Weed Science

www.cambridge.org/wsc

Atmospheric deposition of dicamba herbicide can cause injury to sensitive soybean

Eric Oseland[1], Mandy Bish[2], Robert Lerch[3] and Kevin W. Bradley[4]

[1]Director of Agronomy and Research, Missouri Soybean Association, Columbia MO, USA; [2]Assistant Professor, Division of Plant Sciences and Technology, University of Missouri, Columbia MO, USA; [3]Soil Scientist, USDA-ARS, Cropping Systems and Water Quality Research Unit, Columbia MO, USA and [4]Professor, Division of Plant Sciences and Technology, University of Missouri, Columbia MO, USA

Research Article

Cite this article: Oseland E, Bish M, Lerch R, Bradley KW (2024) Atmospheric deposition of dicamba herbicide can cause injury to sensitive soybean. Weed Sci. **72**: 422–431. doi: 10.1017/wsc.2024.9

Received: 22 September 2023
Revised: 27 December 2023
Accepted: 5 February 2024
First published online: 20 February 2024

Associate Editor:
Timothy L. Grey, University of Georgia

Keywords:
Deposition; dicamba; herbicide injury; off-target movement

Corresponding author:
Kevin W. Bradley;
Email: BradleyKe@missouri.edu

Abstract

The herbicide dicamba has injured millions of hectares of sensitive plant species in the United States since 2017. This injury has coincided with the commercialization of dicamba-resistant soybean [*Glycine max* (L.) Merr.] and cotton (*Gossypium hirsutum* L.). We quantified atmospheric deposition and mass flux of dicamba in 12 soybean production regions of Missouri. Dicamba was routinely detected in weekly deposition samples collected during agriculturally intensive spray periods. Observed concentrations were indicative of both local (<1 km) and long-distance transport (>1 km) of airborne dicamba. High-deposition events (>100 μg m^{-2}) occurred annually in southeast Missouri, and peak dicamba deposited at these sites (12.5 to 84.0 μg m^{-2}) was sufficient to injure non–dicamba resistant soybean. Adoption rate of dicamba-resistant crops and atmospheric stability explained much of the variance, and it is difficult for a herbicide product label to address these variables. Overall, these results demonstrated that dicamba was commonly deposited from the atmosphere during the growing season, and observed concentrations and fluxes were strongly related to the timing and magnitude of rainfall events and the amount of dicamba usage near collection sites.

Introduction

Movement of dicamba herbicide from the site of application to unintended locations has become one of the most controversial and problematic issues in row-crop production in the United States (Association of American Pesticide Control Officials 2020; USEPA 2020). In 2017, an unprecedented number of herbicide injury complaints (approximately 2,700) were filed with state departments of agriculture due to movement of dicamba onto non-targeted plants (i.e., off-target movement) (Bish et al. 2020). Complaints included nearly 1.5 million ha of non–dicamba resistant (non-DR) soybean [*Glycine max* (L.) Merr] and a variety of other plant species such as fruit and nut trees, grapes (*Vitis* spp.), commercial gardens, specialty crops, and residential properties (Bish et al. 2020; Bradley 2018). This issue was the featured topic in many major news outlets (*New York Times*, *Washington Post*, *Chicago Tribune*, NPR, etc.). Issues were not resolved in the next growing seasons, with 1,400 and 1,345 official complaints reported to state departments of agriculture in 2018 and 2019, respectively. A significant amount of additional damage was believed to have been unreported (USEPA 2020). Many scientists referenced the injury as “landscape level,” indicating damage in many occurrences was uniform across large regions with no discernible source or gradient (Bish et al. 2019b, 2020). Historically, similar types of injury were referred to as “air mass damage,” which indicated a herbicide-contaminated air mass had settled across the landscape (Reisinger and Robinson 1976). In recent years, the U.S. Midsouth States has been one of the most heavily impacted areas. Other regions such as Illinois and Iowa have reported similar damage severity in recent years (Association of American Pesticide Control Officials 2020; Wechsler et al. 2019). This sudden increase in injury complaints correlated with development and commercial release of dicamba-resistant (DR) cotton (*Gossypium hirsutum* L.) and soybean.

DR crops were developed to provide producers with chemical options for control of broadleaf weed species in broadleaf crops and to provide control of glyphosate-resistant weeds. Weeds are the most problematic biological threat to crop yield loss in global agricultural production, and they greatly influence humanity’s ability to produce food, fiber, and fuel (Hildebrand 1946; Oerke 2006). Proliferation of herbicide-resistant (HR) weed species has resulted in a substantiated appreciable threat to agricultural production worldwide (Gould et al. 2018; Hicks et al. 2018; Palumbi 2001). A primary method by which agricultural seed and chemical manufacturers have responded to the issue of weed resistance is by genetically engineering crops to withstand currently registered herbicides, such the development of DR cotton and soybean (Behrens et al. 2007; Nandula 2019). Dicamba is a synthetic auxin herbicide (WSSA Group 4) that has been used for more than 50 yr to control broadleaf weeds in pastures, turf, and cereal crops (Shaner 2014) and has a low frequency of weeds evolving resistance compared with other herbicides of similar age (Heap 2021). DR cotton and soybean were commercialized by 2016; however, dicamba could not legally be applied to crops until 2017 (Bish et al. 2019a).

Historically, dicamba formulations were subject to volatility (evaporation from the leaf or soil surface) and could be transported to off-target locations (Behrens and Lueschen 1979; Egan and Mortensen 2012). Consequently, two new dicamba formulations were developed concurrently with the DR cotton and soybean trait to reduce volatility. These new formulations are the only dicamba products approved for use in DR cotton and soybean (Macinnes 2016; Xu et al. 2012). The first independent studies to evaluate these new dicamba formulations showed that volatility was reduced compared with older formulations, but still occurred (Bish et al. 2019a; Jones et al. 2019; Mueller and Steckel 2019). Dicamba has been shown to volatilize from both products in detectable amounts for up to 96 h after application (Bish et al. 2019a).

Other factors that have contributed to the millions of hectares of off-target dicamba injury include physical drift of herbicide droplets due to wind during the application; spray equipment contamination with herbicide remnants; and use of older, unapproved, more-volatile dicamba formulations. Many broadleaf plant species such as non-DR soybean, peaches [*Prunus persica* (L.) Batsch], grapes, and others are highly sensitive to very low doses of dicamba. Only a small amount of this herbicide needs to volatilize and redeposit on sensitive soybean for injury symptoms to occur (Al-Khatib et al. 1992, 1993; Al-Khatib and Peterson 1999; Andersen et al. 2004; Dintelmann et al. 2020; Egan et al. 2014; Kniss 2018; Solomon and Bradley 2014).

Once herbicides enter the atmosphere they can exist in the gaseous or particulate-bound phase and, in either phase, are subject to wet and dry deposition (Glotfelty and Caro 1975; Majewski 1996). Pesticides are typically detected in higher concentrations during intensive agricultural production seasons and at locations with high usage of pesticides (Goolsby et al. 1997; Hatfield et al. 1996; Hill et al. 2002; Richards et al. 1987). However, data are lacking on meteorological conditions associated with pesticide deposition from the atmosphere and whether pesticides deposited from the atmosphere occur at sufficient concentrations to cause injury to sensitive species. Therefore, the objectives of this study were to analyze dicamba concentrations in bulk deposition samples, survey producers to understand what regions are applying the most dicamba, develop models that identify atmospheric variables associated with weekly and seasonal dicamba flux, and identifiy the conditions most likely to result in increased dicamba deposition and potential injury to sensitive plants.

