








Dicamba air concentrations in eastern Arkansas and impact on soybean

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Research Article

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Abstract

Damage to non-dicamba resistant (non-DR) soybean [*Glycine max* (L.) Merr.] has been frequent in geographies where dicamba-resistant (DR) soybean and cotton (*Gossypium hirsutum* L.) have been grown and sprayed with the herbicide in recent years. Off-target movement field trials were conducted in northwest Arkansas to determine the relationship between dicamba concentration in the air and the extent of symptomatology on non-DR soybean. Additionally, the frequency and concentration of dicamba in air samples at two locations in eastern Arkansas and environmental conditions that impacted the detection of the herbicide in air samples were evaluated. Treatment applications included dicamba at 560 g ae ha⁻¹ (1X rate), glyphosate at 860 g ae ha⁻¹, and particle drift retardant at 1% v/v applied to 0.37-ha fields with varying degrees of vegetation. The relationship between dicamba concentration in air samples and non-DR soybean response to the herbicide was more predictive with visible injury (generalized $R^2 = 0.82$) than height reduction (generalized $R^2 = 0.43$). The predicted dicamba air concentration resulting in 10% injury to soybean was 1.60 ng m⁻³ d⁻¹ for a single exposure. The predicted concentration from a single exposure to dicamba resulting in a 10% height reduction was 3.78 ng m⁻³ d⁻¹. Dicamba was frequently detected in eastern Arkansas, and daily detections above 1.60 ng m⁻³ occurred 17 times in the period sampled. The maximum concentration of dicamba recorded was 7.96 ng m⁻³ d⁻¹, while dicamba concentrations at Marianna and Keiser, AR, were ≥ 1 ng m⁻³ d⁻¹ in six samples collected in 2020 and 22 samples in 2021. Dicamba was detected consistently in air samples collected, indicating high usage in the region and the potential for soybean damage over an extended period. More research is needed to quantify the plant absorption rate of volatile dicamba and to evaluate the impact of multiple exposures of gaseous dicamba on non-targeted plant species.

Introduction

Dicamba-resistant (DR) cotton (*Gossypium hirsutum* L.) and soybean [*Glycine max* (L.) Merr.] were rapidly adopted following the commercial introduction of the technology in 2015 and 2016, respectively (Werle et al. 2018). In 2017, new dicamba formulations were approved by the U.S. Environmental Protection Agency (USEPA 2020) to be used exclusively for over-the-top applications on DR crops. According to survey results of the 2017 season, approximately 50% and 85% of the soybean and cotton, respectively, produced in Arkansas, Missouri, Mississippi, and Tennessee were DR cultivars (Steckel et al. 2017). The adoption of DR technology could be attributed to the expansion of weeds with resistance to multiple herbicide modes of action, particularly Palmer amaranth (*Amaranthus palmeri* S. Watson); meanwhile, several weed populations remained susceptible to dicamba despite the fact the herbicide has been commercialized for decades (Behrens et al. 2007; Heap 2023). Before the development of DR cultivars, the herbicide was primarily applied in preplant burndown and postemergence weed management on cereal crops (Shaner 2014).

The expansion of DR technology increased the use of dicamba products in postemergence applications and shifted the off-target movement toward the growing season, impacting sensitive plants (Jones et al. 2019a; McCown et al. 2018; Werle et al. 2018). Reports of damage to non-targeted sensitive vegetation, including non-DR soybean, have occurred in the past (Auch and Arnold 1978) but not to the magnitude that followed the commercialization of dicamba in DR

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crops (Bradley 2017, 2018; Hager 2017; Hartzler and Jha 2020; Steckel 2018, 2019). For instance, according to state authorities, 2,708 complaints were recorded, accounting for approximately 1.46 million ha of damaged soybean impacted by the off-target movement of dicamba in 2017 (Bradley 2017). Additionally, growers reported a 10% to 20% yield loss due to multiple exposures to dicamba off-target movement (Steckel et al. 2017).

The off-target movement of pesticides and atmospheric loading have been reported and were attributed to agricultural areas associated with heavy use of these chemicals (Waite et al. 2005). Atmospheric loading of pesticides is an emerging hypothesis to explain the impact of the off-target movement on a large scale; however, more research is needed to differentiate this mechanism from others, elucidating the fate of these chemicals. Other pesticides, such as glyphosate and atrazine, have been detected in the atmosphere and rainfall (Alonso et al. 2018; Chang et al. 2011; Hill et al. 2002). Research has shown off-target dicamba movement to occur via primary drift, secondary movement, and tank contamination (Cundiff et al. 2017; Jones et al. 2019b; Maybank et al. 1978; Teske et al. 2002). Research has shown that one of the main sources of the secondary movement of dicamba is volatility (Castner et al. 2022; Egan and Mortensen 2012; Jones et al. 2019b; Mueller and Steckel 2019b, 2021; Oseland et al. 2020b; Soltani et al. 2020; Zaccaro-Gruener et al. 2022), and characteristics of the compound are important to consider for this type of transport.

Important physicochemical characteristics concerning the off-target movement of dicamba are the higher vapor pressure (VP = 4,500 μ Pa) and a coefficient of dissociation (pKa) corresponding to 1.87 (Shaner 2014). In comparison to the VP of dicamba, glyphosate and atrazine have VP at least 100 times lower, indicating a low tendency to become volatile. Considering the pKa of dicamba is approximately 2, and according to the acid–base equilibria described by Henderson-Hasselbalch (Aronson 1983), a dicamba solution at pH = 2 has a 50:50 equilibrium of ionic (acidic) to anionic molecules. Therefore, changes in the pH of the solution with dicamba could impact the dissociation of formulated dicamba and the formation of dicamba acid prone to volatilization (Mueller and Steckel 2019b; Riter et al. 2021). Under the acid–base equilibrium, dicamba solutions at pH 4 have 99% undissociated to 1% acid molecules; at pH 5, 0.1% of the molecules would be in the acid form and 99.9% non-dissociated. Other factors may exacerbate dicamba volatility, such as spray tank partners and meteorological conditions following the application. For instance, growers want to add glyphosate to dicamba to increase the weed control spectrum from a single application; however, this mixture (glyphosate with dicamba) reduces solution pH and increases the volatility potential of dicamba (Mueller and Steckel 2019b). Early research considering dicamba volatility reported that high temperatures and low relative humidity, typical in the summer, allow the dissociation of dicamba acid, increasing volatility (Behrens and Lueschen 1979). A recent study reported that average and low air temperature and wind speed on the day of application and the following day were factors associated with significant off-target movement of dicamba during temperature inversions (Oseland et al. 2020b). Moreover, stable air and temperature inversions during and following application with dicamba were found to impact secondary movement (Bish et al. 2019a, 2019b). However, environmental conditions are dynamic, and their impact on volatility is complex.

Researchers have attempted to quantify dicamba volatility using laboratory and field methods. According to early studies, 13% of radiolabeled dicamba acid volatilized from plachets containing sandy loam soil incubated at 35 °C for 7 d (Burnside and Lavy 1966). Later, researchers used soybean as a bioindicator of dicamba emissions after dimethylamine (DMA) salt formulation was applied in the field and laboratory studies, including enclosed chambers (Behrens and Lueschen 1979). In recent field trials, the diglycolamine (DGA) salt of dicamba further reduced volatility compared with the DMA salt formulation (Egan and Mortensen 2012). Most recently, research comparing the secondary movement of DGA salt to *N,N*-bis-(3-aminopropyl) methylamine salt (BAPMA) of dicamba reported further reduction but not the elimination of dicamba volatility (Anonymous 2022a; Jones et al. 2019b). One attempt to reduce dicamba volatility involved the addition of acetic acid:acetate solution (VaporGrip®), to the DGA salt formulation, which inhibits the formation of dicamba acid (Anonymous 2022b, 2022c; MacInnes 2017). Typically, solutions containing the above formulations have a pH greater than 5.0, which minimizes the formation of the volatile dicamba acid (Mueller and Steckel 2019b). Federal regulations only allow salt formulations of dicamba with BAPMA or DGA with VaporGrip® for in-season applications on DR crops (Anonymous 2022a, 2022b, 2022c). Furthermore, a 2020 modification of federal labels required that every application of dicamba in DR technology have the addition of a volatility reduction agent (VRA) to help stabilize higher pH in the tank solution, reducing volatility potential (USEPA 2022). The latest research has focused on using air-sampling techniques to examine and model factors that impact the secondary movement of dicamba, as these formulations did not prevent landscape damage in several locations in the United States (Bish et al. 2021).

