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Dicamba emissions under field conditions as affected by surface condition

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Abstract

The evolution and widespread distribution of glyphosate-resistant broadleaf weed species catalyzed the introduction of dicamba-resistant crops that allow this herbicide to be applied POST to soybean and cotton. Applications of dicamba that are most cited for off-target movement have occurred in June and July in many states when weeds are often in high densities and at least 10 cm or taller at the time of application. For registration purposes, most field studies examining pesticide emissions are conducted using bare ground or very small plants. Research was conducted in Knoxville, TN, in the summer of 2017, 2018, and 2019 to examine the effect of application surface (tilled soil, dead plants, green plants) on dicamba emissions under field conditions. Dicamba emissions after application were affected by the treated surface in all years, with the order from least to most emissions being dead plants < tilled soil < green plant material. In fact, dicamba emissions were >300% when applied to green plants compared to other surfaces. These findings suggest that dicamba applications made to bare ground will likely underestimate what may occur under normal field use conditions when POST applications are made and the crop canopy or weed groundcover is nearly 100% green material. A potential change to enhance the accuracy of current environmental simulation models would be to increase the theoretical findings to allow for the effect of green plant material on dicamba emissions under field conditions.

Introduction

One response to the increase in glyphosate-resistant weed species was the introduction of dicamba-resistant soybean and cotton (Monsanto Company, St Louis, MO) that allow for the POST application of dicamba (Pucci 2017). New formulations of dicamba have been registered for use in these dicamba-resistant crops. BASF has introduced the *N*,*N*-Bis-(aminopropyl) methylamine (BAPMA) formulation of dicamba (Hager 2017), whereas Monsanto introduced a diglycolamine (DGA) salt of dicamba that includes a pH modifier (Hemminghaus et al. 2017; Macinnes 2017). At a soil pH <6.5, there was no difference in soybean bioassay plant response between the DGA formulation and the newer dicamba formulations (Oseland et al. 2020).

Although the broadleaf weed control from this system has been good, extensive off-target movement (OTM) and injury to sensitive nontarget broadleaf vegetation has also been reported (Bradley 2017; Hager 2017). The OTM of dicamba that has occurred since the introduction of dicamba-resistant crops could have been caused by a number of factors, including the use of nozzles that produce very small droplets that stay suspended for many minutes after application. Another possibility could have been spraying into temperature inversions where small droplets do not disperse readily and stay suspended in cool air. A third possibility is that spray material could deposit on soil or plant material in the target field but move later via wind or water while on the soil or plant material as dislodgeable residues. These reports of dicamba OTM injury to broadleaf plants could also be due to volatility (Behrens and Lueshcen 1979; Mueller et al. 2013; Riter et al. 2020). All of these potential avenues for dicamba movement from the target can be described as dicamba emissions, and we will refer to them as such in this paper.

Numerous researchers have reported volatility of different dicamba salts (Behrens and Lueschen 1979; Busey et al. 2003; Egan and Mortensen 2012; Johnson et al. 2012; Penner and Michael 2014; Sciumbato et al. 2004; Strachan et al. 2010). Behrens and Lueschen (1979) were among the first to investigate the effects of air temperature, sprayed surface, relative humidity, and several other factors on dicamba drift, especially vapor drift. Their research primarily used soybean bioassay indicator plants. Egan and Mortensen (2012) utilized similar methods to measure dicamba movement under field conditions and reported a substantial reduction in dicamba vapor drift when using the DGA formulation compared to the dimethylamine (DMA). They also reported that temperature appeared to be directly correlated to the DMA dicamba vapor drift.

The majority of these studies have utilized plant bioassays as indicators of dicamba activity (Egan and Mortensen 2012; Penner and Michael 2014; Sciumbato et al. 2004). Although the sensitivity of these bioassays is more than adequate, a quantitative assessment via air sampling

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followed by chemical extraction and analysis may yield more direct indications of herbicide behavior (Mueller et al. 2013; Mueller 2015). In a multi-state dicamba field flux study, dicamba OTM was reported at all locations, and up to 0.3% of applied dicamba was measured (Riter et al. 2020; Sall et al. 2020). There was no apparent relationship between recorded meteorological and soil conditions for each trial and the observed dicamba OTM. Eleven of the studies in this research consisted of applications made to bare ground with varying amounts of plant refuse present. The remaining studies reportedly had less than 10% green plant material, usually in the form of small cotton plants. The average vertical flux emanating from the surface did not differ between bare ground and plots that contained actively growing crops; however, the authors indicate that this response may be due to the low ground coverage in the studies that contained green plant material.

