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Dicamba off-target movement from applications on soybeans at two growth stages

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Abstract

The objective of this study was to evaluate dicamba off-target movement during and after applications over soybean at two growth stages. Dicamba-tolerant soybean [*Glycine max* (L.) Merr.] at V3 and R1 growth stages in Nebraska and Mississippi fields were treated with diglycolamine salt of dicamba (560 g ae ha^{-1}), potassium salt of glyphosate (1260 g ae ha^{-1}), and a drift-reducing adjuvant (0.5% v v^{-1}). Filter papers positioned outside the sprayed area were used to determine primary movement and air samplers positioned at the center of sprayed area were used to calculate dicamba flux from 0.5 up to 68 hours after application (HAA). Flux was calculated using the aerodynamic method. Soybean growth stage did not affect dicamba deposition on filter papers from 8 to 45 m downwind from the sprayed areas. At 33 m downwind (i.e., distance of the labeled buffer zone), a spray drift of less than 0.0091% (0.05 g ae ha^{-1}) of applied rate is estimated. Dicamba secondary movement may not be affected by soybean growth stage during the application. Although dicamba was detected in air samples collected at 68 HAA, the majority of the secondary movement was observed in the first 24 HAA. Dicamba cumulative loss was lower than 0.77% of applied rate. Results suggest the more stable the atmospheric conditions, the higher the dicamba flux. Thus, meteorological conditions after applications must be considered, and tools to predict the occurrence of temperature inversion are needed to minimize secondary movement of dicamba.

1 | INTRODUCTION

Dicamba has been used for almost 60 years to control broadleaf weeds mainly in corn (*Zea mays* L.) and pastures. In the last few years, its use intensified due to the occurrence of glyphosate-resistant weeds (Heap, 2014) and the development of dicamba-tolerant (DT) crops such as cotton (*Gossypium hirsutum* L.) and soybean [*Glycine max* (L.) Merrill] (Feng & Brinker, 2010; Weekes et al., 2006) which were

Abbreviations: AD, aerodynamic; DRTs, drift reduction technologies; DT, dicamba tolerant; GC-MS, gas chromatograph-mass spectrometer; HAA, hours after application; IBL, internal boundary layer; NOAEC, no observable adverse effect concentration; NOEL, no observed effect level; OTM, off-target movement; PUF, polyurethane foam; US EPA, United States Environmental Protection Agency; VMD, volumetric median diameter.

commercially launched in 2016 (US EPA, 2018a). DT new cultivars have allowed dicamba to be applied during the growing season (including postemergence applications), which has increased problems with off-target movement (OTM) onto susceptible crops including non-DT soybeans (Mortensen et al., 2012).

Pesticide applications always lead to spray drift from the target as either droplets or vapors (Matthews et al., 2014), especially when pesticides are applied under windy conditions (Wang & Rautman, 2008); volatile formulations are sprayed under higher temperature and low humidity conditions; residues are difficult to be completely removed from the sprayer system; and drift reduction technologies (DRTs) are not used. Pesticide OTM may occur as primary (during and/or shortly after application) and secondary movement (an extended period after the application) (Jones et al., 2019a). According to these authors, primary movement occurs at the time of application with the physical movement of droplets, and secondary movement occurs due to molecule volatilization after application. However, secondary movement can also be characterized by suspended droplets that may not evaporate for some time and molecules attached to the dust and water in the air. Additionally, liquid or solid particles deposited on the target could move off the target area following environmental conditions conducive for small particles (i.e., high wind speeds).

Synthetic auxin herbicide spray drift was reported to cause visible plant injury up to 200 m away in light wind conditions, highlighting the potential for negative consequences to susceptible vegetation (Byass & Lake, 1977), especially when insufficient DRTs are used. Nevertheless, it is important to mention that symptomology does not necessarily lead to yield loss, particularly for soybean. Foster et al. (2019), in developing a model to predict soybean yield loss from dicamba exposure, found that visual injury by itself was not an adequate parameter to be included in the model because such a rating system would be subjective and vary among individuals. Egan et al. (2014) reported that visible injury ratings overestimated soybean yield loss, and that plants exposed in the vegetative stage can generally recover from low to moderate injury. Management of spray drift is crucial to reduce the risks of environmental contamination and exposure of susceptible species (Vieira et al., 2018) and the potential resulting yield loss, which emphasizes the importance of understanding the mechanisms that cause dicamba OTM.

Many studies have been reported in literature about dicamba drift and its effects on sensitive crops (Dittmar et al., 2016; Egan et al., 2014; Everitt & Keeling, 2009; Hatterman-Valenti et al., 2017; Jones et al., 2019a, 2019b); however, there is lack of information stating which type of drift (primary or secondary movement) has the largest contribution on crop damages and how much of the secondary movement is particle (solid or liquid) versus vapor. For many dicamba drift cases reported, the underlying cause of the sensitive crop exposure is never found or is assumed without having any evidence that the purported cause actually led to the exposure. According to Olszyk et al. (2004), it is very difficult to accurately estimate the frequency and severity of non-target crop damage through vapor or other routes of exposure.

Core Ideas

- Soybean growth stage had minor influence on off-target movement of dicamba.
- The highest dicamba flux was observed in the first 30 h after application.
- Dicamba cumulative loss was lower than 0.77% of applied rate.

Pesticide primary movement has been well characterized and applicators are familiar with causes such as applications made during windy conditions, nozzle types that produce very fine droplets, high boom heights, and lack of DRTs (Alves et al., 2017; Bish & Bradley, 2017). However, the pattern of symptomology in some dicamba-injured fields was inconsistent with historical reports of how primary movement presents based on weather data (Bish et al., 2019a), suggesting that more research needs to be conducted to evaluate the causes of secondary movement. It is known that atmospheric conditions affect dicamba OTM, specifically temperature (Behrens & Lueschen, 1979; Bish et al., 2019a; Mueller et al., 2013), wind speed, and wind direction (Alves et al., 2017). Bish and Bradley (2017) suggested that spraying dicamba during inversion conditions was likely one contributor to OTM. Contrasting results have been found while considering relative humidity. Behrens and Lueschen (1979) and Mueller et al. (2013) found that dicamba OTM could be reduced with increasing relative humidity while Bish et al. (2019b) suggested more moisture in the atmosphere could increase OTM. In short, more studies need to be conducted in different environmental conditions to address the impact of relative humidity on dicamba OTM.

Several techniques have been used to estimate pesticide spray drift in wind tunnels (Alves et al., 2017; Ellis et al., 2017), test benches (Balsari et al., 2006; Gil et al., 2014), and fields (Bueno et al., 2017; Foster et al., 2018) using Mylar cards, Petri dishes, filter papers, and monofilament lines. Mueller et al. (2013) and Bish et al. (2019b) used a more precise technique based on portable air samplers equipped with polyurethane foam (PUF) to detect dicamba in the air after application by using a gas chromatograph-mass spectrometer (GC-MS) for quantification. As these studies were conducted in fields less than 0.5 ha in size, more results are needed from larger fields sprayed using conventional hydraulic sprayers, such as those reported by Riter et al. (2020) and Sall et al. (2020).

