This is a "preproof" accepted article for Weed Science. This version may be subject to change in the production process, *and does not include access to supplementary material.*
DOI: 10.1017/wet.2020.106

Short Title: surface effects on dicamba

Dicamba Emissions under Field Conditions as Affected by Surface Condition

Thomas C. Mueller and Lawrence E. Steckel

[1]Professors, Department of Plant Sciences, University of Tennessee, Knoxville, TN 37996. Author for correspondence: Tom Mueller, 2505 Chapman Drive, Knoxville, TN, 37996 (Email: tmueller@utk.edu)

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 greater 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 groundcocver 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.

Nomenclature: Dicamba; soybean, *Glycine max* L. Merr.

Keywords: environmental fate, volatility

Downloaded from https://www.cambridge.org/core. University of New England, on 24 Sep 2020 at 13:03:28, subject to the Cambridge Core terms of use, available at https://www.cambridge.org/core/terms. https://doi.org/10.1017/wet.2020.106

One response to the increase in glyphosate-resistant weed species was the introduction of dicamba-resistant soybean and cotton (Monsanto Company, St Louis, MO, USA) 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) while 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).

While the broadleaf weed control from this system has been good, extensive off-target movement (OTM) and injury to sensitive non-target broadleaf vegetation has also been reported (Bradley 2017; Hager 2017; Steckel 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 will be referred to as such by the authors in this paper.

Numerous researchers have reported volatility of different dicamba salts (Behrens and

Downloaded from https://www.cambridge.org/core. University of New England, on 24 Sep 2020 at 13:03:28, subject to the Cambridge Core terms of use, available at https://www.cambridge.org/core/terms. https://doi.org/10.1017/wet.2020.106

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 one of 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 employed plant bioassays as indicators of dicamba activity (Sciumbato et al. 2004; Egan and Mortensen 2012; Penner and Michael 2014). While the sensitivity of these bioassays is more than adequate, a quantitative assessment via air sampling 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 (Sall et al. 2020; Riter 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.

Downloaded from https://www.cambridge.org/core. University of New England, on 24 Sep 2020 at 13:03:28, subject to the Cambridge Core terms of use, available at https://www.cambridge.org/core/terms. https://doi.org/10.1017/wet.2020.106

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, 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

Downloaded from https://www.cambridge.org/core. University of New England, on 24 Sep 2020 at 13:03:28, subject to the Cambridge Core terms of use, available at https://www.cambridge.org/core/terms. https://doi.org/10.1017/wet.2020.106

(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 months (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 3 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 days before dicamba application. Tilled soil plots were disked approximately 14 days 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 days 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 hr^{-1}. Boom height was 60 cm above the top of

Downloaded from https://www.cambridge.org/core. University of New England, on 24 Sep 2020 at 13:03:28, subject to the Cambridge Core terms of use, available at https://www.cambridge.org/core/terms. https://doi.org/10.1017/wet.2020.106

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 minutes 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. 2019; Prueger et al. 2017). Wind speed at application was < 2 km hr^{-1}. Larger plots (900 or 2000 m^2) and a limited number of air samplers dictated that a typical randomized complete block design with 4 replications could not be used, due to 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-year 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, USA) were utilized for air sampling in all experiments. Key components of the samplers included the air sampler main unit (CF-1002BRL-DIG) that included digital readouts for cumulative airflow and for time interval sampling, a microfiber filter paper holder (part number FHA–4CF), and a PUF sampling module (part number HIQ-1002-CF). The sampling media used was a 10-cm diameter 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).

Downloaded from https://www.cambridge.org/core. University of New England, on 24 Sep 2020 at 13:03:28, subject to the Cambridge Core terms of use, available at https://www.cambridge.org/core/terms. https://doi.org/10.1017/wet.2020.106

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 hr after treatment (HAT). The exact amount of time was recorded for each sampler (Tables 2). The samplers automatically measured the cumulative flow and elapsed time. For each surface condition, there were two air samplers per plot. A non-treated control plot also contained an air sampler to validate a lack of contamination. Dicamba 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 media 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 towards 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 meters from the end of the treated plot to try and avoid edge effects. This sampler arrangement is similar to those of Mueller et al. 2013.