Materials and Methods

Sampling Locations and Description of Weather Stations

Samples from the accumulated water collection from the prior week were collected from 12 geographically distinct locations in Missouri (Figure 1). Sampling locations were positioned in regions of Missouri where row-crop agricultural production of corn (*Zea mays* L.), soybean, and/or cotton occur, except one location at Cook Station, MO. This location is in the Missouri Ozark Region, and less than 500 ha of row-crop production occurs annually in this county. The site was selected as a negative control and to provide an understanding of the extent of long-distance dicamba transport. Samplers were placed farther than 365 m away from the nearest possible source of dicamba (corn, soybean, or cotton field) to avoid possible contamination from droplet drift. Each sampling location was in close proximity (<100 m) to a weather station owned and maintained by the University of Missouri. Meteorological data were collected in 3-s increments and averaged into 5-min means. Instrumentation utilized included a Vaisala/Campbell Scientific air temperature/relative humidity probe (model HMP60-L1-PT, Logan, UT) at 305 cm above ground level (AGL) and a three-cup anemometer for wind speeds at this same height. Weather stations contained rainfall gauges that allowed for monitoring of precipitation. A subset of weather stations were equipped to monitor for temperature inversions with Vaisala probes at 46 and 168 cm AGL. Information on the inversion monitoring stations and weather station maintenance protocols can be found in Bish et al. (2019b).

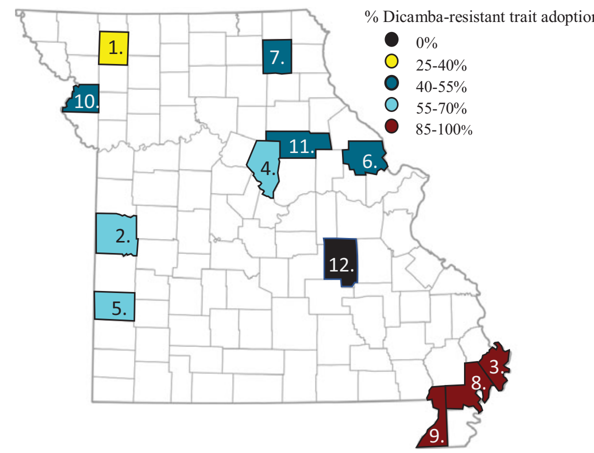

Figure 1. The geographic distribution of bulk atmospheric deposition sampling sites in Missouri in 2019 and 2020. Color-coded counties indicate the adoption of dicamba-resistant soybean in each county. Numbers correspond to sampling locations in Table 1.

Sampler Design

Design of deposition samplers was derived and modified from Waite et al. (1995). The deposition pan was a 100 by 100 cm aluminum sheet gently curved to slope toward a 2.5-cm center opening. The pan was secured to a wooden frame at 121 cm AGL, and the wooden frame was secured to the ground using 60-cm metal stakes. Once the pan was positioned, a plastic funnel attached to a 60-cm polycarbonate tube was secured directly beneath the center opening of the deposition pan. The tube was then inserted into the 2.5-cm opening of a 22.7-L glass carboy housed within the wooden frame. All rainwater from each 7-d sampling period drained through the center opening and was stored in the carboy until the weekly collection occurred. Each carboy could store up to 5 cm of rainfall. On weeks when high rainfall amounts occurred, the overflow was not collected. Metal siding was secured on all four sides of the wooden frame to shade the sample and prevent photolysis of dicamba. Funnels, polycarbonate tubes, and carboys were replaced each season.

Sample Collection

Sample collection began April 22, 2019, and April 13, 2020. Each week and at each location, 1 L of water from the glass carboy was collected in a plastic bag. On weeks when <4 mm of rainfall occurred, dry deposition was collected by adding 1.9 L of distilled

https://doi.org/10.1017/wsc.2024.9 Published online by Cambridge University Press

water across the deposition pan. On weeks when >4 mm of rainfall occurred, the deposition pan was not rinsed. Justification for this approach stems from previous research. This methodology prevents further dilution of samples by introducing additional purified water (Farenhorst et al. 2015; Waite et al. 1995, 2004). The majority of herbicide has been shown to deposit from the wet portion, with the dry deposition contributing only marginal amounts (Dämmgen et al. 2005; Epple et al. 2002). Following weekly collection, each carboy was replaced with a clean carboy. Sample collection occurred through the peak pesticide application season until September 9, 2019, and September 7, 2020, similar to previous studies on herbicide deposition (Scheyer et al. 2007; Waite et al. 1995). Samples were collected weekly by a trained group of individuals who were careful to avoid any contamination from clothing, skin, or other equipment. Upon arrival at each site, water samples were transferred immediately from the collection carboy before any additional cleaning or maintenance of the collector to ensure no unintended dicamba residues could be introduced into the sample. Field blanks were included weekly to monitor contamination. Following collection, samples were transported to a freezer and stored in the dark at −5 C until analysis, which occurred <4 mo after collection. Weekly and cumulative season dicamba flux (in μg m^{-2}) were computed using sample volume, dicamba concentration in the rainfall, and area of the deposition pan.

Dicamba Extraction, Quantification, Quality Control, and Assurance

A solid-phase extraction (SPE) method utilizing straight barrel anion exchange cartridges (Bond Elut SAX SPE 500 mg, 6 ml; Agilent Technologies, Santa Clara, CA) was used to extract dicamba. SPE columns were conditioned with 5 ml of MeOH followed by 5 ml of 0.1 M NaCl solutions followed by 5 ml of deionized water each. All solvents were high-performance liquid chromatography (HPLC) grade. From each rainwater sample, a 200-ml portion was extracted by the SPE columns at a flow rate of 10 ml min^{-1}. Ultra-pure N_2 gas (99.99%) was used to dry the column for 10 min. The SPE cartridge was eluted with 5 ml of NH_4OH at 10 ml min^{-1} and collected into glass test tubes. Between each sample, SPE lines and plungers were cleaned with MeOH and deionized water. Collection tubes containing SPE processed samples were concentrated to dryness using ultra-pure N_2 gas at 30 C and then reconstituted using 0.5 ml of MeOH, resulting in a 400-fold concentration from the original sample.