Pesticide volatilization from field surfaces is an important aspect to the environmental fate of applied chemicals, but there are few published reports with adequate detail. Greater atrazine and lindane volatility was reported from plant material compared to soil (Dorfler et al. 1991). Metolachlor volatility was found to be mainly regulated by surface soil moisture condition and ranged from 5% to 63% of the applied product (Prueger et al. 2017). Fenpropimorph displayed lower volatilization from soil compared to plant surfaces (Muller et al. 1996).

Few studies have been conducted that compare dicamba movement from different surface conditions such as bare ground or green plant material. Dicamba applications are commonly made to bare soil and/or soil surfaces that contain some dead plant residue in early-season applications prior to planting. POST applications are also typically made later in the season to green vegetation such as soybean, corn (*Zea mays* L.), or cotton plants and the various weed species present in those fields.

For registration purposes, most flux studies are conducted using bare ground or very small plants for ease of operation (Corbin et al. 2006). Our hypothesis is that surface condition affects dicamba emissions after application. If the dicamba were to volatilize or move substantially more from green plant surfaces compared to other surfaces, then the actual dicamba OTM issues could be substantially higher. The objective of this research was to examine the effect of application surface on dicamba emissions under field conditions. Data generated from this research will provide insight into one of the factors that may influence dicamba OTM following a spray application.

Materials and Methods

This research was conducted in Knoxville, TN, in the summers of 2017, 2018, and 2019 (Table 1). Research methods were largely based on a previously reported method (Mueller et al. 2013). All research was conducted at a site with Sequatchie loam soil that had no previous dicamba use in the previous 12 mo (34% sand, 48% silt, 18% clay, 1.3% organic matter, pH 6.2, and cation exchange capacity = 11 mEq g^{-1}).

Herbicide Application

The DGA formulation of dicamba was applied to field plots that were 30 by 30 m in 2017 and 45 by 45 m in 2018 and 2019. The field study had three main plots: tilled plots with no plant residue, dead plants on the soil surface, and green plants. The previous year of field management for all plots was no-till soybean with some weeds present. Tilled plots were first sprayed with glyphosate at 1.0 kg ae ha^{-1} approximately 45 d before dicamba application. Tilled-soil plots were disked approximately 14 d later and then tilled multiple times prior to herbicide application to the point that no plant cover remained. This treatment is designated as "none" in tables and graphs, indicating no plant residue present (actual amount in all plots <5%). Plots denoted as "dead plants" were allowed to become covered with weedy plant vegetation, and then paraquat (Gramoxone®; Syngenta Crop Protection Inc., Greensboro, NC) was applied at 840 g ha^{-1} approximately 28 and 7 d before dicamba spraying to kill all existing vegetation. Plots denoted as "green plants" were allowed to become covered with the indigenous weedy plants, which were primarily common lambsquarters (*Chenopodium album* L.) and horseweed [*Conyza canadensis* (L.) Cronq.] in 2017 and 2018, and in 2019 was primarily little barley (*Hordeum vulgare* L.) with some lambsquarters and Palmer amaranth (*Amaranthus palmeri* S. Watson). Green plant cover was 60% to 100% over the plot area.

Herbicide treatments were applied using a tractor-mounted boom with TTI 8002 nozzles operated at 275 kPa and a ground speed of 5.2 km h^{-1}. Boom height was 60 cm above the top of the plant canopy or soil. Applications were made at 6:00 AM on the day of application and then the samplers moved into the treated areas 30 min after the application. Previous studies reported that this time interval was sufficient to allow for small droplets to settle upon the treated surface (Brain et al. 2019; Munjanja et al. 2020; Prueger et al. 2017). Wind speed at application was <2 km h^{-1}. Larger plots (900 or 2,000 m^2), and a limited number of air samplers dictated that a typical randomized complete block design with four replications could not be used because of limitations of plot area and samplers. Duplicate air samples were located in the center of each treated plot, and each sampler was considered a block in the model. The entire study was also replicated three times over the 3-yr period.

The DGA formulation of dicamba was used for all treatments; the same spray mixture was applied to all three soil/plant surface conditions. Dicamba dose was 1.0 kg ae ha^{-1}. No additional herbicides, surfactants, drift control agents, or adjuvants were added.

