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Dicamba Losses to Air after Applications to Soybean under Stable and Nonstable Atmospheric Conditions

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Abstract

Challenges to control broadleaf weeds in broadleaf crops prompted development of soybean [*Glycine max* (L.) Merr.] and cotton (*Gossypium hirsutum* L.) with dicamba resistance. As a result of an unprecedented number of dicamba-related injury cases in the United States, the movement of dicamba was studied in an applied research setting. High-volume air samplers were used to determine concentrations of dicamba in air after treatment to soybean. In the first set of experiments, new commercial dicamba formulations were applied to soybean. Applications were made at the same time with treated areas at least 480 m apart to avoid cross-contamination. Similar levels of dicamba were detected for both formulations, and the highest amounts (22.6 to 25.8 ng m^{-3}) were detected in the first 8 h after treatment (HAT). A second set of experiments involved comparisons of mid-day applications, when the atmosphere was unstable, to later applications under stable atmospheric conditions. Dicamba detected in the first 8 HAT was nearly threefold higher in applications made under stable atmospheric conditions. All experiments resulted in detection of dicamba through the last time point 72 HAT, indicating that volatility occurred regardless of application timing or formulation. Applications that included glyphosate resulted in higher dicamba concentrations than applications lacking glyphosate. These results provide field-level data that new commercial dicamba formulations can volatilize over time and that atmospheric conditions at application affect dicamba concentrations. Pesticide applicators need to be familiar with these factors to reduce off-target movement of dicamba.

Core Ideas

- The highest dicamba detections were associated with stable atmospheric conditions.
- Addition of glyphosate to dicamba increased dicamba losses to air.
- New low-volatile dicamba formulations were detected at similar levels in the air.
- Dicamba was detected in the air for 72 h after each experimental application.

The herbicide dicamba has been widely used for the control of broadleaf weed species in pastures and many cereal crops since the early 1960s (Egan and Mortensen, 2012). Weeds have continued to develop resistance to commonly applied herbicides; however, most species have been slow to evolve resistance to dicamba and other synthetic auxin herbicides (Heap, 2018; Mithila et al., 2011; Sterling and Hall, 1997). Delayed resistance combined with current challenges to control broadleaf weeds in broadleaf crops prompted development of soybean [*Glycine max* (L.) Merr.] and cotton (*Gossypium hirsutum* L.) with resistance to dicamba (DR soybean and DR cotton) (Behrens et al., 2007). However, the synthetic auxin herbicides, including dicamba, have historically been associated with volatility and movement from intended plants to adjacent sensitive plant species, resulting in damage (Behrens and Lueschen, 1979; Egan et al., 2014; Reisinger and Robinson, 1976; Robinson and Fox, 1978; Waite et al., 2002; Yao et al., 2008). Dicamba in the acid form is volatile, and two new formulations of dicamba were developed in conjunction with the DR soybean and cotton to minimize dicamba volatility. One of the new formulations has dicamba bound to the salt *N*,*N*-bis-(3-aminopropyl)methylamine salt (BAPMA salt). The size of the BAPMA salt and strength of the bond reduce the ability of dicamba to dissociate from the salt and scavenge for free hydrogen protons once in spray solution (Westberg and Adams, 2017). The second formulation used an older form of dicamba bound to diglycolamine salt (DGA) mixed with a new proprietary solution known as VaporGrip (MacInnes, 2016). VaporGrip consists of an acetic acid buffer that scavenges free protons in the dicamba spray solution (Abraham, 2018). Both formulations were shown to be lower in volatility than previous formulations in humidome studies (MacInnes, 2016; Westberg and Adams, 2017). However, in 2017, the new formulations and the DR soybean and cotton were approved for use together for the first time, and in the same year, state departments of agriculture reported over 2200 claims of suspected dicamba injury to sensitive plants, such as grapes (*Vitis vinifera* L.), tomatoes (*Solanum lycopersicum* L.), and non-DR soybean (BASF Corporation, 2017; Bradley, 2017; Monsanto Company, 2017; USDA-APHIS, 2015a, 2015b). For

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Abbreviations: a.e., acid equivalent; AGL, above ground level; BAPMA, *N*,*N*-bis-(3-aminopropyl)methylamine salt; DGA, diglycolamine salt; DR, dicamba resistant; HAT, hours after treatment; HPLC, high-performance liquid chromatography; 2,4-D, 2,4-dichlorophenoxyacetic acid; PUF, polyurethane foam.

perspective, in Missouri alone, there were 210 cases representing a roughly 700% increase over total Missouri Department of Agriculture investigations in previous years (K.W. Bradley, personal communication, 2017). The unprecedented number of dicamba investigations with these new formulations highlights the importance of understanding how dicamba is moving from target to nontarget plants in the field setting.