Dicamba concentrations were quantified using an HPLC with a photodiode-array detector (Shimadzu Nexera XR 20A, Shimadzu USA Manufacturing, Columbia, MD) and external standard calibration. Compound separation was achieved using a Zorbax Eclipse XDB-C18 column (narrow bore 2.1 by 250 mm, 3.5 μm, Agilent). Mobile phases consisted of 0.1% phosphoric acid and 100% acetonitrile pumped at isocratic flow rates of 0.24 and 0.16 ml min^{-1}. The column oven temperature was set to 40 C, and the injection volume was 5 μl. Dicamba was detected at 205 nm. The retention time under these conditions was 4.20 (+ 0.11) min. Calibration standards included in each HPLC run ranged from 5 to 1,000 μg L^{-1} using analytical grade (>95%) standards of each compound (Sigma Aldrich, St. Louis, MO). Positive detections were based on retention time and match to reference spectra of dicamba obtained from 500 μg L^{-1} standards. Reference spectra were obtained at 1-nm increments from 190 to 400 nm and a scan interval of 240 ms. Spectral matches were based on a Similarity Index feature in the instrument software, which is scaled from 0 to 1, with 1 representing a perfect fit to the reference. For these analyses, the Similarity Index was set to 0.95 as a screening threshold and ≥0.98 for positive identification. Based on the latter criteria, the instrument detection limit for dicamba was 5 μg L^{-1}, resulting in a method detection limit of 0.0125 μg L^{-1} on a water basis. Quality control and assurance of HPLC and SPE runs were achieved by including blank HPLC-grade methanol standards on a routine basis to confirm prevention of cross-contamination or errors in sample labeling or placement. Spiked field samples were included at 1 μg L^{-1} to determine dicamba recoverability throughout the experiment. Recovery of dicamba in spiked samples ranged from 88% to 104%. No corrections to data were made based on these recoveries. An additional screening confirmed photolysis and microbial degradation of dicamba did not influence the results of this study. Any analyte concentrations that exceeded the linear calibration range of the HPLC were diluted 5:1 methanol to sample and were reanalyzed.

Soybean Response to Dicamba-contaminated Rainfall Events

Soybeans were exposed to simulated rainfall events contaminated with dicamba. Dicamba-sensitive soybean seeds (‘Pioneer P44A37L’) were grown in blow-molded plastic pots measuring 19 by 17 m (3.8 L Custom-Tainer 400C, Hummert International, Earth City, MO). Pots were filled with 3 kg of an 80:20 ratio of field soil: commercial potting medium (Pro-Mix with mycorrhizae, Premier Tech Horticulture, Quakertown, PA). Commercial potting medium was necessary for adequate porosity, root development, and water infiltration. Seeds were planted to a 1.9-cm depth. Plants were maintained in a greenhouse at 30 C and watered daily. Natural light was supplemented with metal-halide lamps (600 μmol m^{-2} s^{-1}). Treatments were applied when soybean reached the V3-V4 stage of growth (approximately 13 to 17 cm in height). Simulated rainfall events were applied using 3.8-L handheld polyethylene adjustable pressure garden sprayers, which were exchanged between treatments to avoid contamination. Each sprayer contained an adjustable nozzle orifice, which allowed for extremely coarse droplet sizes to simulate rainfall droplets. Treatments included 1, 10, 100, 1,000, 10,000, and 100,000 μg L^{-1} of the commercially available DGA (diglycolamine salt of dicamba) plus VaporGrip® dicamba formulation (XtendiMax®, Bayer Crop Science, Creve Coeur, MO). The rates of 1,000, 10,000, and 100,000 μg L^{-1} were purposely exaggerated and are substantially higher than any detections from the study. Treatments included single-application treatments and sequential-application treatments that simulated repeated exposure to dicamba in consecutive weeks as was observed in data collected from the rainfall deposition study. For the 1, 10, and 100 μg L^{-1} dicamba treatments, the sequential applications occurred either one or both 1 and 2 weeks following initial application. Before all applications, pots were weighed to ensure each pot maintained the same field water capacity. A 1-min simulated rainfall event was applied to achieve the same amount of water as a 1.3-cm rainfall event. A 35-cm-tall plastic cone was positioned on the inner edges of the pot to force water droplet contact with either soybean plant tissue or the soil surface. This application allowed for tissue and root uptake of dicamba solution, similar to a rainfall event. A plastic collection container was placed under each pot to contain any water that leached through the soil column following treatment application. No additional water was applied for 24 h after treatment. Once supplemental watering was reinitiated, care was taken to ensure field capacity of the soil was not exceeded. This was

https://doi.org/10.1017/wsc.2024.9 Published online by Cambridge University Press

Table 1. Dicamba mass flux in Missouri bulk atmospheric deposition samples in 2019 and 2020

	2019/2020			
	Weekly max. (wk)[a]	Cumulative[b]	Weeks with detections[c]	Dicamba-resistant soybean adoption[d]
Location[e]	——— μg m^{-2}) ———		——— % ———	
Albany (1)	1.2 (5)/5.8 (8)	2.3 /17	21/26	30/37
Butler (2)	9.4 (4)/10 (5)	52/31	52/57	68/61
Charleston (3)	174 (12)/326 (2)	494/584	95/73	91/86
Columbia (4)	14 (14)/7.9 (8)	28/14	63/21	61 /38
Lamar (5)	7.3 (13)/19 (5)	12/56	42/57	67/54
Moscow Mills (6)	11 (10)/14 (12)	26/49	47/42	48/39
Novelty (7)	12 (5)/14 (16)	49/44	52/52	44/28
Portageville (8)	1,098 (6)/142 (4)	2,228/730	78/89	85/87
Senath (9)	717 (6)/354 (3)	1,754/741	84/68	89/89
St Joseph (10)	5.0 (8)/13 (2)	11/41	42/52	51/38
Vandalia (11)	11 (9)/14 (8)	14/39	26/52	51/29
Cook Station (12)	<DL/2.1 (9)	<DL/5.3	0/21	0/ 5

[a]Weekly max.: the weekly maximum dicamba flux in bulk deposition samples for each year; (wk): week of sampling in which the weekly maximum occurred.
[b]Cumulative dicamba flux for the entirety of the sampling season.
[c]Percentage of weeks throughout sampling periods each year when detectable amounts of dicamba occurred.
[d]Dicamba-resistant soybean adoption as determined by survey described in “Materials and Methods.”
[e]Numbers in parentheses correspond to the location of sampling sites shown in Figure 1.

accomplished by weighing pots 1 h after saturation to determine field capacity and then ensuring pots were not watered to exceed that weight. This process was repeated in the same manner for sequential-application timings. Treatments were arranged in a completely randomized block, and plants were allowed to grow for 14 d following the final sequential treatment. At that time, a previously characterized rating scale was utilized to assess visual soybean injury from dicamba (Behrens and Lueschen 1979). This experiment was repeated once to result in two experimental runs. Visual injury data were subject to ANOVA using PROC GLIMMIX in SAS (SAS v. 9.4, SAS Institute, Cary, NC) and means were separated using Fisher’s protected LSD ($P < 0.05$).

Survey to Determine the Adoption of DR Technology by Missouri Soybean Producers

Herbicide usage data at the county level were not accessible for both years of this research; therefore, an external survey method was utilized to collect information on adoption of DR technology in each sampling region of Missouri. Previous research showed that surveying agricultural professionals that routinely make crop seed and herbicide decisions can provide useful and accurate information (Bish and Bradley 2017; Werle et al. 2018). The survey was distributed via email to all certified pesticide applicators in Missouri and consisted of two questions: (1) In which county or counties do you apply pesticides or influence pesticide application decisions? (2) What percentage of soybean planted in (2019/2020) do you estimate contained the dicamba-resistant trait (0–100%)? There were 1,107 total survey responses in 2019 and 432 responses in 2020. Results of the survey are shown in Figure 1 and Table 1. County-level usage data from 2019 (https://water.usgs.gov/nawqa/pnsp/usage/maps/county-level) align well with the results from this survey ($R^2 = 0.83$).