A research method was published to quantify the flux of dicamba volatility in field conditions by employing small-volume air samplers (3 L min⁻¹) (Riter et al. 2020). Other research used air samplers to measure volatility potential in humidomes and acrylic chambers (Mueller and Steckel 2019a; Ouse et al. 2018). The main benefit of controlled environment experiments is that they allow evaluations using different treatment combinations. However, these conditions do not represent field environments where dicamba applications would be made and impacted by multiple interacting factors.

Dicamba is a synthetic auxin mimic herbicide (Group 4), where an overproduction of auxins in susceptible broadleaf plants can culminate in plant death (Grossmann 2010). Exposure to low doses of dicamba by susceptible plants results in epinasty, leaf crinkling, cupping, and malformation, which could be severe (Behrens and Lueschen 1979; Wax et al. 1969; Weidenhamer et al. 1989). Studies associated with injury to non-DR soybean from exposure to dicamba are abundant (Auch and Arnold 1978; Behrens and Lueschen 1979; Griffin et al. 2013; Jones et al. 2019a; McCown et al. 2018; Robinson et al. 2013; Sciumbato et al. 2004; Solomon and Bradley 2014; Wax et al. 1969). Treatments as low as 0.028 g ae ha⁻¹ resulted in visible injury and height reduction of non-DR soybean treated at vegetative and blooming growth stages (Solomon and Bradley 2014). However, most field studies involving the effect of dicamba on non-DR soybean were conducted by direct foliar applications of the herbicide over a range of doses.

Meanwhile, the impact of indirect exposure by volatile dicamba is unclear, as is the effect on non-DR soybean by the amount of

Table 1. Location, soil series, time of application, weather conditions, and solution pH of the herbicide treatment applied in 16 site-years during the 2018 and 2019 growing seasons.

Year-trial	Location	Soil series	Initiation date and time	Solution pH ^a	Air temperature	Soil temperature	Relative humidity	Wind speed ^b
					—C—		—%—	—km h ⁻¹ —
2018-1	Fayetteville, AR	Pembroke silt loam	May 7, 2018, 9:55 AM	—	19.4	17.2	79	0.69
2018-2	Fayetteville, AR	Pembroke silt loam	May 21, 2018, 9:35 AM	—	20.6	16.1	92	2.40
2018-3	Fayetteville, AR	Pembroke silt loam	May 28, 2018, 10:45 AM	—	29.4	25.0	64	5.26
2018-4	Fayetteville, AR	Pickwick silt loam	June 4, 2018, 11:04 AM	4.75 (7.11)	26.7	23.9	51	6.33
2018-5	Fayetteville, AR	Captina silt loam	June 11, 2018, 11:00 AM	4.79 (7.36)	27.2	23.9	64	6.78
2018-6	Fayetteville, AR	Captina silt loam	July 31, 2018, 8:40 AM	4.86 (7.26)	21.7	22.8	80	0.25
2018-7	Fayetteville, AR	Captina silt loam	September 4, 2018, 10:50 AM	5.01 (8.20)	27.2	25.6	72	10.23
2018-8	Fayetteville, AR	Pickwick silt loam	September 11, 2018, 1:55 PM	4.99 (7.83)	26.7	25.6	40	4.32
2019-1	Prairie Grove, AR	Summit silty clay	May 14, 2019, 1:15 PM	4.89 (7.93)	23.9	21.1	60	5.94
2019-2	Prairie Grove, AR	Cherokee silt loam	May 27, 2019, 9:19 AM	4.93 (7.92)	23.9	22.8	71	5.10
2019-3	Prairie Grove, AR	Summit silty clay	June 3, 2019, 11:49 AM	4.89 (8.08)	26.1	22.2	68	8.43
2019-4	Prairie Grove, AR	Cherokee silt loam	June 13, 2019, 8:39 AM	4.81 (7.84)	16.5	21.1	80	3.81
2019-5	Prairie Grove, AR	Summit silty clay	June 18, 2019, 11:50 AM	4.75 (7.10)	25.6	23.9	70	3.95
2019-6	Prairie Grove, AR	Cherokee silt loam	June 24, 2019, 3:05 PM	4.70 (7.20)	27.8	26.1	59	6.59
2019-7	Prairie Grove, AR	Summit silty clay	July 3, 2019, 5:00 PM	4.72 (7.08)	31.7	28.3	58	6.56
2019-8	Prairie Grove, AR	Cherokee silt loam	July 18, 2019, 9:50 AM	4.78 (7.94)	28.9	26.7	74	7.98

^aTreatment solution contained 560 g ae ha⁻¹ dicamba + 860 g ae ha⁻¹ glyphosate + 1% v/v Intact™ (drift reduction adjuvant). The number in parentheses represents the pH of water before the mixture with herbicides and adjuvant. No treatment solution samples were taken from trials 2018-1, 2018-2, and 2018-3.

^bWind speed for a labeled application is 4.8 to 16 km h⁻¹.

gaseous herbicide in the air, particularly under field conditions. More research is necessary to evaluate the influence of volatilized dicamba on soybean response and how environmental factors impact dicamba detection in air samples. Field research was conducted with the following objectives: (1) to understand the influence of dicamba volatilization (concentration in air samples) on the response of soybean, (2) to determine which main environmental factors impact the dicamba concentration in air samples, and (3) to determine the frequency of detection and concentration of dicamba in eastern Arkansas during the summer months.

Material and Methods

Dicamba Application in Field and Herbicide Deposition

Sixteen trials were conducted on fields located at the Milo J. Shult Agricultural Research and Extension Center of the University of Arkansas, near Fayetteville, AR (36.098889°N, 94.179167°W) and at a producer field located near Prairie Grove, AR (35.969167°N, 94.297222°W) during the 2018 and 2019 growing seasons. The fields at the Fayetteville location had different soil classifications: Captina silt loam (fine-silty, siliceous, active, mesic Typic Fragiudults; 32.2% sand, 55.3% silt and 12.5% clay, 1.16% organic matter, and pH 6.8), Pembroke silt loam (fine-silty, mixed, mesic Ultic Paleudalfs; 11.3% sand, 67.7% silt and 21% clay, 2.4% organic matter and pH 6.6), and Pickwick silt loam (fine-silty, mixed, semiactive, thermic Typic Paleudults; 14% sand, 69% silt and 17% clay, 1.75% organic matter and pH 5.7). The soils at Prairie Grove were a Summit silty clay loam (fine, smectitic, thermic Oxyaquic Vertic Argiudolls; 8.7% sand, 62.1% silt and 29.2% clay, 4.78% organic matter, and pH 5.8) and Cherokee silt loam (fine, mixed, active, thermic Typic Albaqualfs; 27.1% sand,

54.4% silt, and 18.5% clay, 1.25% organic matter, and pH 6.2) (soil analysis for both locations at the University of Arkansas Agricultural Diagnostic Laboratory, Fayetteville, AR). Table 1 features the field location and soil texture for each trial.

An area equivalent to 0.37 ha (60.6 m by 60.6 m) was treated with 560 g ae ha⁻¹ of dicamba (XtendiMax® with VaporGrip® Technology, Bayer, St Louis, MO) plus glyphosate at 860 g ae ha⁻¹ (Roundup PowerMax®, Bayer) with a drift-reducing adjuvant (DRA) at 1% v/v (Intact™, Precision Laboratories, Waukegan, IL). Current label requirements include the addition of a volatility reduction agent (VRA) with in-crop dicamba applications (Anonymous 2022c); however, no VRAs were included in these experiments. The applications were made using a Mudmaster tractor-mounted sprayer (Bowman Manufacturing, Newport, AR) utilizing TTI 11003 VS nozzles (TeeJet® Spraying Systems, Wheaton, IL) calibrated to deliver 140 L ha⁻¹. A 50-ml sample of each treatment solution was collected before application for pH measurement. The pH of each treatment solution was noted once the measurement was constant for 3 min (HI 2211 pH Meter, Hanna Instruments, Woonsocket, RI). Detailed information about the pH of the treatment solution, the date, and the weather at trial initiation is included in Table 1. Applications were made to the field in distinct stages of production, including preplant (after soil cultivation) or vegetative soybean growth stages. A DR soybean cultivar (AG 47X6 RR2X, Asgrow Seed, Creve Coeur, MO) was planted at 350,000 seeds ha⁻¹ at some field sites in Fayetteville on a 91-cm-wide row spacing and in a 19-cm-wide row at Prairie Grove. Conditions of groundcover composition and percentage of living vegetation at the target area at the application were recorded. The treated area of the experimental replications included nine weed-free and tilled replicates, six replicates with DR soybean, and one that was non-cropped and weedy (Supplementary Table S1). Trial applications