Although volatility of the new formulations was shown to be reduced, changes in the pH of spray solution could occur once dicamba is mixed in the spray solution, increasing the likelihood of dicamba volatility. Most field applications of dicamba are likely to include glyphosate as part of the mixture to control a broader spectrum of weeds; however, recent work by Mueller and Steckel (2019) has shown the addition of glyphosate to either of the new formulations lowers pH.

Another route for dicamba movement from intended plants to unintended plants may be applications made into stable air masses. In a subset of the dicamba-related investigations, injury of non-resistant soybean was uniform across fields, and in some regions of the Mid-South, dicamba movement was described as having a "landscape effect" in which injury was not localized but occurred over large regions. In the 1970s, a similar description of widespread injury due to movement of 2,4-dichlorophenoxyacetic acid (2,4-D), another synthetic auxin herbicide, occurred in Washington vineyards (Reisinger and Robinson, 1976; Robinson and Fox, 1978). Many incidences of the 2,4-D injury lacked typical, localized, physical drift patterns and resulted in uniform damage across vineyards in the Yakama Valley. Movement of 2,4-D was associated with stable air masses forming that prohibited herbicide dispersion (Reisinger and Robinson, 1976; Robinson and Fox, 1978). The topography of the soybean and cotton growing regions varies greatly from the grape growing regions of Washington State. However, stable air masses can be caused by a variety of factors including surface temperature inversions, which have been shown to occur routinely in the high-production soybean and cotton geographies of the United States (Hosler, 1961; Bish et al., 2019). Yassin et al. (2018) found that when the atmosphere becomes more stable, concentrations of many pollutants increase; thus, it would be reasonable to conclude that similar effects may occur when dicamba is applied during stable conditions.

Furthermore, the volume of dicamba required to injure many sensitive plants was shown to be much less than that for other herbicides used for weed control in cotton and soybean (Al-Khatib et al., 1992a, 1992b; Al-Khatib and Peterson, 1999; Behrens et al., 2007; Kruger et al., 2012; Sciumbato et al., 2004a, 2004b). Application rates as low as 1/20,000th of a labeled use rate (0.028 g acid equivalent [a.e.] ha^{-1}) have caused visual injury and height reduction to sensitive soybean (Solomon and Bradley, 2014). For comparison, glyphosate and glufosinate, two common, post-emergence herbicides, required 1/10th of the standard use rate to result in any injury to soybean (Al-Khatib and Peterson, 1999). Therefore, only a small amount of dicamba would need to be present in the air to become problematic relative to other herbicides.

Although multiple studies have been conducted to quantify the amount of dicamba in the environment (Waite et al., 1995, 2002, 2005; Messing et al., 2014a, 2014b; Tuduri et al., 2006; Cessna et al., 2000), few studies have evaluated dicamba concentrations in the air after application (Mueller et al., 2013). To our knowledge, no research has been conducted to detect dicamba concentrations as they relate to stable air masses.

Objectives of this research included the use of air sampling analysis to quantify dicamba in the air after application, characterize potential differences between newly approved commercial dicamba formulations, produce regression models to assess relationships between dicamba concentrations and weather variables, and assess the influence of glyphosate on dicamba concentrations.

Materials and Methods

General Trial Information

Air sampling studies were conducted at the University of Missouri Bradford Research Center near Columbia, MO (38°89′ N, 92°21′ W). Dicamba-resistant soybean were planted on 28 Apr. 2017 and 1 May 2018, using common agricultural practices, including no-till seeding, rows spaced 76 cm apart, and seeding rates of 56,680 seeds per ha^{-1}. Three locations were planted each year and were spatially isolated a minimum of 480 m apart, but all within 600 m of a University of Missouri-maintained weather station. The soil type for all experiments was a Mexico silt loam (fine, smectitic, mesic Vertic Epiaqualfs) with 1.9% organic matter and pH of 6.3. Dicamba applications were made between June and September of 2017 and 2018 (Supplemental Table S1). All treatments were applied using a CO_2–powered backpack plot sprayer equipped with 11003 turbo Teejet induction flat fan nozzles (TeeJet, Spraying Systems Company) delivering 140 L ha^{-1} at 138 kPa. All treatments included drift-reducing adjuvants according to label requirements.

In one experiment, the two new low-volatile dicamba formulations, DGA plus VaporGrip and BAPMA salt, were applied at the same time in different regions of the research center. Dicamba was applied at the labeled rate of 560 g a.e. ha^{-1} and included 840 kg a.e. ha^{-1} glyphosate potassium, which is commonly applied in mixture with dicamba. This formulations experiment was repeated four times; three were conducted during the evening, and one during the afternoon.

