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2,4-D; glyphosate; giant ragweed, *Ambrosia trifida* L. AMBTR; horseweed, *Conyza canadensis* (L.) *Cronq.* ERICA; Palmer amaranth, *Amaranthus palmeri* S. Wats. AMAPA; tall waterhemp, *Amaranthus tuberculatus* (Moq.) *Sauer* (=*A. rudis*) AMATU; soybean, *Glycine max* (L.) Merr.; tomato, *Solanum lycopersicum* L.

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Glyphosate plus 2,4-D Deposition, Absorption, and Efficacy on Glyphosate-Resistant Weed Species as Influenced by Broadcast Spray Nozzle

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Abstract

The introduction of 2,4-D–resistant soybean will provide an additional POST herbicide site of action for control of herbicide-resistant broadleaf weeds. The introduction of this technology also brings concern of off-site movement of 2,4-D onto susceptible crops such as sensitive soybean and tomato. The 2,4-D formulation approved for use in 2,4-D–resistant soybean restricts application of the herbicide to nozzles that produce very coarse to ultra-coarse droplet spectrums. The use of larger droplet spectrums for broadcast applications can reduce herbicide deposition onto target weeds and thus influence herbicide efficacy. Field experiments were conducted to evaluate the influence of nozzle design on herbicide deposition onto target plants and the resulting efficacy of a POST application of 280 g ha^{-1} glyphosate plus 280 g ha^{-1} 2,4-D. The TTI11004 nozzle produced an ultra-coarse droplet spectrum and reduced coverage and deposition density on spray cards as compared with the XR11004 and TT11004 nozzles that produced medium droplet spectrums. The AIXR11004 nozzle also reduced deposition density on spray cards but did not reduce coverage. Herbicide solution deposition onto glyphosate-resistant Palmer amaranth, tall waterhemp, giant ragweed, and horseweed ranged from 0.28 to 0.72 µl cm^{-2} and was not influenced by nozzle design. Herbicide efficacy was reduced by the TTI11004 nozzle on Palmer amaranth and horseweed compared with the AIXR11004, TT11004, and XR11004 nozzles when applications were made to either high densities of plants or plants exceeding the labeled height. The use of the AIXR11004 and TTI11004 nozzles that are listed as approved nozzles for glyphosate plus 2,4-D applications on 2,4-D–resistant soybean did not reduce herbicide deposition onto four of the most troublesome broadleaves and did not reduce herbicide efficacy when applied in conjunction with lower weed densities and smaller weeds.

Introduction

Palmer amaranth, tall waterhemp, and horseweed are considered three of the most troublesome weeds in the United States, with horseweed ranked as the most troublesome in soybean (Van Wychen 2016). Rapid growth rates, prolific seed production, and obligate outcrossing contributing to wide genetic diversity are characteristics that make the two *Amaranthus* species especially troublesome in U.S. row-crop grain production (Franssen et al. 2001; Schwartz et al. 2016; Sellers et al. 2003). Variable emergence patterns, high seed production, and long-distance seed dispersal are characteristics that make horseweed problematic in soybean (Davis and Johnson 2008). Giant ragweed is considered one of the most problematic weeds in Indiana soybean (Gibson et al. 2005; Van Wychen 2016). The ability of giant ragweed to emerge across a wide range of conditions and its overall competitiveness in soybean make giant ragweed a major pest for soybean producers (Abul-Fatih and Bazzaz 1979; Baysinger and Sims 1991). All four weed species have also shown the ability to evolve herbicide resistance, with the *Amaranthus* species exhibiting resistance to six herbicide sites of action each; horseweed, resistance to four sites of action; and giant ragweed, resistance to two sites of action (Heap 2017). Horseweed and giant ragweed have been predominant dicot species in Indiana soybean for several decades. Palmer amaranth and tall waterhemp incidence and resistance has increased over the past 5 yr, with more than half of the state's counties confirmed to have Palmer amaranth, 26 counties with glyphosate-resistant tall waterhemp, and 10 counties with protoporphyrinogen oxidase inhibitor-resistant tall waterhemp (TR Legleiter and WG Johnson, personal communication). The introduction of soybean resistant to 2,4-D will provide an additional herbicide site of action for at-planting and POST control of these troublesome weeds, which are susceptible to this growth regulator herbicide (Craigmyle et al. 2013; Robinson et al. 2012; Wright et al. 2010).

The introduction of soybean resistant to 2,4-D also raises the concern of off-site movement of the growth regulator herbicide to sensitive vegetation in adjacent areas, especially during

POST applications, when more susceptible vegetation is actively growing, as compared with the traditional burndown timing, when susceptible species are not as abundant or actively growing (Johnson et al. 2012). The concern of off-site movement is especially heightened with 2,4-D, a phenoxy herbicide that is active on dicot plants at relatively low doses and that cause unique injury symptoms of leaf cupping, epinasty, and leaf malformation (Marth and Mitchell 1944; Robinson et al. 2013). Fields of soybean lacking the 2,4-D resistance trait that are adjacent to 2,4-D–resistant soybean fields and will be prone to crop injury due to off-site movement (Robinson et al. 2013; Wax et al. 1969). High-value crops such as tomatoes grown on 3,000 ha in Indiana, often within close proximity to soybean fields, are especially prone to off-site movement, due to their high sensitivity to growth regulator herbicides, and yield reductions, especially during reproductive stages when POST applications are likely to occur (Jordan and Romanowski 1974; USDA 2014). The preservation of 2,4-D–resistant soybean as a viable technology for control of tough broadleaves will depend on the applicator's ability to minimize off-target movement of the herbicide.

