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DOI: 10.1017/wet.2024.34

Adsorption of spray droplets reduced adsorption of dicamba spray droplets on leaves as droplet size increases

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Abstract

Off-target movement of growth regulator herbicides can cause severe injury to susceptible plants. Apart from not spraying on windy days or at excessive boom heights, making herbicide applications using nozzles that produce large droplets is the preferred method for reducing herbicide drift. Although large droplets maintain a higher velocity and are more likely to reach the leaf surface in windy conditions, their ability to remain on the leaf surface is poorly understood. Upon impact with the leaf surface, droplets may shatter, bounce, roll-off, or be retained on a leaf surface. We examined how different nozzles, pressures, and adjuvants impact spray droplet adsorption on the leaf surface of common lambsquarters and soybean. Plants were grown in a greenhouse and sprayed in a spray chamber. Three nozzles (XR, AIXR, and TTI) were evaluated at 138, 259, and 379 kPa. Dicamba (0.14 kg ae ha^{-1}) was applied alone and with methylated seed oil (MSO), a non-ionic surfactant, silicone-based adjuvant, crop oil concentrate, or a drift reduction adjuvant. A 1, 3, 6, 8-pyrene tetra sulfonic acid tetra sodium salt was added as a tracer. Dicamba spray droplet adsorption when using the XR nozzle, which produced the smallest spray droplets, was 1.75 times greater than when applied with the TTI nozzle with the largest spray droplets. Applying dicamba with MSO increased adsorption on leaf surfaces nearly four times the amount achieved without an adjuvant. The lowest application pressure (138 kPa) increased dicamba spray volume adsorbed more than 10% compared to the higher pressures 259 and 379 kPa. By understanding the impacts of these application parameters on dicamba spray droplet adsorption, applicators can select application parameters, equipment, and adjuvants that will maximize the amount of dicamba spray volume retained on the target leaf surface while minimizing dicamba spray drift.

Nomenclature: dicamba; common lambsquarters, *Chenopodium album* L., soybean; *Glycine max* (L.) Merr.

Keywords: Droplet size, herbicide, adjuvant, off-target movement; retention, 3,6-dichloro-2-methoxybenzoic acid;

Introduction

Glyphosate-resistant weeds have developed due to selection pressure applied to weed populations by the extensive use of glyphosate within corn (*Zea mays* L.), soybean, and cotton (*Gossypium hirsutum* L.) production systems (Johnson et al. 2009; Gage et al. 2019; Green and Siehl 2021). In response to increasing glyphosate resistance, alternative weed management strategies including herbicide-resistant (HR) crop traits are being integrated that use various herbicide modes-of-action that otherwise would not be an option. This includes development of crops resistant to 2,4-D (2,4-dichlorophenoxyacetic acid), 4-hydroxyphenylpyruvate dioxygenase (HPPD) inhibitor and particularly dicamba (3,6-dichloro-2-methoxybenzoic acid) (Green and Siehl, 2021), such as dicamba-resistant soybean varieties, which have been commercially available since 2017 (Alves et al. 2017; EPA 2019).

Dicamba is a selective herbicide from the benzoic acid family of chemicals (Alves et al. 2017), used as preplant burndown or postemergence to selectively control broadleaf weeds in grass crops. Dicamba susceptible crops are vulnerable to off-target movement of dicamba and are often grown adjacent to areas sprayed with dicamba (Nunes et al. 2023). Previous research has reported dicamba drift injury on cotton (Centner 2022), soybean (Nunes et al. 2023), potato (*Solanum tuberosum*), field bean (*Phaseolus vulgaris*), and tomato (*Lycopersicon esculentum*) (Lyon and Wilson 1986; Marple et al. 2008; Kruger et al. 2012; Centner 2022; Nunes et al. 2023), eggplant, cucumber, and snap bean (Wasacz et al. 2022). Injury symptoms of phenoxy herbicides such as dicamba include cupping and curling of leaves as well as stem epinasty. These injury symptoms are easily recognizable and readily manifest the occurrence of phenoxy herbicide drift (Centner 2022; Nunes et al. 2023). The increased use of dicamba to control weeds in herbicide-resistant crops has increased the likelihood of non-target injury of adjacent crops within these systems.

Physical herbicide drift occurs when spray droplets are displaced from their intended flight path due to wind. Application variables that can impact herbicide drift include the use of a hooded sprayer boom (Wolf et al. 1993), the use of drift control agents (Bode et al. 1976), or by lowering the spray boom closer to the ground (Combellack et al. 1996).

Apart from not spraying on a windy day, the most influential factor related to herbicide drift is droplet size (Bird et al. 1996; Ozkan et al. 1997; Carlsen et al. 2006; Nuyttens et al. 2007). Larger droplets maintain their direction and momentum longer and are less prone to be displaced by the wind whereas smaller droplets quickly lose their momentum and become suspended in the air (Nuyttens et al. 2009). Creech et al. (2015a) identified nozzle type as the most important factor determining spray droplet size followed by operating pressure, herbicide spray solution, nozzle orifice size, and carrier volume rate. Increasing the spray pressure decreases droplet size, yet herbicide drift may decrease depending on nozzle design due to the dominance of droplet velocity (Nunes et al. 2023).

The use of spray droplets discharged from a nozzle is the method most often used to deliver the herbicide active ingredient to a weed target. The droplet must first travel the distance from the spray boom to the target. Spray droplets leave the nozzle traveling at velocities of 15 to 25 m s^{-1} (Dombrowski and Johns 1963). When a droplet impacts a plant surface, it will either be retained through adhesion, bounce, shatter, or roll off.

Droplets that are not retained can continue through the canopy and may be retained on a lower leaf or may impact the ground (Schou et al. 2012). Monocotyledons predominantly have a vertical structure and are more likely to retain smaller droplets than larger droplets (Knoche 1994). Nairn et al. (2014) observed lower adhesion of droplets to hairy leaves due to an increase in the incidence of droplet shatter. Growth stage and growing conditions can alter the wettability of a plant and decrease droplet adsorption on the leaf surface (Forster and Leeuwen 2005). The ability of spray droplets to remain on a plant surface determines the quantity of herbicide potentially available to be taken up by the plant. Herbicide performance increased more frequently on difficult-to-wet species as droplet size decreased in a meta-analysis than easy-to-wet species (Knoche 1994). Other variables that impact droplet adsorption include plant morphological characteristics such as leaf angle and pubescence as well as droplet surface tension (Ennis et al. 1952). Adsorption of spray droplets is more dependent upon dynamic surface tension than equilibrium surface tension (Anderson et al. 1987; De Ruiter et al. 1990; Abbott et al. 2021). By changing the surface tension of a spray droplet, adjuvants allow spray droplets to spread and remain over a normally repellent leaf surface (Monaco et al. 2002). Thus, adjuvants can increase droplet adsorption by causing more uniform spreading and wetting of the plant surface and assisting spray droplets to stick to plants (Monaco et al. 2002). For this reason, adjuvants are often added to postemergence spray solutions to enhance spray solution characteristics and/or herbicide activity. Applicators select adjuvants based on many factors such as cost, phytotoxicity risk, compatibility with tank-mix partners, and recommendations from herbicide labels and industry consultants.

In order to mitigate off-target movement of dicamba, herbicide labels recommend applicators use nozzles designed to produce large diameter droplets (Anonymous 2013a; EPA 2019). While increasing the spray droplet size of a herbicide application may be effective at mitigating off-target movement (Bode 1987), increasing the spray droplet size of an application can impact herbicide efficacy (Knoche 1994). In addition, the dicamba herbicide label recommends the use of adjuvants and lists many different types that may be used (EPA 2019). While this approach allows an applicator the ability to tailor an application according to specific needs, without sufficient knowledge proper selection of the most appropriate adjuvant can be difficult due to the complexity of the system (Zollinger 2000). Although these recommendations are on the dicamba label, researchers have not explored the impact they might have on the adsorption of spray droplets on their intended targets.

The objective of this experiment was to determine the impact of droplet size, application pressure, and adjuvant type on the spray droplet adsorption of dicamba on a leaf surface. This will provide applicators with information to allow them to make improved decisions when making dicamba applications to keep more spray volume on the leaf surface.

Materials and Methods

This experiment was conducted during the fall of 2014 at the Pesticide Application Technology Laboratory (PAT Lab) of the University of Nebraska-Lincoln located at the West Central Research and Extension Center in North Platte, NE. The experiment had five replications and two runs separated temporally for each plant species evaluated. A dicamba (0.14 kg ae ha^{-1}) spray solution was applied alone (NONE) and with methylated seed oil (MSO), a non-ionic surfactant (NIS), silicone-based adjuvant (Silicone), crop oil concentrate (COC), or a drift reduction adjuvant (DRA) (Table 1).