No research has been reported on dicamba OTM as it relates to soybean growth stage during the application. Hewitt (2001) reported the collection efficiency promoted by crop leaves is sensitive to leaf area index and geometry and is often unpredictable. Henry et al. (2021) observed that dicamba secondary movement was affected by the presence of dew on soybean leaves after a dicamba application. The hypothesis of this research was that late-stage soybean (with a high leaf area index) would cause greater dicamba OTM due to less airflow through the canopy and greater deposition of the pesticide at the top of the canopy. Therefore, the objective of this research was to evaluate dicamba OTM during and after applications on large-scale fields (4 ha) with DT soybean at two growth stages (V3 and R1) under different environmental conditions, geographies, and/or landscape positions.

2 | MATERIALS AND METHODS

2.1 | Field locations

A field study was conducted in two sites (Roscoe, NE, and Brooksville, MS) and two fields (blocks) were used at each site. Geographic coordinates of each location is shown in Figure S1. In Nebraska and Mississippi, blocks were located 800 and 1700 m apart of each other, respectively, to ensure that no cross-contamination occurred between blocks. In Nebraska and Mississippi, areas were located at a commercial soybean production field (Nelson Farm Co.) and in Mississippi areas were located at the Black Belt Branch Experiment Station of Mississippi State University. According to Köppen–Geiger climate classification, both locations have a fully humid and hot summer climate. Climates in Nebraska and Mississippi sites are classified as Dfa (snow climate) and Cfa (warm temperate climate), respectively (Kottek et al., 2006). Soil of the sprayed areas in Nebraska is classified as Norwest loam (fine-loamy, mixed, superactive, mesic Aeric Calciaquolls) (82%) and Lex loam (fine-loamy over sandy or sandy-skeletal, mixed, superactive, calcareous, mesic Fluvaquentic Endoaquolls) (18%) in Block 1 and Santana loam (fine-loamy, mixed, superactive, mesic Aridic Argiustolls) (44.7%), and Duroc silt loam (fine-silty, mixed, superactive, mesic Pachic Haplustolls) (55.3%) in Block 2. In Mississippi, the soil is classified as Brooksville silty clay (fine, smectitic, thermic Aquic Hapluderts) (100%) in Block 1 and Brooksville silty clay (65%) and Okolona silty clay (fine, smectitic, thermic Oxyaquic Hapluderts) (35%) in Block 2 (Soil Survey Staff, n.d.).

The two separate blocks at each site had different DT soybean growth stages during the application timing. In Nebraska, DT soybean Asgrow AG27 × 7 (Asgrow Seed Co., LLC, St. Louis, IL) was planted at 250000 seeds ha^{-1} (2 cm depth and 0.76 m row spacing) on May 7, 2018 (Block 1) and May 25, 2018 (Block 2). The sprayed area of each block was 4.04 ha (201 × 201 m). In Mississippi, DT soybean Asgrow AG47 × 6 (Asgrow Seed Co., LLC, St. Louis, IL) was planted at 321,000 seeds ha^{-1} (2.5 cm depth and 0.19 m row spacing) on May 15 (Block 1) and June 6, 2018 (Block 2). Fields in Mississippi were not square due to geographic limitations. The sprayed areas of Block 1 and Block 2 were 3.64 ha (202 × 180 m) and 3.87 ha (295 × 100 × 254 × 189 m), respectively (Figure S1).

2.2 | Application and field design

Applications were made on DT soybean at R1 (Block 1) and V3 (Block 2) growth stages (Fehr & Caviness, 1977). Soybean heights at R1 stage were 61 cm in Nebraska and 58 cm in Mississippi, whereas at the V3 stage soybean was 36 cm in Nebraska and 25 cm in Mississippi. In each site, both blocks were sprayed at the same time using two different self-propelled sprayers with a similar set up. Two John Deere R4038 sprayers (Deere and Co., Moline, IL) equipped with a 36.6-m boom and 38-cm nozzle spacing were used in Nebraska site. In Mississippi, two John Deere 6700 sprayers (Deere and Co., Moline, IL) equipped with a 18.3-m boom and 51-cm nozzle spacing were used. In both locations, a 140 L ha^{-1} carrier volume was sprayed through TTI11004 nozzles (Teejet Technologies Spraying Systems Co., Glendale Heights, IL) at 276 kPa and positioned 61 cm above canopy level. Travel speeds of sprayers were 4.7 m s^{-1} in Nebraska and 3.5 m s^{-1} in Mississippi.

Spray solutions were a tank mixture of dicamba, glyphosate, and a drift-reducing adjuvant. Diglycolamine (DGA) salt of dicamba (Xtendimax with VaporGrip, Bayer Co., St. Louis, MO) and potassium salt of glyphosate (Roundup Powermax, Bayer Co., St. Louis, MO) were applied at rates of 560 g acid equivalent (ae) ha^{-1} and 1260 g ae ha^{-1}, respectively. In addition, a polyethylene glycol adjuvant (Intact, Precision Laboratories, LLC, Waukegan, IL, MO) and a polymer adjuvant (FS Intention, Growmark, Inc., Bloomington, IL, MO) were added to the solution at 0.5% v v^{-1} rate in Nebraska and Mississippi, respectively. Volumetric median diameter (VMD) of droplets and volume percentage of droplets finer than 200 µm (V_{200}) were measured at the Pesticide Application Technology Laboratory of the University of Nebraska–Lincoln in North Platte, following a similar methodology described by Butts et al. (2019). Solution and nozzle combination used in Nebraska produced a VMD of 1010 µm and V_{200} of 0.42%, whereas the solution and nozzle combination used in Mississippi produced a VMD of 906 µm and V_{200} of 0.68%.

Meteorological conditions (air temperature, relative humidity, wind speed, and wind direction) at each site/block were collected at 1-min intervals using a HOBO RX3000 Weather Station (Onset Computer Co., Bourne, MA) positioned in the center of each block (Figure S2). Sensors were positioned at 0.15, 0.33, 0.56, 0.89, and 1.50 m above the canopy level. Wind speed and direction data were collected using 2D WindSonic anemometers (Gill Instruments, Lymington, UK). Sensors were also positioned 2 m above the soil surface outside the sprayed area. Conditions were recorded from the time when applications commenced until drift sampling was completed. A temperature gradient (ΔΘ) between 0.15 and 1.50 m above canopy was calculated as an indicator of atmospheric stability. Additionally, sensors were positioned outside the sprayed area at 2 m above ground level. In Nebraska, applications commenced at 4:02 p.m. and lasted for 10 min on July 7, 2018, whereas in Mississippi, applications commenced at 5:30 p.m. and lasted for 15 min on June 27, 2018. No rainfall was observed during data collection.