A number of herbicide application factors, including weather conditions, boom height, herbicide formulation, and droplet size, can influence the amount of off-site movement or drift during application (Carlsen et al. 2006; Combellack 1982). Applicators cannot control the weather conditions, but rather must wait until conditions are favorable to minimize off-site movement. Other factors that contribute to spray drift can be controlled directly by the applicator and will be an important focus for herbicides labeled for 2,4-D–resistant soybean. The only herbicide labeled specifically for use in 2,4-D–resistant soybean is Enlist Duo® (Dow AgroSciences, 9330 Zionsville Road, Indianapolis, IN 46268), a mixture of 2,4-D choline salt and glyphosate. The label requires the use of specific combinations of nozzle type, nozzle orifice size, and spray pressure during herbicide applications (Anonymous 2017). Nozzle type, nozzle orifice size, and pressure all contribute to spectrum of droplet sizes in the spray pattern during application (Combellack 1982; Nuyttens et al. 2007). Droplet spectrum or droplet size has a large impact on herbicide drift, because larger droplets are less apt to move horizontally due to their larger mass and reduced time in the state of fall to their intended target (Bode 1987). A majority of the nozzles allowed for use by the Enlist Duo® label include pre-orifice and/or air-induction designs that produce larger droplet spectrums as compared with single-stage flat-fan nozzles with similar orifice sizes (Anonymous 2017; Johnson et al. 2006).

The use of pre-orifice and air-induction design nozzles will minimize drift, although it is well documented that increasing droplet size generally decreases herbicide coverage and herbicide performance (Knoche 1994). The effect of spray coverage on target plants for foliar herbicide efficacy largely depends on the type of herbicide. Systemic herbicides such as glyphosate and 2,4-D are less effected by decrease in coverage due to the use of nozzles producing large droplets (Ramsdale and Messersmith 2001). Knoche (1994) suggested that while droplet size is a major factor of herbicide coverage, the specific herbicide formulation, targeted plant species, and any interfering filters such as a crop canopy must be considered. A majority of studies on the effect of droplet size on herbicide coverage exclude the influence of crop canopy, although a couple of studies have shown that a soybean canopy can filter droplets and reduce spray coverage lower in the canopy (Bradley and Sweets 2008; Hanna et al. 2008).

The use of 2,4-D–resistant soybean varieties and subsequent POST applications of 2,4-D are likely to be adopted first in fields with tough-to-control and glyphosate-resistant weeds such as Palmer amaranth, tall waterhemp, giant ragweed, and horseweed (Norsworthy et al. 2012). The use of PRE herbicides in combination with a timely POST herbicide application will be recommended to provide greater control of glyphosate-resistant Palmer amaranth, tall waterhemp, horseweed, and giant ragweed as compared with a POST-only strategy and to relieve pressure on the POST herbicide application (Legleiter et al. 2009; Whitaker et al. 2010). The use of a PRE herbicide will delay the timing of sequential POST application, which will therefore be made to soybean with greater plant heights and more developed canopies (Legleiter et al. 2009).

The objective of the experiments described here was to evaluate the influence of spray-droplet spectrums on the deposition, absorption, and efficacy of POST 2,4-D choline plus glyphosate (Enlist Duo®) applications on glyphosate-resistant Palmer amaranth, tall waterhemp, giant ragweed, and horseweed occurring in soybean, including the evaluation of two traditional flat-fan nozzles and two label-required air-induction nozzles.

Materials and Methods

Field Sites

Field experiments were conducted in 2014, 2015, and 2016 at locations with glyphosate-resistant horseweed, giant ragweed, tall waterhemp, and Palmer amaranth. Experiments were conducted for 2 site-years for each species, with the exception of Palmer amaranth, which had 3 site-years of herbicide-efficacy data collected. Locations and years of field experiments can be found in Table 1. Glyphosate-resistant soybean ('Asgrow® 2933,' Monsanto, St. Louis, MO) was planted at all sites in a 38-cm row spacing at seeding rates between 321,000 and 370,000 seeds ha^{-1}. Planting dates for each location are listed in Table 1. Any vegetation in the experiment site at planting was removed either with tillage or an application of paraquat, with the exception of the 2016 Brookston horseweed site, which was planted into an existing stand of horseweed. Due to a known high seedbank population at the Twelve Mile Palmer amaranth site, acetochlor (Warrant®, Monsanto) at 840 g ha^{-1} was applied to suppress Palmer amaranth emergence and allow for soybean emergence and canopy development before the POST applications.

Herbicide Applications and Experiment Design

Plots measured 3-m wide by 8-m long and were arranged in a randomized complete block design with six replications. Treatments were applied using an all-terrain vehicle fitted with a 2-m side-mounted boom with four nozzles positioned at 50-cm spacing. To mimic a commercial application, the nozzles orifices had an output of 1.5 L min^{-1}, the vehicle travel speed was 19 km h^{-1}, and the system pressure was 276 kPa for a total output of 94 L ha^{-1}.