The XR 110025 (XR), AIXR 110025 (AIXR), and TTI 110025 (TTI) nozzles (Teejet Technologies, Spraying Systems Co., Springfield, IL 62703) were operated at 138, 259, and 379 kPa to deliver 94 L ha^{-1}. A 1, 3, 6, 8-pyrene tetra sulfonic acid tetrasodium salt (PTSA) was added as a tracer dye at 6 mg/ml as recommended by Hoffmann et al. (2014) for agricultural sprays. Treatments were applied using a single nozzle track sprayer (Generation III Research

Track Sprayer DeVries Manufacturing, Hollandale, MN 56045). Before conducting the experiment, each nozzle and pressure combination was calibrated to ensure equal deposition by mass at the same height and location within the spray pattern where the plant species would be placed. This was completed by using a 15 cm petri dish and making 20 spray passes over the dish. The dish would then be weighed, and the speed of the track sprayer would be adjusted until the nozzles each had the same deposition at the target site. This method of calibration was used because it was recognized that measuring the output of each nozzle for a period of time would be an insufficient means of calibration for this study because of variations of spray patterns among nozzles at the target site.

Common lambsquarters and Asgrow® A3253 soybeans were grown in SC10 cone-tainer cells (Stuewe and Sons Inc., Corvallis, OR 97389) that were filled with Professional Growers Mix potting soil (Ball Horticulture Company, West Chicago, IL, 60185). Plants received supplemental nutrition (Scotts Miracle-Gro® LiquaFeed® All Purpose, The Scotts Company, Marysville, OH, 43041) once per week. Supplemental lighting (NeoSolTM DS 300W, Illumitex, Austin, TX, 78735) was provided for 14 h days. Soybean plants were sprayed with dicamba treatments when the two unifoliate leaves were fully developed, and common lambsquarters plants had at least four large leaves. For each species, this occurred when plants were 15 to 20 cm tall. Before spraying the plants, any foliage above the target leaves was clipped and removed to ensure the spray droplets were not impeded from the target leaves.

Plants were placed individually in the center of the track sprayer 50 cm below the tip of the nozzle. In addition, a 15 cm petri dish was placed at the height of the plant canopy to collect spray deposition. This was used to verify that equal amounts of deposition were applied across all treatment combinations. If any differences were observed, data was corrected to ensure equal comparison across treatment factors and that no spray volume bias was present. After a plant was sprayed, it was removed from the track sprayer and treated leaves were clipped into pre-labeled plastic sealable bags. The leaves were then rinsed immediately with 40 ml of a 9:1 distilled water to isopropyl alcohol solution that was added to the bag using a bottle top dispenser (Model 60000-BTR, LabSciences, Inc., Reno, NV, 89510). This solution provided the maximum recovery of PTSA deposits in a study by Hoffmann et al. (2014). After the PTSA dye was successfully suspended in the liquid, a two ml sample was drawn with a pipette to fill a glass cuvette. The cuvette was placed in a PTSA module inside a fluorometer (Trilogy Laboratory

Fluorometer, Turner Designs, Sunnyvale, CA, 94085), and fluorescence data were collected. The leaves were then removed from the bags and dried using paper towels. The total leaf area for all leaves used for each plant was determined using an LI-3100 leaf area meter (LI-COR, Lincoln, NE, 68504) and used to standardize fluorometer data across experimental units.

For the fluorescence data to be useful in understanding the quantity of spray volume adsorbed on a leaf surface, the recoverable amount of PTSA dye needed to be measured. To accomplish this, 20 µl of each spray solution was pipetted directly onto the leaves of each species. The leaves were then clipped into plastic bags, rinsed, and processed in the same manner as sprayed leaf samples with 40 ml of distilled water and isopropyl alcohol solution and analyzed to determine the fluorescence of the sample. Likewise, 20 µl of each spray solution was pipetted directly into bags. The same recovery method was used with these bags without leaves and the fluorescence of each was measured. This process of measuring recovered PTSA dye from a known quantity of spray solution with and without leaves validated our ability to measure PTSA dye in the solution and provided any needed correction factor.

The spray droplet spectrum for each treatment combination was evaluated in 2014 using the low-speed wind tunnel at the PAT Lab. The system and process used to collect the spray droplet data have been described extensively in a previous manuscript (Creech et al. 2015b). The laser can classify the spray droplet spectrum into several different categories to compare the spray droplet spectra of different treatments. The treatments in this study were compared using the Dv10, Dv50, and Dv90 parameters representing the droplet size such that 10, 50, and 90% of the spray volume is contained in droplets of equal or smaller values, respectively. The amount of spray volume contained in droplets smaller than 200 µm (<V200) and 730 µm (<V730) was also used for comparison. The spray classifications used in this manuscript were derived from reference curves created from reference nozzle data at the PAT Lab as described by ASAE S572.1 (ASABE 2009) (Figures 1 and 2). The use of reference nozzles and curves allows for the comparison of data obtained from other laboratories or methods (Fritz et al. 2014).

Statistical Analysis

Data analysis was performed in R (R Core Team 2023, version 4.3.0) with Rstudio as an integrated development environment. A multivariate exploratory analysis was performed on the droplet size characteristics of the dicamba experiment treatments. A factor analysis of mixed data

(FAMD) was used to understand the relationship between the spray droplet size (quantitative variables; Dv10, Dv50, and Dv90, RS and <V200) and the adjuvants, nozzles, pressures, and spray classification (categorical variables), using the packages ‘FactoMineR’ (Husson et al. 2014) and ‘factoextra’ (Kassambara and Mundt 2016) with the relationship between variables shown in a biplot. FAMD is a principal component method dedicated to analyzing a data set containing both quantitative and qualitative variables at the same time. FAMD algorithm can be seen as a mixture of principal component analysis (PCA) and multiple correspondence analysis (MCA). Both quantitative and qualitative variables are normalized during the analysis in order to balance the influence of each set of variables.

Results from common lambsquarters and soybean spray droplet adsorption on leaf surfaces were analyzed separately because the treatments were applied at different times. Spray droplet adsorption rates were calculated as a percent of the applied rate as determined from the spray collected in the adjacent petri dish and adjusted by leaf area and recoverable amount of PTSA.

The effect of adjuvants, nozzles, pressures, and their interactions on the spray droplet adsorption were investigated by general linear mixed models (GLMM). The models were adjusted using a Gamma distribution and model fitting was analyzed using the packages ‘car’ (Fox and Weisberg 2019) and ‘performance’ (Lüdecke et al. 2021). Data from the runs of each species were combined within each experiment because they did not differ significantly. Replication was considered a random effect in the model. LS means were compared for significant fixed effects at an alpha level of 0.05.

For additional insights, to identify determinants of maximum dicamba spray droplet adsorption across all treatment combinations, the integration of the studied variables, namely, spray droplet size characteristics of dicamba (Dv10, Dv50, and Dv90, RS, <V200 and <V730) and spray droplet adsorption, for common lambsquarters and soybean, were explored separately by a PCA. The packages ‘FactoMineR’ (Husson et al. 2014) and ‘factoextra’ (Kassambara and Mundt 2016) compute PCA with the relationship between different adjuvants, nozzles, pressures and spray classification visualized on biplots. PCA was used to study the correlations between parameters.

Results and Discussion

Spray Droplet Size

Initially, due to the large number of treatment combinations and variables, a multivariate exploratory analysis was performed to identify determinants of the droplet size characteristics. A factor analysis of mixed data was performed to understand the relationships between the two types of variables, i.e., categorical (adjuvants, nozzles, pressures and spray classification) and the quantitative variables of spray droplet size characteristics of dicamba (Dv10, Dv50, and Dv90, RS and <V200). The first two principal components in the FAMD accounted for 32.2% and 10.5% of the total variation, respectively, and together explained 42.7% of the total variation (Figure 1; Supplementary Figure S1).

Overall, the different treatment combinations among adjuvants, nozzle and pressure were mostly separated both on first (PC1) and second (PC2) dimensions of the PCA, respectively, due to the high positive correlation of all quantitative variables, i.e., Dv50, Dv90, Dv10, RS and <V200, respectively, on PC1 along with a high positive correlation of spray classification and nozzles on PC1 and PC2 and a low positive correlation of adjuvant and pressure on both PCs (Figure 1).

In general, regardless of the adjuvant type, treatment combinations in the first axis comprised by TTI nozzle, in part linked to a low pressure and with an Ultra Coarse spray classification were grouped, being thus related to large droplet size. In contrast, the first axis opposes treatments embracing XR nozzle, in part linked to a high pressure, which had spray classification varying from Very Fine to Medium was associated with droplets less than 200 μm when applications were made, in general, at 379 kPa. In addition, treatments applied with an AIXR nozzle, regardless of pressure, had a spray classification Coarse to Extremely Coarse and were grouped together, representing an intermediate droplet size (Figure 1). Understanding these principles and the spray droplet characteristics of the treatment variables described in Supplementary Table S1, will give further clarity and reasoning to the results presented hereafter.

