of-fit test, and a P-value ≥ 0.05 was considered an acceptable description of the data by the fitted non-linear model (Ritz et al. 2015). A 95% confidence interval for *ED50* at each treatment was calculated.

Results and Discussion

Spray deposition study

Table 2 presents the meteorological data for each experiment, including temperature and air relative humidity, along with the corresponding linear equation and coefficient of determination. The air temperature and relative humidity were adequate during the treatment applications. All linear equations had a coefficient of determination (R^2) of 0.99, indicating a good fit to the model (Table 2).

Table 2
Meteorological data for temperature (T ºC) and air relative humidity (RU %) at treatment application, linear equation, and coefficient of determination.

Experiments - weed	**Application day**	**T ºC**	**RU (%)**	**Linear equation**	**R^2**
Exp.1 - *E. heterophylla*	Feb 22, 2021	27 ± 1.0	68 ± 2	[dye] = 7.74 × abs – 0.181	0.99
Exp. 1 - *D. insularis*	Mar 04, 2021	25 ± 0.5	79 ± 2	[dye] = 7.59 × abs – 0.179	0.99
Exp. 2 - *E. heterophylla*	Mar 09, 2021	26 ± 1.0	80 ± 1	[dye] = 7.66 × abs – 0.156	0.99
Exp. 2 - *D. insularis*	Mar 11, 2021	26 ± 1.0	70 ± 5	[dye] = 7.78 × abs – 0.199	0.99

T ºC: Air temperature; RU: air relative humidity; [dye]: dye concentration (mg L^{-1}); Abs: absorbance. Exp. 2 - duplicate

The average amount of spray deposition and CV values determined on *E. heterophylla* and *D. insularis* sprayed respectively with diquat and glufosinate, associated with different classes of adjuvants, are described in Fig. 1. The results indicated that spray solutions with adjuvants significantly increased the amount of spray deposition on *E. heterophylla* (F: 27.2, $P < 0.01$) and *D. insularis* (F: 699.7, $P < 0.01$).

For *E. heterophylla*, all treatments containing adjuvants resulted in higher deposition amounts than the control, except for Ochima. Among the adjuvants, Fixade stood out with deposition values approximately twice as high as the control treatment, significantly differing from the other treatments. The spray deposition for *E. heterophylla* followed the order: Fixade > Silwet = Nimbus = Agral > Ochima = Control (Fig. 1a). Similar results were observed for *D. insularis*, where all treatments with adjuvant showed higher deposition amounts than the control. The adjuvant Nimbus provided the highest deposition values on *D. insularis*, significantly differing from the other treatments except for the adjuvant Fixade. The amount of spray deposition for *D. insularis* followed the order of Nimbus = Fixade > Silwet > Agral > Ochima > Control (Fig. 1b).

Overall, adding adjuvants to herbicide solutions significantly increased spray deposition in both weeds, but this increase was more pronounced in *D. insularis* than in *E. heterophylla*. An increase in spray deposition of 1.6 and 2.8-fold (average of all treatments with adjuvant) for the weeds sprayed with adjuvant compared to the Control was observed for *E. heterophylla* and *D. insularis*, respectively. The proportionally higher spray deposition found in *D. insularis* when adjuvants were added to the spray solution is probably associated with the plant morphology, which has a more upright leaf orientation and narrower leaves than *E. heterophylla*, with predominantly horizontal and broad leaves. According to observations by Gitsopoulos et al. (2014), when detached grass leaves were placed in an upright position, spray droplets without adjuvant easily slid off and fell from the leaf surface. In contrast, droplets with adjuvants remained firmly adhered to the surface and later spread across it. When the treatment with the highest deposition (Nimbus) is compared with the lowest (Control), the spray deposition increases approximately four times. Higher spray deposition implies more herbicide solution on the weed, which may increase herbicide performance. Previous studies have shown a trend of increased spray deposition by adding adjuvants to the spray solution (Guo et al. 2022; Song et al. 2022). For example, Song et al. (2022) reported higher droplet deposition on wheat leaves when insecticide solution was associated with adjuvants, indicating a relationship between low surface tension and wetting the target surface provided by adjuvants with higher values of droplet deposition. Although the surface tension of the solutions was not determined, all classes of adjuvants used in this study reduce the surface tension of aqueous solutions to different intensities depending on the physicochemical properties of each adjuvant (Prado et al. 2016; Gitsopoulos et al. 2018; Gao et al. 2022).