Four 110° broadcast flat-fan nozzles from TeeJet® (TeeJet Technologies, Glendale Heights,IL) were selected as treatments based on their designs to represent: a traditional flat-fan nozzle with no drift-reduction attributes (XR11004); a pre-orifice and turbulence chamber design flat-fan nozzle (TT11004); a pre-orifice and air-induction design flat-fan nozzle (AIXR11004); and a pre-orifice, air-induction, and turbulence chamber design

Table 1. Planting date, date of herbicide application, and application parameters for the Palmer amaranth, tall waterhemp, giant ragweed, and horseweed site-years.

Site-year[a]	Weed species	Planting date	Treatment date	Soybean stage	Weed height	Weed density	Temperature	Relative humidity	Wind speed
				Trifoliate	cm	m^{-2}	C	%	km h^{-1}
TWM 2014	AMAPA	May 6	June 13	4	10–15	5–15	21	43	16
EVV 2014	AMAPA	May 28	June 25	6	15–20	5–10	31	50	5
MDV 2015	AMAPA	May 20	July 15	8	5–15	0.5–2	23	74	10
MGS 2014	AMATA	May 8	June 22	6	15–20	10–20	24	76	6
MGS 2015	AMATA	May 14	June 28	5	10–15	20–50	22	64	0
WL 2015	AMBTR	May 29	June 19	2	10–15	2–5	21	91	8
WL 2016	AMBTR	April 25	June 3	3	10–15	1–5	25	56	0
MGS 2015	ERICA	May 7	June 20	4	10–15	2–3	22	92	2
BRK 2016	ERICA	May 20	June 11	1	8–30	50–70	29	58	8

[a] Abbreviations: BRK, Brookston, IN; EVV, Evansville, IN; MDV, Medaryville, IN; MGS, Meigs South Research Facility, IN; TWM, Twelve Mile, IN; WL, West Lafayette, IN.

flat-fan nozzle (TTI11004). The AIXR11004 and TTI11004 nozzles both represented drift-reduction technologies (DRTs) that are on the list of required flat-fan nozzles for POST applications of Enlist Duo®.

The herbicide spray solution consisted of Enlist Duo® at a rate of 560 g ae ha^{-1} (280 g ae ha^{-1} glyphosate plus 280 g ha^{-1} 2,4-D) plus ammonium sulfate (N-Pak® AMS Liquid, Winfield Solutions, St Paul, MN) at 5% v/v. A lower than labeled herbicide rate was used to maximize any efficacy differences between treatments. Pink foam marker dye (Vision Pink™, Garrco Products, Converse, IN) was also included in the spray mixture at a 0.25% v/v, as was a 1,3,6,8-pyrenetetrasulfonic acid (PTSA) fluorescent dye (Spectra Trace SH-P, Spectra Colors, Kearny, NJ) at 600 μg ml^{-1}.

Spray Droplet–Spectrum Analysis

An analysis of the spray-droplet spectrum for each of the nozzle treatments evaluated in the field experiment was conducted to broaden the applicability of the data beyond the four specific nozzles. Spray droplet–spectrum analysis was conducted using the same herbicide mix that was used in the field at the discriminating rate (glyphosate at 280 g ae ha^{-1} plus 2,4-D at 280 g ha^{-1}) and the full labeled rate (glyphosate at 1,120 g ae ha^{-1} plus 2,4-D at 1,120 g ha^{-1}).

Spray-droplet analysis was conducted at the Pesticide Application Technology laboratory at the University of Nebraska West Central Research and Extension Center (UNL PAT). Analysis of each nozzle type was conducted on one randomly selected nozzle of the four nozzles that were used in the field. Nozzle tips were flow rated before analysis to ensure that damage had not occurred to the tip orifice during field applications. Laser diffraction with a Sympatec Helos Vario KR particle-size analyzer equipped with an R7 lens was used to analyze spray-droplet size. The entire spray plume was analyzed three times by traversing the nozzle vertically through the laser in a low-speed wind tunnel with air velocities of 24 km h^{-1} to evacuate droplets from the laser path after analysis. The analysis output report included the Dv10, Dv50, and Dv90, which report the percentage (10, 50, and 90, respectively) of droplets in the spray volume that are at or below the reported diameter. A reference curve established at the UNL PAT lab per the American Society of Agricultural and Biological Engineers (ASABE) S542.1 was used to classify each nozzle into a droplet category based on the Dv10 and Dv50 values.

Data Collection and Analysis

Spray-Solution Coverage and Deposition Density

Spray-solution coverage and deposition density collected using Kromekote-coated card stock (Kromekote C1S by CTI, Glodan, Mount Carmel, PA) showed definite marking of deposition from the foam marker dye included in the spray solution. Five 5-cm by 7.6-cm cards were placed at the height of the target weed species on metal holders inserted in a diagonal pattern between two soybean rows to capture spray deposition at all positions between soybean rows. Cards were placed on holders immediately before the herbicide application. Following application, the spray solution was allowed to dry, and cards were then placed in plastic bags and stored until analysis.