Another experiment was conducted to detect dicamba in the air after applications in the daytime, when the atmosphere is typically unstable, and near sunset, when atmospheric conditions tend to be more stable. Given the logistics of available land, only the DGA plus VaporGrip formulation was used for these studies, and stable applications were made in the evening to ensure more stable atmospheric conditions. During each set of these experiments, a daytime and an evening application were made within a 24-h time period. On a subset of experiments, smoke bombs were used to visually confirm stable atmosphere conditions (data not shown). The atmospheric stability experiment was repeated 10 times.

Five additional applications were made that lacked glyphosate in the spray mixture. Data from these applications were used in comparison with determine the effects of glyphosate on dicamba concentrations. Information pertaining to all 19 applications can be found in Supplemental Table S1.

Sample Collection

In all experiments, air samples were collected from two or three high volume air samplers (Model CF-1001BRL, Hi-Q Environmental Products Company) positioned equidistantly in 6-m × 31-m plots. Each sampler was fitted with a polyurethane foam (PUF) substrate header attachment, and machines were calibrated with a Hi-Q flow-rate calibration unit to maintain a flow rate of 250 L min^{-1}. Sampling media consisted of glass fiber filter paper 102 mm in diameter (Hi-Q Environmental Products Company) and PUF media, TE-1015 7.62 × 3.81 cm, (Tisch Environmental). Sampling height was maintained at 20 cm above crop canopy to prevent contamination from the treated plants. Air samplers were cleaned with methanol and calibrated before initiation of each experiment. Prior to each treatment, high-volume air samplers were operated for ≥2 h to identify contaminates and to serve as controls for experimental comparisons. After background collection, air samplers were removed from the plot and transported to an isolated location where filters and PUF were removed and replaced with new media. Thirty minutes after herbicide application, air samplers were placed back in the plots. This interval was used to allow sprayed dicamba droplets time to settle (Mueller et al., 2013). Sampling intervals were 0.5, 8, 16, 24, 48, and 72 h after treatment (HAT). Media was collected and replaced with new collection media at each time interval.

Sample Extraction and Analysis

Dicamba was extracted from the media by adding 50 mL of high-performance liquid chromatography (HPLC)-grade methanol and shaking samples at room temperature at 100 rpm for 2 h. Samples were then centrifuged in 50 mL conical tubes (Thermo Fisher Scientific) at 9000 rpm for 4 m to collect substrates. Individual samples were transferred to concentration tubes and evaporated to <1 mL using a TurboVap II (Caliper Life Sciences), with a bath temperature of 30°C and 193 kPa of nitrogen flow. Concentrated samples were reconstituted with 1 mL of HPLC-grade methanol, vortexed for 10 s, sonicated for 10 m to remove resin from concentration tubes with an FS60 sonicator (Fisher Scientific), vortexed for an additional 10 s, and transferred to 2.5 mL HPLC vials (Thermo Scientific). Transfers were performed using Norm-Jet 5 mL with Luer-Lock syringes (Fisher Scientific) equipped with Whatman 0.45-μm polypropylene filtering media (GE Healthcare Life Sciences). The extracts were kept in cold storage at <2°C until analysis.

Samples were analyzed using HPLC (Shimadzu) coupled with a photodiode array (PDA) detector and external standard calibration. The separation of dicamba was achieved on a Zorbax Eclipse XDB-C18 column (narrow bore 2.1 × 250 mm, 3.5 μm) (Agilent). The mobile phase consisted of 0.1% phosphoric acid and acetonitrile pumped at an isocratic flow of 0.24 and 0.16 mL m^{-1}, respectively, with a column oven temperature of 40°C. Method run time was 6 m with ultraviolet detection of dicamba at a wavelength of 205 nm. Sample injection volume was 4 μL and retention time was 4.4 m. Dicamba standard was purchased from Sigma Aldrich. Standards ranged from 0.005 to 10 mg L^{-1} and were included with each experimental run to generate calibration curves. The limit of detection was 0.005 mg L^{-1}; however, samples with <0.05 mg L^{-1} were rarely observed. Blank HPLC-grade methanol samples were included on a routine basis at different stages of sample preparation and analysis to confirm that cross-contamination between samples did not occur.

Computations and Statistics

Statistical analyses were performed using SAS 9.4 (SAS Institute). The PROC univariate procedure was used to test normality of untransformed, log-transformed, and square-root-transformed data. The Shapiro–Wilk W test ($p = 0.05$) was used for evaluation, and log-transformed data were used for further analyses. Analysis of variance was performed using a generalized linear mixed model procedure (PROC GLIMMIX). Fixed effects for the formulations comparisons were herbicide formulation, HAT, and herbicide formulation × HAT. Time of application was considered a random effect, allowing for comparison of the two formulations across application conditions. Fixed effects for the atmospheric stability experiment were HAT and time of application. Fixed effects for the influence of glyphosate were glyphosate, HAT, and glyphosate × HAT. Least squares means were obtained and separated with a Fisher's protected LSD at $p \leq 0.05$. This procedure was also used to test the effects of glyphosate in the spray solution.