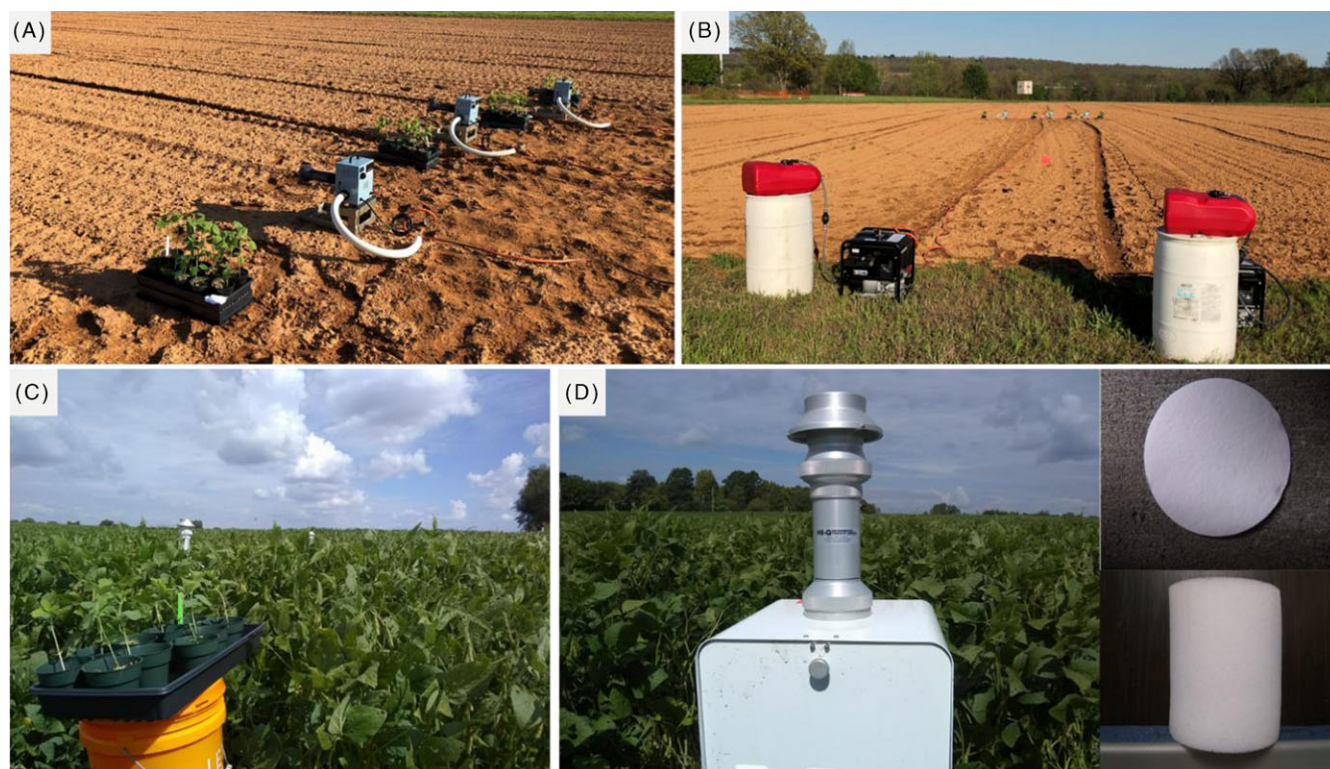


Figure 1. (A–C) High-volume air samplers and soybean bioindicators placed inside the treated area during different volatility experiments. (D) A close-up of an air sampler during collection and the filtering media used to trap volatile dicamba (glass-fiber filter paper and polyurethane foam, top and bottom right, respectively).

were separated by at least 5 d, and a minimum of 3 mm of rainfall occurred between each replication, except for two trials in 2018 (2018-4 and 2018-6; data not shown).

Before application, four filter papers measuring 110 mm in diameter (VWR International, Radnor, PA) were fixed to a 150 mm by 150 mm cardboard sheet placed horizontally at the target level (weedy or weed-free soil or soybean canopy) in the treated area to determine the concentration of dicamba applied. Wind speed data were collected every 3 s using a handheld anemometer device during each application. At 30 min following spraying, the filter papers were collected and placed inside separate 50-ml tubes (VWR International) and stored inside labeled ziplock bags to avoid cross-contamination. Samples were stored in coolers for transport to a -20°C freezer before analysis. Environmental conditions were evaluated while air sampling occurred. Air and soil temperature, dew point temperature, rainfall, and relative humidity were recorded using a weather station approximately 30 m from the treated area (Supplementary Figures S1–S3). Wind speed and direction data were not reported due to sensor failure. Weather sensors of air temperature, relative humidity, and the dew point were at 1.6 m from the soil surface, and the soil temperature was at 1-cm depth.

Analysis of Dicamba in Air Samples and Deposition within the Treated Area

Previous research evaluated volatile herbicides following field application utilizing air-sampling devices of different capacities, sample extraction from filtering media, and laboratory analysis using liquid chromatography and spectroscopy techniques (Mueller et al. 2013; Soltani et al. 2020). Dicamba volatility was evaluated using high-volume air samplers (Hi-Q Environmental

Products, San Diego, CA) placed inside the treated area. For each replicated trial, three and two air samplers were placed inside the treated area in 2018 and 2019, respectively. Each air sampler was equipped with a glass-fiber filter paper of 102 mm in diameter (Hi-Q Environmental Products) placed in series with a polyurethane foam (PUF) sorbent that measured 6 cm by 8 cm (diameter and length) (cat. no. 22954, Restek, Lancaster, PA). At 30 min after application, the air samplers were placed inside the treated area (Figure 1). The air sampler had the flow rate programmed to run constantly at 185 L min^{-1} to collect volatile dicamba emitted from the treated field. The samplers displayed the cumulative volume of air sampled and the time elapsed. Figure 1 illustrates air samplers in the field and filtering media used to trap the volatile herbicide. Previous research has shown that this experimental setup effectively traps volatile dicamba (Zaccaro-Gruener et al. 2022). The sampling height was 60 cm above the target. An additional air sampler was established as a control measurement approximately 1 km from the treated plot. Air sampler components were cleaned utilizing methanol before a trial and between each collection. Filters and PUFs were collected at 24, 48, 72, and 96 h after application (HAA) on trials replicated in 2018; in 2019, the trials ended at 48 HAA. The samples from each time interval were placed in labeled plastic bags and kept at -20°C until analysis.

Samples of application deposition (filter papers) and air-sampler PUFs and filter papers samples were sent to the University of Tennessee in Knoxville, TN. The method for dicamba extraction was based on Mueller and Steckel (2019a). An aliquot of 400 ml of methanol was added to the PUF samples before homogenizing and transferring them into a 1-L bottle. The bottle was secured to a shaker for an overnight extraction process. The filter paper samples were extracted using 40 ml of methanol for 2 h on

the same shaker. The extract solution was filtered and concentrated before resuspension with 5 ml of methanol. The solution was then filtered through a 0.45- μm filter before a 1-ml aliquot was dispensed in a 2-ml vial compatible with the liquid chromatography–mass spectroscopy (LC-MS) instrument. Samples of herbicide deposition were extracted using 40 ml of methanol and diluted 1/20 times before LC-MS analysis. External standards of dicamba acid dissolved in methanol were used to verify the dicamba concentration. Analysis was conducted by high-performance liquid chromatography using an Agilent Liquid Chromatograph (model 1290, Agilent Technologies, Santa Clara, CA) in tandem with single-quadrupole MS. Analytical results showed that the retention time of dicamba acid was 5.0 min, and the minimum quantitation limit was equivalent to 0.1 ng ml⁻¹ of solvent. Quality control included fortified samples, blank matrix, and duplicates to evaluate carry-over after each injection. Recovery was approximately 90%, and results were corrected for dilutions. Results of the average herbicide deposited on filters (ng) placed on the target area are summarized in Supplementary Table S1. The total dicamba detected (ng) in air samples was found by adding the amount detected in the PUF to the amount found on the filter papers that compose the air-sampler filtering media analyzed. Results were converted to concentration (in ng m⁻³) according to the air volume sampled at each collection interval.