The deposition cards were converted into 600 by 600 dpi, 24-bit color digital images using a duplex scanner (Image Center™ ADS-2000, Brother InternationalBridgewater, NJ). Digital images were analyzed using APS ASSESS v. 2.0 (ASSESS 2.0–Image Analysis Software for Plant Disease Quantification, American Phytopathological Society, St Paul, MN) to separate the pink depositions from the white card background. Output from the ASSESS analysis included area of deposition coverage (mm^2) and deposition counts. The area of deposition coverage was manually converted to percent coverage, and counts were converted to deposition density using the known size of the cards. Individual cards were treated as subsamples of the whole plot, differences in percent deposition coverage and density were determined with ANOVA using SAS v. 9.4 PROC MIXED (SAS Institute, Cary, NC), and means were separated at $\alpha = 0.05$ adjusted for Tukey's honest significant difference (HSD). Spray coverage and deposition density means within a species were pooled across site-years when differences between site-years did not occur.

Herbicide Solution Deposition on Target Weeds

Immediately following the herbicide application, one target weed, representative of the average height, was cut at the soil surface and washed with 200 ml of a nonionic surfactant (Triton™ X-100, EMD Chemicals, Gibbstown, NJ) and water (1:1000) solution. Due to a large variation in horseweed height at the 2016 Brookston site, crewmembers were instructed to collect horseweed plants in the 10- to 15-cm height range and with minimal overhead interference from larger plants. Wash procedures consisted of using a syringe to pull 40 to 50 ml of wash solution from the collection vial, grasping the target with forceps and cutting it at soil level, and then placing the plant material into the wash solution and agitating it for 30 s, after which the plant was rinsed with the solution in the syringe upon removal from the vial. Forceps were washed with a methanol and water solution (1:1) between treatments to avoid cross contamination. Washed plants were placed in paper envelopes and transported to the laboratory, where whole plant leaf area (cm^2) was analyzed using a leaf-area meter LI-3100 (Li-Cor, Lincoln, NE).

Wash solutions were quantified for raw fluorescence with a laboratory fluorometer (Trilogy Laboratory Fluorometer, Turner Designs, San Jose, CA) equipped with a PTSA-specific module. Raw fluorescence values were plotted on a previously established standard curve (0.0001 to 1 $\mu g\ ml^{-1}$) to determine the quantity of PTSA in the wash solution. Spray-solution deposition on the target plant surface ($\mu l\ cm^{-2}$) was calculated using the PTSA in the wash solution ($\mu g\ ml^{-1}$), known volume of the wash solution (200 ml), known rate of PTSA in the spray solution (600 $\mu g\ ml^{-1}$), and the leaf area of the plant (cm^2). Differences in deposition of the spray solution on the target surface were determined with ANOVA using SAS v. 9.4 PROC MIXED, means were separated with Tukey's HSD at $\alpha = 0.05$. Herbicide solution deposition means within a species were pooled across site-years when differences between site-years were not significant.

2,4-D Concentration on Leaf Surface

Immediately following the herbicide application and at 2, 4, 6, and 24 h after herbicide applications, one leaf from a target species plant that was separate from the plants analyzed in the previous section was collected from each replication. The leaf was selected from a plant of the target height described in the previous section, and the leaf harvested was the node below the newest fully expanded leaf. The leaf was washed in 50 ml of 1:1 water and high-performance liquid chromatography–grade methanol solution. A syringe was used to pull 10 ml of clean solution from the 50-ml vial before introducing any leaf material, and the leaf was agitated in the remaining solution for 30 s. The leaf was then rinsed with the solution from the syringe as it was pulled from the wash solution vial. Wash solutions were stored a climate-controlled laboratory in closed cardboard boxes until preparation and analysis. The leaf area and biomass of the leaves were measured in the lab following collection. Leaf wash solutions were collected from all six replication, although the following sample preparations and analysis were only conducted on three of those replicates.

Wash solutions were prepared for analytical analysis by taking a 1-ml aliquot of wash solution and adding 500 ng of d_5-2,-D (CDN Isotopes, Pointe-Claire, QC, Canada) as an internal standard. The samples were then dried in a vacuum concentrator, derivatized by adding 40 µl anhydrous pyridine and 60 µl n-methyl-n-(trimethylsilyl) trifluoroacetamide, and finally heated for 1 h at 60 C.

Levels of 2,4-D were determined using a gas chromatography/mass spectrometry– mass spectrometry analysis. The gas chromatograph was a 1310 Thermo TRACE™ (Thermo Fisher Scientific, Waltham, MA) using a Thermo TG-SQC column (15 m by 0.25 mm by 0.25 µm). A 1-µl injection volume was used with an inlet temperature of 250 C with a 10:1 inlet split ratio and column flow of 1.5 $ml\ min^{-1}$. The thermal gradient had an initial temperature of 120 C, held for 1 min, then 20 C min^{-1} increases up to 320 C, and then held for 3 min. The retention time for 2,4-D was 4.1 min.

Analytes were then quantified with a Thermos TSQ Evo 8000 triple-quadrupole mass spectrometer. Positive chemical ionization mode was used with a methane flow rate of 1.0 $ml\ min^{-1}$. Quantitation was based on multiple reaction monitoring. A transition of 292 to 257 was used for 2,4-D and 297 to 262 for d_5-2,4-D. A collision energy of 5 V was used for all transitions. Data were collected and analyzed with Thermo Chromeleon v. 7.2 SR4 software. Responses for 2,4-D were normalized and quantitated against their respective internal standards.

Quantities of 2,4-D from the wash samples were then converted to nanograms of 2,4-D per square centimeter of leaf surface area using the previously measured leaf areas. A two-factor ANOVA was used to evaluate differences in nanograms of 2,4-D per square centimeter between nozzles and collection times. Analysis was conducted using SAS v. 9.4 PROC MIXED. Means were pooled across years for each species to maximize the replications per treatment. Mean separation was performed using Tukey's HSD, $\alpha = 0.05$.