Air Sampling Media Collection

Hi-Q Model CF-1002BRL-Digital portable high-volume air samplers (Hi-Q.net, San Diego, CA) were utilized for air sampling in all experiments. Key components of the samplers included the air sampler main unit (CF-1002BRL-DIG), which included digital readouts for cumulative airflow and for time interval sampling, a microfiber filter paper holder (part number FHA–4CF), and a polyurethane foam (PUF) sampling module (part number HIQ-1002-CF). The sampling media used were a 10-cm diam HEPA-type high-purity binder-less 99.99%-efficiency borosilicate glass fiber filter paper (part number FPAE–102) and an 8-cm-long polyurethane vapor collection substrate (part number HIQ–3PUF). Additional parts included glass cartridges with stainless-steel screens for the PUF head sampler (part number HIQ-1009) and the associated single Teflon end caps with silicone O-rings (part number HIQ-1026).

The samplers operated at 185 L min^{-1}. Sampling intervals for all studies were 0 to 6, 6 to 12, 12 to 24, and 24 to 36 h after treatment (HAT). The exact amount of time was recorded for each sampler (Table 2). The samplers automatically measured the cumulative flow and elapsed time. For each surface condition, there were two air samplers per plot. A nontreated control plot also contained an air sampler to validate a lack of contamination. Dicamba

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Table 1. Year, surface residue, average temperature, and relative humidity of studies conducted to examine dicamba emissions following application under field conditions.

			Average temperature				Relative humidity			
Year	Date	Surface residue	0–6	6–12	12–24	24–36	0–6	6–12	12–24	24–36
			C				%			
2017	June 1	None	25.4	31.9	18.3	26.4	75.8	50.3	99.0	78.3
		Dead plants	27.8	33.7	19.1	28.1	67.5	47.0	99.1	78.7
		Green plants	24.6	33.6	19.3	27.4	78.7	53.0	95.6	79.4
2018	May 23	None	28.7	36.9	20.0	34.9	73.7	46.8	92.5	52.8
		Dead plants	29.3	37.3	20.4	34.7	66.6	45.7	94.1	53.4
		Green plants	28.5	36.5	19.5	34.5	68.9	49.4	92.9	54.9
2019	May 16	None	23.6	30.6	16.9	26.6	71.2	63.6	96.9	81.2
		Dead plants	25.5	32.9	16.2	28.1	57.0	45.1	96.3	71.4
		Green plants	26.7	31.8	16.5	28.7	69.9	66.6	96.9	82.1

concentrations in these control plots ranged from 0 (none detected) to 1.7 ng m^{-3}, with an average of 0.15 ng m^{-3}. At the end of a designated sampling interval, the entire microfiber filter and the PUF were removed and fresh sampling media inserted within the air sampler. Each measurement was an independent assessment of dicamba emissions at that specific location. Sampling medium was placed directly into a small container upon collection at respective intervals, then into a cooler at 0 C and stored in a –20 C freezer for subsequent chemical analysis. The air samplers were placed inside the treated area and oriented toward the soil surface so as to measure the direct emission of dicamba from the treated surface. The distance from the treated surface to the air sampler intake was approximately 30 cm. Field plot size was adequate to have the sampler at least 12 m from the end of the treated plot to minimize edge effects. This sampler arrangement is similar to those of Mueller et al. (2013).

Chemical Analysis of Sample Media

The microfiber filter papers were extracted with methanol for 1.0 h on a reciprocating shaker operated at 80 cycles min^{-1}. Extraction efficiency was approximately 90% for filter media, and data were not corrected for recovery (data not shown). An aliquot of each extraction was passed through a 0.45-µm filter directly into a 2.0-ml vial for later chemical analysis. Dicamba detections on the PUF were inconsistent, and were seldom appreciable compared to the amount collected on the filter papers (<10%). Analysis of PUF sampling media has proven to be problematic for dicamba (Mueller 2015). Data presented are from the filter paper matrix only.

Dicamba concentrations were determined using an external standard technique of analytical standards of dicamba acid (chemservice.com) dissolved in methanol. For 2017 and 2018 samples, an Agilent Liquid Chromatograph (1100 series) in line with an Agilent single quad 6120 mass spectrometer was used for analysis. A 25-cm by 4.6-mm C-18 column (phenomenex.com) at 35 C was used to separate components of interest from the matrix. The mobile phase (0.7 mL min^{-1}) used a gradient program of acetonitrile and water. Both components were fortified with 0.1% formic acid. Initial conditions were 50% acetonitrile/50% water, followed by a linear gradient to 95% acetonitrile at 4 min, held constant at 95% acetonitrile for 9 min, and then returned to original conditions for equilibration prior to the next injection. The parameters for this mass spectrometer were drying-gas flow of 12.0 L min^{-1}, 35-bar nebulizer pressure, 250 C drying-gas temperature, 200 C vaporizer temperature, 2,500-volt capillary voltage, 0-volt corona current, 1,200-volt charging voltage, and single-ion monitoring at 219.0 from 4.0 to 7.0 min. The retention time of dicamba acid in the system was 5.0 min, with a limit of detection of 0.1 ppb. Samples from the 2019 experiment were analyzed using similar methods but with an Agilent 1260 LC coupled with a 6470 MSMS detector. Once samples were extracted, they were stored in a dark freezer at –20 C and were analyzed within 3 d. Within each analytical sequence, numerous solvent blanks were included to verify that dicamba carryover from previous injections was not present (data not shown).