Non-DR Soybean Bioindicators

Non-DR soybean plants (Credenz® 4748 LL, BASF, Research Triangle Park, NC) were grown in a greenhouse until the V1 or V2 growth stage. At 30 min following application for each experiment, the bioindicator plants were placed inside the treated area. The bioindicator plants were kept on trays to prevent contact with any treated surface (see Figure 1). The bioindicator sampling intervals were 0.5 to 24 h, 0.5 to 48 h, 0.5 to 72 h, 0.5 to 96 h, 24 to 48 h, 48 to 72 h, and 72 to 96 h in 2018; in 2019, the experiments ran up to 48 h. An additional set of plants was placed by the control air sampler to be used as a nontreated reference. Each sampling interval had 8 to 10 individual plants (pseudo-replicates). Preventive measures were taken to prevent the potential for cross-contamination with the treated surface and among the plant sets. Bioindicator plants were returned to the greenhouse following the predetermined exposure intervals and maintained until evaluation. Evaluations consisted of a dicamba injury score (0% = no effect to 100% = complete plant death) as represented in Figure 2, and height (cm) measured at 21 \pm 2 d after treatment (DAT). Aboveground biomass was collected at termination (21 DAT) and weighed after drying at 60 C for 5 d until constant mass. Average height and biomass data were converted to percentage relative reductions to a nontreated control for each trial to account for differences in growing conditions. Positive values indicate a reduction of height and biomass, while negative reduction values indicate that plants were taller or heavier than the nontreated reference.

Frequency of Dicamba Detection and Concentration Level in Air in Eastern Arkansas

In 2020 and 2021, air samplers were placed in a covered area in the vicinity of the main building of the Lon Mann Cotton Research Station, near Marianna, AR (34.732778°N, 90.766389°W), and the Northeast Research & Extension Center, in Keiser, AR (35.674167°N, 90.086667°W). Commercial dicamba applications within 1.6 km of both facilities are prohibited (Unglesbee 2021).

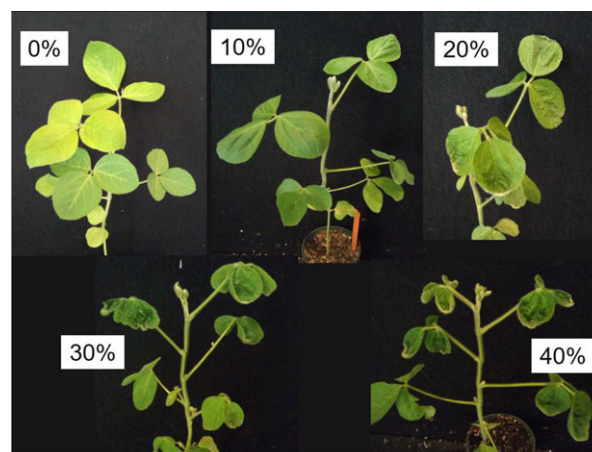


Figure 2. Representative pictures of the symptomology of non-dicamba-resistant soybean seedlings and the resulting injury rating (%) at 21 d after being exposed to volatilized dicamba emitted from a field treated with dicamba at 560 g ae ha⁻¹, glyphosate at 860 g ae ha⁻¹, and 1% v/v of a drift reduction adjuvant evaluated in 2018 and 2019 growing seasons.

Low-volume air pumps (model 220-5000TC, SKC, Eighty Four, PA) were connected to a 76-mm sorbent PUF contained within a 22 mm by 100 mm glass tube (cat. no. 226-92, SKC) using clear 15-cm plastic tubing (6.35-mm inner diameter, 9.53-mm outer diameter). The pumps ran continuously, and the air samplers were programmed to sample for a 24-h period (midnight to midnight). The airflow setting of the samplers was 5 L min⁻¹ (Check-mate Calibrator, SKC). The morning following sample collection completion, the PUF cartridge was collected and stored in a labeled plastic bag and kept at -20 C until analysis. Air-sampling components were cleaned after each collection using methanol, and a new cartridge was installed for subsequent sampling intervals. In 2020, sample collection was performed from June 3 until July 21 near Marianna and from June 6 until July 21 in Keiser, generating 37 and 38 samples in Keiser and Marianna, respectively. In 2021, collections were performed from June 6 until July 30 in Marianna and from June 10 until July 29 in Keiser, which generated 47 and 48 samples per location, respectively. Malfunction of the pump occurred a few days each year, resulting in failure to collect samples daily within this period. Samples were sent to the Mississippi State Chemistry Laboratory (Starkville, MS) for analysis of dicamba content in the PUF samples. Sample extraction and quantification were conducted following Soltani et al. (2020). The analytical quantitation limit for the small PUFs was equivalent to 0.3 ng ml⁻¹ of solvent. Analytical results were converted (to total ng m⁻³ d⁻¹) based on the constant airflow reported earlier. Dicamba content results were displayed separately by location and year. Additionally, environmental data were obtained from weather stations located at each research station. Maximum air temperature, average relative humidity, wind speed, and accumulated rainfall with dicamba detection were included by sampling date, location, and year.

Statistical Analysis

The total dicamba concentration in air (ng m⁻³ d⁻¹) detected by the three air samplers was averaged in each sampling interval. Data distributions were analyzed and selected based on the lowest log-likelihood fit and the corrected Akaike information criterion (AICc) using the distribution platform of JMP Pro v. 16.1 (SAS

Institute, Cary, NC). Dicamba concentration in air samples had lognormal distribution. The field experiment had 16 unique environments over the 2018 and 2019 seasons, with data organized by site-year. Statistical analysis was performed only considering data from 0.5 to 48 HAA, as this period was replicated in both years. Natural logarithmic transformation of dicamba detection was done to improve the homogeneity of variance. The impact of ground-cover type (vegetation or soil), percentage of groundcover from living vegetation, and sampling intervals were tested, considering site-years as a random variable. ANOVA was performed in JMP using the Mixed models of the Fit Model platform, and the least-squares means were compared using Fisher's protected LSD ($\alpha = 0.05$) (SAS Institute Inc. 2022). Dicamba detection results were back-transformed to simplify the interpretation of results. The relationships between weather variables (averaged 24-h intervals) and dicamba detections were evaluated using Spearman's correlation coefficients. The relationship between relative humidity and sampling timing with dicamba detection was investigated using Mixed models in the Fit Model platform ($\alpha = 0.05$). However, correlations were discussed because relative humidity did not satisfy the requirements for inclusion in the model to result in a generalized $R^2 \geq 0.2$ (data not shown).

Bioindicator results of soybean injury (%), relative height, and biomass reductions (% of nontreated) were analyzed using JMP. Injury followed a beta distribution, while relative height and biomass reductions exhibited normal distributions. Results of dicamba in air samples ($\text{ng m}^{-3} \text{ d}^{-1}$) were analyzed by collection timing (up to 48 HAA) and trial. Relationships between injury, height, and biomass reductions with dicamba in air samples were explored using a Generalized Regression model in the Fit Model platform with the Lasso estimation method and AICc as the validation method. The best model of the relationship between injury and dicamba concentration was nonlinear. The prediction model of injury by dicamba concentration had limitations below 0.2 ng m^{-3} , because every air sample analyzed from the treated area resulted in a detection (lowest = 0.1 ng m^{-3}), and every plant exposed to the treated plot showed symptomatology. The Generalized Regression analysis resulted in values of generalized R^2 to the relationships, in which a value closest to 1 indicates a perfect relationship (Nagelkerke 1991; SAS Institute Inc. 2022). Previous research also utilized nonlinear models to explain soybean injury resulting from low-dose applications of dicamba (Robinson et al. 2013). Regression models of height and biomass impacted by dicamba detection followed linear relationships. Analyses of predicted dicamba concentrations over a 24-h period that would result in 10%, 15%, 20%, and 50% soybean injury and 5% and 10% height reduction were conducted.

Dicamba concentration data from Marianna and Keiser were analyzed in JMP Pro v. 16.1. Statistical analysis only considered data when dicamba was detected. ANOVA was performed to assess the impact of location, year, and the interaction on dicamba concentrations in air samples using Mixed models of the Fit Model platform in JMP, considering the sampling date as a random variable. Natural logarithmic transformations were applied to improve the homogeneity of variance of the quantification data. Weather variables were analyzed in the Multivariate platform of JMP against the results of dicamba concentration in air samples. Data considered in this analysis included times when no herbicide was detected to evaluate the impact of weather conditions on dicamba detection. Relationships among these variables were explored using Spearman's correlation coefficients. Generalized regression analysis of dicamba concentration in the air of

Marianna and Keiser was performed considering maximum air temperature, average relative humidity, and the frequency of rain events; however, the poor generalized R^2 value (<0.2) was deemed not appropriate; therefore, only correlations were discussed. Additional analyses included hypothesis tests (t -test) of dicamba concentration contrasting days with measurable rain events versus clear days and the concentration when more than 2 d elapsed since a rain event versus fewer than 2 d.