The different nozzle types had the greatest variability among Dv50 values when averaged over adjuvant and pressure, confirming the results reported by Creech et al. (2015a) that nozzle is the primary determinant of spray droplet size. The XR, AIXR, and TTI nozzles had average Dv50 values of 237, 505, and 812 μm, respectively (Supplementary Table S1). The difference in spray droplet size among nozzles is also apparent when comparing the spray volume contained in droplets less than 200 µm. The TTI nozzle typically had less than one percent, while the XR nozzle had nearly 50% of its spray volume contained in droplets less than 200 µm when applications were made at 379 kPa (Figure 2; Supplementary Table S1).

Increasing the application pressure decreased spray droplet size as determined by Dv50 values from 629 µm to 495 and 430 µm averaged across nozzle type and spray solution for 138, 259, and 924 kPa, respectively (Figure 2; Supplementary Table S1).

Although our treatments were thus mostly separated on both PCs by the spray classification of nozzles and pressure, we observed that, in general, the addition of a silicone adjuvant to dicamba produced the smallest spray droplets, followed by MSO, DRA, COC, NIS, and dicamba without an adjuvant. These spray solutions had Dv50 values of 482, 489, 507, 524, 546, and 559 µm, respectively, when averaged over nozzle type and pressure. Visual representation of the Dv50 data of all treatment combinations of nozzle, adjuvants and pressures is in Figure. 2.

Spray droplets are the most common method used to deliver a lethal dose of chemicals to the target plant species. Furthermore, the spray droplet size is highly correlated to the droplet velocity (Nuyttens et al. 2009) and the rate of change of size with distance from spray release. Smaller droplets may initially have a high velocity when emitted through the nozzle, but their low mass allows them to decelerate rapidly. At the plant location, these small droplets, with their relatively slower velocities, are more readily adsorbed on a leaf surface (Ramsdale and Messersmith, 2001).

Common lambsquarters

Common lambsquarters was used for this experiment because it has a leaf surface composed of crystalline epicuticular wax, which makes it difficult to wet (Harr and Guggenheim 1995). A significant three-way interaction ($P<.001$; Table 2) was observed among nozzle type, pressure, and spray solution related to dicamba spray droplet adsorption on common lambsquarters leaves.

Principle component analysis conducted on several spray droplet size characteristics of dicamba (Dv10, Dv50, and Dv90, RS, <V200 and <V730) along with the spray droplet adsorption for common lambsquarters captured 91.5% of the variability on the first two axes of

the PCA across the different treatment combinations. PC1 accounted for 79.4% of the total variation, and PC2, 12.2% (Figure 3; Supplementary Figure S2).

The biplot exhibited separation of the different treatment combinations among adjuvants, nozzle, pressure along with their respective spray classifications, due to the positive correlation of Dv10, Dv50 and Dv90 and the inverse contribution of <V200, <V730 and RS on PC1 along with a positive correlation of adsorption on the PC2 (Figure 3).

Due to the large number of treatment interactions, the many differences will not be covered individually, rather trends will be discussed. The use of adjuvants significantly increased the amount of spray volume adsorbed on the surface of common lambsquarters (Figure 3A; Figure 4; Supplementary Table S2). Of the top ranked 15 treatments for dicamba spray adsorption, MSO accounted for six instances, followed by COC, NIS, and silicone with four, three, and two instances, respectively. These 15 highest ranked treatments had an average spray adsorption of 24% of the applied rate (Figure 3A; Figure 4; Supplementary Table S2). Dicamba applied without an adjuvant, ranked near the bottom compared to other treatments with adjuvants with less than 10% spray adsorption on common lambsquarters leaf surfaces (Figure 3A; Figure 4; Supplementary Table S2). The addition of DRA to the dicamba solution only moderately increased adsorption compared to dicamba alone (Figure 3A; Figure 4; Supplementary Table S2). These two treatments had less than half the dicamba spray volume adsorption that the top-ranked 15 treatments had. For the most part, using NIS and silicone with dicamba was most often ranked near the middle of all the treatments for adsorption.

Overall, our results revealed that treatment combinations such as (52), NONE-TTI-low; (53), NONE-TTI-medium; (54), NONE-TTI-high, for which the dicamba was applied alone, were poorly correlated to the second axis, showing thus the lowest adsorption among all the treatments. These treatments had a spray classification as Ultra Coarse. On the opposite side, treatments such as 1 (MSO-XR-low), 4 (MSO-AIXR-low) and 9 (MSO-TTI-high), had the greatest adsorption with spray classification varying from Medium to Extremely Coarse. In general, the use of MSO as an adjuvant increased the amount of dicamba adsorption compared to other adjuvants tested or when dicamba was applied alone (Figure 3).

In most instances, the spray droplet classifications for the dicamba alone and with DRA treatments ranked in the last 15 were Coarse, Extremely Coarse, and Ultra Coarse (Figure 3; Figure 4; Supplemental Table S2). These treatments were applied with TTI and AIXR nozzles

(Figure 4) Supplemental Table S2). The few exceptions were the treatments applied with the XR nozzle that produced Fine and Medium spray classifications. Although these XR nozzle treatments had smaller spray droplets, it was not enough to overcome the poor adsorption when the dicamba spray solution contained only dicamba or dicamba with DRA. Conversely, 10 of the 15 highest-ranked treatments for spray adsorption were applied with XR nozzles with spray classifications of Very Fine to Medium (Figure 4; Supplemental Table S2). Of the remaining five highest-ranked treatments (Figure 4; Supplemental Table S2), three were attributed to the AIXR nozzle with Coarse to Extremely Coarse spray classifications, and two were applied with the TTI nozzle with Extremely Coarse and Ultra Coarse spray classifications. It would be expected that larger spray droplets would not remain on the leaf surface as easily as smaller droplets. These five treatments were either applied with MSO, with a low pressure, or both.

The top four treatments with the greatest spray adsorption were each applied at the lowest pressure evaluated, 138 kPa (Figure 4). Treatments applied at 138 kPa had, on average, 25% more spray adsorption on common lambsquarters leaves (Figure 4; Supplemental Table S2). Differences between 259 and 379 kPa were more subtle, and no general trend was obvious other than that they were ranked in the middle to last in most instances. Smaller spray droplets slow down faster than larger droplets because of air drag (Goering et al. 1972). At 50 cm below the nozzle tip, spray droplets 120 μm and smaller have velocities at or less than 2 m s^{-1} (Nuyttens et al. 2009). Thus, any reduction in spray droplet adsorption caused by increasing the application pressure would impact the TTI and AIXR nozzle more, which had less than 10% of their spray volume contained in droplets less than 200 μm (Supplemental Table S1). In comparison, the XR nozzle had as much as 59% of its spray volume contained in droplets less than 200 μm and droplet velocity would not have been as important as a variable.

Soybean

PCA conducted on several spray droplet size characteristics of dicamba and the spray droplet adsorption for soybean captured 91.6% of the variability on the first two axes of the PCA across the different treatment combinations. PC1 accounted for 80% of the total variation, and PC2, 11.6% (Figure 5).

The biplot exhibited separation of the different treatment combinations among adjuvants, nozzle, pressure along with their respective spray classifications, due to the positive correlation of Dv10, Dv50, and Dv90 and the inverse contribution of <V200, <V730 and RS on PC1 along with a positive correlation of adsorption on the PC2 (Figure 5; Supplemental Table S3).

Our results revealed that treatment combinations such as 1 (MSO-XR-low), 4 (MSO-AIXR-low) and 6 (MSO-AIXR-high) were highly correlated to the second axis and displayed the greatest adsorption with spray classification varying from Medium to Extremely Coarse. On the contrary, treatment combinations such as (52), NONE-TTI-low; (53), NONE-TTI-medium; (54), NONE-TTI-high, with dicamba applied alone, were poorly correlated to the second axis, showing thus the lowest adsorption among all the treatments. PCA analysis for soybean also revealed that the use of MSO as an adjuvant had a significant impact on the dicamba spray adsorption compared to other adjuvants tested in our experiment or when dicamba was applied alone (Figure 5).

The dicamba spray adsorption on soybean leaves as influenced by adjuvant, nozzle type, and application pressure was similar to that observed with common lambsquarters. A significant three-way interaction (P = 0.0074; Table 2) was observed among the three variables as they relate to dicamba spray droplet adsorption on soybean leaves.