Chemical analysis of sample media

The micro-fiber filter papers were extracted with methanol for 1.0 hr on a reciprocating shaker operated at 80 cycles min^{-1}. Extraction efficiency was approximately 90% for filter media and data was 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

Downloaded from https://www.cambridge.org/core. University of New England, on 24 Sep 2020 at 13:03:28, subject to the Cambridge Core terms of use, available at https://www.cambridge.org/core/terms. https://doi.org/10.1017/wet.2020.106

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 x 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 four minutes, held constant at 95% acetonitrile for nine minutes, 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, 2500 volt capillary voltage, 0 volt corona current, 1200 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 minutes, 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 days. 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

Downloaded from https://www.cambridge.org/core. University of New England, on 24 Sep 2020 at 13:03:28, subject to the Cambridge Core terms of use, available at https://www.cambridge.org/core/terms. https://doi.org/10.1017/wet.2020.106

soil surface. In 2017 there was a single sensor, and in 2018 and 2019 there were 2 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 amongst the samplers (± 0.1% when tested at 20, 30, 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 (ng) determined in that sampling interval and means were separated using LSD at the 5% significance level (Table 2). Additionally, the ng m^{-3} emitting from a treated area was determined by taking the dicamba in ng and dividing 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 non- linear sigmoidal regression equation (Equation 1). In this equation, parameter a = maximum dicamba measured at asymptote while parameter c = time in hours required for inflection of curve from increasing to decreasing dicamba amounts.

$$\text{Equation 1. } y = a/(1+\exp(-(\text{hours}-c)/b))$$

For each year and surface condition combination, the regression parameters for that line were derived (Table 3). To compare the relative dicamba OTM potential, each time interval for each year was normalized to the no plant residue treatment for that individual time frame (Table

Downloaded from https://www.cambridge.org/core. University of New England, on 24 Sep 2020 at 13:03:28, subject to the Cambridge Core terms of use, available at https://www.cambridge.org/core/terms. https://doi.org/10.1017/wet.2020.106

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 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.

In order to determine if temperature and relative humidity impacted 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 days before herbicide application, thus the soil was moist at the time of spraying. There was also an 8 mm rainfall 12 hours 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 hr^{-1}, and maximum wind gusts each year from 8 to 11 km hr^{-1}. The wind speed was usually higher in the middle of the day.

Downloaded from https://www.cambridge.org/core. University of New England, on 24 Sep 2020 at 13:03:28, subject to the Cambridge Core terms of use, available at https://www.cambridge.org/core/terms. https://doi.org/10.1017/wet.2020.106

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 years, 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).

One difference among the years was that in 2017 at approximately 12 hours after treatment, 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.

Relating the dicamba emissions to the measured environmental factors in this study was attempted (Table 4). The challenge is that the dicamba data is a single value for a given time interval, while the environmental data consists of many numbers over the same time interval. After considering several approaches, the authors 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

Downloaded from https://www.cambridge.org/core. University of New England, on 24 Sep 2020 at 13:03:28, subject to the Cambridge Core terms of use, available at https://www.cambridge.org/core/terms. https://doi.org/10.1017/wet.2020.106

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 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. It 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 it took 25 to 50% (7 to 8 hours in 2017 compared with 9.3 to 15 hours in 2018 and 2019) more time before the rate of dicamba leaving the treated area started to decrease. This would result in more time to potentially expose sensitive vegetation around the treated field.

Downloaded from https://www.cambridge.org/core. University of New England, on 24 Sep 2020 at 13:03:28, subject to the Cambridge Core terms of use, available at https://www.cambridge.org/core/terms. https://doi.org/10.1017/wet.2020.106

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

Downloaded from https://www.cambridge.org/core. University of New England, on 24 Sep 2020 at 13:03:28, subject to the Cambridge Core terms of use, available at https://www.cambridge.org/core/terms. https://doi.org/10.1017/wet.2020.106

2017 to the highest of 2019, being > 20X greater in 2019 (Table 3). In 2019 there was more difference between the three surface conditions with respect to the temperature especially in the 6- to 12-hour 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 two years that consisted mainly of horseweed and lambsquarters. Another potential explanation is the temperature measurements were taken at the soil surface 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, while soil moisture and evaporation of the soil water mainly influenced evaporation from soil (Stork et al. 1998). Having the dicamba flux being modulated by different primary mechanisms based on the surface applied would possibly explain our results.