All the treatments containing adjuvants showed lower CV values for both weeds when compared to the Control. Regarding the uniformity of spray deposition distribution on *E. heterophylla* plants, the adjuvant Fixade showed the lowest CV of 34%, followed by Nimbus (35%), Silwet (37%), Agral (47%), Ochima (52%), and Control (60%). The lowest CV values for *D. insularis* were observed in the treatments with adjuvants Silwet and Nimbus, which were 21%. A higher CV was observed for the Control treatment at 36%

(Table 3). Lower CV values mean that the amount of spray deposited on the weeds is more uniform, which is essential in herbicide application programs. Weeds that receive less spray deposition of herbicide solution probably will not be effectively controlled, and weeds with spray deposition higher than necessary are effectively wasted (Prado et al. 2024; Oliveira et al. 2019). In this study, the adjuvants improve the spray deposition and the uniformity of *E. heterophylla* and *D. insularis* (Table 3).

Bioefficacy study

Table 3 presents meteorological data, including temperature and relative humidity during treatment application. The air temperature and relative humidity were adequate during the treatment applications except for the relative humidity of Exp. 21 – *E. heterophylla* and Exp. 1 – *D. insularis*, which was above the recommended herbicide label.

Table 3
Meteorological data for temperature (T°C) and air relative humidity (RH%) at treatment application.

Experiments - Weed	Temperature °C	Relative humidity (%)	Application date
Exp. 1 - *Euphorbia heterophylla*	23 ± 2	64 ± 2	May 06, 2021
Exp. 2 - *Euphorbia heterophylla*	29 ± 1	52 ± 1	May 29, 2021
Exp. 1 - *Digitaria insularis*	28 ± 2	37 ± 1	Nov 23, 2021
Exp. 2 - *Digitaria insularis*	27 ± 2	58 ± 1	Dec 04, 2021

Temperature and relative humidity were measured at a height of 1 m above ground.

In the first experiment, all adjuvants tested increased diquat efficacy by up to 76% (Table 4). The adjuvants Fixade and Nimbus led to the highest increases in diquat efficacy, with 95% and 94% improvements, respectively. The treatment with adjuvant Ochima showed the smallest increase in efficacy (76%). In the second experiment, increased diquat efficacy was observed in all treatments except for the Silwet treatment (*ED50* = -5%). The increase in diquat efficacy was more pronounced in the first experiment compared to the second (Table 4). The more favorable meteorological conditions during the first experiment, with lower temperatures and higher relative humidity, likely contributed to the enhanced diquat performance.

Table 4

The parameters of the log-logistic equations[1] used to estimate the *ED50* and *ED90* (g ai ha^{-1}) values of diquat with different adjuvants in reducing *Euphorbia heterophylla* plants' dry weight.

Treatments	***ED50*** (g a.i. ha^{-1})	***ED90*** (g a.i. ha^{-1})	***b***	***c***	***d***	**Lack-of-fit** ***F*-test**	***P*-value *(ED50)***	**IE** ***(ED50)***
Exp. 1								
Fixade	7.3 (1.5)	44.8 (13.8)	1.2 (0.2)	0.040 (0.007)	1.7 (0.4)	0.2817	0.046	95
Agral	21.4 (4.9)	57.6 (8.6)	2.2 (0.4)	0.061 (0.009)	1.8 (0.3)	0.4769	< 0.001	86
Silwet	22.1 (7.8)	63.5 (19.4)	2.1 (0.8)	0.082 (0.014)	1.6 (0.3	0.9934	0.009	86
Nimbus	9.4 (3.5)	72.4 (18.5)	1.1 (0.2)	0.030 (0.008)	1.8 (0.3)	0.4761	0.012	94
Ochima	36.5 (7.6)	74.7 (13.0)	3.1 (0.9)	0.063 (0.008)	1.5 (0.2)	0.8519	< 0.001	76
Control	152.3 (16.4)	363.2 (48.1)	2.5 (0.5)	0.071 (0.010)	1.5 (0.1)	0.7855	< 0.001	-
Exp. 2								
Fixade	14.4 (2.7)	31.8 (3.9)	2.8 (0.4)	0.007 (0.001)	1.2 (0.2)	0.2389	< 0.001	75
Agral	15.6 (3.9)	51.8 (8.2)	1.8 (0.3)	0.010 (0.004)	1.4 (0.2)	0.5979	< 0.001	73
Silwet	60.6 (8.0)	130.2 (19.0)	2.9 (0.8)	0.010 (0.003)	1.2 (0.2)	0.3121	< 0.001	-5
Nimbus	34.1 (7.6)	103.8 (16.2)	2.0 (0.3)	0.010 (0.004)	1.2 (0.1)	0.6800	< 0.001	41
Ochima	15.6 (4.9)	46.8 (8.7)	2.0 (0.4)	0.020 (0.003)	1.1 (0.2)	0.2166	0.003	73
Control	57.9 (7.0)	136.7 (19.7)	2.6 (0.6)	0.020 (0.005)	1.3 (0.2)	0.3777	< 0.001	-