The use of adjuvants significantly increased the amount of spray retained on the surface of soybean (Figure 6). Of the top-ranked 15 treatments for dicamba adsorption in soybean, MSO accounted for eight instances, followed by NIS and silicone with three and COC with one. These 15 highest-ranked treatments had an average spray adsorption of 37% (Figure 6; Supplemental Table S3). Like common lambsquarters, dicamba applied without an adjuvant or with DRA occupied the 15 lowest rankings with less than 15% spray adsorption on average (Figure 6; Supplemental Table S3). The addition of DRA to the dicamba solution only moderately increased absorption compared to dicamba alone. In comparing the spray adsorption of adjuvants applied with dicamba to soybean and common lambsquarters, the biggest difference was that NIS and silicone had greater adsorption on average than COC on soybean. The opposite is true for common lambsquarters with greater dicamba droplet adsorption when using COC.

Eight of the ten treatments ranked the highest for spray droplet adsorption were applied using the XR nozzle that produced spray classifications from Very Fine to Medium (Figure 5; Supplemental Table S1). The remaining two positions of the top ten ranked treatments were the AIXR nozzle when applying dicamba with MSO. The TTI nozzle, when applying dicamba and MSO spray solution, ranked 11th, 12th, and 13th with spray classifications of Extremely Coarse and Ultra Coarse (Figure 5; Supplemental Table S3). Although the TTI nozzle produces large droplets compared to the other nozzles evaluated, the use of MSO was able to overcome the antagonistic properties of large droplets relating to spray adsorption on a leaf surface. The next time the TTI nozzle appears in the table was when applications were made with silicone at 259 kPa.

The smaller droplets of XR nozzles compensated for the low leaf adsorption of dicamba alone or dicamba with DRA. As previously reported, dicamba alone or with DRA had very low spray droplet adsorption on soybean leaves (Figure. 5; Supplemental Table S3). The highest ranked treatments when using either dicamba alone or with DRA were all achieved when using the XR nozzle producing Fine to Medium spray droplets. Soybean leaves, especially on young plants, are pubescent. Reduced spray adsorption has been observed on hairy leaves due to an increase in the incidence of droplet shatter (Nairn et al. 2014). Thus, smaller droplets, with less velocity and momentum, are less likely to shatter and therefore may be more disposed to remain on the leaf surface similar to what was observed with the XR nozzle.

Similar to the results observed with common lambsquarters, spray droplet adsorption increased on soybean leaves when applied at 138 kPa in most instances (Figure 5; Supplemental Table S3). Spray droplets larger than 400 µm in diameter have a relatively constant velocity as pressure increases (Nuyttens et al. 2009). When averaged across treatments, the TTI nozzle had less than 10% of its spray volume contained in droplets less than 400 µm (Supplemental Table S1).

Because of this, increasing application pressure when using the TTI nozzle had no significant effect, and in most cases, the adjuvant treatments were ranked almost identically (Figure 5; Supplemental Table S3). Nuyttens et al. (2009) reported that the velocity droplets with diameters between 200 and 400 µm were most responsive to increasing spray pressure 50 cm below the nozzle tip. Because the spray droplet spectrums ranged from Very Fine to Ultra Coarse depending on the treatment, the influence of increasing application pressure varied. Moreover, as spray pressure increases, droplet size decreases, which would reduce the influence of droplet velocity on spray droplet adsorption on a leaf surface.

Adding adjuvants to the dicamba spray solution had the greatest impact on spray droplet adsorption. Adsorption increased on average 4.5 and 3.7 times by adding MSO to the dicamba spray solution for common lambsquarters and soybean, respectively. Using a DRA purportedly reduces the number of fine droplets and increases spray droplet deposition (Anonymous 2013b). While spray droplet deposition is a necessary requirement for herbicide activity on targeted plants, of equal or greater importance is the amount retained on the leaf surface. In this study, using the DRA with dicamba increased the amount of spray retained on the leaf surface by 34 and 40% for common lambsquarters and soybean, respectively, when averaged over other treatment variables. Compared to dicamba alone, this is a significant increase, but compared to other adjuvants, the increase was minimal. Whether this increase is due to increased spray deposition, adsorption, or both is unknown. As mentioned earlier, NIS and silicone with dicamba were most often ranked near the middle of all the treatments for adsorption. When applying the spray solutions to leaf surfaces manually to calculate recovery, it was visually evident that silicone has high spreading capabilities. This would permit the spreading of spray droplets applied to the upper surface of leaves to cover a wide area and spread around the leaf margin to the underside of the leaves. Although the other spray solutions did not observe this level of spreading, silicone was consistently ranked near the middle of the spray solutions evaluated. Spreading may deflect some of the spray droplet momentum from rebounding or shattering when impacting the leaf surface, however, it may lead to excessive runoff.

The interaction between spray solution and nozzle type can change the risk of drift and may impact spray droplet adsorption and herbicide efficacy in some circumstances (Nunes et al. 2023). Nozzles are the most influential component of a spray application process in the determination of spray droplet size (Creech et al. 2015a). Alves et al. (2017) evaluated drift from dicamba applications using flat-fan nozzles (XR, TT, AIXR and TTI), under three wind speeds in a wind tunnel (0.9, 2.2, 3.6 and 4.9m s^{-1}), observed that TTI nozzle produced the lowest percentage of dicamba drift at 2.2, 3.6 and 4.9m s^{-1} wind while dicamba spray drift from XR, TT and AIXR nozzles was greater as droplet size decreased.

Adsorption with the XR nozzle, which produces Very Fine to Medium spray droplets, was nearly 2 times greater than the TTI nozzle, which produced Extremely Coarse to Ultra Coarse spray droplets. This demonstrated the impact droplet size can have on droplet adsorption on the leaf surface. However, it is important to recognize that this experiment was conducted under ideal conditions in a spray chamber with no apprehension of herbicide drift. Under normal field conditions, applicators must weigh the risks of herbicide drift from the application while maintaining high spray droplet deposition, adsorption, and herbicide efficacy. Bode (1987) reported the significance of the diameter of a spray droplet related to particle drift as a 100 µm diameter droplet can travel 7.5 times further off-target than a 500 µm droplet in 5 kph wind speed. For this reason, the use of an XR nozzle is not justifiable in many scenarios. The same is especially true when applying a product similar to dicamba with a nozzle that produces Fine droplets that can cause severe damage to sensitive plants. On the other hand, droplets too large are difficult to retain on a leaf surface or to achieve high number densities of droplets because as one increases droplet diameter by a factor of 2, there is a reduction of 8x the number of droplets.

Increasing the application pressure had the smallest effect on droplet adsorption. This may be explained by first understanding that the trend with the nozzle types in this study is that as pressure increases, spray droplet size decreases, both of which are counteractive. Secondly, velocities for droplets with diameters between 200 and 400 µm are highly responsive to increasing spray pressure when those velocities are measured at a distance close to that of the ground, i.e. ~50 cm below the nozzle tip (Nuyttens et al. 2009). Thus, changes in application pressure to droplets with diameters below and above that range of droplet sizes would have minimal effect on changing the droplet velocity near the target leaves. Applications at 138 kPa had greater spray droplet adsorption than the other pressures. This could be attributed to the fact that herbicide solutions applied at lower pressures have spray droplets beginning at a slower velocity and reaching their sedimentation velocity quicker than when sprayed at higher pressures (Nuyttens et al. 2009). In the scenario of making applications at 138 kPa, droplets would impact the leaf surface with relatively low velocity and momentum, thus reducing droplet bounce and shatter.

Practical Implications

As environmental concerns instigated by the risk of herbicide spray drift shift the pendulum to larger spray droplet sizes, the proper selection and use of adjuvants and operating pressure can help ensure herbicide efficacy is not marginalized.

This experiment found that applying dicamba with no additional adjuvant significantly reduced the amount of spray droplets retained on leaf surfaces. The addition of adjuvants, particularly MSO, increased spray adsorption to the leaf surface. This research also found that coarser sprays are poorly retained on leaf surfaces, as compared to finer sprays. Additionally, lower-pressure applications increase adsorption compared to those at higher pressures. Although the XR nozzle should not be used for a dicamba application in the field, it helped to illustrate that smaller droplets are better retained on a leaf surface than larger droplets. Based on the results from this research, if applicators use the nozzle and adjuvant types and scenarios in this experiment, they should consider using Coarse to Extremely Coarse droplets at lower pressures to reduce drift potential while using MSO to achieve maximum droplet adsorption on the leaves. By understanding the impacts of these application parameters on dicamba spray droplet adsorption, applicators can select application parameters, equipment, and adjuvants that will maximize the amount of dicamba spray retained on the target leaf surface while minimizing dicamba spray drift potential.