Environmental Data Collection

Within each plot, a temperature and relative-humidity sensor probe was placed onto the soil surface. In 2017 there was a single sensor, and in 2018 and 2019 there were two sensors on the soil surface within each plot. The temperature samplers (HOBO model PRO V2) were set to operate at 30-min intervals. These units were re-zeroed prior to each study. Temperature and relative-humidity data were time stamped. The start time was synchronized to the initiation of each study. Previous calibrations of the HOBO units showed acceptable accuracy and agreement among the samplers (± 0.1% when tested at 20 C, 30 C, and 40 C, data not shown). The environmental data presented are for the mean over the sampled time interval averaged over the sensors for that plot. Additionally, there was a permanent weather station adjacent to the plots (<200 m) that measured wind speed and rainfall.

Statistical Analysis

Within each study, the dicamba concentration was expressed as the amount (in nanograms) determined in that sampling interval, and means were separated using LSD at the 5% significance level (Table 2). Additionally, the nanograms per cubic meter being emitted from a treated area was determined by dividing the nanograms of dicamba by the volume of air for that respective sampling interval.

The cumulative dicamba amounts over time were regressed using SigmaPlot 14 (SYSTAT Software, Chicago, IL) to provide a nonlinear sigmoidal regression equation (Equation 1):

$$y = a/(1 + \exp(-(\text{hours} - c)/b)) \quad [1]$$

where parameter a = maximum dicamba measured at asymptote, and parameter c = time in hours required for inflection of curve from increasing to decreasing dicamba amounts.

For each year and surface condition combination, the regression parameters for that line were derived (Table 3). To compare

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Table 2. Field studies from 2017, 2018, and 2019 in Knoxville, TN, to examine the effect of field surface condition on dicamba emissions after application.[a]

Year	Sampling interval	Surface condition	Actual time	Dicamba	Dicamba concentration	Percent no residue[c]
	HAT[b]		h	ng	ng m^{-3}	%
2017	0–6	No plant residue	6	71b	1.1b	100
		Dead plants	6.1	31b	0.5b	44
		Green plants	6.2	292a	4.4a	411
		LSD	0.2	48	0.8	
		P = 0.05				
2017	6–12	No plant residue	5.1	146b	2.6b	100
		Dead plants	4.9	90b	1.6b	62
		Green plants	4.8	732a	13.5a	503
		LSD	0.1	104	1.4	
		P = 0.05				
2017	12–24	No plant residue	10.8	12ab	0.1ab	100
		Dead plants	10.8	0b	0b	0
		Green plants	10.9	41a	0.4a	336
		LSD	0.46	18	0.2	
		P = 0.05				
2017	24–36	No plant residue	10.4	57b	0.5b	100
		Dead plants	10.3	0b	0b	0
		Green plants	10.3	210a	1.9a	372
		LSD	0.08	36	0.5	
		P = 0.05				
2018	0–6	No plant residue	6.6	502a	8.8a	100
		Dead plants	6.6	93a	1.7b	19
		Green plants	6.4	433a	7.7a	86
		LSD	0.4	292	5	
		P = 0.05				
2018	12–24	No plant residue	6.1	1,377b	16b	100
		Dead plants	6.1	394c	6c	29
		Green plants	6.1	4,453a	67a	323
		LSD	NS	490	4	
		P = 0.05				
2018	24–36	No plant residue	12	567b	3.7b	100
		Dead plants	12.6	252c	1.5c	44
		Green plants	12.3	1,000a	6.6a	176
		LSD	0.5	158	1.2	
		P = 0.05				
2018	24–36	No plant residue	5.4	370b	2.8b	100
		Dead plants	5.3	143b	1.1b	39
		Green plants	5	1,005a	7.9a	272
		LSD P=0.05	0.2	224	1.6	
2019	0–6	No plant residue	6.5	700b	11b	100
		Dead plants	6.4	230c	3b	33
		Green plants	6.4	4,400a	78a	629
		LSD	0.8	400	6	
		P = 0.05				
2019	6–12	No plant residue	5.9	2,700b	38b	100
		Dead plants	5.9	700b	9b	26
		Green plants	5.9	10,800a	166a	400
		LSD	NS	2,900	11	
		P = 0.05				
2019	12–24	No plant residue	9.1	770b	3b	100
		Dead plants	9	390b	6b	51
		Green plants	9.2	3,500a	30a	455
		LSD	0.5	1,200	1.2	
		P = 0.05				
2019		No plant residue	12	2,370b	18b	100
	24–36	Dead plants	12	560b	4.2b	24
		Green plants	11	8,690a	70a	367
		LSD	0.2	2,400	20	
		P = 0.05				
			% min	% avg		
All	All	Dead plants	0	31		
All	All	Green plants	86.1	361		