[1] $Y = c + (d - c)/\{1 + \exp [b (\log x - \log ED50)]\}$ (four-parameters). *Y* = dry weight reduction concerning the untreated control, *c* = lower limit, *d* = *upper limit*, *b* = slope of the curve, *x* = herbicide concentration, and *ED50* = herbicide concentration at the inflection point. IE: increase efficacy = 100 × (*ED50* diquat − *ED50* diquat + adjuvant) ÷ *ED50* diquat.

In the first experiment, all treatments containing adjuvants showed a lower *ED50* than the Control treatment, as indicated by the confidence interval (Fig. 2). Among the adjuvants analyzed, the *ED50* of Fixade was the lowest, showing a value 21 times lower than that of the Control treatment (Fig. 2 and Table 4).

In the second experiment, except for the adjuvants Silwet and Nimbus, all others presented significantly lower *ED50* than the Control treatment, differing significantly by the confidence interval. As in the first experiment, the treatment with adjuvant Fixade presented the lowest *ED50* value (Fig. 2).

From the results of the dose-response study, it is clear that there is a need to mix adjuvants in a diquat solution to increase the control efficacy against *E. heterophylla*. Experiments showed that the herbicide dose of diquat can be reduced to get the same control effect when adjuvants are mixed. Among the adjuvant classes assessed, all increased the control efficacy of diquat except for Silwet in the second experiment. The lower performance of the adjuvant Silwet may be related to the low relative humidity and high temperature at the time of spraying (Table 3), which were at the limit considered suitable for spraying pesticides. Adjuvants belonging to the organosilicon class can drastically reduce the solution's surface tension to values close to 20 mN m^{-1} (Prado et al. 2016; Cação et al. 2019; Gao et al. 2022). The lower surface tension may have contributed to the greater spreading of the droplets over the plant/leaves and, combined with the low air relative humidity, contributed to the faster solution evaporation (Xu et al. 2011), reducing the absorption of the diquat active ingredient due to the short time to penetrate plant tissue.

Our study reports increased diquat efficacy against *E. heterophylla* when associated with adjuvants, corroborating previous findings by Gitsopoulos et al. (2014) and Gitsopoulos et al. (2018). Gitsopoulos et al. (2018) also noted that adding organosilicon surfactants to diquat spray solutions improved weed control efficacy, but it was not the most effective adjuvant among those studied. In the context of the present study, it is evident that simply reducing the surface tension of the spray solution is not the sole factor influencing the biological efficacy of diquat. Mohassel et al. (2011), in their study on optimized herbicide doses with adjuvants, observed that factors beyond the reduction in surface tension may contribute to improved herbicide control efficacy.

The *E. heterophylla* plants were controlled entirely at 44.4 g ai ha^{-1} of the herbicide diquat associated with the adjuvant Fixade (Fig. 3a). In contrast, in the Control treatment, the plants were not fully controlled at 133.3 g ai ha^{-1} (Fig. 3b).

The spray solution amount deposited on *E. heterophylla* plants probably positively influenced the phytotoxicity of the herbicide diquat. In both experiments, the highest deposition values were observed when diquat was associated with the adjuvant Fixade (Fig. 1a), the same treatment that obtained the lowest *ED50*. In this sense, adopting the most appropriate adjuvant can further contribute to managing *E. heterophylla* with diquat.

In general, adding adjuvants to the glufosinate herbicide solution decreased the phytotoxicity of *D. insularis* in both experiments, with the lowest *ED50* and *ED90* observed in the Control treatment, with some exceptions (Table 5).

Table 5

The parameters of the log-logistic equations[1] were used to estimate the *ED50* and *ED90* (g ai ha^{-1}) values of diquat with different adjuvants in reducing *Digitaria insularis* plants' dry weight.