Herbicide Efficacy

All efficacy ratings and measurements were taken 21 d after application. Plots were visually evaluated for control, with 0 representing no control and 100 representing complete control. Height measurements were taken for 3 plants $plot^{-1}$ and for 3 plants within the untreated strips of each replication in the Palmer amaranth, tall waterhemp, and horseweed experiments. Height measurements were not taken in the giant ragweed experiments due to overall high efficacy and lack of measurable plants. Height measurements were treated as subsamples and converted to percent height reduction using the untreated strip heights.

Visual evaluations and height reduction data were analyzed with ANOVA using SAS v. 9.4 PROC MIXED, means were separated using Tukey's HSD at $\alpha = 0.05$. Visual evaluation means of Palmer amaranth, tall waterhemp, and giant ragweed were pooled across site-years within each species due to similarities in mean differences. Percent height reduction means of tall waterhemp were pooled across site-years due to similarities in treatment mean differences.

Results and Discussion

Spray Droplet–Spectrum Analysis

As expected, the lowest Dv50 occurred with the single-stage XR11004 nozzle, and the highest occurred with the TTI11004, which has three drift-reduction design elements (Table 2). The two designated DRT nozzles that appear on the Enlist Duo® label both had Dv10 values above 200 µm, indicating both nozzles produce less than 10% driftable fines. The broadcast-nozzle droplet spectrums were placed into classification categories in accordance with ASABE S542.1 for both the discriminating dose used in the field experiment and a full dose or labeled rate that will be used for commercial agricultural applications. The XR11004 nozzle produced a medium droplet spectrum for

Table 2. Dv10, Dv50, Dv90, and the spray classification category for each nozzle at discriminating and full rates of glyphosate plus 2,4-D.

Nozzle	Herbicide rate[a]	Dv10[b]	Dv50[b]	Dv90[b]	Spray classification category[c]
			——————————— μm ———————————		
XR11004	Discriminating	140	279	445	Medium
	Full	134	271	433	Medium
TT11004	Discriminating	162	327	543	Medium
	Full	172	390	683	Coarse
AIXR11004	Discriminating	244	462	693	Very coarse
	Full	239	472	732	Very coarse
TTI11004	Discriminating	349	674	1,018	Ultra-coarse
	Full	434	867	1,315	Ultra-coarse

[a] Discriminating rate: 280 g ha^{-1} glyphosate plus 280 g ha^{-1} 2,4-D; full rate: 1,120 g ha^{-1} glyphosate plus 1,120 g ha^{-1} 2,4-D.
[b] Dv10, Dv50, and Dv90: the percentage (10, 50, and 90, respectively) of droplets in the spray volume that are at or below the reported diameter.
[c] Spray classification categories assigned using reference curve generated at the UNL PAT lab in accordance with ASABE S542.1.

both rates, while the two DRT nozzles, AIXR11004 and TTI11004, produced very coarse and ultra-coarse droplet spectrums at both rates, respectively (Table 2). The TT11004 nozzle was the only nozzle that produced differing droplet spectrum classifications between the discriminating and full herbicide rate, with the discriminating rate producing a spectrum of medium droplets and the full rate producing a coarse droplet spectrum. These droplet classifications were compared with categories computed by the UNL PAT lab Web calculator for the same nozzles and pressures using a water solution. All of the nozzles tested fell within the same category as calculated by the Web tool, with the exception of the XR, which was in the fine category on the calculator and medium in our analysis. When the Dv50 numerical values were compared, the full herbicide rate was higher than that of the discriminating rate for all nozzles except the XR11004. These differences can be attributed to the Enlist Duo® formulation, because pesticides and adjuvants can alter the droplet spectrum (Miller and Ellis 2000). The increased rate of this formulation had the added benefit of increasing the droplet size, even if only slightly, and as to not change the droplet size classification with the exception of one nozzle.

Although the following deposition and efficacy results were obtained using discriminating doses and a limited number of nozzles, the spray classification allows for a comparison of deposition and efficacy within a spray-droplet category rather than for a specific nozzle. The similarities of the droplet spectrum categories between herbicide rates for the two DRT nozzles also allows us to evaluate the deposition data without concern for the herbicide rate.

Spray-Solution Coverage and Deposition Density

Spray-solution coverage was decreased by the ultra-coarse TTI11004 nozzle in the 2015 tall waterhemp, giant ragweed, and horseweed sites as compared with the other nozzles evaluated (Table 3). The TTI11004 also reduced coverage as compared with the AIXR11004 in the 2014 Palmer amaranth experiment, although coverage was similar to that of the two non-DRT nozzles. The AIXR11004 nozzle that produced very coarse droplets and is a required DRT nozzle did not differ in coverage as compared with the two smaller droplet–producing non-DRT nozzles across all species and site-years (Table 3).