2.3 | Off-target movement sampling

Prior to applications, 125 mm diameter Whatman n.1 filter papers (Whatman, Maidstone, UK) were secured outside the sprayed area on horizontal stands at the canopy level in all four directions (Figure S2), in order to determine primary OTM. Filter papers were placed downwind at 4, 8, 16, 31, and 45 m from the edge of the sprayed area in three lines 15-m apart. In addition, filter papers were placed upwind at 4, 8, and 16 m from the edge of the sprayed area. The central line was positioned in the middle point of the application area and perpendicular to its respective direction.

Thirty minutes after completing the application, all filter papers were carefully collected and individually put into a 50 mL screw cap tube (Sarstedt AG & Co., Nümbrecht, DEU) previously identified and then stored in a freezer at −10˚C or a container with dry ice until analysis. Special care was taken to avoid cross-contamination among samples, during either the collection or transportation, which included double bagging samples and changing gloves between the collection of each sample.

Five air samplers were positioned in the middle of the sprayed area on a center mast at the same heights used for weather station sensors. The center mast and weather station were placed 3 m apart. To determine secondary OTM, samples were collected 30 min after the application. An air sampler consisted of an air pump (SKC Inc., AirCkeck 224–52, Eighty Four, PA), a rechargeable battery (Anker Innovations, Powercore+ 20100 USB-C, Shenzhen, Guangdong, China), and a PUF (SKC Inc., Cat. no. 226–92, Eighty Four, PA), positioned on a horizontal stand (Figure S3) at each height. Six air sampling intervals were taken at both sites. In Nebraska, the intervals were 0.5 to 3, 3 to 16, 16 to 29, 29 to 42, 42 to 55, and 55 to 68 hours after application (HAA), whereas in Mississippi, they were 0.5 to 4, 4 to 16, 16 to 27, 27 to 39, 39 to 50, and 50 to 63 HAA. Interval duration varied based on field logistics and constraints. At the end of each sampling period, PUFs were collected and replaced with a new one. The airflow rate traveling through the air pumps and PUFs was kept between 2.9 and 3.1 L min^{-1} and monitored using a Check-mate Calibrator (SKC Inc., Eighty Four, PA) at the beginning and end of each sampling interval. Additionally, air samplers operated for 24 h prior to applications to identify contaminants in the air. Once collected, PUFs were individually put into a 50 mL screw cap tube following a similar procedure used for filter papers. Due to a limited number of air samplers and the high cost of analysis, only one replication was used.

2.4 | Dicamba quantification

All samples were shipped overnight in coolers containing dry ice at −20˚C to the Mississippi State Chemical Laboratory at Mississippi State University in Starkville, MS, for analysis. Dicamba was extracted and analyzed using a method described in Soltani et al. (2020). In brief, 30 mL methanol fortified with 0.100 mL of 0.1125 μg mL^{-1} 13C6-labeled dicamba (CAS no.:1173023-067; Sigma Aldrich, St. Louis, MO) as an internal standard. PUF samples were homogenized with a SPEX SamplePrep Geno/Ginder (OPS-Diagnostics, Lebanon, NJ). Supernatant was concentrated with a Turbo-Vap to 1 mL, filtered, evaporated, and solvent exchanged to an appropriate volume of 25% acetonitrile in water solution, resulting in a sample concentration of 50×. Quality-control samples included a blank matrix sample (either a PUF or filter) devoid of dicamba and a matrix sample spiked with 0.100 mL of an 0.100 μg mL^{-1} dicamba solution. The spiked matrix sample was used to determine batch extraction efficiency. Recoveries ranged between 80% and 120%, and the level of quantitation was 0.3 ηg PUF^{-1} and 0.3 ηg filter^{-1}. All samples were carefully managed to avoid the potential for cross-contamination and stored at −20˚C until analysis.

Dicamba was quantified using an Agilent 1290 liquid chromatograph coupled with an Agilent 6460 C triple quadrupole mass spectrometer (Agilent Technologies, Santa Clara, CA). Chromatographic separation was performed using an Agilent Zorbax Eclipse Plus 100-mm column. Mobile phases consisted of 0.1% formic acid in water for the aqueous phase (A) and 0.1% formic acid in acetonitrile as the organic phase (B). Flow rate was 0.3 mL min^{-1} with the following gradient program: 0 to 0.5 min of 25% B, 0.5 to 1 min of 50% B, and 1 to 4 min of 60% B. Ionization of dicamba was performed using electrospray ionization in negative mode with an auxiliary gas (N_2), source temperature of 200˚C, and a gas flow rate of 10 L min^{-1}.

2.5 | Dicamba flux determination

Using the amount of dicamba collected in the PUFs, flux and cumulative loss were calculated using the aerodynamic (AD) method as recommended by the US Environmental Protection Agency at Guideline OCSPP 835.8100 (US EPA, 2018b). Similar methods were used by Riter et al. (2020) and Sall et al. (2020) and are well described by Anderson et al. (2019). Calculations were made using Excel 2016 worksheets (Microsoft Corporation, Redmond, WA) as provided by US EPA (US EPA, 2018b).

Dicamba flux was calculated according to Equations (1)and (2) (Majewski et al., 1990):

$$P = \frac{-(0.42)^2 \left(c_{z\text{top}} - c_{z\text{bottom}}\right)\left(u_{z\text{top}} - u_{z\text{bottom}}\right)}{\Phi_m \Phi_p [\ln\left(\frac{z_{\text{top}}}{z_{\text{bottom}}}\right)]^2} \quad (1)$$

where P is the flux (μg m^{-2}·s^{-1}); $c_{z\text{top}}$ (μg m^{-3}) is the concentration at the top sampler adjusted according to the regression of concentration versus ln (height); $c_{z\text{bottom}}$ (μg m^{-3}) is the concentration at the bottom sampler adjusted according to the regression of concentration versus ln (height); $u_{z\text{top}}$ (m s^{-1}) is the wind speed at the top sampler adjusted according to the regression of wind speed versus ln (height); $u_{z\text{bottom}}$ (m s^{-1}) is the wind speed at the bottom sampler adjusted according to the regression of wind speed versus ln (height); z_{top} and z_{bottom} are heights (m) of top and bottom samplers, respectively; Φ_m and Φ_p (dimensionless) are the internal boundary layer (IBL) stability correction terms determined according to the following conditions based on the calculation of the Richardson number, R_i:

$$R_i = \frac{(9.8)\left(c_{z\text{top}} - c_{z\text{bottom}}\right)\left(T_{z\text{top}} - T_{z\text{bottom}}\right)}{[\left(\frac{T_{z\text{top}}+T_{z\text{bottom}}}{2}\right) + 273.16] + \left(u_{z\text{top}} - u_{z\text{bottom}}\right)^2} \quad (2)$$

where R_i (dimensionless) is Richardson number, $T_{z\text{top}}$ (°C) is the temperature at the top sampler adjusted according to the regression of temperature versus ln (height); $T_{z\text{bottom}}$ (°C) is the temperature at the bottom sampler adjusted according to the regression of temperature versus ln (height).