[a]The diglycolamine (DGA) salt of dicamba was applied at 1.0 kg ae ha^{-1} to all plots. Mean separation within a column grouping with a different letter is different at 5% significance level.
[b]Abbreviation: HAT, h after treatment.
[c] Percent of dicamba captured in comparison to no residue treatments.

the relative dicamba OTM potential, each time interval for each year was normalized to the no-plant-residue treatment for that individual timeframe (Table 3). This normalization was based on the fact that most Environmental Protection Agency (EPA) studies require the use of bare ground (no plant residue) in their field assessments, and some previous studies have also had bare

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Table 3. Regression paramters for dicamba emissions for applied surface conditions of no residue, dead plants, or green plants from field studies in Knoxville, TN in 2017 to 2019.[a]

Year	Surface condition	Parameter *a*	Parameter *c*	r^2	*a* Compared to no residue
		Dicamba ng	Hours		%
2017	No residue	257	7.7	0.85	100
2017	Dead plants	122	7	0.93	48
2017	Green plants	1,170	8	0.94	456
2018	No residue	2,390	9.3	0.94	100
2018	Dead plants	815	10.5	0.98	34
2018	Green plants	6,390	9.6	0.88	267
2019	No residue	6,820	15	0.92	100
2019	Dead plants	1,850	13.5	0.94	27
2019	Green plants	27,390	12.9	0.88	402
All	Dead plants				36.2
All	Green plants				374.8

[a]Parameter *a* = maximum dicamba measured at asymptote, and parameter *c* = time in hours required for inflection of curve from increasing to decreasing dicamba amounts. Parameter *a* data were also normalized to compare no-residue values to those with dead plants or green plant material.

Table 4. Correlation coefficients and (probability levels in parentheses) comparing three surface conditions (no residue, dead plants, or green plants) to measured dicamba emissions, relative humidity, and temperature measured at the soil surface of each plot.[a]

	Dicamba ng m^{-3}	Relative humidity	Temperature
Surface condition	0.395 (0.0018)	0.021 (0.8759)	0.0358 (0.785)
Dicamba ng m^{-3}	1	–0.019 (0.883)	0.153 (0.244)
Relative humidity		1	–0.929 (<0.0001)

[a]Environmental data used were the average over that particular sampling interval.

ground in their methodology (Riter et al. 2020). This comparison of the normalized data provides a framework to discuss the effect of surface conditions on observed dicamba concentrations.

To determine whether temperature and relative humidity affected the amount of dicamba detected, a correlation was run in Proc Corr procedure in SAS (ver. 9.4; SAS Institute; Cary, NC). between average temperature and relative humidity during the specific time interval to dicamba detected in that time. Results shown include correlation coefficients and probability levels (Table 4).

Results and Discussion

The normal relationship between temperature and relative humidity was observed in this study, with the diurnal pattern of higher temperature and lower relative humidity during the daylight hours (Table 1). The overnight time interval (12 to 24 HAT) had lower temperatures and substantially higher relative humidity. In 2017, there was a 16-mm rainfall event 2 d before herbicide application, thus the soil was moist at the time of spraying. There was also an 8-mm rainfall 12 h after spraying in 2017; the effects of this precipitation will be discussed in subsequent sections. There was no other rainfall on any of the other studies (data not shown). Wind speed each year was similar, with constant wind speed of 0 to 3 km h^{-1}, and maximum wind gusts each year from 8 to 11 km h^{-1}. The wind speed was usually higher in the middle of the day.