Determination of Factors Influencing Atmospheric Deposition of Dicamba

Regression analyses were conducted to identify relationships between dicamba flux and factors that influence deposition. Two analyses were conducted. The first was to identify factors that may influence cumulative dicamba deposition over the entire growing season. The second was to identify factors that may influence weekly dicamba flux in regions with high DR trait adoption and higher dicamba detections throughout the growing season. Independent variables included in the first analysis were: percent DR soybean trait adoption in the county where sampling occurred (derived from previously described survey), percentage of sampled period in which wind speeds were <4.8 km per hour (kph), percentage of sampled period in which daily high temperatures exceeded 29 C, and average relative humidity for the sampled period. Wind speed and temperature thresholds were selected based on requirements within the approved dicamba herbicide labels and because previous research showed each factor to influence either dicamba volatility or particle suspension in air (Bish et al. 2019a; Egan and Mortensen 2012; Hill et al. 2002; Oseland et al. 2020). The analysis was conducted using PROC REG in SAS v. 9.4 with a stepwise selection. A priori significance levels selected for entry and removal from the model were $P \leq 0.15$, as this threshold has been found to improve the model and provide further predictive ability (Shtatland et al. 2001). Dicamba fluxes were subject to PROC UNIVARIATE to test for normality conditions, and a logarithmic transformation was necessary to achieve normalized distributions. Models were considered significant at $P \leq 0.05$.

The second regression analysis utilized weekly meteorological data from the Heyward and Charleston sampling locations in southeastern Missouri. These locations had the highest DR trait adoption in both 2019 and 2020 and had consistent and substantial dicamba deposition through most of the growing seasons. Conditions for entry and removal from the model as well as model and variable significance criterion were identical to those described for the first regression analysis. However, data before May 1 and following July 15 were excluded for practical reasons. Dicamba labels restrict use after July 15. We also removed weeks in which <1 ppb of dicamba was detected. Independent variables included average daily high temperature for the week, midday wind speeds (1200 to 1600 hours), average weekly relative humidity, and weekly frequency of inverted temperature conditions. Temperature inversion conditions were met once air temperatures at 305 cm AGL exceeded air temperatures at 46 cm AGL by 0.5 C or more, as described previously in Bish et al.

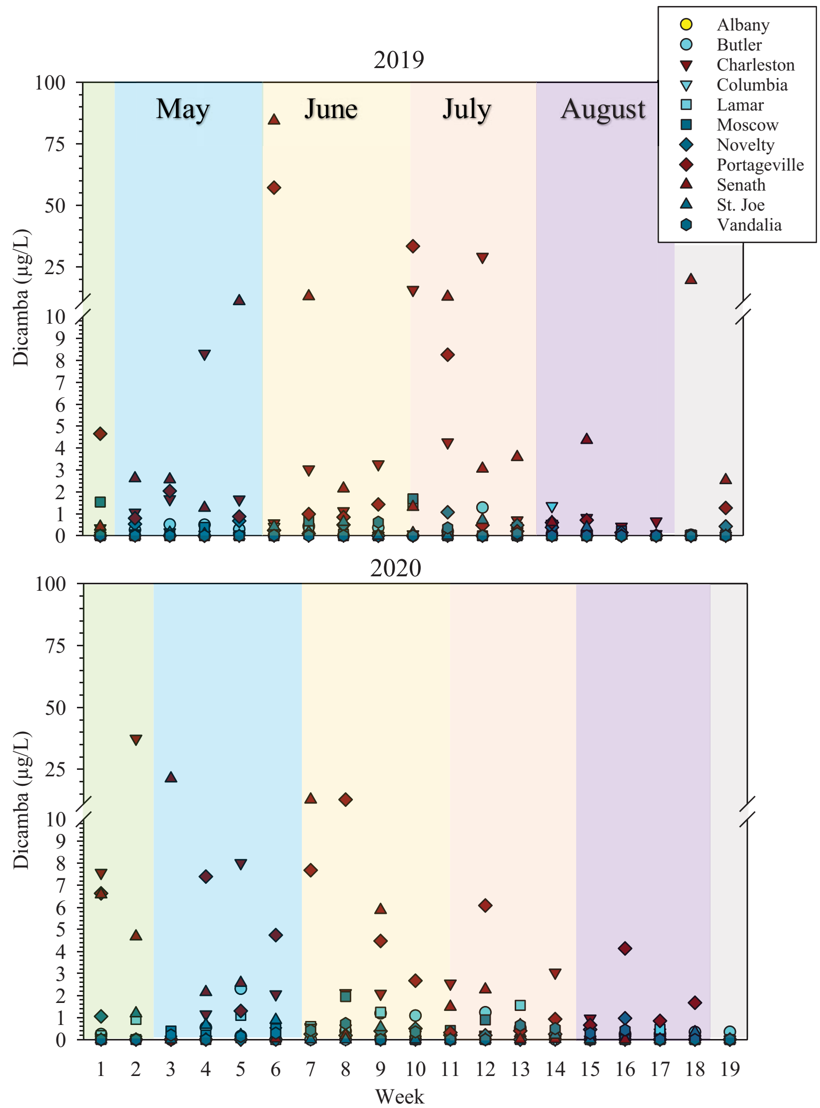

Figure 2. Weekly dicamba concentrations in bulk atmospheric deposition samples in 2019 and 2020. Color-coded symbols correspond with dicamba-resistant soybean adoption levels depicted in Figure 1. Sampling began April 22, 2019, and April 13, 2020. Cook Station was not included in the figure.

(2019b). Unfortunately, the Senath, MO, location could not be included in the analysis, as routine quality-control assessments of the weather data generated from this station indicated biases in probes and resulted in faulty temperature inversion data.

Results and Discussion

We detected dicamba in deposition samples from each of the 12 locations in both 2019 and 2020, with the exception of the Cook Station site in 2019. Cook Station has little to no DR soybean or cotton (Figure 1) and fewer than 1,000 ha of total agricultural row-crop production (USDA-NASS 2019). Detected concentrations varied among locations and years. The highest concentration detected in 2019 was in southeast Missouri at the Senath site and occurred on June 3 (84 µg L^{-1}; Figure 2; Table 1). The highest concentration detected in 2020 was also in southeast Missouri at the Charleston site and occurred on April 30 (37 µg L^{-1}; Figure 2). Weekly detection frequency ranged from 21% to 95% in 2019 and from 26% to 89% of the sampled weeks in 2020 (Table 1). For both years, the highest mass fluxes on a weekly and annual bases occurred at the three sites in southeast Missouri (Sites 3, 8, and 9; Figure 1). These sites had peak weekly fluxes >140 µg m^{-2}, with the highest weekly mass flux in 2019 observed at Portageville (Site 8) on June 3 (1,098 µg m^{-2}; Table 1) and the highest in 2020 at Senath (Site 9) on May 4 (354 µg m^{-2}, Table 1).