Treatments	***ED50*** (g a.i. ha^{-1})	***ED90*** (g a.i. ha^{-1})	***b***	***c***	***d***	**Lack-of-fit *F*-test**	***P*-value *(ED50)***	**AE *(ED50)***
Exp. 1								
Fixade	158.1 (29.2)	443.1 (47.4)	2.1 (0.4)	0.018 (0.010)	2.9 (0.2)	0.0547	< 0.001	-5.7
Agral	100.0 (28.3)	282.2 (46.9)	2.1 (0.3)	0.035 (0.011)	3.1 (0.5)	0.8156	< 0.001	33.2
Silwet	160.7 (34.9)	521.4 (45.6)	1.9 (0.5)	0.037 (0.008)	3.1 (0.2)	0.5650	< 0.001	-7.4
Nimbus	151.1 (26.4)	424.9 (42.0)	2.1 (0.3)	0.025 (0.008)	3.0 (0.2)	0.0947	< 0.001	-1.0
Ochima	341.7 (33.2)	563.6 (75.2)	4.4 (1.2)	0.050 (0.013)	2.9 (0.1)	0.0820	< 0.001	-128
Control	149.6 (14.6)	218.4 (24.2)	5.8 (1.1)	0.057 (0.005)	2.8 (0.3)	0.0510	< 0.001	-
Exp. 2								
Fixade	171.1 (19.3)	318.7 (35.0)	3.5 (0.6)	0.033 (0.013)	2.2 (0.1)	0.9604	< 0.001	-22.7
Agral	133.2 (10.9)	207.8 (17.6)	4.9 (0.8)	0.027 (0.003)	1.8 (0.2)	0.0718	< 0.001	4.4
Silwet	98.7 (20.9)	378.7 (47.6)	1.6 (0.4)	0.012 (0.122)	2.2 (0.1)	0.8293	< 0.001	29.2
Nimbus	172.6 (24.6)	445.4 (52.7)	2.3 (0.4)	0.025 (0.013)	2.0 (0.1)	0.1016	< 0.001	-23.8
Ochima	255.0 (30.1)	519.9 (26.4)	3.1 (0.4)	0.023 (0.003)	1.9 (0.1)	0.0651	< 0.001	-82.9
Control	139.4 (16.8)	370.9 (50.3)	2.2 (0.4)	0.026 (0.016)	2.1 (0.1)	0.5440	< 0.001	-

[1] $Y = c + (d - c)/\{1 + exp\ [b\ (log\ x - log\ ED50)]\}$ (four-parameters). *Y* = dry weight reduction concerning the untreated control, *c* = lower limit, *d* = *upper limit*, *b* = slope of the curve, *x* = herbicide concentration, and *ED50* = herbicide concentration at the inflection point. EI: efficacy increase = 100 × (*ED50* diquat – *ED50* glufosinate + adjuvant) ÷ *ED50* glufosinate.

The estimated *ED50* values of glufosinate associated with different classes of adjuvants in reducing the DW of *D. insularis* are presented in Fig. 4. The first experiment showed that the treatment with the adjuvant Agral presented the lowest *ED50*, differing significantly from the Control and the other treatments. The treatment with adjuvant Ochima showed the highest *ED50*, which differed from the other treatments. The *ED50* of Ochima was approximately 2.3 times higher than that of the Control treatment (Table 5 and Fig. 4), demonstrating an antagonist effect. A similar performance concerning treatment with Ochima was observed in the second experiment, with the highest *ED50* differing significantly from the Control treatment. Except for Ochima, no other adjuvant treatment differed significantly from the Control (Fig. 4).

In general, the results indicated that adding adjuvants to the glufosinate spray solution had an antagonistic effect on reducing the DW of *D. insularis* plants (Fig. 4). Although treatments with adjuvants significantly increased spray deposition on *D. insularis* plants (Fig. 1b), this did not translate into improved DW reduction. Notably, the increase in spray deposition on *D. insularis* plants does not necessarily imply better performance of glufosinate. In the treatment Control, the plants of *D. insularis* were controlled entirely at 400 g ai ha^{-1} (Fig. 5b). When the glufosinate solution was associated with the adjuvant Ochima, the plants sprayed at a 400 g ai ha^{-1} dose showed nonexistent or minor damage by herbicide (Fig. 5a).