If $R_i > 0$ (for stagnant/stable IBL):

$$\Phi_m = \left(1 + 16R_i\right)^{0.33} \text{ and } \Phi_p = 0.885\left(1 + 34R_i\right)^{0.4} \quad (3)$$

If $R_i < 0$ (for convective/unstable IBL):

$$\Phi_m = \left(1 - 16R_i\right)^{-0.33} \text{ and } \Phi_p = 0.885\left(1 - 22R_i\right)^{-0.4} \quad (4)$$

2.6 | Data analysis

Data collected from filter papers placed downwind was fitted to the three-parameter log-logistic model of the *drc* package in R, version 3.2.3 (R Foundation for Statistical Computing, Vienna, Austria) at 95% confidence interval according to Equation (5) (Ritz et al., 2015):

$$y\ (x) = c + (d - c)\, exp^{\frac{-x}{e}} \quad (5)$$

in which y is the dicamba deposition (ηg m^{-2}); c and d are the lower and upper limits (ηg m^{-2}), respectively; e is the steepness of the curve; and r is the downwind distance (m). This was the top model based on log likelihood of the function *mselect* in the *drc* package. Data collected from filter papers placed upwind was analyzed using SigmaPlot Software, version 14.0 (Systat Software Inc., Chicago, IL) and comparisons were made using 95% confidence interval.

3 | RESULTS AND DISCUSSION

3.1 | Meteorological conditions

Air temperature and relative humidity were consistent with little variation in both blocks in each location from the commencement of the applications until collection of filter papers (Figure 1). Applications were made earlier in the afternoon in Nebraska, which may help in explaining observations of higher temperature and lower relative humidity (32.5°C and 40%) compared with Mississippi (31.0°C and 70%). Greater variability was observed for wind speed and wind direction among blocks, especially in Mississippi where applications were made under lower wind speeds (from 1.0 to 2.0 m s^{-1}) than in Nebraska (from 1.2 to 2.7 m s^{-1}). Wind direction in Nebraska ranged from 187 to 258 degrees (average 207 degrees in Block 1 and 227 degrees in Block 2), whereas in Mississippi it ranged from 51 to 131 degrees (average 64 degrees in Block 1 and 111 degrees in Block 2). For that reason, downwind directions in Nebraska were set at the north and east sides of both blocks, and in Mississippi they were set at the south and west sides in Block 1 and at the North and West sides in Block 2 (Figure S1).

When summarizing meteorological data up to 68 HAA, increases in ΔΘ and reduced wind speeds serve as indicators of stable atmospheric conditions (Bish et al., 2019b). This suggests the meteorological conditions in Mississippi were more stable than in Nebraska during sampling intervals (Figures 2 and 3). Wind speeds ranging from 2 to

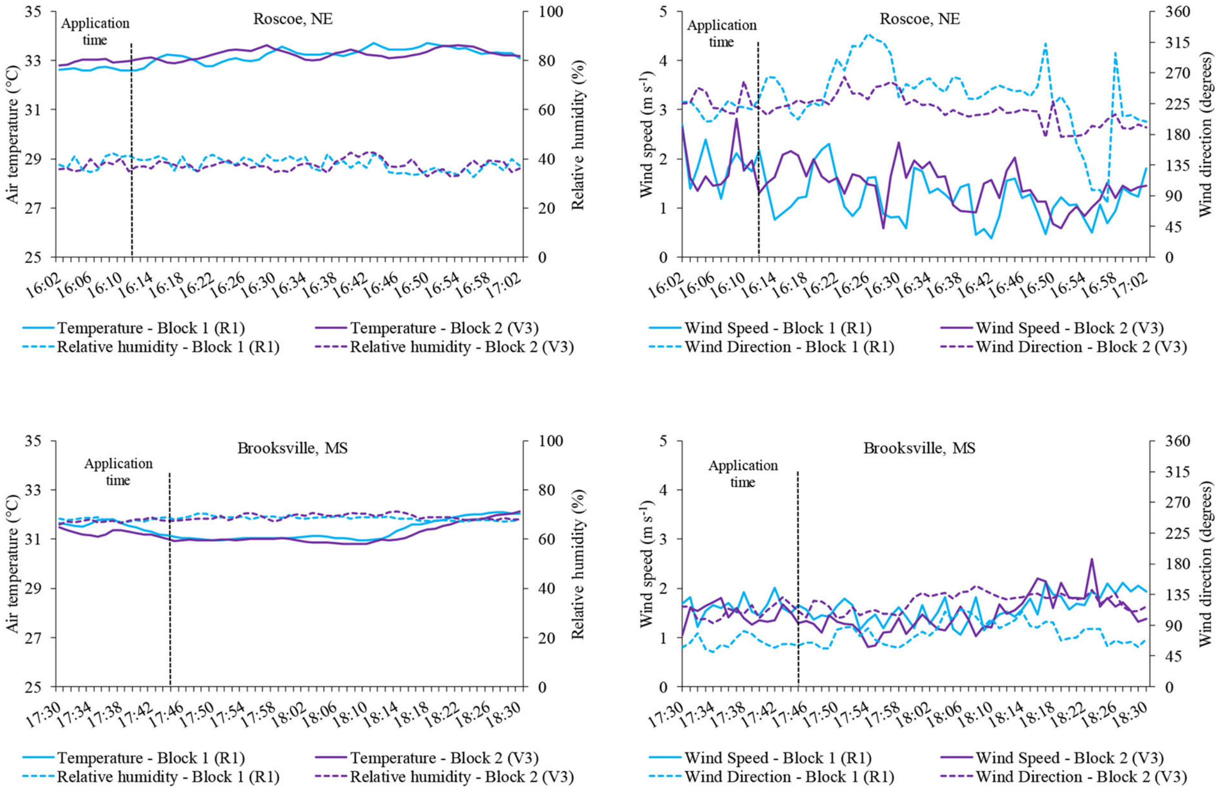

FIGURE 1 Meteorological conditions during and up to 1 h after applications in Nebraska and Mississippi.