Downloaded from https://www.cambridge.org/core. University of New England, on 24 Sep 2020 at 13:03:28, subject to the Cambridge Core terms of use, available at https://www.cambridge.org/core/terms. https://doi.org/10.1017/wet.2020.106

More dicamba OTM from green plant material would be consistent with field observations by scientists in recent years where applications made during warmer temperatures in late June and July correlated with more dicamba OTM complaints (Bradley 2017; Hager 2017; Steckel et al. 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 years 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 postemergence where 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.

ACKNOWLEDGEMENT

The project was conducted under Hatch project TEN00526 and was partially funded by the Tennessee Soybean Promotion Board. No conflicts of interest have been declared. Technical assistance by Joe Beeler, David Kincer, Abigail Vickers, Trey Clark, Luke Shoffner and Anna Ekene Davis Tharpe is gratefully acknowledged.

Downloaded from https://www.cambridge.org/core. University of New England, on 24 Sep 2020 at 13:03:28, subject to the Cambridge Core terms of use, available at https://www.cambridge.org/core/terms. https://doi.org/10.1017/wet.2020.106

REFERENCES

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

Bradley KW (2017) How to proceed in 2018: a university perspective. Proceedings of the North Central Weed Science Society 53:245

Brain R, Goodwin G, Abi-Akar F, Lee B, Rodgers C, Flatt B, Lynn A, Kruger G, Perkins D, (2019) Winds of change, developing a non-target plant bioassay employing field-based pesticide drift exposure: a case study with atrazine. Science of the Total Environment 678:239-252

Busey P, Broschat TK, Johnston DL (2003) Injury to landscape and vegetable plants by volatile turf herbicides. Hort technology 13:650-652

Burnside OC, Lavy TL (1966) Dissipation of dicamba. Weeds 14:211-214

Carlsen, SCK, Spliid NH, Svensmark B (2006) Drift of 10 Herbicides after tractor spray application. 1. secondary drift (evaporation). Chemosphere 64:787-794

Corbin M, Eckel W, Ruhman M, Spatz D, Thurman N (2006) NAFTA guidance docment for conducting terrestrial field dissipation studies. Sourced 5/30/2020 https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/nafta-guidance-document-conducting-terrestrial-field#IIC

Downloaded from https://www.cambridge.org/core. University of New England, on 24 Sep 2020 at 13:03:28, subject to the Cambridge Core terms of use, available at https://www.cambridge.org/core/terms. https://doi.org/10.1017/wet.2020.106

Culpepper AS, York AC (1998) Weed management in glyphosate tolerant cotton. J. Cotton. Sci. 2: 174-185

Dorfler U, Adler-Kohler R, Schneider P, Scheunert I, Korte F (1991) A Laboratory Model System for Determining the Volatilty of Pesticides from Soil and Plant Surfaces. Chemosphere 23:485-496

Egan JF, Mortensen DA (2012) Quantifying vapor drift of dicamba herbicides applied to soybean. Environmental Toxicology and Chemistry 31:1023-1031

Hager A (2017) Observations of midwest weed extension scientist. Proceedings of the North Central Weed Science Society 72:240

Hemminghaus JW, Macinnes AWD, Zhang J (2017) Low volatility herbicidal compositions. United States Patent US 9,743,664 B2

Johnson VA, Fisher LR, Jordan DL, Edmisten KE, Stewart AM, York AC (2012) Cotton, peanut, and soybean response to sublethal rates of dicamba, glufosinate, and 2,4-D. Weed Technol 26:195-206

MacInnes A (2017) Vaporgrip technology: How it works and its benefits. Abstract of the Weed Science Society of America 57:353

Mueller TC (2015) Methods to measure herbicide volatility. Weed Sci 63:116-120.

Downloaded from https://www.cambridge.org/core. University of New England, on 24 Sep 2020 at 13:03:28, subject to the Cambridge Core terms of use, available at https://www.cambridge.org/core/terms. https://doi.org/10.1017/wet.2020.106

Mueller TC, Steckel LE (2019) Dicamba volatility in humidomes as affected by temperature and herbicide treatment. Weed Technol 3:541-546.