This research can serve as a basis for future experiments as researchers attempt to define the ideal nozzle-adjuvant-pressure combination that will maximize herbicide performance by increasing spray droplet adsorption and transferring lethal doses to the plant while minimizing off-target movement due to spray drift. The adjuvants evaluated were applied at a single rate and were not combined with other adjuvants. Further research is needed to know if other rates or adjuvant combinations can be used to achieve a greater amount of droplet adsorption.

Acknowledgments

This research received no specific grant funding from any funding agency, commercial or not-for-profit sectors. The authors express their appreciation for the support received from members of Dr. Kruger’s lab in conducting this research.

Funding

This research received no specific grant from any funding agency, commercial or not-for-profit sectors.

Competing Interest

Competing interests: The author(s) declare none.

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Table 1. Source of materials used in spray droplet adsorption study.

Common name	Trade name	Treatment rate	Manufacturer
Dicamba	Clarity®	0.14 kg ae ha^{-1}	BASF Corporation, Research Triangle Park, NC, 27709
Methylated seed oil	Super Spread MSO®	1.0% v/v	Wilbur-Ellis Company, Fresno, CA, 94596
Non-ionic surfactant	R-11®	0.25% v/v	Wilbur-Ellis Company, Fresno, CA, 94596
Silicone adjuvant	Syl-Coat®	0.95 L ha^{-1}	Wilbur-Ellis Company, Fresno, CA, 94596
Crop oil concentrate	R.O.C. ®	1.0% v/v	Wilbur-Ellis Company, Fresno, CA, 94596
Drift agent	In-Place®	0.3 L ha^{-1}	Wilbur-Ellis Company, Fresno, CA, 94596

Table 2. ANOVA results from GLMMs analyzing the effect of the factors nozzles, pressure, and adjuvants on the spray droplet adsorption on common lambsquarters and soybean. Significant at $P < 0.05$.

Source of variation	X^2	Df	*P*-value
Lambsquarters			
Adjuvant	1572.19	5	<.001
Nozzle	440.73	2	<.001
Pressure	99.96	2	<.001
Adjuvant x Nozzle	254.94	10	<.001
Adjuvant x Pressure	58.02	10	<.001
Nozzle x Pressure	25.82	4	<.001
Adjuvant x Nozzle x Pressure	81.65	20	<.001
Soybean			
Adjuvant	1241.28	5	<.001
Nozzle	408.02	2	<.001
Pressure	28.43	2	<.001
Adjuvant x Nozzle	221.20	10	<.001
Adjuvant x Pressure	23.97	10	0.0076 **
Nozzle x Pressure	19.71	4	0.0005 ***
Adjuvant x Nozzle x Pressure	38.59	20	0.0074 **

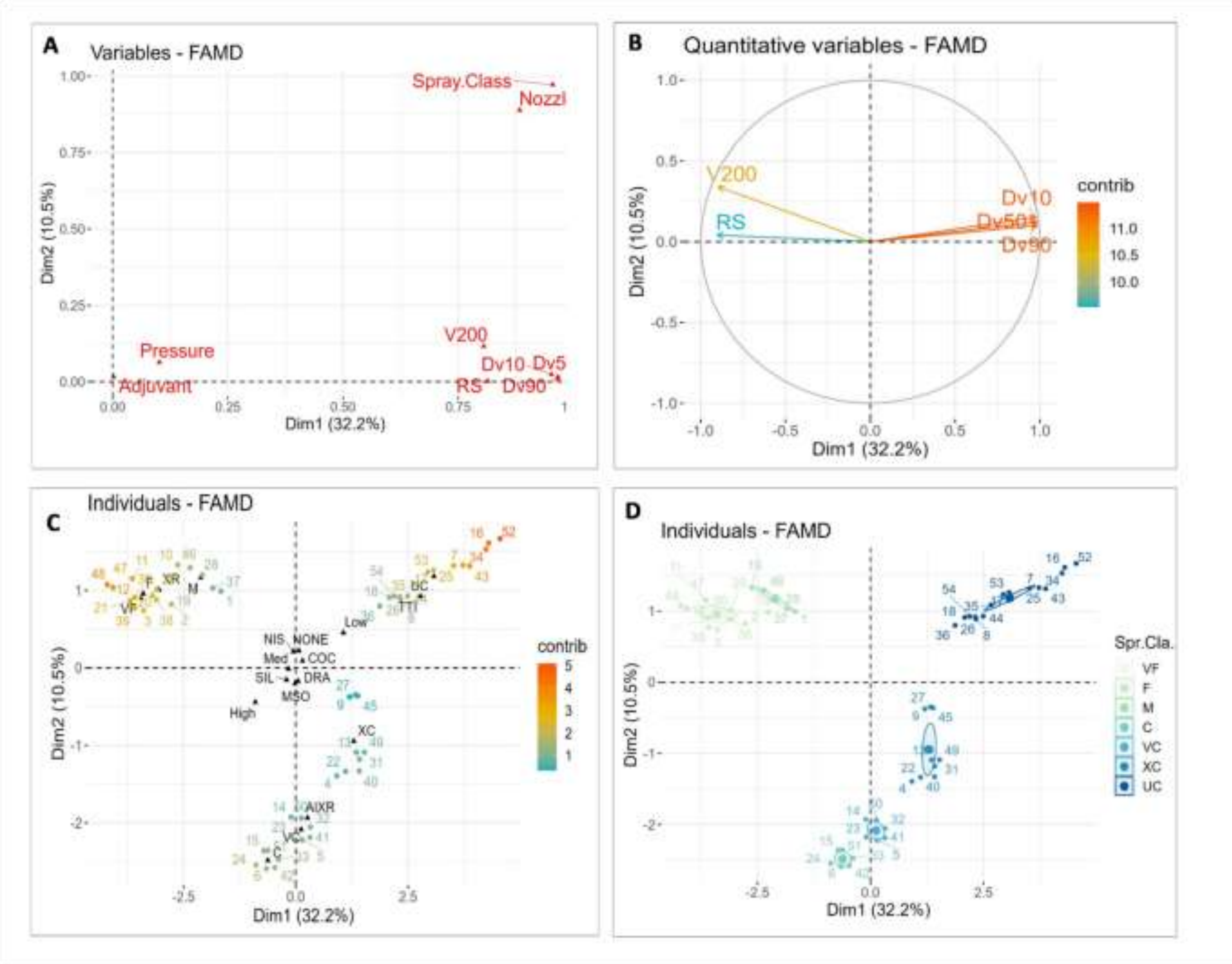

Figure 1. Results of the Factor Analysis of Mixed Data (FAMD) for the categorical (adjuvants, nozzles, pressures, and spray classification) and the quantitative (Dv10, Dv50, and Dv90, RS and <V200) variables. Dv10, Dv50, and Dv90 values represent the droplet diameter at which 10, 50, and 90% of the total spray volume, respectively, is composed of droplets of equal or lesser diameter; <V200 value represent the percentage of spray volume contained in droplets less than 200 µm for each adjuvant, nozzle, and pressure combination used. Variables representation (A); correlation circle underlining quantitative variables and their contribution to the first and second dimensions (B); individuals factor map underlining all variables and their projection to the first and second dimensions and all the 54 treatment combinations among adjuvant, nozzle, and pressure, respectively, (C) and individuals colored by spray classification (D). Individuals represent all 54 the treatment combinations are as follows: (1), MSO-XR-low; (2), MSO-XR-medium; (3), MSO-XR-

high; (4), MSO-AIXR-low; (5), MSO-AIXR-medium; (6), MSO-AIXR-high; (7), MSO-TTI-low; (8), MSO-TTI-medium; (9), MSO-TTI-high; (10), NIS-XR-low; (11), NIS-XR-medium; (12), NIS-XR-high; (13), NIS-AIXR-low; (14), NIS-AIXR-medium; (15), NIS-AIXR-high; (16), NIS-TTI-low; (17), NIS-TTI-medium; (18), NIS-TTI-high; (19), SIL-XR-low; (20), SIL-XR-medium; (21), SIL-XR-high; (22), SIL-AIXR-low; (23), SIL-AIXR-medium; (24), SIL-AIXR-high; (25), SIL-TTI-low; (26), SIL-TTI-medium; (27), SIL-TTI-high; (28), COC-XR-low; (29), COC-XR-medium; (30), COC-XR-high; (31), COC-AIXR-low; (32), COC-AIXR-medium; (33), COC -AIXR-high; (34), COC-TTI-low; (35), COC-TTI-medium; (36), COC-TTI-high; (37), DRA-XR-low; (38), DRA-XR-medium; (39), DRA-XR-high; (40), DRA-AIXR-low; (41), DRA-AIXR-medium; (42), DRA-AIXR-high; (43), DRA-TTI-low; (44), DRA-TTI-medium; (45), DRA-TTI-high; (46), NONE-XR-low; (47), NONE-XR-medium; (48), NONE-XR-high; (49), NONE-AIXR-low; (50), NONE-AIXR-medium; (51), NONE-AIXR-high; (52), NONE-TTI-low; (53), NONE-TTI-medium; (54), NONE-TTI-high. MSO (methylated seed oil), NIS (non-ionic surfactant), SIL (silicone), COC (crop oil concentrate), DRA (drift reduction agent), and NONE (Dicamba only, 0.14 kg ae ha^{-1}), denotate the six adjuvants. XR, AIXR, and TTI represent three nozzles and high, medium and low correspond to the three pressures, i.e., 138, 259, and 379 kPa. Spray classification was determined in accordance with ASAE S572.1 standards from reference curves generated using the same methods to determine spray quality of the treatments. Spray classification categories were derived from reference curves generated at the Pesticide Application Technology Laboratory per ASAE S572.1 where VF = Very Fine, F = Fine, M = Medium, C = Coarse, VC = Very Coarse, XC = Extremely Coarse, and UC = Ultra Coarse.