It was expected that at least the mineral oil-based adjuvant would enhance the efficacy of glufosinate, as the manufacturer recommended its use for controlling *D. insularis*. Results similar to those observed in this study were reported by Polli et al. (2022), who found low reductions in dry biomass and mortality of several weed species or even an antagonistic effect when adjuvants were added to glufosinate solutions. Sobiech et al. (2020) reported that the adjuvant methylated rapeseed oil can increase the effectiveness of sulcotrione herbicide by reducing the contact angle and surface tension of liquid spray droplets. As observed in this study for *D. insularis*, the reduction of surface tension and contact angle provided by adjuvants did not improve glufosinate efficacy. The lower performance of glufosinate against *D. insularis* is likely associated with the plant's active ingredient absorption since treatments with adjuvants considerably increased spray deposition (Fig. 1b). Since the efficacy of the herbicide glufosinate is proportional to uptake and translocation levels (Takano et al., 2020), adding adjuvants to the glufosinate spray solution did not contribute to *D. insularis* glufosinate uptake.

The results observed in this study emphasize the challenges of selecting the appropriate adjuvant to enhance herbicide efficacy. As noted by several researchers (Gitsopoulos et al. 2014; Polli et al. 2022; Zhang et al. 2022), herbicide efficacy against weeds depends on the interaction of numerous factors, including the adjuvant, weed species, herbicide, and environmental conditions, making it difficult, if not impossible, to generalize recommendations for a specific adjuvant with a particular herbicide. Therefore, targeted studies are essential to understand these interactions better and improve herbicide-based weed management.

Conclusion

Herbicide tank-mix adjuvants are crucial in optimizing post-emergence herbicide spray deposition and biological efficacy against weeds. In conclusion, the adjuvants Fixade, Agral, Silwet, Nimbus, and Ochima improved herbicide spray deposition and distribution uniformity on *E. heterophylla* and *D. insularis* weeds. Except for Silwet in the second experiment, all adjuvants enhanced diquat performance against *E. heterophylla*, with Fixade showing the best performance. The addition of adjuvants Fixade, Agral, Silwet, and Nimbus did not improve the efficacy of glufosinate. The adjuvant Ochima provided an antagonistic effect on the performance of glufosinate.

Declarations

Conflict of interest

The authors declare that they have no conflict of interest.