Results and Discussion

Dicamba Detections after Application and the Environmental Impact

Replications of the field experiment to evaluate the impact of volatile dicamba on susceptible soybean response were initiated from May 7 to September 11, 2018, and May 14 to July 18, 2019, from 8:40 AM to 5 PM (Table 1). Air temperature during herbicide applications ranged from 16.5 to 31.7 °C; relative humidity ranged from 40% to 92%; and wind speed peaked at 10.23 km h^{-1} (Table 1). The pH of solutions used on treatments was collected before application and analyzed in all but three replicated trials (2018-1, 2018-2, and 2018-3; see Table 1). The solutions containing the herbicide treatments (dicamba plus glyphosate with a particle DRA) were acidic, as pH measurements ranged from 4.75 to 5.01. According to the Henderson-Hasselbalch acid-base equilibrium (Aronson 1983), a solution pH between 4 and 5 has 1% to 0.1% of dicamba molecules in the acid form, prone to volatilize, and 99% to 99.9% of the molecules in nonionized form. Previous research has examined the impact of herbicide formulations and additives on the stability of dicamba in solution and conversion to the volatile acid form (Mueller and Steckel 2019b). The authors established that adding potassium salt of glyphosate to dicamba was a key contributor to reducing the solution pH up to 2.1 units. They concluded that the increase in the formation of dicamba acid occurs due to the pH reduction, increasing volatility potential. The present research showed a smaller change in the solution pH than the study mentioned, implying that the off-target movement observed could be impacted not only by volatilization. It is possible that suspended spray particles could have remained in the area after application.

Results of dicamba deposited on filter papers positioned on the treated plot (soil or vegetation canopy) during application ranged from 205,982 to 523,372 ng of dicamba per filter paper, which equated to 217 to 551 g ae ha^{-1} (Supplementary Table S1). This variation could be expected, as coverage variability could occur during applications over a small area of the filter paper (95 cm^2), or reflect the impact of wind gusts during application, reducing herbicide deposition on the filter papers positioned on the target beneath the sprayer. However, the deposition results were within acceptable limits for applications of 560 g ha^{-1} of dicamba using a large-scale sprayer.

Results of dicamba concentration in air samples over the treated field in 2018 ranged from 0.384 to $6.536 \text{ ng m}^{-3} \text{ d}^{-1}$ from 0.5 to 24 HAA, 0.13 to $2.581 \text{ ng m}^{-3} \text{ d}^{-1}$ from 24 to 48 HAA, 0.258 to $1.486 \text{ ng m}^{-3} \text{ d}^{-1}$ from 48 to 72 HAA, and from 0.1 to $1.045 \text{ ng m}^{-3} \text{ d}^{-1}$ from 72 to 96 HAA (Table 2). Most of the herbicide collected in air samples occurred from 0.5 to 48 HAA (56% to 87% of total herbicide detected over replicated trials). Therefore, trials in 2019 lasted up to 48 HAA for logistic and cost reasons; however, this sampling period still accounted for the majority of potential dicamba emitted. As expected, most

Table 2. Dicamba concentration in air samples at 24-h intervals, up to four different timings starting at 0.5 to 24, 48, 72, and 96 h after application (HAA) in the 2018 and 2019 growing seasons.

	Hourly intervals of exposure after application ^a			
	0.5–24	24–48	48–72	72–96
Dicamba concentration in air				
Trial code	ng m ⁻³			
2018-1	1.276	1.186	0.824	0.608
2018-2	1.721	2.581	1.486	0.757
2018-3	3.803	1.882	0.466	0.575
2018-4	3.045	0.688	0.981	0.766
2018-5	6.536	0.130	0.389	0.627
2018-6	2.632	1.183	0.922	1.045
2018-7	1.767	0.315	0.258	0.100
2018-8	0.384	0.321	0.455	0.100
2019-1	1.369	0.29	—	—
2019-2	3.012	0.506	—	—
2019-3	1.475	0.25	—	—
2019-4	8.598	9.42	—	—
2019-5	7.716	1.342	—	—
2019-6	0.679	0.156	—	—
2019-7	0.811	1.706	—	—
2019-8	5.705	1.617	—	—

^aTrials conducted in 2018 were terminated at 96 HAA, while trials in 2019 lasted up to 48 HAA. Trial code equals year and replicate.

replicated trials showed that the concentration of dicamba in air samples was the highest at the first sampling interval and decreased with time, except for trials 2018-2, 2019-4, and 2019-7. These results were consistent with previous research, which reported that dicamba concentrations were the greatest following an application and decreased until the last evaluation at 72 HAA (Bish et al. 2019a). For trials conducted in 2019, the range of dicamba concentrations was broad, ranging from 0.679 to 8.598 ng m⁻³ from 0.5 to 24 HAA and 0.156 to 9.42 ng m⁻³ from 24 to 48 HAA (Table 2). Weather conditions could have impacted the variability in dicamba concentration in air samples during each experimental run.

The impacts of sampling interval, groundcover type, and percentage of living vegetation were analyzed, considering experimental runs as random (Table 3). Data from the second sampling interval of the 2019-4 trial were considered to be an outlier and excluded from statistical analysis. The treated area groundcover varied considerably (Supplementary Table S1); therefore, comparisons were made between the type of treated surfaces as vegetated (combining DR soybean and non-crop weedy cover) versus non-vegetated (bare soil) and the percentage of living vegetation on these surfaces. Results showed no statistical differences in dicamba concentration by surface type (P-value = 0.56; Table 3); dicamba concentration averaged 2.71 and 1.90 ng m⁻³ on vegetated and soil surfaces, respectively (data not shown). Previous studies reported higher dicamba volatility after applications to vegetated surfaces than soil (Mueller and Steckel 2021). Researchers hypothesized that dicamba volatility was higher in vegetated surfaces due to several factors, including a greater surface area to absorb and emit herbicide, and that water transpiration could promote herbicide emissions from plant surfaces. The percentage groundcover of living vegetation (P-value = 0.51; Table 3) did not significantly impact dicamba concentration in air samples. The groundcover composition of the present trials varied substantially, particularly considering trials with vegetation present; the amount of living vegetation varied from 5% to 99%, and no significant differences could be observed regarding groundcover conditions (Supplementary Table S1). Statistical results showed that site-years

Table 3. Influence of fixed effects on dicamba concentration in air samples (ng m⁻³) and probability values.

Effects ^a	Treatments ^b	Average dicamba concentration ^c	P-value
		—ng m ⁻³ —	
Sampling interval	0.5–24 HAA ^c 24–48 HAA	2.27 a 0.67 b	0.0010*

^aThe effects of groundcover composition and % living vegetation of groundcover were not significant (P-value = 0.56 and 0.51, respectively) and are not shown. Statistical analysis included data from 0.5 to 48 HAA and considered experimental runs a random variable. Asterisk (*) indicates a significance of treatment effects at P = 0.05.

^bHAA, hours after application.

^cDicamba concentration represents back-transformed values of least-squares means. Means followed by a different letter differ according to Fisher's protected LSD ($\alpha = 0.05$).

Table 4. Spearman's correlation coefficients associated with dicamba concentration (ng m⁻³) in air samples collected across 16 experimental runs between 2018 and 2019 and environmental factors.^a

Parameter	Average air temperature	Min. atmospheric relative humidity	Rainfall	Max. dew point temperature
Correlations	0.08	-0.39	0.14	-0.12

^aData included herbicide detections collected across experimental runs from 0.5 to 48 h after application. Values nearest to 1 correspond to the strongest relationships. Correlation value in bold is significant at P = 0.05. The average soil temperature at 1-cm depth is not shown, as the correlation coefficient was not significant and below 0.10.

were not different for dicamba detections (P-value = 0.3197; data not shown), and only the sampling interval affected dicamba concentration in air (P-value = 0.0010). According to these results, dicamba concentration in air samples was 2.27 ng m⁻³ from 0.5 to 24 HAA and decreased to 0.67 ng m⁻³ by 24 to 48 HAA (Table 3).