Cumulative dicamba flux over the growing season illustrated the timing of dicamba deposition (Figure 3). High flux periods were observed throughout the growing season of both years, particularly at the three southeast Missouri sites, which had multiple high weekly deposition events (>100 µg m^{-2}) and high cumulative fluxes over both growing seasons (Figure 3). Cumulative flux primarily increased until herbicide applications diminished in early July. All other sites had peak flux events of <20 µg m^{-2}, but several sites (2, 4, 5, 6, 7, 10, and 11) had at least 1 yr with cumulative growing season fluxes >25 µg m^{-2}. At the three southeast Missouri sites, annual variation in cumulative flux showed that dicamba deposition in 2019 was dominated by a few large events, while in 2020 deposition occurred via multiple, smaller events. Typically, dicamba applications occur either before planting in April or after crop emergence in June. Although other

https://doi.org/10.1017/wsc.2024.9 Published online by Cambridge University Press

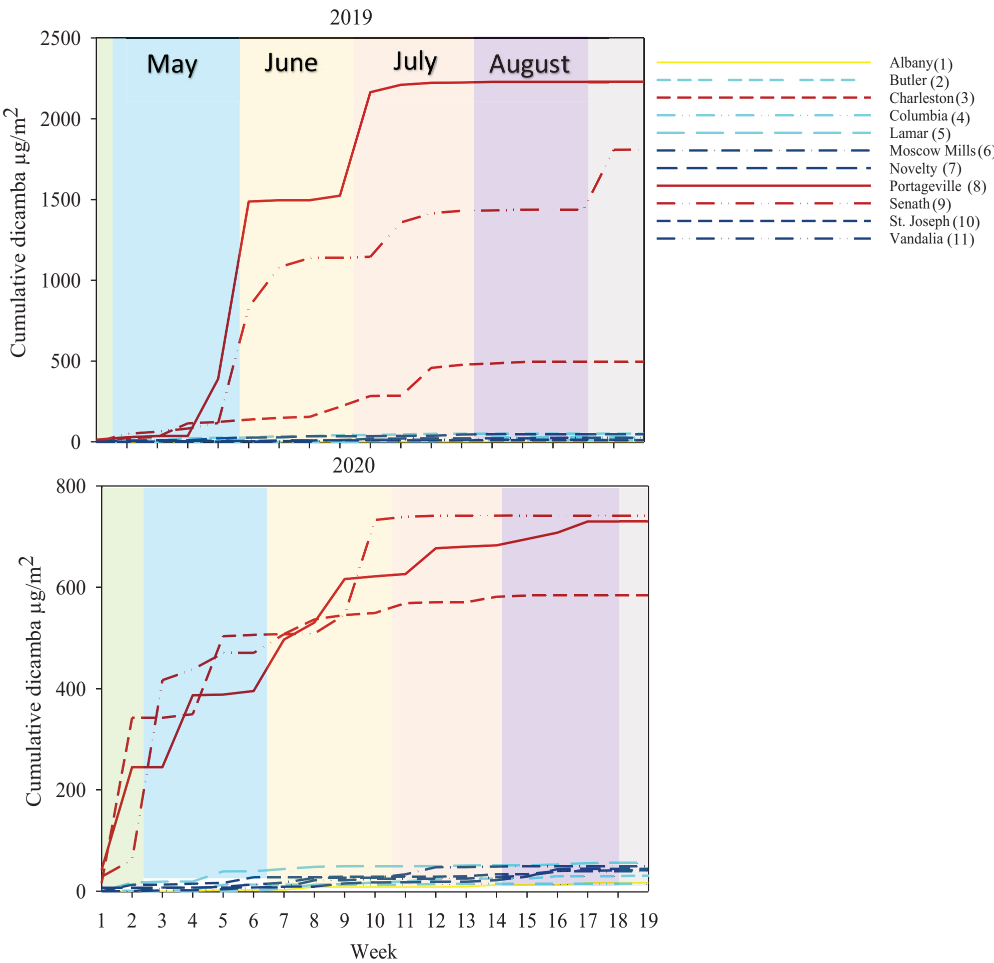

Figure 3. Cumulative dicamba mass flux in 2019 and 2020. Line colors are in accordance with dicamba-resistant soybean in Figure 1. Week 1 sampling began April 22, 2019, and April 13, 2020. Cook Station was not included in the figure.

authors have reported patterns of greater herbicide concentrations in the atmosphere during intensive application periods (Dubus et al. 2000; Waite et al. 1995), the flux data presented here indicated consistent dicamba application occurred at several sites from April to July. Overall, these results demonstrated that dicamba was commonly deposited from the atmosphere during the growing season, and observed deposition and fluxes were strongly related to DR soybean adoption near collection sites and the timing of rainfall events (Figure 3; Table 1).

Simulating Dicamba-contaminated Rainfall Events

Results from the simulated rainfall assay revealed that soybean exposed to dicamba concentrations of 10 µg L^{-1} or less in one simulated rainfall event showed minimal symptoms of visible injury (<1%; Figure 4). However, repeated simulated rainfall events with at least 10 µg L^{-1} dicamba resulted in more prominent injury symptoms. Soybean treated with 10 µg L^{-1} dicamba in two consecutive weeks had 7% visible injury symptoms, while soybean treated with 10 µg L^{-1} dicamba in three consecutive weeks had 16% injury. There were multiple weeks in southeast Missouri when >10 µg L^{-1} of dicamba was collected in the bulk deposition samples (Figure 2; Table 1). A concentration of 10 µg L^{-1} simulated at 1.3 cm would be equivalent to a 47.2 µg m^{-2} deposition event in our study. Others have reported repeated exposures over time increase the likelihood of dicamba symptomology on sensitive soybean plants when dicamba is in the air (Zaccaro-Gruener et al. 2023). Thus, it is plausible that rainfall is transporting dicamba from the atmosphere in sufficient concentrations to contribute to the dicamba injury observed on sensitive plant species like non-DR soybean in regions where landscape-level injury has been reported.

Identifying Variables That Contribute to Dicamba Deposition

Finally, we utilized two separate stepwise linear regression models to determine the influence of seasonal environmental conditions and regional DR soybean adoption on dicamba deposition. The first model was based on cumulative dicamba flux over the growing season to identify factors that influenced deposition differences among the locations (Table 2). Adoption of DR soybean and the percentage of the growing season when wind speeds were ≤4.8 kph were selected in the regression model ($R^2 = 0.71$). The most influential factor was DR trait adoption ($R^2 = 0.65$), and this factor was positively correlated with dicamba fluxes. DR soybean adoption was >85% for both years in the three southeast Missouri counties where dicamba fluxes were highest. While dicamba applications do not occur on every hectare with DR technology, a previous Nebraska survey showed that approximately 80% of growers who planted soybean with the DR trait made an application of dicamba to their soybean (Werle et al. 2018). Others have found similar positive

https://doi.org/10.1017/wsc.2024.9 Published online by Cambridge University Press