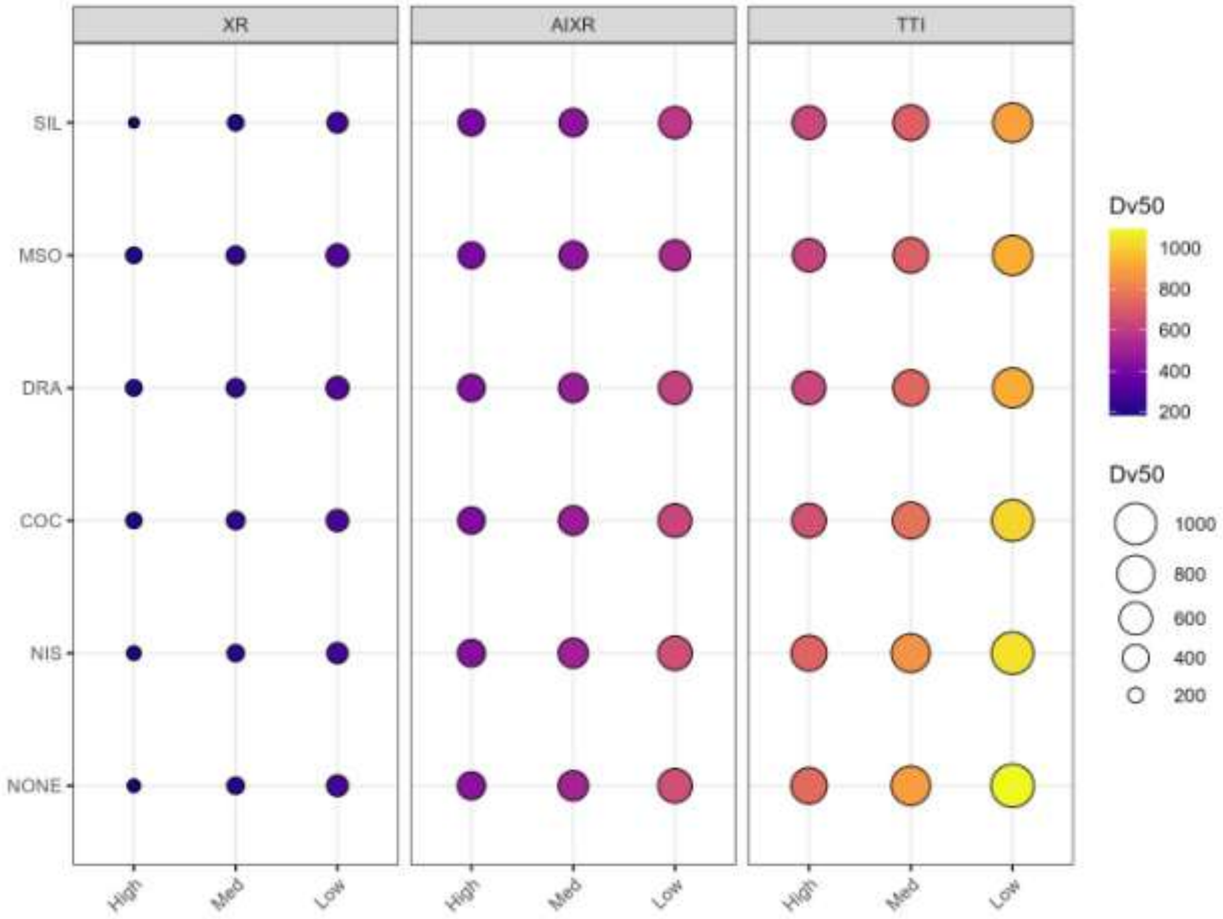

Figure 2. Representation of the volume median diameter (Dv50) polled over adjuvants and pressures by nozzles. Dv50 represents the droplet size diameter of equal of lesser value comprising 50% of the total spray volume. SIL (silicone), MSO (methylated seed oil), DRA (drift reduction agent), COC (crop oil concentrate), NIS (non-ionic surfactant), and NONE (Dicamba only, 0.14 kg ae ha^{-1}), denotate the six adjuvants. XR, AIXR, and TTI represent three nozzles and high, medium and low correspond to the three pressures, i.e., 138, 259, and 379 kPa.