Stepwise linear regression models were generated using the PROC REG procedure to identify key factors contributing to dicamba concentrations in air. Independent variables included presence or absence of glyphosate, HAT, soil temperature under residue (15 cm), bare soil temperature (5 cm), bare soil temperature difference (10–5 cm), air pressure, solar radiation, average dew point temperature at 46 and 305 cm above ground level (AGL), average relative humidity at 46 and 305 cm AGL, maximum air temperature at 46 and 305 cm AGL, air temperature difference (ΔT) between 305 and 46 cm (ΔT 305–46 cm), ΔT between 168 and 46 cm (ΔT 168–46 cm), and ΔT between 305 and 168 cm. The first 24 h of each experiment with the DGA plus VaporGrip formulation of dicamba was used for analysis. Weather variables were averaged over the course of each 8-HAT interval (0.5 to 8 HAT, 8 to 16 HAT, and 16 to 24 HAT). The a priori significance level chosen for variables to be included and remain in the model was $\alpha = 0.15$. Wind speed was not conducive to the stepwise regression, given the finite starting points of zero. Therefore, Spearman's correlation coefficients were produced to explore the relationship between wind and dicamba concentrations.

Results

Comparisons of New, Commercial Dicamba Formulations

When applied simultaneously, the DGA plus VaporGrip and BAPMA salt of dicamba were detected at similar levels over the time course (Fig. 1). The highest concentrations for each formulation occurred 0.5 to 8 HAT. Concentration of the DGA plus VaporGrip was 22.6 ng m^{-3} whereas that of the BAPMA salt was 25.8 ng m^{-3}. Both formulations showed similarly rapid dissipation in air, with dicamba concentrations decreasing from >20 ng m^{-3} at 0.5 to 8 HAT to <7 ng m^{-3} at 8 to 16 HAT. By 24 to 48 HAT, dicamba concentrations were ~2 ng m^{-3} and remained at that concentration through 72 HAT. Literature is lacking with regards to dicamba dissipation rates in the air. First-order kinetics were tested for these formulations but did not satisfactorily describe the dissipation of dicamba in air over time for either formulation (data not shown). Both formulations were detected through the end of each experimental run at 72 HAT, indicating that both formulations volatilized over time. Previous work with older dicamba formulations and recent work with the DGA plus VaporGrip has shown that dicamba can remain on leaf surfaces for 24 h to days after applications, providing opportunity for volatilization over time (Chang and Vanden Born, 1971; Cessna, 1993; Long et al., 2016; Bish and Bradley, 2019).

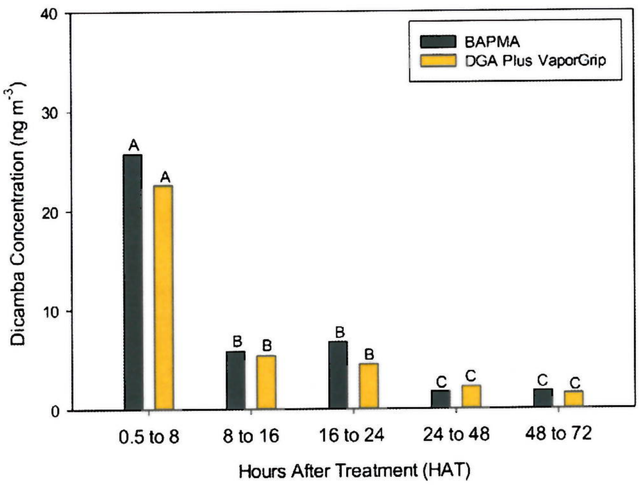

Fig. 1. Comparison of the *N,N*-bis-(3-aminopropyl)methylamine salt of dicamba (BAPMA salt) formulation (black bars) to the diglycolamine salt (DGA) of dicamba bound to VaporGrip (gray bars). Applications were made of the 1 × rate of dicamba (560 g acid equivalent [a.e.] ha^{-1}) and included glyphosate (840 kg a.e. ha^{-1}) (n = 119). Letters above bars represent means separation using Fisher's protected LSD at $p \leq 0.05$.