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Figures

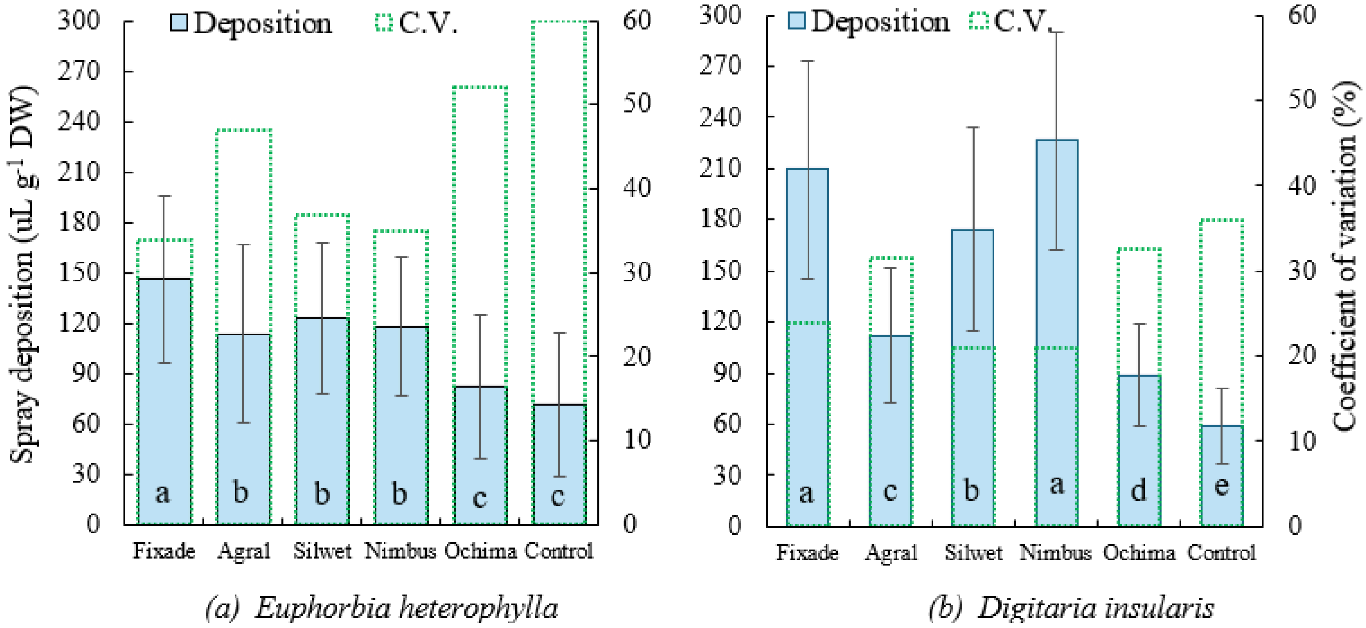


Figure 1

Means spray deposition (mean ± SD) and coefficient of variance (CV %) after spraying the herbicide diquat on *Euphorbia heterophylla* (a) and glufosinate on *Digitaria insularis* (b) associated with different adjuvants. Means with different letters are significantly different by Scott-Knott at 5% probability. CV: Coefficient of variation %. Bars represent the mean standard deviation.

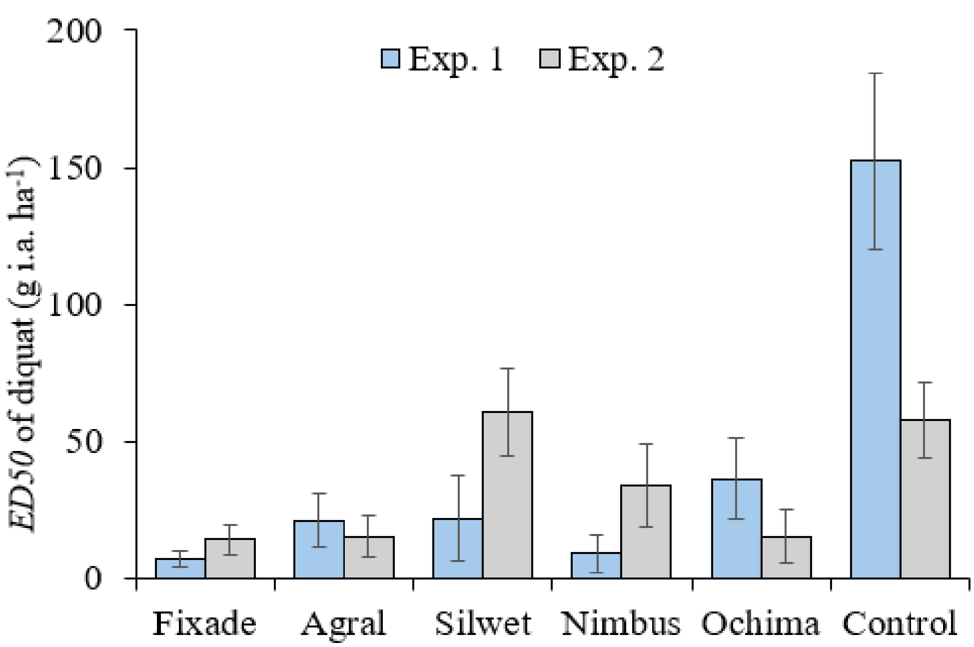


Figure 2

ED50 values of diquat estimated by the log-logistic equation sprayed alone or mixed with different classes of adjuvants on *Euphorbia heterophylla* aboveground dry weight reduction. The vertical bar represents the 95% confidence interval.

Figure 3

Images of pots with *E. heterophylla* plants 20 days after treatment of diquat associated with the adjuvant Fixade (a) and Control (b) in the second experiment. From left to right, the diquat doses are 3,600, 1,200, 400, 133.3, 44.4, 14.8, 4.9, and 0 g ai ha^{-1}.