The impact of weather on dicamba concentration detected was explored by monitoring air and soil temperatures, relative humidity, and dew point temperature reported by site-year (Supplementary Figures S1 and S2) and the accumulated hourly results of rainfall by replicated trial (Supplementary Figure S3). Sensor failure prevented wind speed data collection during these experiments; meanwhile, data gathered during application showed that wind lower than 4.8 km h⁻¹ occurred in 6 of 16 experimental runs. Therefore, stable air conditions could have impacted these field trials similarly to reports in which stable air during a temperature inversion exacerbated the secondary movement of dicamba (Bish et al. 2019a). Previous studies reported that higher atmospheric temperatures, lower relative humidity, or conditions with temperature inversions and stable air had been associated with dicamba detections (Behrens and Lueschen 1979; Bish et al. 2019a; Egan and Mortensen 2012). The minimum relative humidity was the only environmental variable correlated with dicamba concentration in air samples across 16 experiments (coefficient = -0.39; Table 4). The relative humidity data ranged from 28% to 100% across site-years (Supplementary Figures S1 and S2), and the average dicamba concentration was reduced as relative humidity increased. Other research reported that low atmospheric relative humidity increases dicamba volatility (Behrens and Lueschen 1979; Gavrilescu 2005; Mueller and Steckel 2021; Mueller et al. 2013); although researchers have hypothesized that high humidity conditions can increase dicamba settlement on plant or soil surfaces (Egan and Mortensen 2012).

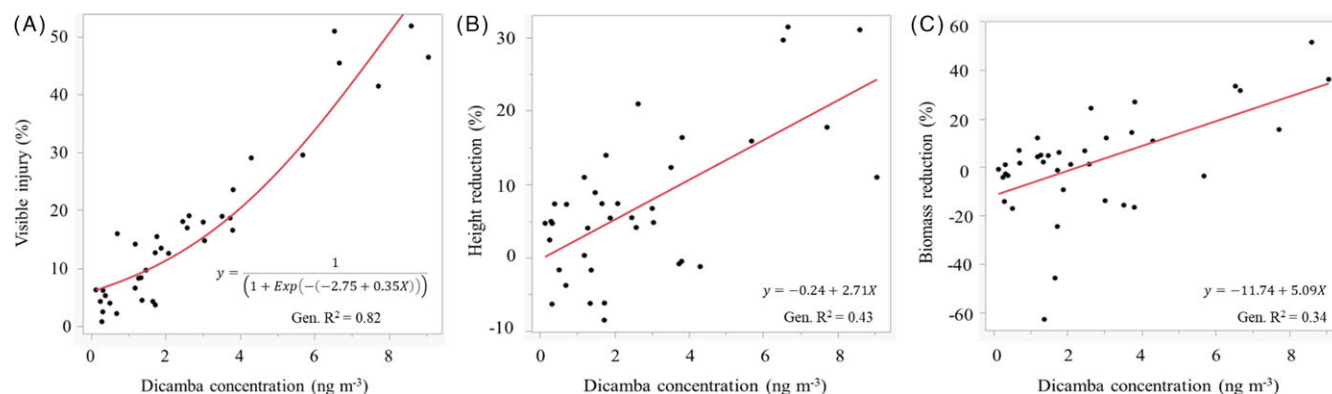


Figure 3. Generalized regression curves fit dicamba concentration in air (ng m^{-3}) and (A) visible injury (%), (B) height reduction (%), or (C) biomass reduction (%) of susceptible soybean at 21 d after treatment across 13 experimental runs between 2018 and 2019. The analysis excluded three experimental runs for which no plants were available for evaluation; data for soybean height and biomass reductions by dicamba concentration both followed normal distributions; meanwhile, soybean injury by dicamba concentration followed a beta distribution.

Response of Non-DR Soybean to Dicamba by Indirect Exposure

Visible injury, height, and biomass reduction were evaluated on non-DR soybean seedlings at 21 d after a single exposure to the field treated with dicamba. Soybean bioindicators from three of 16 trials (2019-6, 2019-7, and 2019-8; Supplementary Table S1) suffered damage (feeding by insects or rodents) and were excluded from these evaluations. Auxin injury symptomology was observed in nearly all plants placed in the field. The set of plants positioned by the control air sampler occasionally showed symptoms of damage (visible injury $\leq 5\%$), and dicamba was detected at approximately $54 \text{ ng} (\pm 24)$ over the entire intervals (96 h in 2018 and 48 h in 2019), equivalent to 0.24 ng m^{-3} in 2018 and 0.14 ng m^{-3} in 2019. Other mechanisms could have impacted the off-target movement of dicamba from the treated area toward the control sampler positioned 1 km away. The main symptoms observed were leaf cupping, epinasty, and sometimes extreme malformation of the apical meristem. Figure 2 shows representative plants with symptoms and ratings of visible injury attributed (ratings of visible injury ranged from 1 to 52%; data not shown). Soybean plants exposed to the field at 0.5 to 24 h, 0.5 to 48 h, 0.5 to 72 h, 0.5 to 96 h resulted in similar responses, but these differed from plants placed on the field at 24–48 h, 48–72 h, and 72–96 h (data not shown). The injury results indicate that the first 24 h following the application had the highest concentration of dicamba in the air. A general trend of lower symptoms was observed after 24 HAA, but this reduction was not significant by exposure timing (data not shown). Analysis of dicamba concentrations with plant responses (injury, height, and biomass) only considered consecutive intervals, 0.5 to 24 and 24 to 48 HAA, collected in 2018 and 2019. According to raw data, all air samples collected resulted in dicamba concentrations greater than $0.1 \text{ ng m}^{-3} \text{ d}^{-1}$ and elicited injury on non-DR soybean placed in the treated field (data not shown). The percent reduction results of height and biomass were lower than the percent visible injury of soybean exposed to the treated field.

According to regression results across site-years, soybean injury and dicamba concentration in air samples followed a strong positive relationship (generalized $R^2 = 0.82$; Figure 3). According to the model, the predicted concentrations of a single exposure to volatile dicamba resulting in 10% and 20% injury were 1.60 and $3.94 \text{ ng m}^{-3} \text{ d}^{-1}$, respectively (Table 5). The level of volatilized

dicamba predicted to result in 50% injury to non-DR soybean was 7.17 to $8.96 \text{ ng m}^{-3} \text{ d}^{-1}$. According to research by Robinson et al. (2013), a foliar application of dicamba at 0.20 to 0.5 g ha^{-1} injured V2 soybean an estimated 10%. Similar research determined that field application of dicamba at 56 g ha^{-1} resulted in an overall 9.3% injury (Sciumbato et al. 2004). It is challenging to compare exposures by volatile herbicides to those of direct applications; furthermore, exposure time is likely to influence plant responses. The absorption of foliar-applied herbicides occurs primarily via diffusion across the cuticle of the upper leaf surface (Zimdahl 2013); meanwhile, stomata penetration is an essential pathway of absorption of volatile compounds (Currier and Dybing 1959; Skoss 1955). Specific research is needed to quantify the absorption rate of volatile dicamba through stomata.

The relationships between soybean height or biomass reductions by dicamba concentrations were not as strong as that with visible injury (Figure 3). Results showed that dicamba detection explained 43% of the height reduction data variability and 34% of biomass reduction variability. Similar to visible injury, height and biomass reductions were slightly lower on plants exposed to the field after 24 HAA (data not shown). Previous research reported that low-dose treatments containing dicamba foliar applied to V3/V4 soybean resulted in a quadratic relationship with soybean height ($R^2 = 0.42$) (Griffin et al. 2013). According to the present research, a 5% reduction in soybean height resulted from a single exposure to a dicamba concentration of $1.94 \text{ ng m}^{-3} \text{ d}^{-1}$, while exposure to dicamba at $3.78 \text{ ng m}^{-3} \text{ d}^{-1}$ reduced height by 10% (Table 5). According to research by Griffin et al. (2013), plant height was reduced by 9% when sprayed directly with dicamba at 17.5 g ha^{-1} . Due to the low generalized R^2 value of the relationship, no predictions were made between the reduction of soybean biomass and dicamba detections (Figure 3). Even though this relationship was not strong, it indicated that increasing dicamba concentration could reduce soybean growth. Auxin mimic herbicides may impact non-DR species by stimulating growth and internode expansion (Zimdahl 2013), which could explain the lower R^2 values for the biomass and height models.

Frequency and Concentration of Dicamba Detected within Air in Eastern Arkansas

The daily concentration of dicamba in air samples was monitored at two locations in eastern Arkansas from June 3 to July 21, 2020,

Table 5. Predicted dicamba concentration in air and the lower and upper 95% confidence intervals (CI) resulted from relationships with soybean injury (%) and height reductions from a onetime exposure.