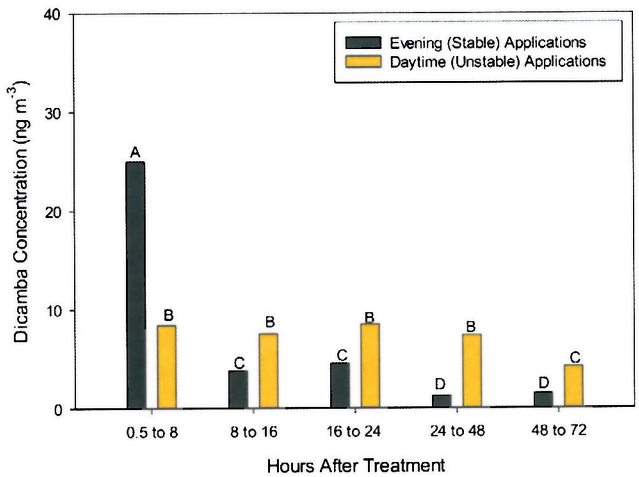

Fig. 2. Dicamba diglycolamine salt (DGA) plus VaporGrip was applied at a 1 × rate with glyphosate during midday when atmospheric conditions should be unstable (gray bars), and during the evening when conditions should be more stable (black) (n = 269). Letters above bars represent means separation using Fisher's protected LSD at $p \leq 0.05$.

Atmosphere Stability

Dicamba concentrations from applications made during unstable conditions in the daytime were similar over all collection intervals with the exception of a decrease from 48 to 72 HAT (Fig. 2). The mean level of dicamba detected was 8.4 ng m^{-3} from 0.5 to 8 HAT and 4.2 ng m^{-3} from 48 to 72 HAT. In contrast, mean dicamba concentration for applications made during stable conditions was highest from 0.5 to 8 HAT (25.0 ng m^{-3}), but concentrations rapidly declined to levels lower than daytime applications at the 8 to 16 HAT. The 8 to 16 and 16 to 24 HAT time points for the evening applications had similar levels of dicamba at 3.8 and 4.5 ng m^{-3}, respectively, and concentrations decreased to <1.5 ng m^{-3} from 24 to 48 and 48 to 72 HAT.

Based on the concentration differences between daytime and evening applications, treatments applied during unstable conditions were less likely to become suspended and move off-target initially. However, daytime applications resulted in significantly higher concentrations detected at the 8 to 16, 16 to 24, and 24 to 48 HAT. These data reveal differences in aerial transport modes of dicamba. Volatilization occurring under turbulent, daytime conditions resulted in steady and more persistent dicamba concentrations over time. The droplets suspended in air after applications made in stable conditions would be subject to movement by horizontal winds. Droplets suspended in the stable air could be the result of applications during stable conditions and/or volatilization of droplets into the stable air mass. Both mechanisms would result in droplets suspended in a stable air mass and would result in a lack of vertical dispersion of droplets.

Relationships between these transport modes and dicamba concentrations were explored further with a series of regression models (Table 1). Data from the 0.5 to 8 HAT time points for both daytime and evening applications were used to identify relationships among weather variables that affect dicamba being suspended in the air initially, whereas data from the 8 to 16 and 16 to 24 HAT time points were used to identify relationships among weather variables and dicamba concentrations that would result from volatility. A simple linear regression model was produced from the 0.5 to 8 HAT data with ΔT (305–46 cm) as the independent variable and dicamba concentrations as the dependent variable. Differences in air temperatures (ΔT) between two heights AGL can serve as an indicator of atmospheric stability; the greater ΔT is then the more stable the atmosphere. The model indicated that every 1°C incremental increase of ΔT (305–46 cm) would result in an increase of dicamba concentration in the air by 1.67 ng m^{-3} (Table 1, Eq. [1]) and explained 58% of variability in dicamba concentrations for the 0.5 to 8 HAT time points. A stepwise regression model was developed to identify all weather variables that may contribute to dicamba concentrations in the air during the 0.5 to 8 HAT (Table 1, Eq. [2]). Maximum air temperature at 46 cm (MTemp 46) and dew point temperature at 305 cm (DP305) satisfied selection requirements for inclusion in the model and, together with ΔT (305–46 cm), accounted for 68% of the variability in dicamba concentrations. The MTemp 46 had a negative relationship with dicamba concentrations; this would be expected, as air temperatures nearest the earth surface should cool rapidly during inversion conditions. The DP305 had a positive relationship with dicamba concentrations. As dew point temperature increases, water vapor in the atmosphere increases. More moisture in the atmosphere could impede or inhibit dicamba molecules suspended in a stable air mass from dispersing by interacting with the dicamba molecules directly and resulting in the reformation of droplets that can settle out, or by interacting with a secondary particle with which dicamba also interacts.

Stable atmospheric conditions are typically associated with reduced wind speeds. Average and maximum wind speeds were negatively correlated with dicamba concentrations for the first 8 HAT, with coefficients of −0.17 and −0.47 respectively (Table 2, Correlation 1). The ΔT was included in the correlation analysis as a control, given that its relationship with dicamba concentration in the first 8 HAT was already determined to be positive. The correlation coefficient was 0.73. Wind speeds did not correlate with dicamba concentrations for the 8 to 24 HAT time points in the correlation analysis (Table 2, Correlation 2). Similarly, the best stepwise regression model of the 8 to 24 HAT time points had an R^2 of 0.32 (data not shown), suggesting that the tested weather variables were insufficient to explain most variability in the observed dicamba concentrations due to volatility. Consistency among the dicamba concentrations detected in the 8 to 16 and 16 to 24 HAT time points across experiments suggests that variations observed in weather variables across these experiments were not significant with regards to explaining volatility.