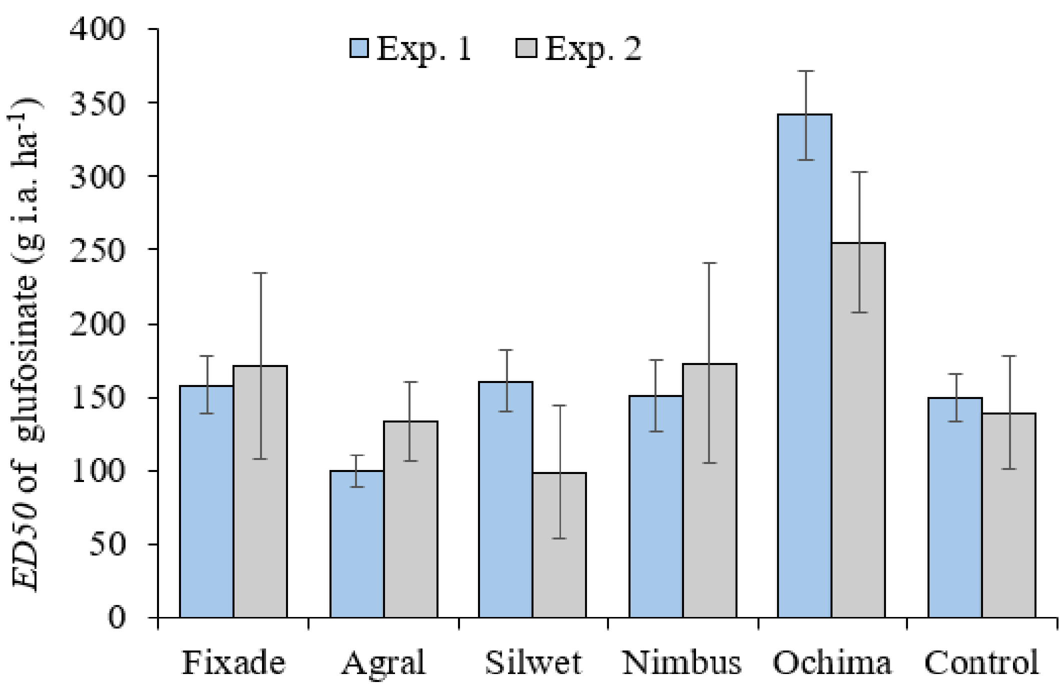
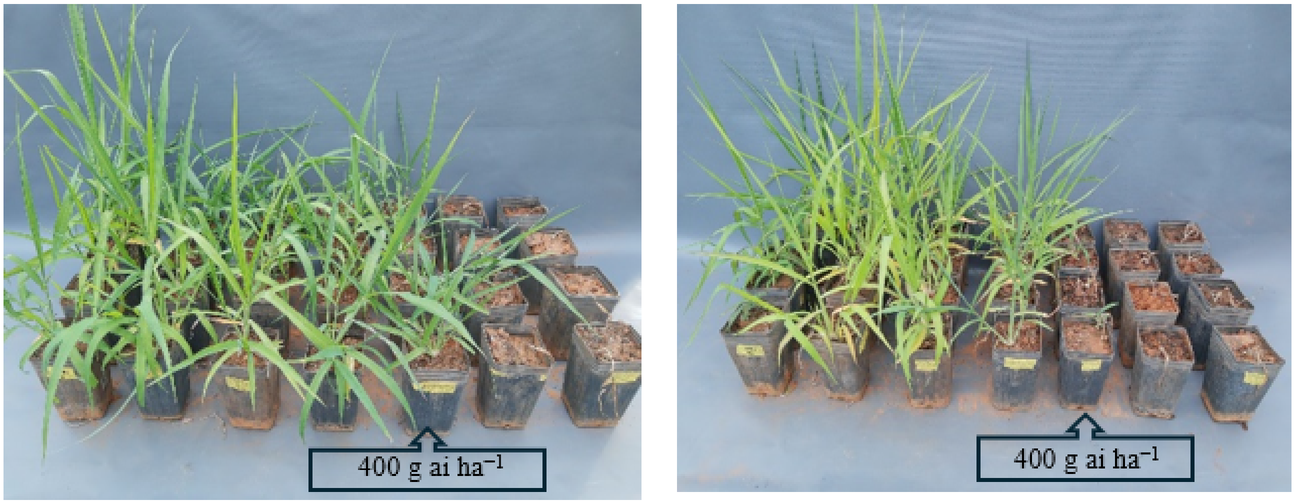


Figure 4

ED50 values of glufosinate estimated by the log-logistic equation sprayed alone or mixed with different classes of adjuvants on *Digitaria insularis* aboveground dry weight reduction. The vertical bar represents the 95% confidence interval.



(a) (b)

Figure 5

Images of pots with *D. insularis* plants 20 days after treatment of diquat associated with the adjuvant Ochima (a) and Control (b) in the first experiment. From right to left, the glufosinate doses are 3,600, 1,200, 400, 133.3, 44.4, 14.8, 4.9, and 0 g ai ha^{-1}.