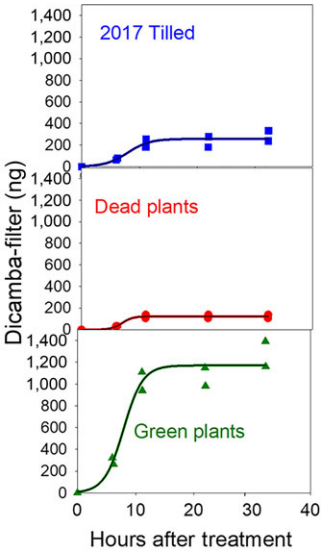


Figure 1. Dicamba emissions in 2017 as affected by surface condition and hours after treatment presented as cumulative nanograms. Regression equation set to $y = a/(1 + \exp(-(\text{hours} - c)/b))$. Parameter *a* = maximum dicamba at asymptote, parameter *c* = time in hours to reach inflection point of curve where dicamba concentration is increasing at a slower rate. Regression parameters are given in Table 3.

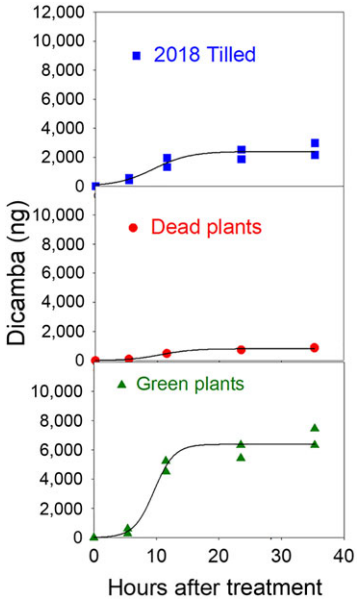


Figure 2. Dicamba emissions in 2018 as affected by surface condition and hours after treatment presented as cumulative nanograms. Regression equation set to $y = a/(1 + \exp(-(\text{hours} - c)/b))$. Parameter *a* = maximum dicamba at asymptote, parameter *c* = time in hours to reach inflection point of curve where dicamba concentration is increasing at a slower rate. Regression parameters are given in Table 3.

Dicamba Emissions

Dicamba emissions following application were affected by the treated surface in all years, with the order from least to most emissions being dead plants < tilled soil < green plant material (Tables 2, 3; Figures 1, 2, 3). The magnitude of dicamba emissions varied greatly over the 3 yr, with much more occurring in 2019 compared to 2018 or 2017. Although the dicamba emitted varied in scale, the relative emissions as affected by the surface applied was consistent (Table 2).

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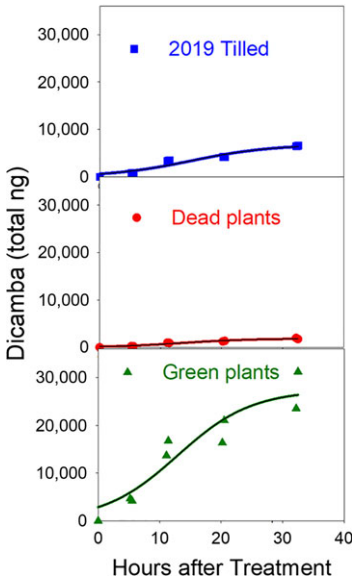


Figure 3. Dicamba emissions in 2019 as affected by surface condition and hours after treatment presented as cumulative nanograms. Regression equation set to $y = a/(1 + \exp(-(\text{hours} - c)/b))$. Parameter a = maximum dicamba at asymptote, parameter c = time in hours to reach inflection point of curve where dicamba concentration is increasing at a slower rate. Regression parameters are given in Table 3.

One difference among the years was that in 2017 at approximately 12 HAT, an 8-mm rainfall event occurred between the second and third sampling interval. This precipitation decreased the amount of dicamba emitted after the rainfall, and the slopes of the line from the last two measurement intervals tended to be less steep than the 0 to 6 and 6 to 12 HAT data points. Burnside and Lavy (1966) reported that dicamba moved through a soil column after a rainfall event. If dicamba was moved into the soil by rainfall, it would result in less on the soil surface for subsequent emissions 12 to 24 HAT and 24 to 36 HAT (Table 2). There was no dicamba detected in the plots that contained dead plants on the surface once this rainfall event occurred.