Deposition density was lowest for the ultra-coarse droplet–producing TTI11004, with 10 to 22 deposits cm^{-2} (Table 4). The very coarse AIXR11004 nozzle had increased densities of 15 to 35 deposits cm^{-2} as compared with the TTI11004 nozzle. The two non-DRT nozzles produced higher spray deposition densities ranging from 24 to 62 deposits cm^{-2} (Table 4). The decreased deposition density with increasing droplet size and a fixed carrier volume would be expected, and is a possible concern for commercial

Table 3. Glyphosate plus 2,4-D solution coverage on spray cards placed at the height of Palmer amaranth, tall waterhemp, giant ragweed, and horseweed at a POST application.

	AMAPA		AMATA			
Broadcast nozzle	2014	2015	2014	2015	AMBTR[a]	ERICA[a]
	——————————————— % coverage[b] ———————————————					
XR11004	16.6 AB	17.0 A	10.7 A	19.9 A	24.2 A	21.6 A
TT11004	16.6 AB	11.4 A	11.4 A	21.6 A	23.0 A	20.8 A
AIXR11004	18.2 A	11.9 A	12.8 A	20.6 A	22.1 A	21.5 A
TTI11004	14.5 B	12.9 A	11.4 A	14.7 B	18.4 B	17.9 B

[a] Means pooled across site-years.
[b] Means within a column followed by a different letter are significantly different using Tukey's HSD ($\alpha = 0.05$).

Table 4. Glyphosate plus 2,4-D deposition counts per square centimeter on spray cards placed at the height of Palmer amaranth, tall waterhemp, giant ragweed, and horseweed at a POST application.

Broadcast nozzle	AMAPA[a]	AMATA 2014	AMATA 2015	AMBTR 2015	AMBTR 2016	ERICA[a]
	——— no. droplet cm^{-2b} ———					
XR11004	38 A	25 A	58 A	55 A	62 A	52 A
TT11004	27 B	24 A	55 A	43 B	58 A	45 A
AIXR11004	19 C	15 B	34 B	29 C	35 B	30 B
TTI11004	12 D	10 C	16 C	16 D	22 C	17 C

[a] Means pooled across site-years.
[b] Means within a column followed by a different letter are significantly different using Tukey's HSD ($\alpha = 0.05$).

applications. The decreased spray coverage with the TTI11004 nozzle that produced ultra-coarse droplets was also expected, as previous research has shown a decrease in coverage as droplet size increases (Knoche 1994).

The use of deposition cards is valuable in showing differences in deposition density and estimation of solution coverage. Although the cards provide an effective estimate of coverage, the differences in plant architectures, leaf angles, and surfaces warrant investigation of spray deposition onto target weeds.

Herbicide Solution Deposition on Weed Species

Deposition of the herbicide solution on Palmer amaranth ranged from 0.52 to 0.62 µl cm^{-2} in 2014 and 0.28 to 0.45 µl cm^{-2} in 2015 (Table 5). Tall waterhemp solution deposition was 0.38 to 0.49 µl cm^{-2} and 0.52 to 0.57 µl cm^{-2} in 2014 and 2015, respectively (Table 5). The range of herbicide solution deposition on giant ragweed was 0.54 to 0.72 µl cm^{-2} in 2015 and 0.4 to 0.53 µl cm^{-2} in 2016 (Table 5). Herbicide solution deposition on horseweed was similar between site-years and ranged from 0.39 to 0.46 µl cm^{-2} (Table 5). The differences in herbicide solution deposition between years for Palmer amaranth, tall waterhemp, and giant ragweed was likely due to differences in soybean canopy development, because the herbicide applications were timed to weed height and cooperating weather conditions rather than soybean canopy development. All three weed species had less herbicide solution deposition in the year in which the soybean canopy had a greater number of trifoliates (Tables 1 and 5). Differences in herbicide solution deposition were expected on horseweed between years, as there was a difference of three trifoliate leaves in soybean canopy development, although solution deposition was similar between years. These similarities between years was likely due to the high density and large range of weed heights at the 2016 Brookston site, which provided canopy coverage that would have been similar to the soybean canopy at the 2015 Meigs site. Variabilities in this experimental design may have also been lessened if more plants per replication had been collected for herbicide solution deposition.

The theoretical maximum herbicide solution deposition is 0.935 µl cm^{-2}, which is a conversion of the field application rate of 94 L ha^{-1} to µl cm^{-2}. The herbicide solution deposition values in these experiments ranged from 30% to 77% of the theoretical maximum. A loss in deposition compared with the theoretical maximum would be expected, because the application is occurring under field conditions and is being applied to a surface of variable leaf angles and structures rather than a flat surface.

Despite differences that occurred between site-years, there were no differences in herbicide solution deposition observed between broadcast-nozzle types within weed species. The DRT broadcast nozzles that produced larger droplet spectrums achieved deposition onto target weed species equivalent to those of traditional smaller droplet–producing broadcast nozzles. The evaluation of herbicide solution deposition onto four troublesome broadleaf weeds across multiples site-years in this experiment showed that differences in deposition are more likely influenced by the development of soybean canopy and weed density than the broadcast-nozzle design and the droplet spectrums that are produced due to those designs.

Table 5. Deposition of glyphosate plus 2,4-D spray solution on target plants of Palmer amaranth, tall waterhemp, giant ragweed, and horseweed.