Mueller TC, Wright DR, Remund KM (2013) Effect of formulation and application time of day on detecting dicamba in the air under field conditions. Weed Sci 61:586-593

Muller T, Kubiak R, Staimer N, Mueller T (1996) Volatilization of 14C-labelled fenpropimorph after application to plants and soil under simulated outdoor conditions. International J of Environ. Anal. Chemistry 65:183-191

Munjanja BK, Naude Y, Forbes PBC (2020) A review of Sampling Approaches to Off-target Pesticide Deposition. Trends in Environ and Anal Chemistry 25:1-9

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. DOI10.1002/ps5887

Penner D, Michael J (2014) Bioassay for evaluating herbicide volatility from soil and plants. In: Sesa, C. (Ed.) Pesticide Formulation and Delivery Systems 33:36-43

Prueger JH, Alfieri J, Gish TJ, Kustas WP, Daughtry ST, Hatlfield JL, McKee LG (2017) Multi-year measurements of field-scale metolachlor volatilization. Water Air Soil Pollut. 228:84-89

Downloaded from https://www.cambridge.org/core. University of New England, on 24 Sep 2020 at 13:03:28, subject to the Cambridge Core terms of use, available at https://www.cambridge.org/core/terms. https://doi.org/10.1017/wet.2020.106

Pucci J (2017) Monsanto sees improved glyphosate prices and more Xtend acres in 2018. Agribusiness Global. https://www.agribusinessglobal.com/agrochemicals/monsanto-sees-improved-glyphosate-prices-more-xtend-acres-in-18/

Rice CP, Nochett CB, Zara P (2002) Volatilization of trifluralin, atrazine, metholachlor, chlorpyifos, α-endosulfan, and β-endosulfan from freshly tilled soil. J Agric Food Chem 50:4009-4017

Riter LS, Sall ED, Pai N, Beachum CE, Orr TB (2020) Quantifying dicamba volatility under field conditions: part 1, methodology. J Agric Food Chem 68:2277-2285

Rudel H (1997) Volatization of pesticides from soil and plant surfaces. Chemosphere 35:143-152

Sall ED, Huang K, Pai N, Schapaugh AW, Honegger JL, Orr TB, Riter LS (2020) Quantifying dicamba volatility under field conditions: part II, comparative analysis of 23 dicamba volatility field trials. J Agric Food Chem 68:2286-2296.

Sciumbato AS, Chandler JM, Senseman SA, Bovey RW, Smith KL (2004) Determining exposure to auxin-like herbicides. II. practical application to quantify volatility. Weed Technol 18:1135-1142.

Downloaded from https://www.cambridge.org/core. University of New England, on 24 Sep 2020 at 13:03:28, subject to the Cambridge Core terms of use, available at https://www.cambridge.org/core/terms. https://doi.org/10.1017/wet.2020.106

Steckel L, Ducar J, York A, Scott B, Barber T, Bradley K (2017) Off-target dicamba in Tennessee: an extension perspective. Proceedings of the North Central Weed Science Society 53: 165

Stork A, Ophoff H, Smelt JH, Fuhr F (1998) Volatilization of clopyralid and terbuthylazine under field conditions: comparison of field and wind tunnel experiments. Z. PflKrankh. PflShutz Sonderh. 16:745-755

Strachan SD, Casini MS, Heldreth KM, Scocas JA, Nissen SJ, Bukun B, Lindenmayer RB, Shaner DL, Westra P, Brunk G (2010) Vapor movement of synthetic auxin herbicides: aminocyclopyrachlor, aminocyclopyrachlor-methyl ester, dicamba, and aminopyralid. Weed Science 58:103-108

Wechsler SJ, Smith D, McFadden J, Dodson L, Willisamson S (2019) The use of genetically engineered dicamba-tolerant soybean seeds has increased quickly, benefiting adopters but damaging crops in some fields. United States Dept of Agriculture Economic Research Service. Sourced 8/30/2020 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/

Young BG (2006) Changes in herbicide use patterns and production practices resulting from glyphosate-resistant crops. Weed Technol 20:301-307