In this study, we attempted to relate the dicamba emissions to the measured environmental factors (Table 4). The challenge is that the dicamba data amount to a single value for a given time interval, whereas the environmental data consist of many numbers over the same time interval. After considering several approaches, we correlated the average temperature and relative humidity to the respective surface condition and dicamba emission (Table 4). Surface condition was significantly related to dicamba emissions but not to temperature or relative humidity. In this study, based upon how the study was conducted, there was no apparent relationship between dicamba emissions and temperature/relative humidity. This result differs from several previous reports (Behrens and Lueschen 1979; Mueller 2013; Mueller and Steckel 2019). The authors of those studies speculate that the surface condition effect is much more pronounced than the effect of temperature or relative humidity, and it appears that factors other than those measured affected dicamba emissions among the years.

The relative dicamba measurements within each sampling interval when compared to the tilled soil were markedly consistent (Table 2). Emissions from plots with dead plants ranged from 0 to 62% with a mean of 31%, and green plant relative emissions ranged from 86% to 629%, with a mean of 361%. An examination of the regression parameter shows a similar relationship when normalized to bare soil (no plant residue) with dicamba emissions from plots with dead plants and green plants being 36% and 375%, respectively (Table 3). Thus, surface condition clearly affected the amount of dicamba that is being released into the air for potential OTM.

The relative shapes of the regression curves for all plots were similar. The fit of the equation to all curves was good, with $r^2 > 0.85$ for all plots (Table 3). Parameter a is a measure of the maximum dicamba concentration, and parameter c is a measurement of the slope of the line as it changes from increasing to decreasing concentrations (Table 3). In general, the parameter c values indicate a similarity in the response of the curves each year. The 2017 plots had a shorter time to maximum contributed by a rainfall event at 12 HAT, which decreased dicamba concentrations in later sampling intervals. These results also showed that in 2018 and 2019, years not interrupted by rainfall, not only was more dicamba captured leaving the treated surface but also that 25% to 50% more time elapsed (7 to 8 h in 2017 compared with 9.3 to 15 h in 2018 and 2019) for the rate of dicamba leaving the treated area began to decrease. This would result in more time to potentially expose sensitive vegetation around the treated field.

The relative responses across the three surface areas were consistent in all 3 yr. However, two fundamental questions arise from these data. First, why is more dicamba being emitted from green plant surfaces compared to the others? Second, why are the absolute amounts of dicamba so remarkably different among the 3 yr? Dicamba measurements were >300% when applied to green plants compared to other surfaces (Tables 2, 3). The temperature and relative humidity data indicate no major differences between the various surfaces in this study (Tables 1, 4). A possible explanation is that the green plant material was much more erect and had a higher surface area, which would exacerbate the emission of dicamba from the treated surface. Differences in plant density, ground cover, and height could also have affected our results. Another potential explanation is that the absorption sites of dead plant material or tilled soil would be more effective at adsorbing the dicamba molecule with a sufficient bond to suppress dicamba emissions.

The water leaving the treated plot could have been a driving force encouraging the dicamba emissions. Water transpiring from green plants could facilitate dicamba movement. Dead plant material acting as a mulch could have reduced water loss, and thus dicamba emissions were reduced by less water loss from "mulched" soil.

The pH of the sprayed surface could also affect dicamba missions; it is possible that the surface chemistry of the green plants is at a lower pH, which could encourage later dicamba emissions. Dicamba is a weak acid (pKa = 1.87), and the state of the molecule, whether protonated or deprotonated, may have a substantial impact on the volatility (MacInnes 2017). Our results are consistent with previous research showing more dicamba movement off plant material (Behrens and Lueschen 1979).

The dicamba concentrations measured over the different years varied from the lowest in 2017 to the highest of 2019, being >20 times greater in 2019 (Table 3). In 2019 there was a greater difference between the three surface conditions with respect to the temperature, especially in the 6- to 12-h time interval (Figure 4). The surface condition in 2019 and the green plants may have been more conducive to dicamba volatility, as little barley was the most abundant weed, with an upright grassy phenotype compared to the previous 2 yr, when weed species present consisted mainly of horseweed and lambsquarters. Another potential explanation is that the temperature measurements were taken at the soil surface

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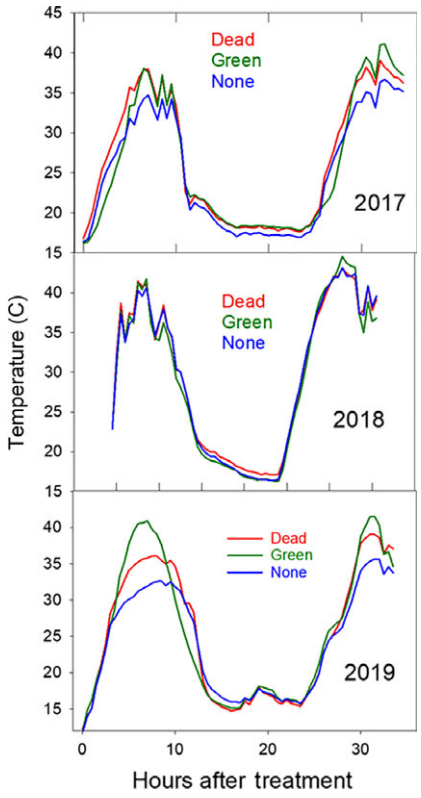


Figure 4. Temperature at soil surface for each surface condition in 2017, 2018, and 2019.