Broadcast nozzle	AMAPA 2014	AMAPA 2015	AMATA 2014	AMATA 2015	AMBTR 2015	AMBTR 2016	ERICA[a]
	——— µl cm^{-2} ———						
XR11004	0.52	0.45	0.40	0.52	0.72	0.40	0.40
TT11004	0.57	0.36	0.38	0.56	0.65	0.53	0.39
AIXR11004	0.53	0.28	0.45	0.57	0.59	0.43	0.46
TTI11004	0.61	0.38	0.49	0.52	0.54	0.42	0.40
P	0.4426	0.7723	0.3687	0.7176	0.3957	0.3365	0.1527

[a] Means pooled across site-years.

2,4-D Concentration on Leaf Surface

The 2,4-D concentration on the leaf surface was not influenced by nozzle or the interaction of nozzle and time after application, although time after application was significant for all four weed species ($P < 0.0001$) (Figure 1). The concentration of 2,4-D on the leaf surface was greatest at the 0 hour time for all four weed species and ranged from 1,154 to 1,806 ng 2,4-D cm^{-2} leaf surface area (Table 6). In comparison to the field application rate of 2,800 ng cm^{-2}, converted from 280 g ha^{-1}, the concentration of 2,4-D on the leaf surface immediately after application was 41% to 65% of the target application, a similar range as was found with fluorescent dye washes. Levels of 2,4-D on the leaf surface were reduced at 4 h on Palmer amaranth and at 2 h for waterhemp, giant ragweed, and horseweed. Concentrations continued to decline over time on the leaf surface for the two amaranth species, while giant ragweed and horseweed levels remained constant from 2 to 24 h (Table 6).

The droplet spectrum size of the nozzle used to make the application did not influence the absorption of 2,4-D in Palmer amaranth, waterhemp, giant ragweed, and horseweed, as the concentrations on the surface of the leaf at all time points were similar between all four nozzles. The use of drift-reduction nozzles that produce very coarse and ultra-coarse droplet spectrums did not influence the absorption of 2,4-D by four glyphosate-resistant dicot species using the methods of this study.

Table 6. Concentration of 2,4-D on the leaf surface of Palmer amaranth, waterhemp, giant ragweed, and horseweed leaves over a 24-h period following herbicide application, pooled over nozzle.

Time	AMAPA	AMATA	AMBTR	ERICA
h after application	———— ng 2,4-D cm^{-2} leaf surface[a] ———			
0	1154 A	1265 A	1806 A	1411 A
2	928 AB	612 B	765 B	408 B
4	743 BC	358 C	613 B	207 B
6	547 C	261 CD	328 B	117 B
24	192 D	53 D	128 B	85 B

[a] Means within a column followed by a different letter are significantly different using Tukey's HSD ($\alpha = 0.05$).

Herbicide Efficacy

Control of Palmer amaranth, tall waterhemp, and giant ragweed ranged from 9% to 12%, 20% to 23%, and 88% to 93%, respectively (Table 7). Control of horseweed ranged from 13% to 19% in 2015 and 12% to 26% in 2016 (Table 7). Differences in control between nozzle types only occurred in the 2016 horseweed site year, with the TTI11004 resulting in less control than the two non-DRT nozzles that produced medium droplet spectrums. Conversely, the other DRT nozzle, AIXR11004, resulted in similar control of horseweed compared with the two non-DRT nozzles at the same site. Visual control ratings are a subjective observation and can vary between individual researchers, so an objective measurement such as height reductions must be used to validate any differences that occurred in the subjective observations.

Plant height reductions were evaluated for Palmer amaranth, tall waterhemp, and horseweed and were not taken for giant ragweed. The efficacy of 2,4-D and glyphosate on giant ragweed was too high, even at discriminating doses, to effectively evaluate