Downloaded from https://www.cambridge.org/core. University of New England, on 24 Sep 2020 at 13:03:28, subject to the Cambridge Core terms of use, available at https://www.cambridge.org/core/terms. https://doi.org/10.1017/wet.2020.106

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

Year	Date	surface residue	Average temperature				Relative humidity			
			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

Downloaded from https://www.cambridge.org/core. University of New England, on 24 Sep 2020 at 13:03:28, subject to the Cambridge Core terms of use, available at https://www.cambridge.org/core/terms. https://doi.org/10.1017/wet.2020.106

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. Percent of dicamba captured in comparison to no residue treatments. DGA dicamba was applied at 1.0 kg ae/ha to all plots. Mean separation within a column grouping with a different letter is different at 5% significance level.

Year	Time Interval	surface condition	actual time	dicamba		dicamba		Pcnt No residue
			hr	ng		ng m^{-3}		%
2017	0-6	no plant residue	6	71	b	1.1	b	100
		dead plants	6.1	31	b	0.5	b	44
		green plants	6.2	292	a	4.4	a	411
		LSD P=0.05	0.2	48		0.8		
2017	6-12	no plant residue	5.1	146	b	2.6	b	100
		dead plants	4.9	90	b	1.6	b	62
		green plants	4.8	732	a	13.5	a	503
		LSD P=0.05	0.1	104		1.4		
2017	12-24	no plant residue	10.8	12	ab	0.1	ab	100
		dead plants	10.8	0	b	0	b	0
		green plants	10.9	41	a	0.4	a	336
		LSD P=0.05	0.46	18		0.2		
2017	24-36	no plant residue	10.4	57	b	0.5	b	100
		dead plants	10.3	0	b	0	b	0
		green plants	10.3	210	a	1.9	a	372
		LSD P=0.05	0.08	36		0.5		
2018	0-6	no plant residue	6.6	502	a	8.8	a	100
		dead plants	6.6	93	a	1.7	b	19
		green plants	6.4	433	a	7.7	a	86
		LSD P=0.05	0.4	292		5		
2018	12-24	no plant residue	6.1	1377	b	16	b	100
		dead plants	6.1	394	c	6	c	29
		green plants	6.1	4453	a	67	a	323
		LSD P=0.05	ns	490		4		
2018	24-36	no plant residue	12	567	b	3.7	b	100
		dead plants	12.6	252	c	1.5	c	44
		green plants	12.3	1000	a	6.6	a	176
		LSD P=0.05	0.5	158		1.2		
2018	24-36	no plant residue	5.4	370	b	2.8	b	100
		dead plants	5.3	143	b	1.1	b	39

Downloaded from https://www.cambridge.org/core. University of New England, on 24 Sep 2020 at 13:03:28, subject to the Cambridge Core terms of use, available at https://www.cambridge.org/core/terms. https://doi.org/10.1017/wet.2020.106

		green plants	5	1005	a	7.9	a	272
		LSD P=0.05	0.2	224		1.6		
2019	0-6	no plant residue	6.5	700	b	11	b	100
		dead plants	6.4	230	c	3	b	33
		green plants	6.4	4400	a	78	a	629
		LSD P=0.05	0.8	400		6		
2019	6-12	no plant residue	5.9	2700	b	38	b	100
		dead plants	5.9	700	b	9	b	26
		green plants	5.9	10800	a	166	a	400
		LSD P=0.05	ns	2900		11		
2019	12-24	no plant residue	9.1	770	b	3	b	100
		dead plants	9	390	b	6	b	51
		green plants	9.2	3500	a	30	a	455
		LSD P=0.05	0.5	1200		1.2		
2019		no plant residue	12	2370	b	18	b	100
	24-36	dead plants	12	560	b	4.2	b	24
		green plants	11	8690	a	70	a	367
		LSD P=0.05	0.2	2400		20		

			% min	% avg
all	all	dead plants	0	31
all	all	green plants	86.1	361

Downloaded from https://www.cambridge.org/core. University of New England, on 24 Sep 2020 at 13:03:28, subject to the Cambridge Core terms of use, available at https://www.cambridge.org/core/terms. https://doi.org/10.1017/wet.2020.106

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. Paramter 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 was also normalized to compare no residue values to those with dead plants or green plant material.