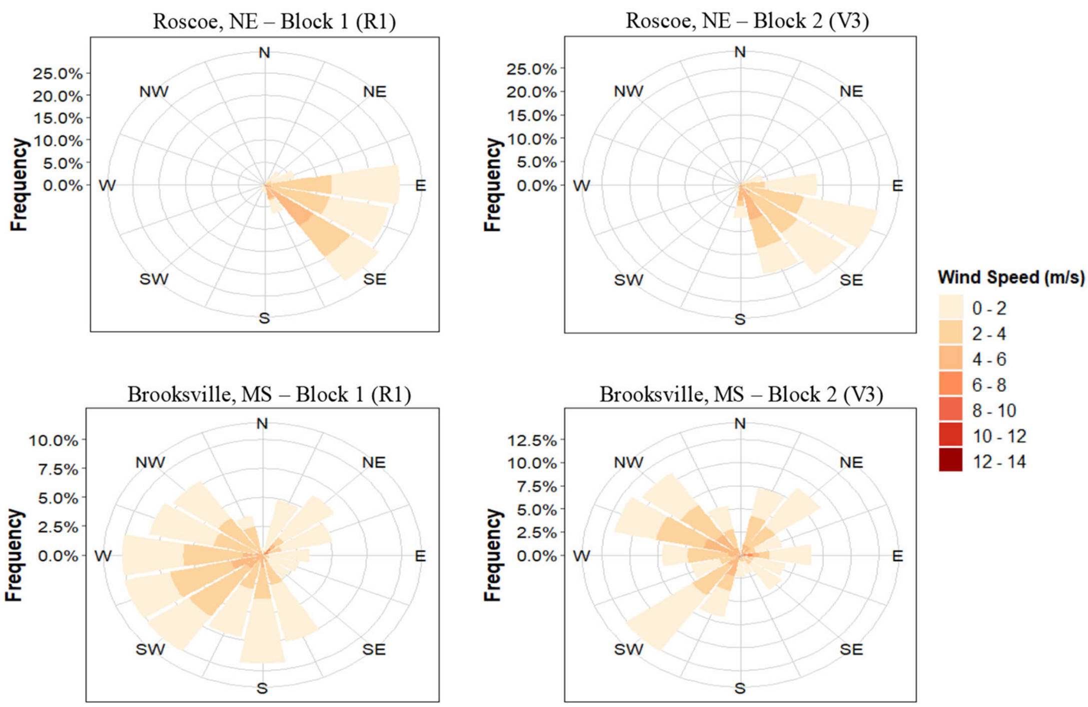

FIGURE 2 Wind rose plots detailing the average wind frequency and wind speed from 1 up to 68 h after application on soybean at two growth stages (R1 and V3) in Nebraska and Mississippi.

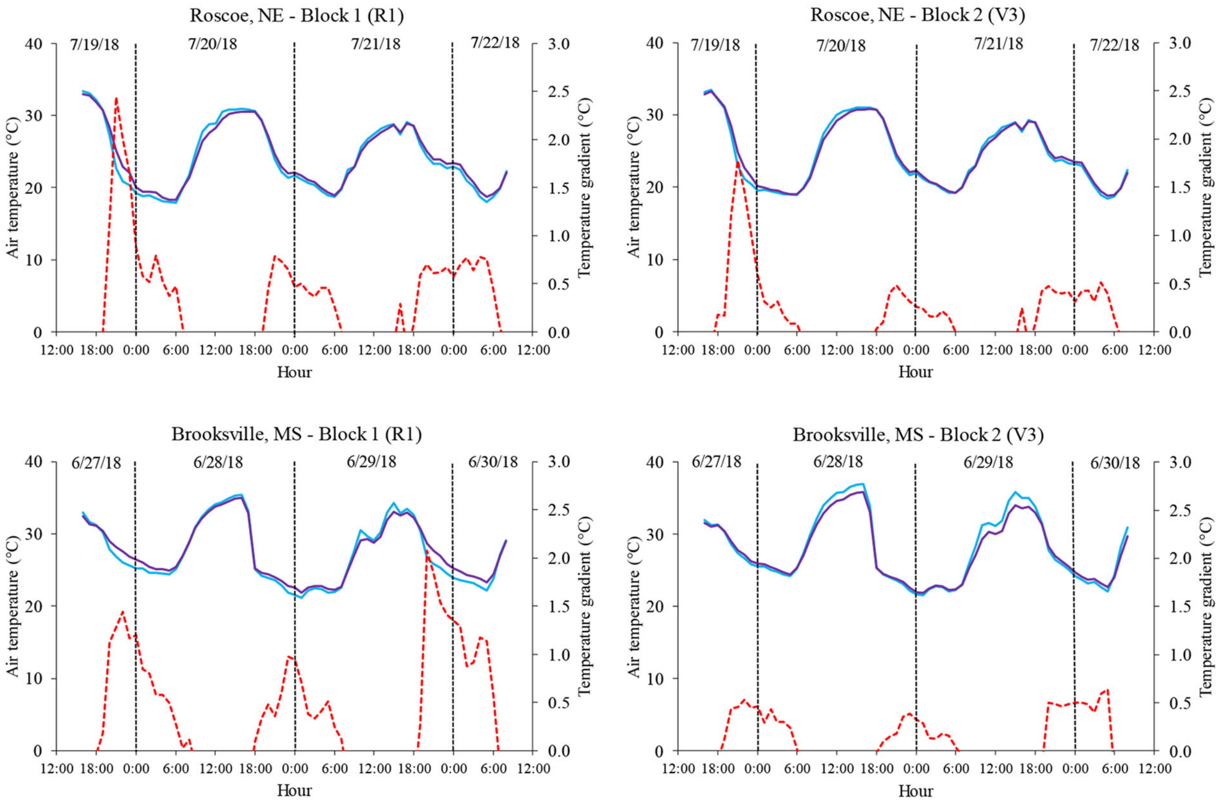

FIGURE 3 Temperature fluctuation observed throughout the sampling collection in Nebraska and Mississippi. *H* and *h* indicate temperatures of the highest and lowest heights of sensors above the canopy, respectively.

4 m s^{-1} were more frequent in Nebraska than in Mississippi, and lower wind speeds in Mississippi led to more variation in wind direction compared to Nebraska (Figure 2). The highest ΔΘ observed in Block 1 in Mississippi suggests this area had the most stable atmospheric conditions (Figure 3). Evidences of temperature inversions from early evenings and mornings were observed across areas, especially in Block 1 in Mississippi. These results suggest a temperature inversion was not associated with the soybean canopy development or growth stage, nor were inversions likely to be present at the time of application.

Temperature inversions happen when the air near the soil's surface is cooler than the air further away from the earth's surface (Enz et al., 2014). Bradley (2019) reported that inversions formed more than 60% of evenings in Missouri across the growing season months of June and July of 2015, 2016, and 2017, and typically began forming between 6:00 and 8:00 p.m., which was also observed in this study. In addition, Bradley (2019) stated that in some geographies, inversions may begin even earlier and recommended that applications end 2 h prior to sunset. Dicamba herbicide label indicates that application should not be made during temperature inversions because small particles may be suspended in the stable air mass and can be moved to unintended targets (Anonymous, 2017).