Variables	Predicted dicamba in air ^a		
	Average	Lower 95% CI	Upper 95% CI
Soybean injury (%)		ng m ⁻³	
10	1.60	1.08	2.03
15	2.93	2.53	3.31
20	3.94	3.55	4.36
50	7.93	7.17	8.96
Soybean height reduction (%)			
5	1.94	0.97	2.89
10	3.78	2.84	5.76

^aPredicted values resulted from an inverse prediction model using the Generalized Regression (see Figure 3). Data comprised dicamba concentration in air samples and soybean response across experimental runs between 2018 and 2019.

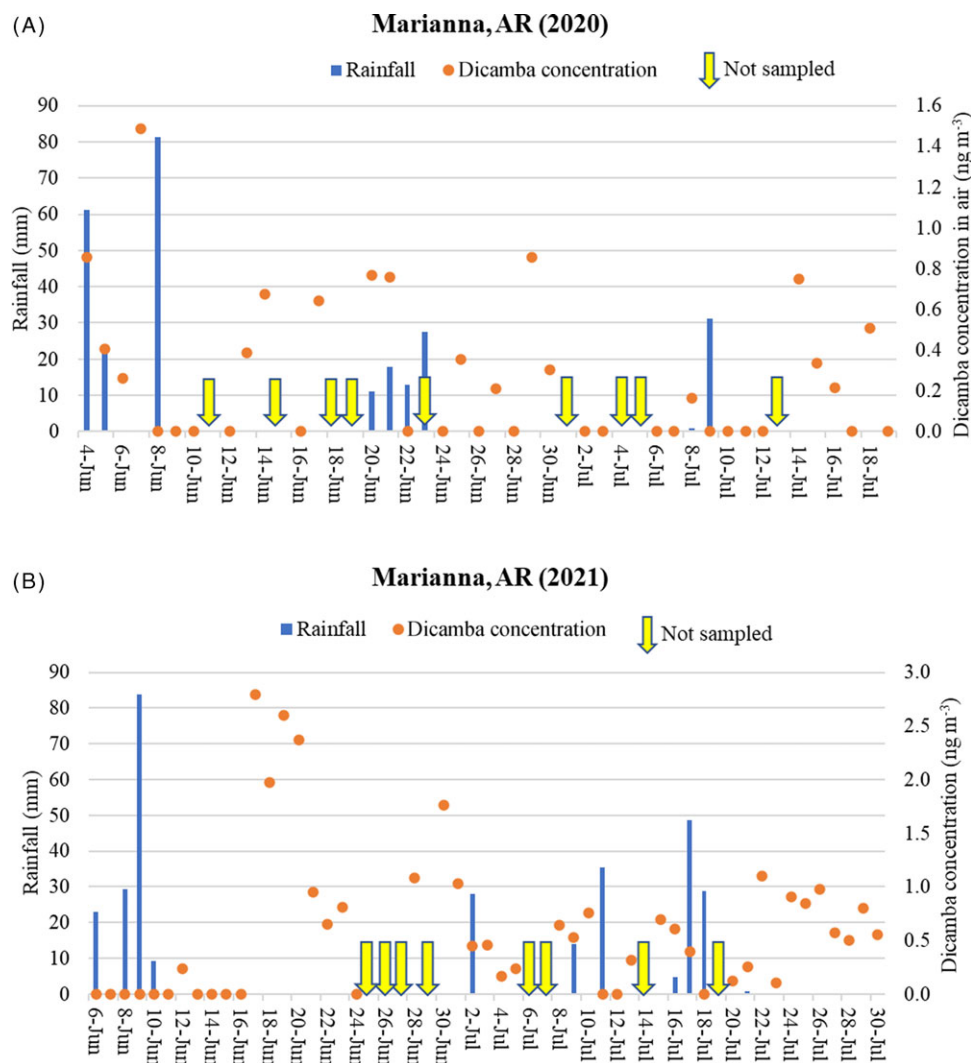


Figure 4. Dicamba concentration in air (ng m⁻³ d⁻¹) at Marianna, AR, and daily rainfall (mm) in 2020 (A) and 2021 (B). Dicamba was detected in 18 of 37 samples in 2020 and 33 of 47 samples in 2021. Yellow arrows indicate days for which no sample was collected.

and June 6 to July 30, 2021, near Marianna and from June 6 to July 21, 2020, and June 10 to July 29 of 2021 in Keiser. The maximum concentration of dicamba in Marianna was 1.49 ng m⁻³ d⁻¹ in 2020 and 2.79 ng m⁻³ d⁻¹ in 2021 (Figure 4). The maximum daily

concentration of dicamba was greater in Keiser: 2.87 ng m⁻³ in 2020 and 7.96 ng m⁻³ d⁻¹ in 2021 (Figure 5). The frequency at which dicamba detection occurred in eastern Arkansas was substantial, especially considering that the state prohibited

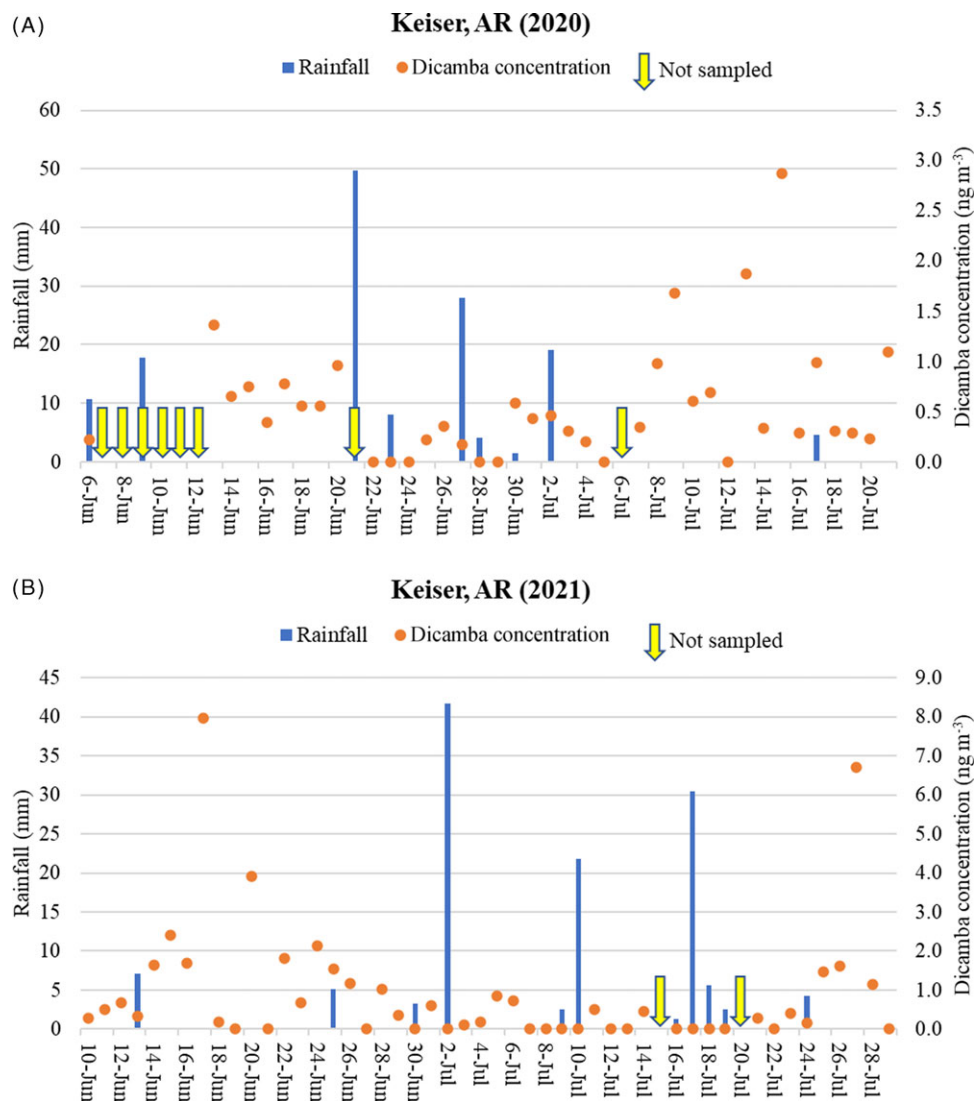


Figure 5. Dicamba concentration in air ($\text{ng m}^{-3} \text{d}^{-1}$) at Keiser, AR, and daily rainfall (mm) in 2020 (A) and 2021 (B). Dicamba was detected in 31 of 38 samples in 2020 and 31 of 48 samples in 2021. Yellow arrows indicate days for which no sample was collected.

dicamba applications in soybean and cotton beyond the cutoff dates of May 25, 2020, and June 30, 2021, and a 1.6-km no dicamba spray buffer around the university research stations was established (Unglesbee 2021). Dicamba detections occurred in 18 of 37 samples (49%) and 33 of 47 samples (70%) at Marianna in 2020 and 2021, respectively (Figure 4). In Keiser, dicamba detections occurred in 31 of 38 samples (82%) in 2020 and 31 of 48 samples (65%) in 2021 (Figure 5). All detections that occurred in 2020 were after the dicamba application cutoff date, while 45% and 70% of the detections in 2021 occurred after the cutoff date in Keiser and Marianna, respectively, which suggests that applications regularly occurred beyond the state-appointed dicamba application cutoff and that volatile dicamba remained in the atmosphere several days after applications. Susceptible soybean in these locations exhibited dicamba injury symptomology (leaf and apical meristem malformation), as seen in Figure 6, taken on June 28, 2021, at the Northeast Research and Extension Center in Keiser, AR. The soybean damage shown in

the picture was likely caused by multiple exposures to low doses of dicamba. Based on dicamba concentrations found in air samples at the Keiser site where the photo was taken in 2021, there were at least nine daily exposures to more than $1 \text{ ng m}^{-3} \text{d}^{-1}$ of dicamba, with one exposure of almost $8 \text{ ng m}^{-3} \text{d}^{-1}$ (Figure 5).