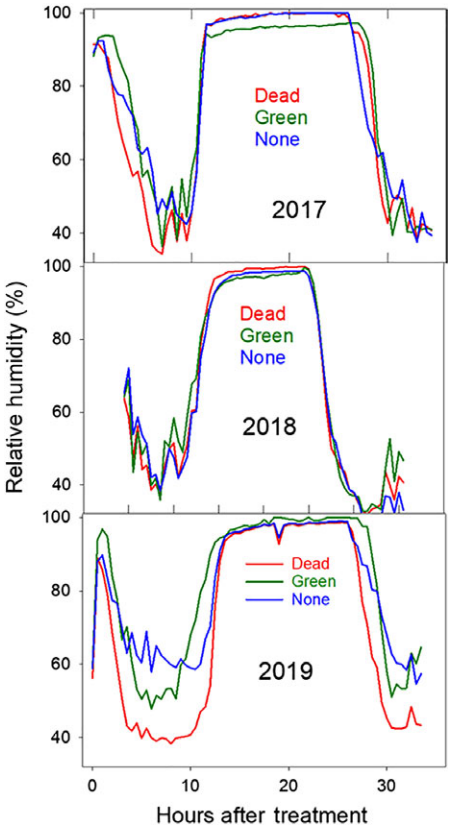


Figure 5. Relative humidity at soil surface for each surface condition in 2017, 2018, and 2019.

rather than within the canopy, and the conditions between the two surfaces could have differed.

Carlsen et al. (2006) reported that pesticide evaporation rates will be the greatest immediately after spraying while the target surface is still saturated and then rapidly decrease to a much lower level. Pesticide vapor pressure and evaporation have been compared and are at times correlated for the tested pesticides (Rudel 1997). Temperature can have a large influence on pesticide evaporation, and the two often are directly correlated. Given the effect of temperature, the evaporation will therefore vary with time of day, season, and latitude; indicating that the time of the year may affect total pesticide volatility. Higher rates of evaporation have been observed from plants when compared to soil surfaces. A possible reason for this greater volatility from plants is the greater air velocity at the altitude of the leaves combined with more turbulent airflow within and around the plant canopy, the plants' greater surface area, and the binding of the pesticide to the soil through absorption to organic matter and clay. A possible scenario in our research is that the air temperatures mainly influenced the evaporation from the plants, whereas soil moisture and evaporation of the soil water mainly influenced evaporation from soil (Stork et al. 1998). The possibility that the dicamba flux was modulated by different primary mechanisms based on the surface to which dicamba was applied would possibly explain our results.

More dicamba OTM from green plant material would be consistent with field observations by scientists in recent years, when applications made during warmer temperatures in late June and July correlated with more dicamba OTM complaints (Bradley 2017; Hager 2017). Late June and July glyphosate and dicamba applications on dicamba-resistant soybean and cotton are often applied to weeds over 10 cm tall and at high densities. This use pattern would be consistent with previous reports on the history of herbicide usage in glyphosate-resistant crops. Culpepper and York (1998) reported that 2 yr after the introduction of glyphosate-resistant cotton in North Carolina, many growers were exclusively relying on glyphosate applied multiple times to manage their weeds. In soybean, Young (2006) reported that from 1995 to 2003, the average weed height at the time of POST applications moved from 12 cm to 21 cm. Our research would suggest that increases in volatility will be more likely if farmers make applications of dicamba to large, dense stands of weeds. The results from this study also are significant, in that EPA modeling studies normally require bare-ground studies for various pesticides to be examined for their flux from treated fields (Corbin et al. 2006). These data suggest that applying dicamba to bare ground as compared to green plant material underestimates what would be expected under normal use conditions. This research would indicate that this is especially true for those applied POST, when the crop canopy would be expected to be essentially 100% green material. Simulation models often have parameters available to adjust the emissions based on the surface characteristics. A potential change to enhance the accuracy of the models would be to increase their theoretical findings to allow for the effect of green plant material on dicamba missions under field conditions.

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