3.2 | Dicamba deposition

Dicamba deposition on filter papers decreased exponentially as the distance from the sprayed area increased in both downwind directions in Nebraska and Mississippi (Figure 4ab). Model parameters are shown in Table 1. Data from the west side of Block 1 in Mississippi was not presented because it showed high amounts of dicamba (up to 139354 ηg m^{-2}), suggesting a possible contamination during field collection or mislabeled sample. This side of the field did not have sufficient area to place all five downwind distances, compromising the deposition modeling. At 4 m downwind from the sprayed area, dicamba was detected in amounts up to 21650 ηg m^{-2} in Nebraska and 35919 ηg m^{-2} in Mississippi. At 33 m, which corresponds to the buffer zone established by the US Environmental Protection Agency (US EPA, 2018a), it is expected to be less than 1889 ng m^{-2} in Nebraska and 5070 ng m^{-2} in Mississippi. These values correspond to 0.0034% (1/29645th) and 0.0091% (1/11045th), respectively, of a labeled use rate (560 g ae ha^{-1}). Application rates as low as 1/20000th of a labeled use rate have caused visual injury and height reduction to non-DT soybean (Solomon & Bradley, 2014). Although applications in Mississippi were made under lower wind speeds compared to Nebraska, greater deposition on filter papers positioned on the west side of Block 2 was

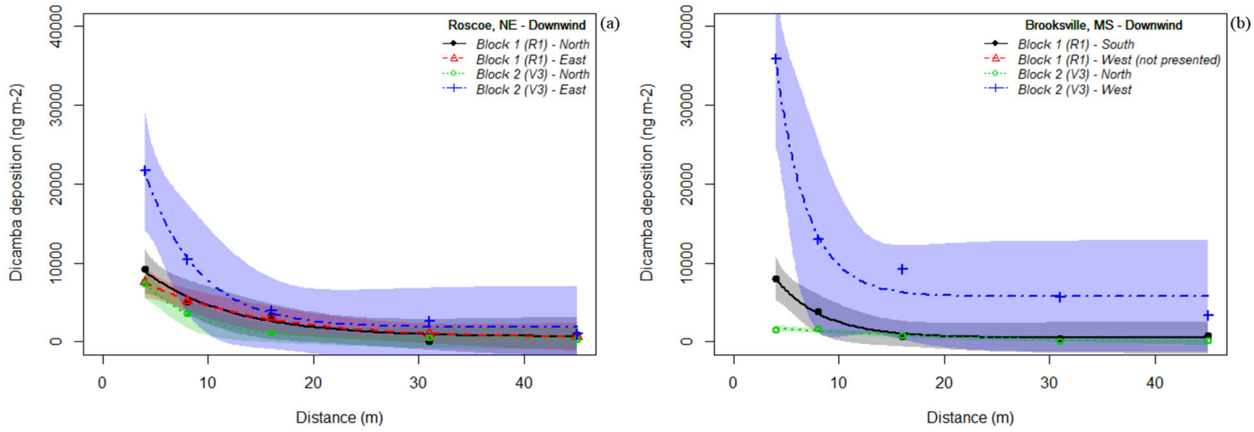

FIGURE 4 Dicamba deposition on filter papers positioned downwind outside the sprayed area in Nebraska (a) and Mississippi (b). Shaded areas represent 95% confidence interval.

TABLE 1 Estimation of three-parameter log-logistic model for dicamba deposition on filter papers positioned downwind outside the sprayed area in Nebraska and Mississippi.

Location	Block (soybean growth stage)	Downwind direction	Model parameter[a]		
			c	*d*	*e*
Roscoe, NE	1 (R1)	North	630.42	13988	8.4094
		East	446.00	10530	11.2009
	2 (V3)	North	443.63	15838	5.0621
		East	1837.00	45778	4.9968
Brooksville, MS	1 (R1)	South	507.28	18684	4.5498
		West	—	—	—
	2 (V3)	North	0.00	2156	21.205
		West	5770.00	121000	2.967

[a] *c* and *d* are the lower and upper limits, respectively, and *e* determines the steepness of the curve.
Abbreviations: R1, reproductive stage; V3, vegetative stage.

observed because the wind direction was more parallel to the transects compared to the other downwind directions.

Greater deposition of dicamba on filter papers placed at 4 m downwind (east in Nebraska and west in Mississippi) was observed when application was made on soybeans at V3 stage in comparison to R1 stage. This observation may be explained due to the difference in leaf area between vegetative and reproductive stages, which may lead to a lower capacity of droplet retention in vegetative stages. No difference in deposition was observed at distances further than 10 m downwind, suggesting the majority of driftable particles were deposited closer to the sprayed area, regardless of soybean growth stage during application.

No dicamba deposition was expected on filter papers placed upwind due to the little variability in wind direction during and up to 30 min after the applications. However, dicamba molecules were detected on filter papers placed upwind from the edge of the sprayed area in both locations, especially in Mississippi where higher values were detected of the herbicide when compared to Nebraska (Figure 5a,b). At 4, 8, and 16 m upwind, dicamba amounts were up to 301, 70, and 130 ηg m^{-2} in Nebraska and up to 1078, 970, and 568 ηg m^{-2} in Mississippi, respectively. Applications made on soybeans at vegetative and reproductive growth stages produced similar deposition upwind, suggesting once again that canopy development did not affect deposition at upwind distances. These results also suggest that droplets may flow against predominant wind direction, most likely with more intensity at lower wind speed conditions (as observed in Mississippi). According to USEPA (2017), low wind speeds are highly variable in direction and gusts frequently blow contrary to the predominant wind direction.

3.3 | Dicamba flux

In Nebraska, the greatest dicamba secondary movement was detected up to 3 HAA, in both blocks (Figure 6). Although dicamba was detected in air samples collected at 68 HAA, the majority of secondary movement in Nebraska was observed in the first 42 HAA. Different from that observed in Nebraska, application on Block 1 in Mississippi produced greater

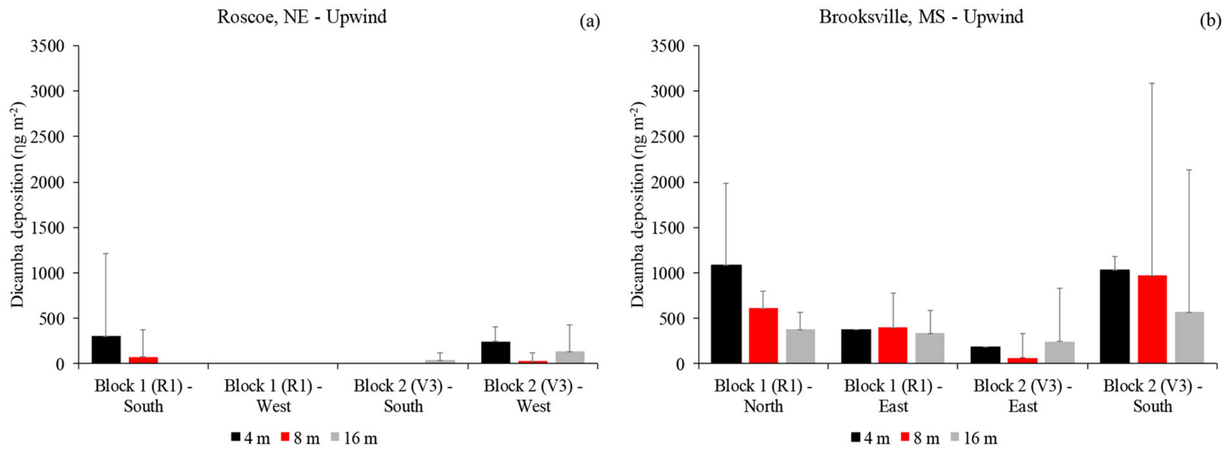

FIGURE 5 Dicamba deposition on filter papers positioned upwind outside the sprayed area in Nebraska (a) and Mississippi (b). Bars represent 95% confidence interval.