ANOVA results of dicamba concentration in air samples collected in eastern Arkansas were impacted only by year (P -value = 0.0463; Table 6). According to statistical analysis with data pooled over locations, average dicamba concentration increased by nearly 50% when comparing samples collected in 2020 ($0.51 \text{ ng m}^{-3} \text{d}^{-1}$) with those collected in 2021 ($0.72 \text{ ng m}^{-3} \text{d}^{-1}$). The increase in dicamba concentrations in the air from year to year indicated that dicamba usage in these locations in east Arkansas most likely increased over time, which is not surprising considering the extension of the dicamba application cutoff date in 2021. Overall, the average concentration of dicamba in air samples was 0.66 and $0.54 \text{ ng m}^{-3} \text{d}^{-1}$ in Keiser and Marianna, respectively (Table 6). Additionally, the sampling date impacted dicamba concentration



Figure 6. Non-dicamba resistant soybean damage at the Northeast Research and Extension Center in Keiser, AR. This photo was taken on June 28, 2021.

in air samples (P -value = 0.0474; data not shown), which could be attributed to weather variations each day that influenced the detection of herbicide.

Daily environmental conditions were monitored as air sampling occurred in Marianna and Keiser and reported by location and year (Figures 4 and 5; Supplementary Tables S2–S5). Spearman's correlation was used to determine relationships between environmental factors and dicamba air concentration in eastern Arkansas. The correlation coefficients were significant and moderate for the maximum air temperature, average relative humidity, accumulated rainfall, and time interval since a rainfall event (Table 7). The maximum air temperature and the time since rain event were positively correlated with the concentration of dicamba in air samples (coefficient = 0.24 and 0.32, respectively). Similarly, previous research reported that higher air temperatures significantly increased dicamba volatility potential (Bish et al. 2019a; Mueller and Steckel 2019a; Ouse et al. 2018). Additionally, findings suggested an increase of dicamba concentration in the air as time elapsed following a rain event. Dicamba concentration in air samples collected in eastern Arkansas was negatively correlated with average relative humidity and accumulated rainfall (coefficient = -0.35 and -0.28 , respectively; Table 7). It may be possible that high relative humidity and rainfall promote the settlement of dicamba vapors in soil and onto plant surfaces, reducing concentration in air samples, which is consistent with previous research (Behrens and Lueschen 1979; Egan and Mortensen 2012; Mueller and Steckel 2021; Oseland et al. 2020a). Considering only the days that dicamba was not detected across years and locations, 58% of these samples were collected the day following a rain event (Figures 4 and 5). Additional analysis showed that average dicamba concentration was reduced from $0.74 \text{ ng m}^{-3} \text{ d}^{-1}$ on clear days to $0.25 \text{ ng m}^{-3} \text{ d}^{-1}$ when rainfall occurred (lowest measurable rain = 0.245 mm d^{-1} ; Table 8). It is possible that detected dicamba was a result of rainfall events later

in the day; hence, the earlier detection. Furthermore, the average dicamba concentration increased from $0.41 \text{ ng m}^{-3} \text{ d}^{-1}$ in less than 2 d from a rain event to $0.83 \text{ ng m}^{-3} \text{ d}^{-1}$ when more than 2 d elapsed after rainfall (Table 8). These results indicated that greater rainfall frequency reduced dicamba detection in the atmosphere by wet herbicide deposition in the soil profile (Gavrilescu 2005).

The experiments conducted throughout this research showed a positive relationship between the concentration of dicamba in air and soybean response, particularly for visible injury and height reductions after a single exposure. For instance, a single exposure to $1 \text{ ng m}^{-3} \text{ d}^{-1}$ of dicamba could result in 8.3% injury and 2.5% height reduction (Figure 3). However, data collected in eastern Arkansas at Mariana and Keiser from June and July resulted in dicamba concentrations in air $\geq 1 \text{ ng m}^{-3} \text{ d}^{-1}$ in 6 samples collected in 2020 and 22 samples in 2021 (Figures 4 and 5).

According to previous research, the loading of pesticides in the atmosphere is relative to the input of agricultural use (Waite et al. 2005). The atmospheric loading of dicamba could result in consecutive exposures of soybean and other susceptible crops grown surrounding DR technology. As shown in this research (Figures 4 and 5) and previous reports, soybean damage resulting from multiple exposures to dicamba could be economically detrimental for farmers not growing the DR technology (Steckel et al. 2017). It is important to note that the dicamba treatment evaluated in this study, the DGA salt with VaporGrip® formulation plus glyphosate and DRA once labeled for DR cropping systems, is not currently a legal application, and it could represent a worst-case scenario. Recent federal and state restrictions on dicamba applications, including limited tank-mix partners, required additional VRA, and establishment of a season cutoff (June 30 for soybean and July 30 for cotton) aim to reduce off-target movement of dicamba (Anonymous 2022c; USEPA 2020). Conditions that

Table 6. Effect of year, location, and their interaction on dicamba concentrations in air samples collected in eastern Arkansas.

Fixed effects ^a	Dicamba concentration in air ^b
Year	—ng m ⁻³ d ⁻¹ —
2020	0.51 b
2021	0.72 a
Location	
Keiser	0.66
Marianna	0.54
Location × year	
Keiser × 2020	0.55
Keiser × 2021	0.81
Marianna × 2020	0.46
Marianna × 2021	0.63

^aAnalysis performed using a Mixed model in JMP Pro v. 16.1, with natural logarithm-transformed dicamba detection and considering sampling date as a random variable. ANOVA for dicamba concentration was impacted by year (P-value = 0.0463) but not by location by year interaction (P-value = 0.7856) or by location (P-value = 0.4689).

^bDicamba concentration represented back-transformed values of least-squares means. Means followed by distinct lowercase letters within the same effect category were different according to Fisher's protected LSD ($\alpha = 0.05$).

Table 7. Spearman correlation coefficients associated with dicamba concentration (ng m⁻³) in air samples collected at Marianna and Keiser, AR, in 2020 and 2021 and environmental factors during sampling.^a

Parameter	Max. air temperature ^b	Avg. relative humidity	Rainfall ^b	Time since rain event
Correlations	0.24	-0.35	-0.28	0.32

^aData included herbicide concentration across locations and years. Values nearest to 1 correspond to the strongest relationships. Correlation values in bold were significant at P = 0.05. The average wind speed correlation was not shown as it was not significant.

^bRainfall is daily rainfall accumulated.

Table 8. Means and t-test results contrasting dicamba concentration in air (ng m⁻³ d⁻¹) for comparisons of clear days vs. days with measurable rain or more than 2 d since a rain event versus fewer than 2 d since a rain event.^a

Contrast	Dicamba concentration in air	P-value
	—ng m ⁻³ d ⁻¹ —	
Clear days vs. days with measurable rain	0.74 vs. 0.25	<0.0001*
>2 d since rain vs. <2 d since rain	0.83 vs. 0.41	0.0059*

^aData averaged over years and locations. The lowest amount of rain accumulated was 0.245 mm. Asterisk (*) indicates a significance of treatment effects at P = 0.05.

increase the potential for dicamba volatility should be avoided to reduce the impacts of off-target movement, and additional research should establish the consequences of multiple low-dose exposures on non-targeted species.

Supplementary material. To view supplementary material for this article, please visit <https://doi.org/10.1017/wsc.2023.22>

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