Influence of Glyphosate on Dicamba Concentrations

Most field applications of dicamba are likely to include glyphosate as part of the mixture. When glyphosate and HAT were tested as fixed effects, both influenced dicamba concentrations (Table 3). Treatments with glyphosate had a mean dicamba concentration of 8.45 ng m^{-3} compared with those that lacked glyphosate with 4.45 ng m^{-3}. Glyphosate × HAT was not a significant effect (data not shown). Glyphosate remained a significant effect for both types of transport studied (0.5 to 8 HAT and 8 to 24 HAT). This was expected for the 8 to 24 HAT time points given the likely relationship between glyphosate and enhancing volatility. However, these results indicate that glyphosate can influence initial movement of dicamba as well.

Discussion

Given the incidences of off-target dicamba movement, questions have arisen regarding how these new dicamba formulations move. Volatility of these new formulations, which have been shown to be less volatile than older dicamba formulations in extensive humidome research, has remained a point of concern (Long et al., 2016: Mueller, 2015). Recent studies of sensitive soybean plants placed in the field 30 min after dicamba applications has indicated that both formulations can volatilize in the field setting (Jones et al., 2019). Air sampling data from this study provide additional support for the ability of each formulation to volatilize in the field. For this study, the distance of the spray boom above the intended target (0.45 m) combined with the size of the droplets leaving the boom (401–500 µm in diameter) should have resulted in droplets reaching the intended

Table 1. Linear regression models to identify independent variables associated with dicamba concentrations.

Equation†	Independent variables‡ x_1	x_2	x_3	Model equation	R^2	*p* value
1	ΔT 305–46	–	–	$y = 22.2 + 1.67x_1$	0.58	<0.0001
2	MTemp 46	DP 305	ΔT 305–46	$y = 38.7 - 0.91x_1 + 1.1x_2 + 1.24x_3$	0.68	<0.0001

† Eq. [1] was a linear regression to describe the relationship between air temperature difference (ΔT) from 305 to 46 cm and dicamba concentrations from 0.5 to 8 h after treatment (HAT) when dicamba was subject to suspension in stable air masses. Equation [2] resulted from a stepwise regression model to describe relationships of multiple weather variables with dicamba concentrations from 0.5 to 8 HAT.

‡ Independent variables that were tested in the stepwise models included soil temperature under residue (15 cm), bare soil temperature (5 cm), bare soil temperature difference (10–5 cm), air pressure, solar radiation, average dew point temperature, maximum wind speed, maximum and average air temperature at 46 cm above ground level (AGL), maximum and average air temperature at 305 cm AGL, average relative humidity, air temperature difference (ΔT) between 305 and 46 cm (ΔT 305–46 cm), and ΔT between 168 and 46 cm (ΔT 168–46 cm). MTemp46 is the maximum air temperature at 46 cm, and DP305 is the average dew point temperature at 305 cm.

Table 2. Spearman correlation coefficients to evaluate relationships between dicamba concentrations and wind speeds.†

Correlation	ΔT‡	Avg. wind‡	Max. wind‡
Correlation 1§	**0.73**	**−0.17**	**−0.47**
Correlation 2	−0.08	0.11	0.05

† Bolded values were significant at the $p < 0.01$ level.

‡ ΔT, air temperature at 305 cm – air temperature at 46 cm; Avg. wind, average wind speed; Max. wind, maximum wind speed.

§ Correlation 1 included data from the 0.5 to 8 h after treatment (HAT) when stable atmospheric conditions contributed to dicamba in the air. Correlation 2 included data from the 8 to 16 and 16 to 24 HAT, which should more closely associate with volatility.

Table 3. Influence of glyphosate on dicamba air concentrations and associated p values.†

Fixed effect	Treatment	Dicamba concentration‡	df	*F*	*p* value
		ng mg^{-3}			
± Glyphosate	+ Glyphosate	8.45a	1, 237	20.5	<0.01
	− Glyphosate	4.45b			
Hour after treatment (HAT)	0.5–8 HAT	12.3a	2, 237	24.7	<0.01
	8–16 HAT	4.59b			
	16–24 HAT	4.08b			
Stable atmospheric conditions (0.5–8 HAT)	+ Glyphosate	16.6a	1, 88	5.83	0.02
	−Glyphosate	9.11b			
Volatility conditions (8–16 and 16–24 HAT)	+ Glyphosate	5.58a	1, 151	14.7	<0.01
	−Glyphosate	3.37b			

† The fixed effect of glyphosate × HAT was not significant ($p = 0.29$) and is not shown. The fixed effect of ± glyphosate was significant when all time points were combined for analysis. Likewise, the fixed effect of HAT was significant when all treatments (± glyphosate) were combined.