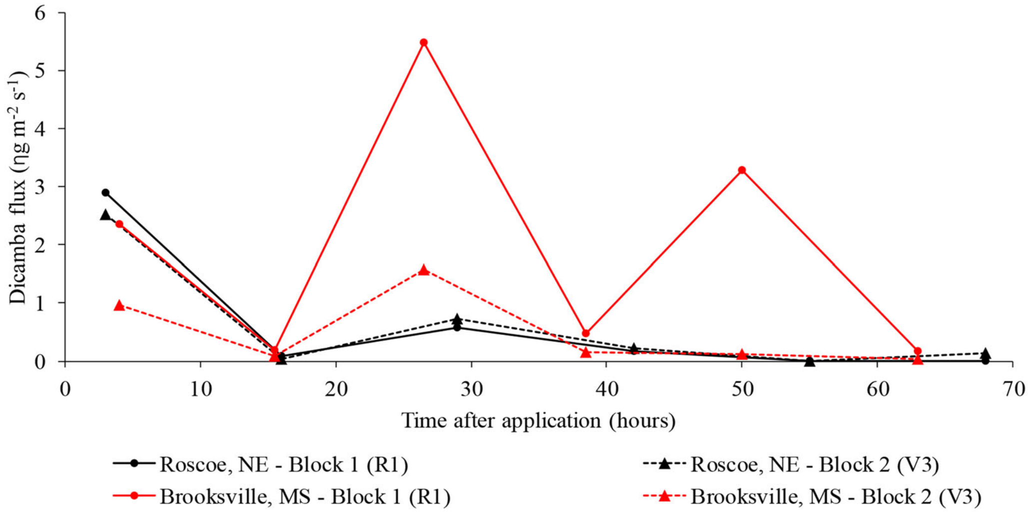

FIGURE 6 Dicamba flux calculated using aerodynamic method from air samples collected in the middle of the sprayed area after application on dicamba-tolerant soybeans at two growth stages (V3 and R1) in Nebraska and Mississippi.

dicamba flux than Block 2 across collections, except at the sampling periods of 16 and 63 HAA. At 4, 27, 39, and 50 HAA, fluxes from Block 1 were 2.3-, 3.4-, 2.5-, and 33.0-fold greater, respectively, than the fluxes from Block 2. Regardless of soybean stage in Mississippi, the greatest fluxes were observed from 16 to 27 HAA. In Mississippi, greater flux at 39 HAA compared to 16 HAA was probably observed in the soybean at R1 stage because sampling periods started at different times prior to sunset (9 p.m. for 16 HAA and 7 p.m. for 39 HAA). By starting an overnight sampling period 2 h prior to sunset, it is probable that air samplers collected dicamba molecules during those two daytime hours which would have diminished effects on diurnal fluxes.

Flux was very similar up to 4 HAA when dicamba was sprayed on soybean at R1 stage in both locations (2.9 ηg m^{-2} s^{-1} in Nebraska and 2.3 ηg m^{-2} s^{-1} in Mississippi). Such similarity between data from Block 1 of both locations was not observed especially from 27 to 55 HAA, where greater flux was observed in Mississippi than in Nebraska. Dicamba flux reached 5.5 ηg m^{-2} s^{-1} in Mississippi at 27 HAA, whereas in Nebraska it was 0.6 ηg m^{-2} s^{-1} at 29 HAA, corresponding to a 9.2-fold difference. Similarly, dicamba flux from Block 2 was 2.1-fold greater in Mississippi than in Nebraska at those sampling periods.

Results suggest that longer periods of stable atmospheric conditions resulted in higher dicamba flux after application, especially considering the $\Delta\Theta$. In general, higher temperature, greater $\Delta\Theta$, and lower temperature span (observed in Block 1 in Mississippi) resulted in the greatest flux values. It is important to emphasize that lower dicamba flux was also observed in stable atmospheric conditions (both blocks in Nebraska). Therefore, the duration of temperature inversion may have an effect on dicamba OTM after applications. Similar results were reported by Bish et al. (2019b), who sprayed two dicamba formulations (*N*,*N*-bis-(3-aminopropyl)methylamine salt (BAPMA) and DGA salt) under stable and unstable conditions. These authors found that both formulations produced similar secondary movement up to 72 HAA, and dicamba was detected in the air (ηg m^{-3}) even when sprayed under unstable conditions. These findings corroborate with Yassin et al. (2018) who stated that when the atmosphere becomes more stable, concentrations of many pollutants increase.

Flux calculations across blocks and locations had a similar tendency for detecting greater dicamba flux during daytime and lower flux at nights. Higher amounts of dicamba detected during the day is likely due to higher air temperatures and wind speeds and lower air relative humidity compared to night conditions. Mueller and Steckel (2019) reported that temperature appears to be a major contributor of secondary movement, with greater dicamba detections in the air at higher temperatures.

Results shown in this study suggest soybean growth stage during the application likely has little or no effect on secondary movement of dicamba. Meteorological conditions during and after applications have a more important role in dicamba movement. Increased moisture in the atmosphere could inhibit dicamba molecules suspended in the air from dispersing, resulting in reformation of droplets that can settle out (Bish et al., 2019b). Egan and Mortensen (2012) observed a correlation between relative humidity and greater injury, which may indicate higher humidity increases residence time of dicamba near the plant surface. Due to the limited size of their dataset, the authors reported that these correlations should be interpreted as suggestive and warrant further investigation. Henry et al. (2021) observed in a controlled-environment study that over a 48-h period after application, dicamba concentration quantified in air samplers increased by 20% when soybeans were exposed to simulated dew for 3 h compared with soybeans that were not exposed to dew. Henry et al. (2021) findings corroborate with Ramsey et al. (2005) who stated that rewetting of leaf surfaces causes short-term interactions between the leaf surface and the environment that are favorable for volatility. These particular hypotheses need to be investigated because results of the current study showed dicamba flux was not necessarily higher in an environment with higher relative humidity. If secondary drift constituents are primarily vapors, it would not be expected that higher relative humidity would increase flux rates. In addition, more appropriate collectors need to be used to detect droplets that remain suspended in the air and can deposit after applications. In short, questions remain regarding what combinations of air temperature and relative humidity are most likely to result in dicamba movement in the field (Bish et al., 2019b) and most, if not all, studies conducted to this point in time cannot clearly differentiate particulate drift from vapor drift of dicamba due to inadequate research techniques available.