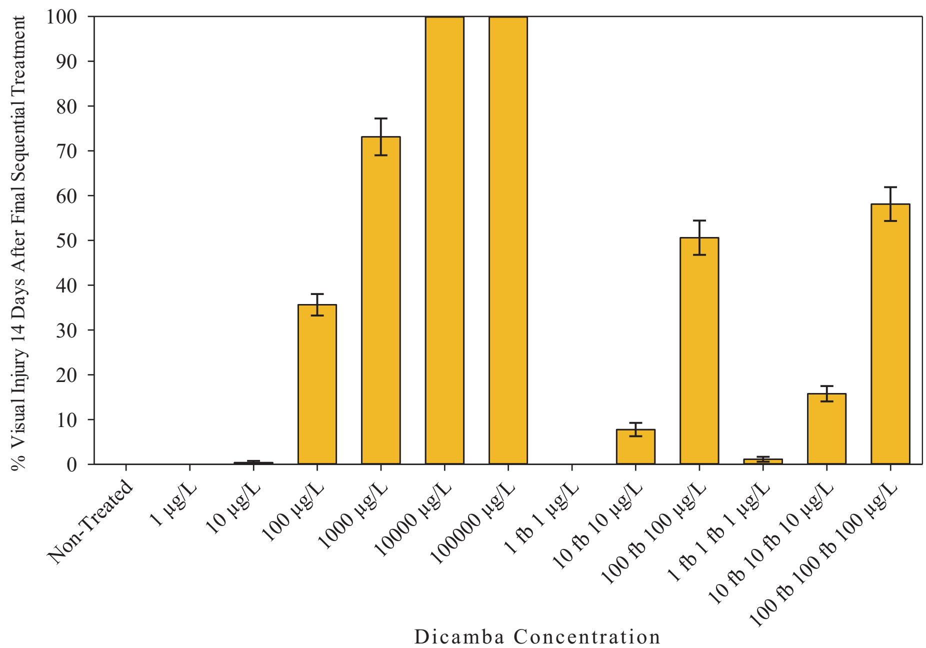

Figure 4. The response of dicamba-sensitive soybean to simulated dicamba-contaminated rainfall events. Sequential treatments were applied 1 wk apart to simulate repeated exposure to dicamba in sequential weeks. These treatments are indicated by fb (= followed by). The treatments of 1,000 ppb and above were to simply elicit a response and were exaggerated beyond any measurements of dicamba recorded in this study. The severity of injury was based on previously reported 0% to 100% scale to measure visible symptoms of dicamba injury on soybeans. Bars include data compiled from two experimental runs, and ratings were taken 14 d after the final sequential treatment

correlations of atmospheric deposition and pesticide usage within a region (Hill et al. 2002).

The influence of wind speed and atmospheric stability on dicamba flux was evaluated further in an additional stepwise linear regression analysis to identify regional-specific factors ($R^2 = 0.41$; Table 3). The best-fit model indicated that weekly dicamba flux was influenced by wind speeds during the middle of the day, the percentage of the week in which inverted temperature conditions occurred, and relative humidity. Inversion frequency and humidity were positively correlated with dicamba flux, while midday wind speeds were negatively correlated. Wind speed is highest at midday and equates to a larger boundary layer, which is the layer of atmosphere in which airborne particles are trapped (Hu 2015; Majewski and Capel 1995). A larger boundary layer allows more area for volatilized particles to disperse. This result builds upon the previous stepwise analysis and provides additional support for the role of stable atmospheric conditions and atmospheric water vapor on dicamba behavior in the atmosphere. These results are similar to findings from Bish et al. (2019a) demonstrating that stable air (i.e., low wind and/or inversions) and higher dew point temperatures (i.e., the temperature at which air is saturated with water) correlated with increased dicamba deposition following dicamba applications. Dew point temperatures are dependent upon variables including relative humidity and increase as relative humidity increases (Lawrence 2005). Increases in volatilization of pesticides from soil due to increased relative humidity have been observed previously (Davie-Martin et al. 2015; Farha et al. 2016). Previous research has shown that stable and humid conditions can restrict dispersion of atmospheric particulates (Yin and Wang 2017). Others have hypothesized that high humidity could increase the settlement of dicamba across a region (Egan and Mortensen 2012) Lower wind speeds and shrinking of the atmospheric boundary layer associated with stable conditions are likely two impediments to dispersion. It was previously speculated that stable and humid conditions could interfere similarly with atmospheric dicamba dispersion (Bish et al. 2019a). Any impediment that prevents dicamba molecules from dispersing could result in concentrated masses of dicamba being readily available for deposition when weather conditions change. A similar mechanism was described by Peterson et al. (1969) in research focused on air pollution. Robinson and Fox (1978) coined the phrase "air mass damage" in the 1960s to describe a similar phenomenon of large-scale deposition events for a synthetic auxin herbicide in Yakima Valley, WA.

Research on dicamba applications at the farm level have resulted in models that associate stable air with an increased likelihood of dicamba moving off-target, as stable air masses are commonly pushed to new locations by gentle horizontal winds (Bish et al. 2020; Oseland et al. 2020). However, to our knowledge, this study is the first to measure dicamba deposition from the atmosphere and correlate those levels directly to atmospheric stability.

Movement of dicamba herbicide from the site of application to non-target areas has been a significant problem in the agricultural industry since the introduction of DR crops in 2016 (Bish et al. 2020). The term "landscape-level injury" has been used to describe the observed dicamba injury in southeast Missouri, northeast Arkansas, western Tennessee, Illinois, and Iowa (Hartzler 2017). Understanding the factors that influence atmospheric dicamba transport and deposition is critical to the responsible use of DR technology, and we used data collected in Missouri to serve as a case study for what may also be occurring in other states with high injury occurrences. We determined that dicamba concentrations detected in bulk deposition samples in southeast Missouri exceeded any reported concentrations in the historical literature (Dubus et al. 2000; Waite et al. 1995). At three sites, dicamba deposition was sufficient to cause injury to sensitive plant species like non-DR soybean, with repeated high-deposition events

Table 2. Results of stepwise linear regression modeling to determine the influence of seasonal environmental conditions and soybean trait adoption on cumulative dicamba flux in bulk atmospheric deposition samples in Missouri.[a]

Variable	Estimate	Partial R^2	Model R^2	*F*-value	Pr > *F*
Intercept	−1.42	—	—	1.73	0.001
Adoption[b]	0.06	0.65	0.65	38.56	<0.001
Low wind[c]	4.72	0.06	0.71	3.84	0.06

[a]Stepwise linear regression included all data from all sampling sites except Cook Station due the inconstancies of soybean production in this region compared with other sites.
[b]Adoption is the percent adoption of dicamba-resistant soybean in the county where sampling occurred based on survey results from Missouri pesticide applicators and influences.
[c]Low wind indicates the percentage of the sampling season that wind speeds reached speeds of 4.8 kph or less.

Table 3. Results of stepwise linear regression modeling to determine the influence of weekly environmental conditions on dicamba flux in bulk atmospheric deposition samples in Missouri.[a]

Variable	Estimate	Partial R^2	Model R^2	*F*-value	Pr > *F*
Intercept	−4.27	—	—	1.22	0.28
% Inversion[b]	9.17	0.19	0.19	6.16	0.02
MidWind[c]	−0.29	0.11	0.30	4.33	0.04
Humidity[d]	0.26	0.11	0.41	4.49	0.04

[a]Stepwise linear regression included 2019 and 2020 data from the Portageville and Charleston Missouri locations where the highest dicamba-resistant soybean adoption occurred during both years of the study.
[b]% Inversion indicates the percentage of the sampled week that temperature-inverted conditions occurred.
[c]MidWind is the average middle of the day (1200–1600 hours) wind speed at the sampling locations.
[d]Humidity is the average relative humidity for the week.

occurring annually. Similar results were observed by Zaccaro-Gruener et al. (2023). Dicamba fluxes at these sites also showed high levels of deposition from April to July each year, which were apparently sustained by widespread dicamba usage during these months. From this research, our models indicate that the adoption of DR soybean and stable atmospheric conditions are two of the most important factors that influence the amount of dicamba deposition. This research is the first to illustrate that dicamba can be deposited from the atmosphere at levels sufficient to cause injury to sensitive soybean and that regional DR soybean adoption and stability of the atmosphere are important in determining those concentrations.