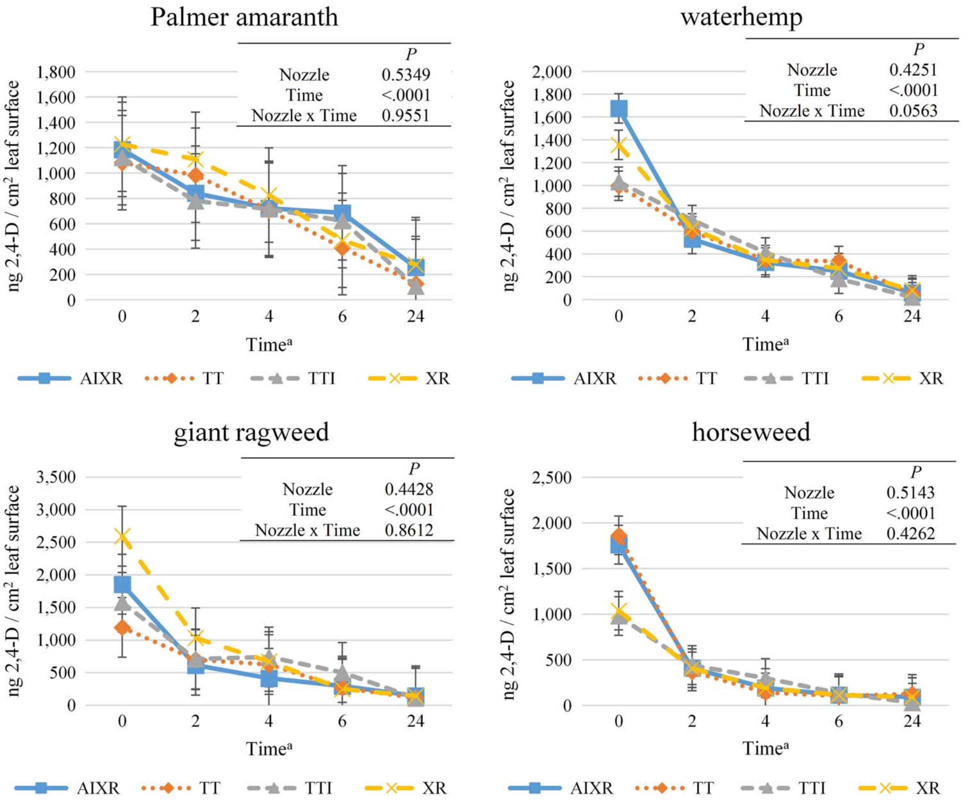

Figure 1. Concentration of 2,4-D on the leaf surfaces of Palmer amaranth, waterhemp, giant ragweed, and horseweed leaves over a 24-h period after herbicide application as influenced by broadcast spray nozzle design. [a] Time = hours after application.

Table 7. Control of Palmer amaranth, tall waterhemp, giant ragweed, and horseweed 21 d after treatment with glyphosate (280 g ha^{-1}) plus 2,4-D (280 g ha^{-1}) as influenced by broadcast nozzle.

				ERICA	
Broadcast nozzle	AMAPA[a]	AMATA[a]	AMBTR[a]	2015	2016
	————————	———— %[b]	————————		
XR11004	12 A	22 A	88 A	18 A	26 A
TT11004	13 A	23 A	93 A	16 A	22 A
AIXR11004	11 A	22 A	90 A	13 A	20 AB
TTI11004	9 A	20 A	92 A	19 A	12 B

[a] Means pooled across site-years.

[b] Means within a column followed by a different letter are significantly different using Tukey's HSD (α = 0.05).

heights; plants were almost completely deceased and necrotic at the time of evaluation. Differences in height reduction did not occur between nozzle types in the following species and site-years: 2014 Twelve Mile Palmer amaranth site, 2015 Palmer amaranth, tall waterhemp and 2015 Meigs horseweed (Table 8). Differences in weed height reduction between nozzle types did occur in the 2014 Evansville Palmer amaranth site and the 2016 Brookston horseweed site, with both having greater plant height reduction with the medium droplet–producing XR11004 compared with the TTI11004 (Table 8).

The TTI11004 nozzle resulted in a reduction in herbicide efficacy on horseweed compared with a medium droplet–producing nozzle when evaluating both visual control and height reduction at the 2016 Brookston site. In addition, a similar trend of the TTI11004 reducing efficacy was evident based on weed height reduction at the 2014 Evansville Palmer amaranth site. Differences in visual control and height reduction due to nozzle design or droplet spectrum size were not observed in any of the other site-years or species. When the application parameters were evaluated (Table 1), horseweed at the Brookston site had a much higher density of plants as well as a large range of plant heights compared with other site-years. The 2014 Evansville Palmer amaranth site had an application delay due to weather conditions, and the heights of Palmer amaranth plants were greater than for the other site-years and fell outside the recommended height range for POST herbicide applications for this species. Therefore, the potential for a loss in herbicide efficacy due to the larger droplets produced by the TTI11004 nozzle is more likely to occur in situations in which weeds exceed the recommended application height or are growing at high densities. The majority of site-years in this experiment used a POST herbicide application following an application of a residual herbicide, with the exception of the 2016 Brookston horseweed site, which replicated a "green" planted site without a residual herbicide.

Table 8. Height reduction of Palmer amaranth, tall waterhemp, and horseweed 21 d after treatment with glyphosate (280 g ha^{-1}) plus 2,4-D (280 g ha^{-1}) as influenced by broadcast nozzle.

	AMAPA[a]				ERICA	
Broadcast nozzle	2014 EVV	2014 TWM	2015	AMATA[b]	2015	2016
	————————	———— %[c]	————————			
XR11004	84 A	48 A	69 A	65 A	65 A	62 A
TT11004	78 AB	43 A	75 A	66 A	66 A	61 AB
AIXR11004	77 AB	45 A	75 A	63 A	64 A	55 AB
TTI11004	55 B	41 A	72 A	66 A	65 A	50 B

[a] Abbreviations: EVV, Evansville, IN; TWM, Twelve Mile, IN.

[b] Means pooled across site-years.

[c] Means within a column followed by a different letter are significantly different using Tukey's HSD (α = 0.05).

In conclusion, the use of DRT broadcast nozzles that use air-induction and pre-orifice designs that produce very coarse to ultra-coarse droplets under the correct conditions can achieve equivalent deposition ,absorption of herbicide solution, and efficacy on Palmer amaranth, tall waterhemp, giant ragweed, and horseweed as compared with non-DRT nozzles. The equivalent deposition, absorption, and efficacy were achieved when the product was applied under ideal scenarios of lower-density weed populations and appropriately sized weeds. The DRT nozzles, especially the ultra-coarse droplet–producing TTI11004, are more likely to reduce efficacy on troublesome broadleaf weeds when used in nonideal scenarios such as high-density weed populations and applications to weeds that are taller than the maximum recommended heights. It should also be noted that this research did not include the inclusion of drift-reduction agents, which would likely affect these results. The required use of DRT nozzles is essential during POST applications to soybean to reduce off-target damage to neighboring species and can effectively provide delivery of the herbicide to the target plants, providing effective control of target species when applied under appropriate parameters.

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