Dicamba cumulative losses were lower than 0.77% and 0.17% of the applied rate (560 g ae ha^{-1}) in Block 1 in Mississippi and in the other sprayed areas, respectively (Figure 7). Considering data from both blocks in Nebraska and Bock 2 in Mississippi, similar results were reported by Riter et al. (2020), who observed less than 0.2 ± 0.05% of applied dicamba (560 g ae ha^{-1}) was volatilized over the 3-day sampling period, with most loss occurring within the first 12 HAA. According to US EPA (2018c), the no observable adverse effect concentration (NOAEC) for non-DT soybean plant height or yield is 138 ηg m^{-3}, which is 5.3- and 3.0-fold greater than the highest concentrations observed in this study in Nebraska (26 ηg m^{-3}) and Mississippi (46 ηg m^{-3}) as shown in Table S1. These results suggest secondary movement may not cause soybean yield loss considering a single-exposure event. The minimum amount of dicamba flux (ηg m^{-2} s^{-1}) capable of causing symptomology and damage to non-target crops under field conditions is unknown. As most of the dose–response studies have been conducted using rates (g ae ha^{-1}) (Egan et al., 2014; Foster & Griffin, 2018; Foster et al., 2018; Kniss, 2018; Weidenhamer et al., 1989; Zhang et al., 2019), more research is needed to evaluate the correlation between dicamba flux and its consequences on soybean. Additionally, the existence of published field studies that consistently report a dose that causes no symptomology or no observed effect level (NOEL) for non-DT soybeans is unknown.

Differences between both locations may also be attributed to adjuvants, droplet size, and row spacing. The solution sprayed in Nebraska produced droplets with 104 μm coarser VMD and lower V_{200} than the solution sprayed in Mississippi. Further research needs to be conducted to better understand the effects of drift-reducing adjuvants on dicamba OTM. These adjuvants are mainly recommended to reduce primary movement (Anonymous, 2017); however, it is unclear how these products may affect secondary movement. It is also unclear how crop row spacing can affect dicamba OTM considering that higher amount of herbicide is exposed to soil surface when wider row spacings are used. Carbonari et al. (2020) reported the relation of dicamba with plant surface is different from that with soil surface. Sall et al. (2020) conducted a 3-year research over a range of locations, field types, and environmental conditions and concluded that soil conditions failed to identify any single soil parameter as a dominant driver of dicamba losses.

In order to reduce secondary movement, it should be noted that current formulations of dicamba either have in-can volatility-reducing agents (VRAs) or require their addition to the spray solution (Anonymous, 2020, 2021). A VRA based on acetic acid/acetate was developed to further decrease the volatility profile of dicamba, eliminating hydrogen ions (H^+) in dicamba spray solution (Hemminghaus et al., 2014). Mueller and Steckel (2019) concluded that VRA is an efficient tool in reducing volatilization, and the largest differences occurred mainly at high temperatures (above 30°C).

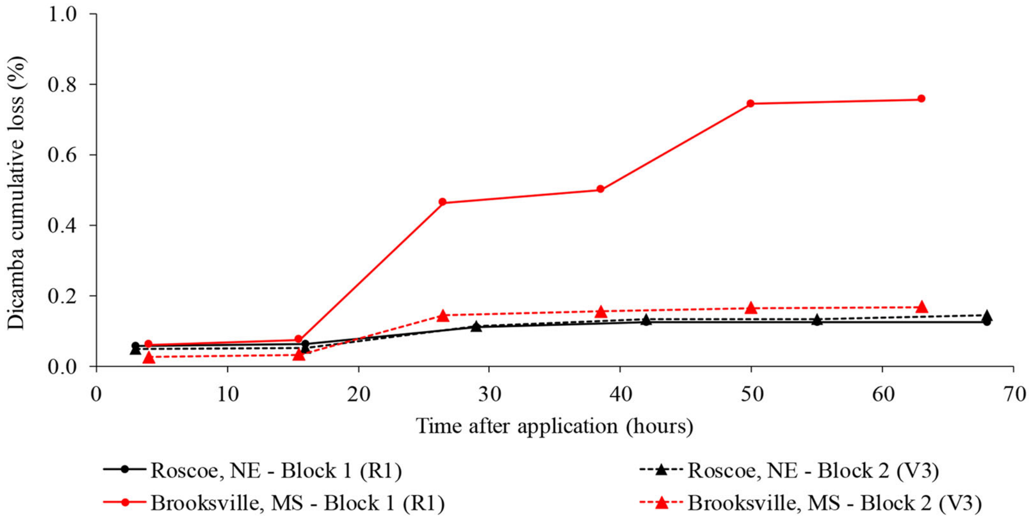

FIGURE 7 Dicamba cumulative loss collected in the middle of the sprayed area after application on dicamba-tolerant soybeans at two growth stages (V3 and R1) in Nebraska and Mississippi.

Carbonari et al. (2022) observed the lowest volatility combination of DGA salt of dicamba with potassium salt of glyphosate and a VRA was the blend with the lowest volatility and is the most suitable combination to recommend to farmers.

Soybean growth stage did not affect dicamba deposition on filter papers from 8 to 45 m downwind from sprayed areas. At 33 m downwind (i.e., distance of the labeled buffer zone), less than 0.0091% of applied rate (560 g ae ha^{-1}) was estimated by using an exponential model. Dicamba molecules were detected on upwind filter papers. Results presented in this study suggest secondary movement of dicamba did not depend on soybean growth stage and was affected by complex interactions between environment and meteorological conditions, especially temperature and relative humidity. Longer periods of stable atmospheric conditions after applications resulted in higher dicamba flux. Overall, the highest dicamba flux was observed on the application day, and air concentrations were below the NOAEC for soybean height and yield. The maximum value of dicamba cumulative loss was 4.3 g ae ha^{-1} (0.77% of the applied rate). Tools to predict the occurrence of stable atmospheric conditions are needed to guide applicators as to when the most appropriate time for dicamba applications should occur in order to mitigate OTM.

AUTHOR CONTRIBUTIONS

Greg R. Kruger: Conceptualization; investigation; funding acquisition; methodology; project administration; resources; supervision; writing–review & editing. **Guilherme S. Alves**: Conceptualization; data curation; formal analysis; writing–original draft; writing –review & editing. **Kasey Schroeder**: Methodology; data curation; writing–review & editing. **Jeffrey A. Golus**: Methodology; data curation; writing–review & editing. **Daniel B. Reynolds**: Conceptualization; investigation; methodology; resources; writing–review & editing. **Darrin M. Dodds**: Conceptualization; investigation; methodology; resources; writing–review & editing. **Ashli E. Brown**: Conceptualization; investigation; methodology; writing–review & editing. **Bradley K. Fritz**: Investigation; methodology; writing–review & editing. **Wesley C. Hoffmann**: Investigation; methodology; writing–review & editing. All authors have read and agreed to the published version of the manuscript.

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

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SUPPORTING INFORMATION

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