Airborne pesticides need wind to disperse. Previous research has found that daily wind speeds in southeast Missouri tend to be lower than in other regions within the state as well as many other regions throughout the United States where dicamba injury has not been as widespread (Pfleeger et al. 2006). This same research has shown that other geographies with a high frequency of off-target injury, such as areas throughout Illinois and Arkansas, are also prone to less-windy conditions (Pfleeger et al. 2006). Our study did not investigate the usage of DR soybean in these regions, but they are known high soybean-producing regions, and some estimates indicate high DR adoption at the time of this research (Wechsler et al. 2019).

At two of three sites in southeastern Missouri, dicamba deposition and fluxes were lower in 2020 than in 2019 (Table 1). A combination of factors may have influenced these observed differences. There were 10 fewer fieldwork days over the duration of our sampling period in 2019 compared with 2020 (USDA-NASS 2020). As DR soybean adoption did not differ in this region between years, it is possible that dicamba applications occurred within a shorter time period in 2019 and resulted in higher deposition compared with 2020, when applications were spread out over more days (Figure 3). Additionally, the U.S. Court of Appeals for the Ninth Circuit interrupted dicamba applications during 2020 due to legal uncertainties involving dicamba label registrations. It is unknown to what extent this affected applications of dicamba in 2020.

The deposition of dicamba via rainfall and dry deposition has broad implications for soybean production regions across the United States. The observed dicamba deposition (Figure 2) was indicative of two main transport patterns: (1) sites with high concentrations were indicative of local transport (<1 km) during or soon after periods of dicamba application combined with high usage; and 2) sites with consistent but low dicamba deposition events throughout the sampling period indicated the potential of medium- to long-range transport (>1 km) or limited dicamba usage near these sites (Scheyer et al. 2007). The results presented are supported by work from Zaccarro-Gruener et al. (2023), who measured dicamba in deposition samples in Arkansas. This work also identified decreased concentrations in days following rain events, indicating rain clears the atmosphere and corresponds to the dicamba detection events observed in our study (Figures 2 and 3). However, this study did not utilize atmospheric stability or wind speeds to correlate dicamba concentrations. This research has highlighted the potential for landscape-level injury to occur to highly sensitive plant species like non-DR soybean from contaminated rainfall events and identified certain factors such as high DR trait adoption and stable atmospheric conditions that likely contribute to atmospheric deposition of dicamba. This research indicates that in some regions of the United States, dicamba can be used for weed management in DR crops without significant concern for atmospheric deposition. However, in other regions, atmospheric stability and increased dicamba usage as a result of high DR trait adoption is likely causing atmospheric deposition that results in injury to a variety of agricultural, ornamental, and tree species.

Acknowledgments. The authors would like to thank Gatlin Bunton, James Heiser, and Delbert Knerr for assistance with sample collection. This research received no specific grant from any funding agency or the commercial or not-for-profit sectors. The authors have no conflicts of interest to declare.

References

Al-Khatib K, Parker R, Fuerst EP (1992) Sweet cherry (*Prunus avium*) response to simulated drift from selected herbicides. Weed Technol 6:975–979

Al-Khatib K, Parker R, Fuerst EP (1993) Wine grape (*Vitis vinifera* L.) response to simulated herbicide drift. Weed Technol 7:97–102

Al-Khatib K, Peterson D (1999) Soybean (*Glycine max*) response to simulated drift from selected sulfonylurea herbicides, dicamba, glyphosate, and glufosinate. Weed Technol 13:264–270

Andersen SM, Clay S, Wrage L, Matthees D (2004) Soybean foliage residues of dicamba and 2,4-D and correlation to application rates and yield. Agron J 96:750–760

Association of American Pesticide Control Officials (2020) Dicamba Archives. https://aapco.org/dicamba-archives. Accessed: March 2021

Behrens MR, Mutlu N, Chakraborty S, Dumitru R, Jiang WZ, LaVallee BJ, Herman PL, Clemente TE, Weeks DP (2007) Dicamba resistance: enlarging and preserving biotechnology-based weed management strategies. Science 316:1185–1188

Behrens R, Lueschen W (1979) Dicamba volatility. Weed Sci 27:486–493

Bish M, Oseland E, Bradley K (2020) Off-target pesticide movement: a review of our current understanding of drift due to inversions and secondary movement. Weed Technol 35:1–43

Bish MD, Bradley KW (2017) Survey of Missouri pesticide applicator practices, knowledge, and perceptions. Weed Technol 31:165–177

Bish MD, Farrell ST, Lerch RN, Bradley KW (2019a) Dicamba losses to air after applications to soybean under stable and nonstable atmospheric conditions. J Environ Qual 48:1675–1682

Bish MD, Guinan PE, Bradley KW (2019b) Inversion climatology in high-production agricultural regions of Missouri and implications for pesticide applications. J Appl Meteorol Clim 58:1973–1992

Bradley K (2018) Dicamba Injured Crops and Plants Becoming More Evident: June 15th Update. https://ipm.missouri.edu/cropPest/2018/6/dicambainjuryupdate/. Accessed: April 2023

Dämmgen U, Erisman JW, Cape JN, Grünhage L, Fowler D (2005) Practical considerations for addressing uncertainties in monitoring bulk deposition. Environ Pollut 134:535–548

Davie-Martin CL, Hageman KJ, Chin Y, Rouge V, Fujita Y (2015) Influence of temperature, relative humidity, and soil properties on the soil-air partitioning of semivolatile pesticides: laboratory measurements and predictive models. Environ Sci Technol 49:10431–10439

Dintelmann BR, Warmund MR, Bish MD, Bradley KW (2020) Investigations of the sensitivity of ornamental, fruit, and nut plant species to driftable rates of 2, 4-D and dicamba. Weed Technol 34:1–11

Dubus IG, Hollis JM, Brown CD (2000) Pesticides in rainfall in Europe. Environ Pollut 110:331–344

Egan JF, Barlow KM, Mortensen DA (2014) A meta-analysis on the effects of 2, 4-D and dicamba drift on soybean and cotton. Weed Sci 62:193–206

Egan JF, Mortensen DA (2012) Quantifying vapor drift of dicamba herbicides applied to soybean. Environ Toxicol Chem 31:1023–1031

Epple J, Maguhn J, Spitzauer P, Kettrup A (2002) Input of pesticides by atmospheric deposition. Geoderma 105:327–349

Farha W, Abd El-Aty AM, Rahman MM, Shin H, Shim J (2016) An overview on common aspects influencing dissipation pattern of pesticides: a review. Environ Monit Assess 188:1–21

Farenhorst A, Andronak L, McQueen R (2015) Bulk deposition of pesticides in a Canadian city: Part 1. Glyphosate and other agricultural pesticides. Water Air Soil Pollut 226:1–11

Glotfelty D, Caro J (1975) Introduction, transport, and fate of persistent pesticides in the atmosphere. Pages 42–62 *in* Majewski MS, Capel PD, eds. Pesticides in the Atmosphere. Distribution, Trends, and Governing Factors. US Geological Survey, Open File Report 94-506. Washington, DC: ACS Publications

Goolsby DA, Thurman EM, Pomes ML, Meyer MT, Battaglin WA (1997) Herbicides and their metabolites in rainfall: origin, transport, and deposition patterns across the midwestern and northeastern United States, 1990−1991. Environ Sci Technol 31:1325–1333

Gould F, Brown ZS, Kuzma J (2018) Wicked evolution: can we address the sociobiological dilemma of pesticide resistance? Science 360:728–732