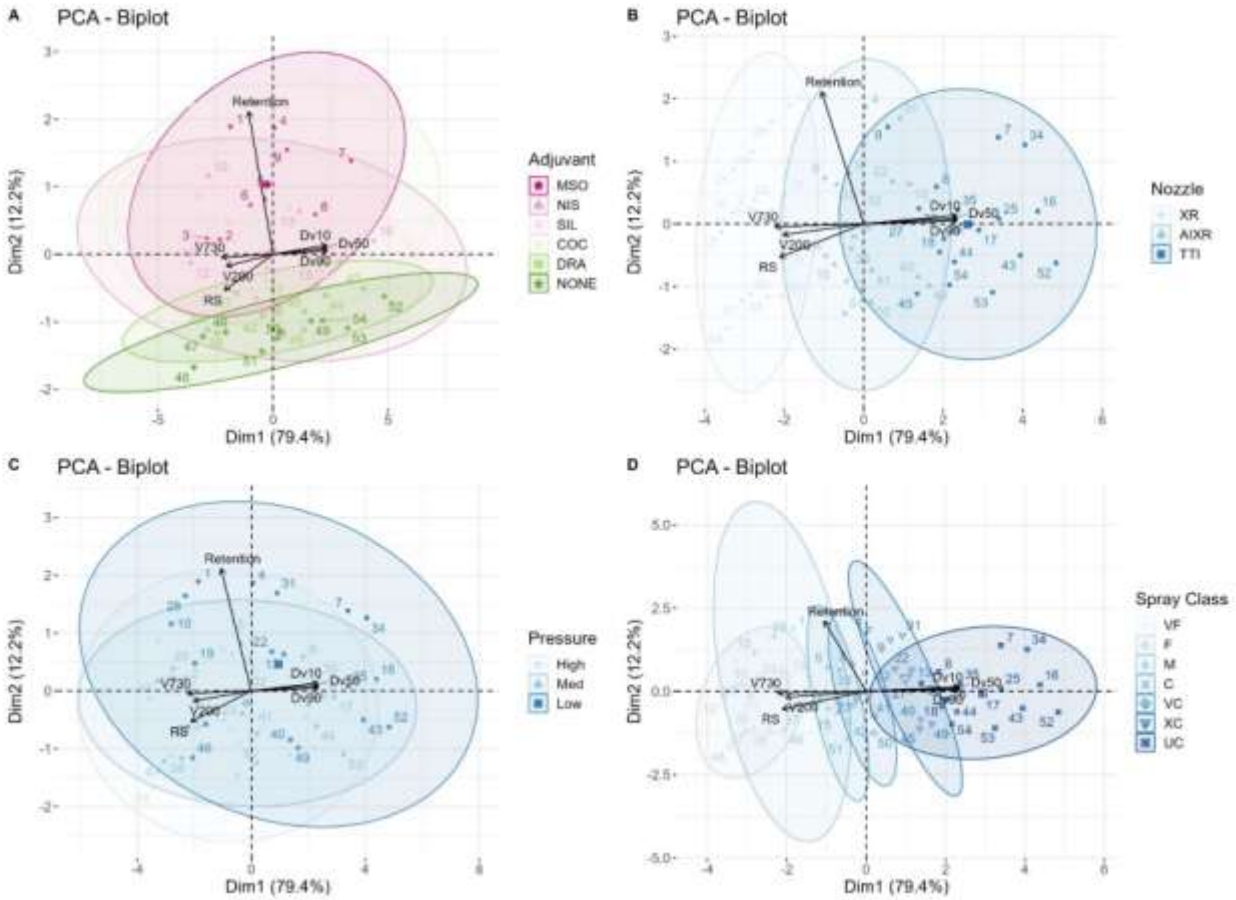

Figure 3. Biplot of the principal component analysis for lambsquarters variables, namely, spray droplet adsorption, Dv10, Dv50, and Dv90, RS, <V200 and <730 showing different groups and spatial distributions. <V200 and <V730 values represent the percentage of spray volume contained in droplets less than 200 µm AND 730 µm for each adjuvant, nozzle, and pressure combination used. MSO (methylated seed oil), NIS (non-ionic surfactant), SIL (silicone), COC (crop oil concentrate), DRA (drift reduction agent), and NONE (Dicamba only, 0.14 kg ae ha^{-1}), denotate the six adjuvants (A); XR, AIXR, and TTI represent three nozzles (B); high, medium and low correspond to the three pressures, i.e., 138, 259, and 379 kPa (C) and spray classification categories were derived from reference curves generated at the Pesticide Application Technology Laboratory per ASAE S572.1 where VF = Very Fine, F = Fine, M = Medium, C = Coarse, VC = Very Coarse, XC = Extremely Coarse, and UC = Ultra Coarse (D). Individuals represent all 54 the treatment combinations among adjuvant, nozzle and pressure, respectively, as follows: (1), MSO-XR-low; (2), MSO-XR-medium; (3), MSO-XR-high; (4), MSO-AIXR-low; (5), MSO-AIXR-medium; (6), MSO-AIXR-high; (7), MSO-TTI-low; (8), MSO-TTI-medium; (9), MSO-

TTI-high; (10), NIS-XR-low; (11), NIS-XR-medium; (12), NIS-XR-high; (13), NIS-AIXR-low; (14), NIS-AIXR-medium; (15), NIS-AIXR-high; (16), NIS-TTI-low; (17), NIS-TTI-medium; (18), NIS-TTI-high; (19), SIL-XR-low; (20), SIL-XR-medium; (21), SIL-XR-high; (22), SIL-AIXR-low; (23), SIL-AIXR-medium; (24), SIL-AIXR-high; (25), SIL-TTI-low; (26), SIL-TTI-medium; (27), SIL-TTI-high; (28), COC-XR-low; (29), COC-XR-medium; (30), COC-XR-high; (31), COC-AIXR-low; (32), COC-AIXR-medium; (33), COC -AIXR-high; (34), COC-TTI-low; (35), COC-TTI-medium; (36), COC-TTI-high; (37), DRA-XR-low; (38), DRA-XR-medium; (39), DRA-XR-high; (40), DRA-AIXR-low; (41), DRA-AIXR-medium; (42), DRA-AIXR-high; (43), DRA-TTI-low; (44), DRA-TTI-medium; (45), DRA-TTI-high; (46), NONE-XR-low; (47), NONE-XR-medium; (48), NONE-XR-high; (49), NONE-AIXR-low; (50), NONE-AIXR-medium; (51), NONE-AIXR-high; (52), NONE-TTI-low; (53), NONE-TTI-medium; (54), NONE-TTI-high.

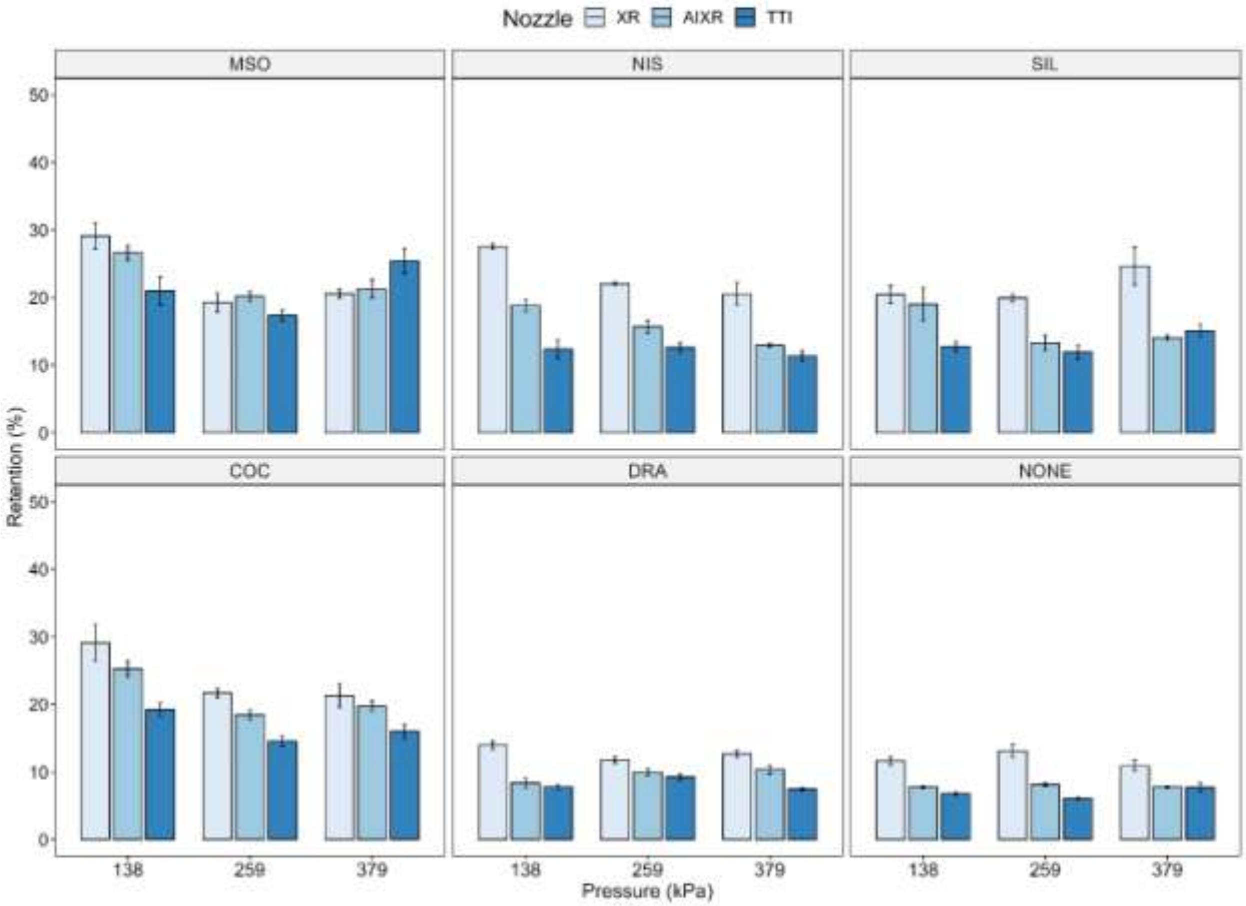

Figure 4. Spray droplet adsorption on common lambsquarters leaves as a percent of the total spray volume applied for each nozzle over pressure for each adjuvant. Values represent means and the bars the standard error of five independent biological replicates (n=5). MSO (methylated seed oil), NIS (non-ionic surfactant), SIL (silicone), COC (crop oil concentrate), DRA (drift reduction agent), and NONE (Dicamba only, 0.14 kg ae ha^{-1}), denotate the six adjuvants. XR, AIXR, and TTI represent three nozzles at 138, 259, and 379 kPa.