‡ Dicamba used for this analysis was Dicamba diglycolamine (DGA) plus VaporGrip; values represent back transformation of the least squares means. For each fixed effect tested, the lowercase letters represent separation of means using Fisher's protected LSD at $p \leq 0.05$.

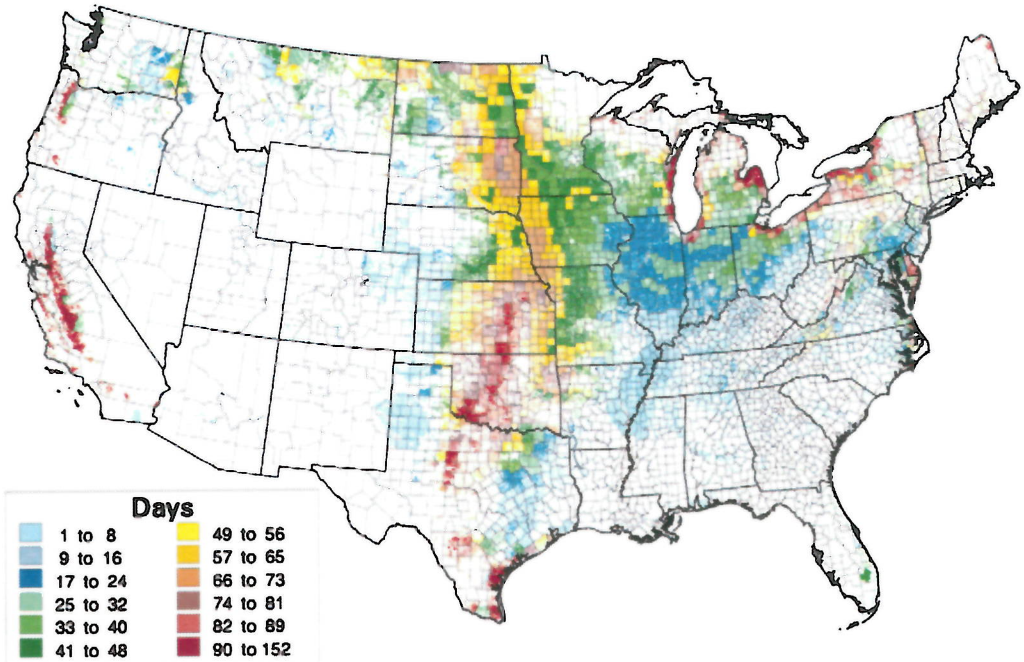

Fig. 3. Yearly average number of days during the typical growing season (1 May to 30 September) from 1994 to 1998 in which wind speeds exceeded 14.4 km h^{-1} (USEPA-generated map modified by Pfleeger et al. 2006). Southeastern Missouri, northeastern Arkansas, and western Tennessee were some of the most heavily affected areas with regards to off-target movement of dicamba and sensitive crop injury. These areas also coincide with some of the least windy agricultural production areas.