Hartzler B (2017) Thoughts on the Dicamba Dilemma. https://crops.extension.iastate.edu/blog/bob-hartzler/thoughts-dicamba-dilemma. Accessed: April 2023

Hatfield J, Wesley C, Prueger J, Pfeiffer R (1996) Herbicide and nitrate distribution in central Iowa rainfall. J Environ Qual 25:259–264

Heap I (2021) The International Herbicide-Resistant Weed Database. www.weedscience.org. Accessed: April 2023

Hicks HL, Comont D, Coutts SR, Crook L, Hull R, Norris K, Neve P, Childs DZ, Freckleton RP (2018) The factors driving evolved herbicide resistance at a national scale. Nat Ecol Evol 2:529–536

Hildebrand E (1946) War on weeds. Science 103:465–492

Hill B, Harker K, Hasselback P, Moyer J, Inaba D, Byers S (2002) Phenoxy herbicides in Alberta rainfall: potential effects on sensitive crops. Can J Plant Sci 82:481–484

Hill BD, Harker KN, Hasselback P, Inaba DJ, Byers SD, Moyer JR (2002) Herbicides in Alberta rainfall as affected by location, use and season: 1999 to 2000. Water Qual Res J 37:515–542

Hu XM (2015) Boundary layer (atmospheric) and air pollution. Air pollution meteorology. Pages 227–236 *in* North GR, Pyle J, Zhang F, eds. Encyclopedia of Atmospheric Sciences. 2nd ed. Amsterdam: Elsevier/Academic Press

Jones GT, Norsworthy JK, Barber T, Gbur E, Kruger GR (2019) Off-target movement of DGA and BAPMA dicamba to sensitive soybean. Weed Technol 33:51–65

Kniss AR (2018) Soybean response to dicamba: a meta-analysis. Weed Technol 32:507–512

Lawrence MG (2005) The relationship between relative humidity and the dewpoint temperature in moist air. A simple conversion and applications. Bull Am Meterol Soc 86:225–234

Macinnes A (2016) VaporGrip technology: how it works and its benefits. *In* Proceedings of the North Central Weed Science Society. Des Moines, IA: North Central Weed Science Society. 215 p

Majewski MS (1996) Pesticides in the Atmosphere: Distribution, Trends, and Governing Factors. Boca Raton, FL: CRC Press. 215 p

Majewski MS, Capel PD (1995) Pesticides in the Atmosphere: Distribution, Trends, and Governing Factors. Open-File Report 94-506. Sacramento, CA: U.S. Geological Survey, Earth Science Information Center

Mueller TC, Steckel LE (2019) Dicamba volatility in humidomes as affected by temperature and herbicide treatment. Weed Technol 33:1–6

Nandula VK (2019) Herbicide resistance traits in maize and soybean: current status and future outlook. Plants 8:337

Oerke E (2006) Crop losses to pests. J Agric Sci 144:31–43

Oseland E, Bish M, Steckel L, Bradley K. (2020) Identification of environmental factors that influence the likelihood of off-target movement of dicamba. Pest Manag Sci 76:3282–3291

Palumbi SR (2001) Humans as the world's greatest evolutionary force. Science 293:1786–1790

Peterson CM, Paulus HJ, Foley GH (1969) The number-size distribution of atmospheric particles during temperature inversions. J Air Poll Cont Assoc 19:795–801

Pfleeger TG, Olszyk D, Burdick CA, King G, Kern J, Fletcher J (2006) Using a geographic information system to identify areas with potential for off-target pesticide exposure. Environ Toxicol Chem 25:2250–2259

Reisinger L, Robinson E (1976) Long-distance transport of 2,4-D. J Appl Meteorol Clim 15:836–845

Richards RP, Kramer JW, Baker DB, Krieger KA (1987) Pesticides in rainwater in the northeastern United States. Nature 327:129–131

Robinson E, Fox LL (1978) 2,4-D herbicides in central Washington. J Air Poll Cont Assoc 28:1015–1020

Scheyer A, Morville S, Mirabel P, Millet M (2007) Pesticides analysed in rainwater in Alsace region (eastern France): comparison between urban and rural sites. Atmos Environ 41:7241–7252

Shaner D (2014) Herbicide Handbook. 10th ed. Lawrence, KS: Weed Science Society of America. 513 p

Shtatland E, Cain E, Barton M (2001) The perils of stepwise logistic regression and how to escape them using information criteria and the output delivery system. Pages 222–226 *in* Proceedings of the Twenty-Sixth Annual SAS Users Group International Conference. Long Beach, CA: SAS Users Group

Solomon CB, Bradley KW (2014) Influence of application timings and sublethal rates of synthetic auxin herbicides on soybean. Weed Technol 28:454–464

[USDA-NASS] U.S. Department of Agriculture–National Agricultural Statistics Service (2019) CropScape: Cropland Data Layer. Published Crop-Specific Data Layer. https://nassgeodata.gmu.edu/CropScape. Accessed: April 2023

[USDA-NASS] U.S. Department of Agriculture–National Agricultural Statistics Service (2020) Missouri Crop Progress and Condition. https://www.nass.usda.gov/Statistics_by_State/Missouri/Publications/Crop_Progress_and_Condition/2019/20190903-MO-Crop-Progress.pdf. Accessed: April 2023

[USEPA] U.S. Environmental Protection Agency (2020) Dicamba Use on Genetically Modified Dicamba-Tolerant (DT) Cotton and Soybean: Incidents and Impacts to Users and Non-users from Proposed Registrations. PC# 100094, 128931. https://www.regulations.gov/document/EPA-HQ-OPP-2020-0492-0003. Accessed: April 2023

Waite D, Cessna A, Grover R, Kerr L, Snihura A (2004) Environmental concentrations of agricultural herbicides in Saskatchewan, Canada. J Environ Qual 33:1616–1628

Waite DT, Sommerstad H, Grover R, Kerr LA, Westcott ND, Irvine DG (1995) Atmospheric deposition of pesticides in a small southern Saskatchewan watershed. Environ Toxicol Chem 14:1171–1175

Wechsler S, Smith D, McFadden J, Dodson L, Williamson S (2019) The Use of Genetically Engineered Dicamba-Tolerant Soybean Seed Has Increased Quickly, Benefiting Adopters but Damaging Crops in Some Fields. https://www.ers.usda.gov/amber-waves/2019/october/the-use-of-genetically-engineered-dicamba-tolerant-soybean-seeds-has-increased-quickly-benefiting-adopters-but-damaging-crops-in-some-fields. Accessed: April 2023

Werle R, Oliveira, MC, Jhala AJ, Proctor CA, Rees J, Klein R (2018) Survey of Nebraska farmers' adoption of dicamba-resistant soybean technology and dicamba off-target movement. Weed Technol 32:754–761

Xu W, Cannan TM, Finch CW, Schnabel G, Bratz M, Bowe SJ, Brommer CL (2012) Advancements in Dicamba Formulation. Pages 329 *in* Proceedings of Weed Science Society of America. Waikoloa, HI: Weed Science Society of America

Yin Z, Wang H. (2017) Role of atmospheric circulations in haze pollution in December 2016. Atmos Chem Phys 17:11673–11681

Zaccaro-Gruener ML, Norsworthy JK, Brabham CB, Barber LT, Roberts TL, Mauromoustakos A, Mueller TC (2023) Dicamba air concentrations in eastern Arkansas and impact on soybean. Weed Sci 71:265–277