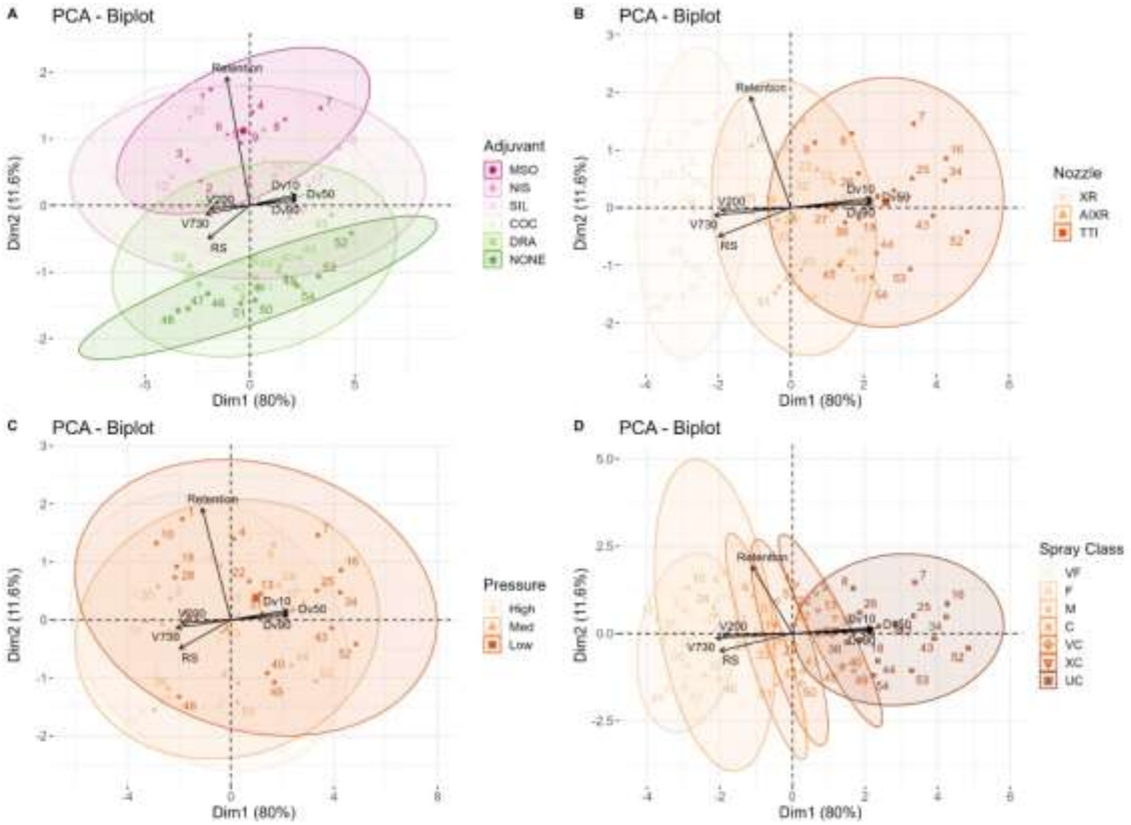

Figure 5. Biplot of the principal component analysis for soybean variables, namely, spray droplet adsorption, Dv10, Dv50, and Dv90, RS, <V200 and <V730 showing different groups and spatial distributions. MSO (methylated seed oil), NIS (non-ionic surfactant), SIL (silicone), COC (crop oil concentrate), DRA (drift reduction agent), and NONE (Dicamba only, 0.14 kg ae ha^{-1}), denotate the six adjuvants (A); XR, AIXR, and TTI represent three nozzles (B); high, medium and low correspond to the three pressures, i.e., 138, 259, and 379 kPa (C) and spray classification categories were derived from reference curves generated at the Pesticide Application Technology Laboratory per ASAE S572.1 where VF = Very Fine, F = Fine, M = Medium, C = Coarse, VC = Very Coarse, XC = Extremely Coarse, and UC = Ultra Coarse (D). Individuals represent all 54 the treatment combinations among adjuvant, nozzle and pressure, respectively, as follows: (1), MSO-XR-low; (2), MSO-XR-medium; (3), MSO-XR-high; (4), MSO-AIXR-low; (5), MSO-AIXR-medium; (6), MSO-AIXR-high; (7), MSO-TTI-low; (8), MSO-TTI-medium; (9), MSO-TTI-high; (10), NIS-XR-low; (11), NIS-XR-medium; (12), NIS-XR-high; (13), NIS-AIXR-low; (14), NIS-AIXR-medium; (15), NIS-AIXR-high; (16), NIS-TTI-low; (17), NIS-TTI-medium; (18), NIS-TTI-high; (19), SIL-XR-low; (20), SIL-XR-medium; (21), SIL-XR-high; (22), SIL-

AIXR-low; (23), SIL-AIXR-medium; (24), SIL-AIXR-high; (25), SIL-TTI-low; (26), SIL-TTI-medium; (27), SIL-TTI-high; (28), COC-XR-low; (29), COC-XR-medium; (30), COC-XR-high; (31), COC-AIXR-low; (32), COC-AIXR-medium; (33), COC -AIXR-high; (34), COC-TTI-low; (35), COC-TTI-medium; (36), COC-TTI-high; (37), DRA-XR-low; (38), DRA-XR-medium; (39), DRA-XR-high; (40), DRA-AIXR-low; (41), DRA-AIXR-medium; (42), DRA-AIXR-high; (43), DRA-TTI-low; (44), DRA-TTI-medium; (45), DRA-TTI-high; (46), NONE-XR-low; (47), NONE-XR-medium; (48), NONE-XR-high; (49), NONE-AIXR-low; (50), NONE-AIXR-medium; (51), NONE-AIXR-high; (52), NONE-TTI-low; (53), NONE-TTI-medium; (54), NONE-TTI-high.

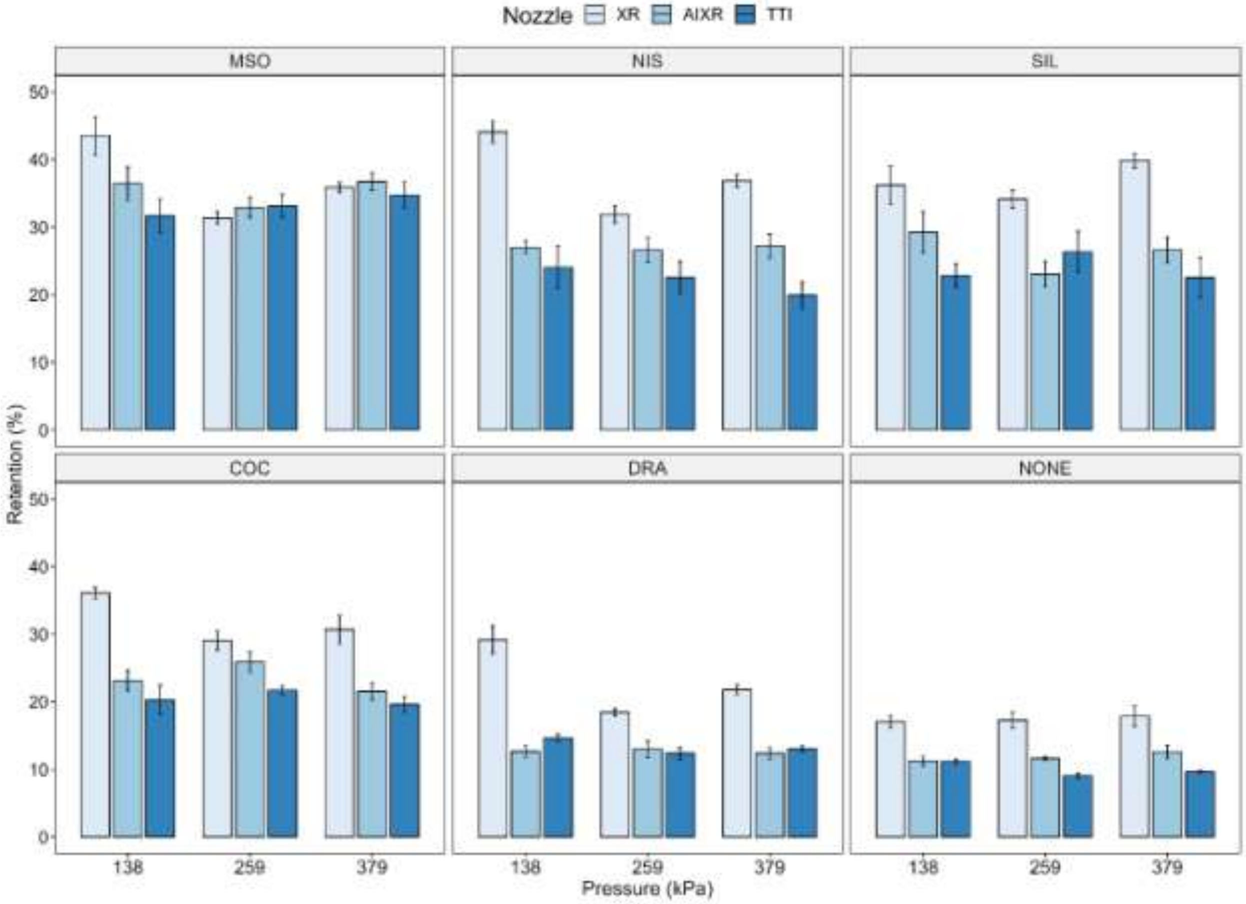

Figure 6. Spray droplet adsorption on soybean leaves as a percent of the total spray volume applied for each nozzle over pressure for each adjuvant. Values represent means and the bars the standard error of five independent biological replicates (n=5). MSO (methylated seed oil), NIS (non-ionic surfactant), SIL (silicone), COC (crop oil concentrate), DRA (drift reduction agent), and NONE (Dicamba only, 0.14 kg ae ha^{-1}), denotate the six adjuvants. XR, AIXR, and TTI represent three nozzles at 138, 259, and 379 kPa.