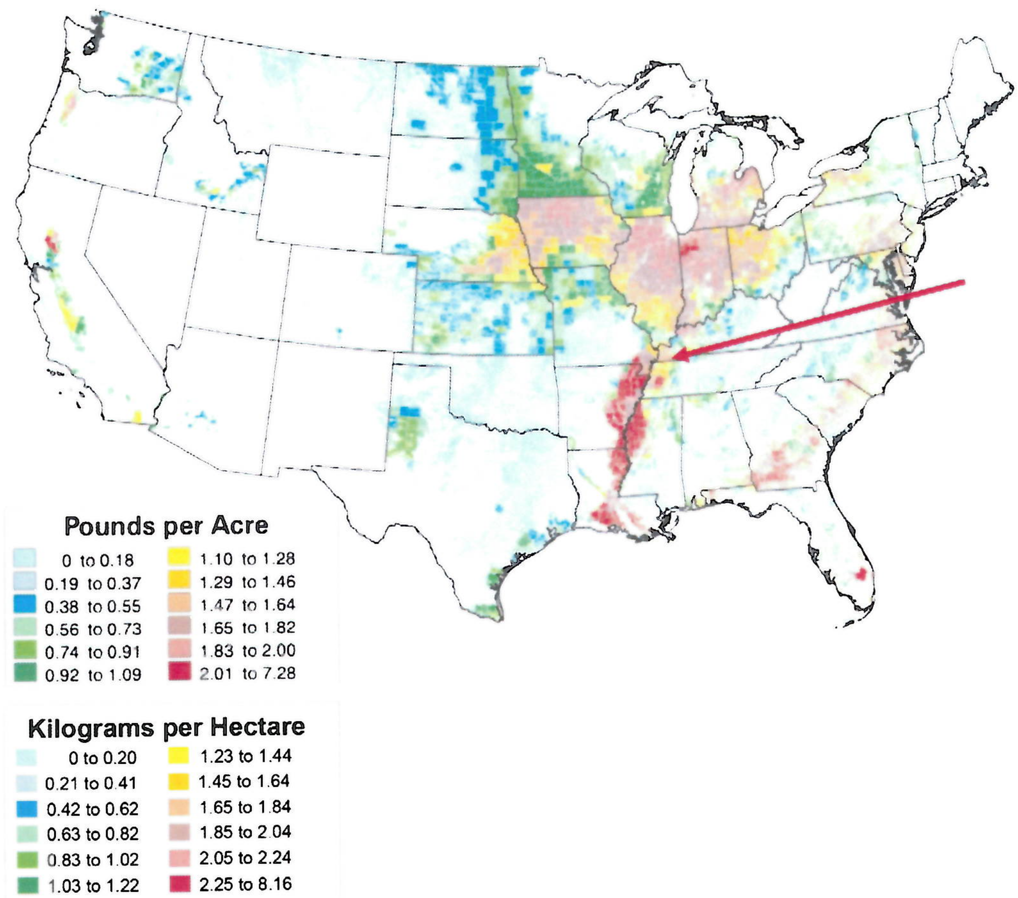

Fig. 4. Annual rate (pounds of active ingredient per acre) of herbicides applied in each county (USEPA-generated map modified by Pfleeger et al., 2006) in 1997. Southeastern Missouri, northeastern Arkansas, and western Tennessee (tip of the red arrow) were some of the most heavily affected areas with regards to off-target movement of dicamba and sensitive crop injury. They also coincide with regions of high herbicide usage.

targets in 0.04 s under ideal conditions (Grisso et al., 2013). Even small droplets known as fines, which are 5 μm or less in diameter, should reach the target in under 10 min. It is unlikely that both formulations were applied and remained suspended in the air for up to 72 HAT, and more plausible that both formulations reached intended targets but volatilized over time. Another mode of transport for dicamba movement could be suspension of dicamba droplets in stable air masses, which can be moved by horizontal wind. In this research, higher concentrations of dicamba were observed in the air when applied during stable conditions compared with unstable, midday conditions. Increases in ΔT (305–46 cm) and decreases in wind speed, both of which serve as indicators of stable conditions, coincided with higher concentrations of dicamba. Traditionally, high wind speed associated with physical drift of herbicides has been the most concerning transport mechanism for off-target pesticide movement (Pfleeger et al., 2006). However, some of the most problematic regions for dicamba injury in 2017 and 2018 were in the Missouri bootheel, northeastern Arkansas, and western Tennessee (Bradley, 2017, 2018). These areas typically have much lower wind speeds relative to other areas (Fig. 3), and this region is prone to inversions during the growing season (Bish et al., 2019). It is possible that the stable atmosphere in these regions would allow herbicides, including dicamba, to remain concentrated in the air and unable to disperse. These regions typically have higher rates of annual herbicide usage compared with other regions (Fig. 4). The combinations of stable atmosphere with high use rates may explain much of the observed "landscape" effects of dicamba damage.

Dicamba levels in the air were increased by glyphosate, regardless of the mode of transport. The addition of glyphosate to spray mixtures is a common practice, and particularly so with synthetic herbicides such as dicamba, because glyphosate controls grassy weed species.

Conclusions

Results from this research identify areas to improve best management practices. First, applicators must have an understanding of stable conditions. A comprehensive survey of >2300 Missouri pesticide applicators revealed a general awareness of drift associated with high winds but a lack of understanding with regards to inversions and stable atmospheric conditions (Bish and Bradley, 2017). Technological advances allow applicators to spray later into the day, which is sometimes favored to avoid physical drift of chemicals due to high winds. However, inversions typically set in near or prior to sunset, and applicators must be aware that calm and still winds may be the worst time to spray dicamba. Second, the ability of both formulations to volatilize over time should be accounted for with regards to nearby sensitive plants. Third, the influence of glyphosate on dicamba concentrations in the air suggests that different strategies or chemical combinations may be needed to control grass weeds in broadleaf crops.

Questions still remain regarding how much dicamba must volatilize to result in injury to sensitive plants, and what combinations of air temperatures and relative humidity are most likely to result in volatilization in the field setting. Therefore, dicamba formulations might be best used in the early stages of the growing season, to control weeds prior to soybean planting instead of controlling weeds once the crops are established. This would limit the number of sensitive crops and plants actively growing at the times of applications, although it is still concerning with regards to sensitive tree species that may be breaking dormancy (Dintelmann et al., 2019).

Supplemental Material

The supplemental material contains an additional table of information about the experiments, including year, dates, and weather conditions at the time of application.

Conflict of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

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