Year	surface condition	parameter a dicamba ng	parameter c hours	r^2	a compared to no residue %
2017	no residue	257	7.7	0.85	100
2017	dead plants	122	7	0.93	48
2017	green plants	1170	8	0.94	456
2018	no residue	2390	9.3	0.94	100
2018	dead plants	815	10.5	0.98	34
2018	green plants	6390	9.6	0.88	267
2019	no residue	6820	15	0.92	100
2019	dead plants	1850	13.5	0.94	27
2019	green plants	27390	12.9	0.88	402
all	dead plants				36.2
all	green plants				374.8

Downloaded from https://www.cambridge.org/core. University of New England, on 24 Sep 2020 at 13:03:28, subject to the Cambridge Core terms of use, available at https://www.cambridge.org/core/terms. https://doi.org/10.1017/wet.2020.106

Table 4. Correlation coefficients and (probability levels in parantehsis) comparing 3 surface conditions (no residue, dead plants or green plants) to measured dicamba emissions, relative humidty and temperature measured at the soil surface of each plot. Environmental data used was the average over that particular sampling interval.

	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)

Downloaded from https://www.cambridge.org/core. University of New England, on 24 Sep 2020 at 13:03:28, subject to the Cambridge Core terms of use, available at https://www.cambridge.org/core/terms. https://doi.org/10.1017/wet.2020.106

Figure captions:

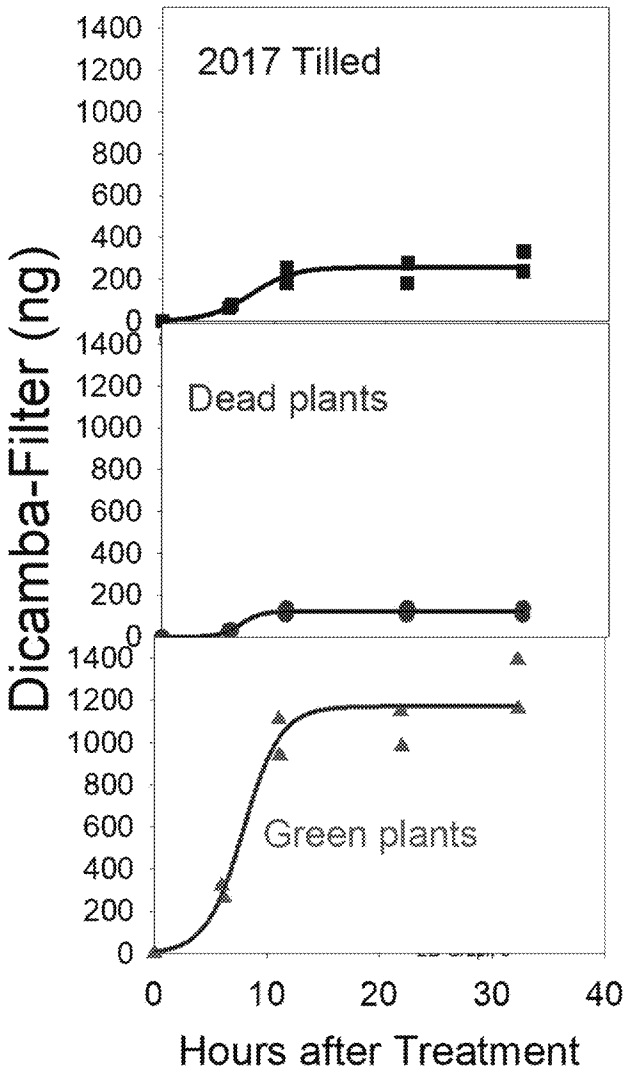

Figure 1. Dicamba emissions in 2017 as affected by surface condition and time after treatment (Hours after Treatment = HAT) presented as cumulative ng. Regression equation set to y = a/(1+exp(-(hours-c)/b)) . Parameter a = maximum dicamba at asymptote, parameter c = time in hours to reach inflection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

Downloaded from https://www.cambridge.org/core. University of New England, on 24 Sep 2020 at 13:03:28, subject to the Cambridge Core terms of use, available at https://www.cambridge.org/core/terms. https://doi.org/10.1017/wet.2020.106

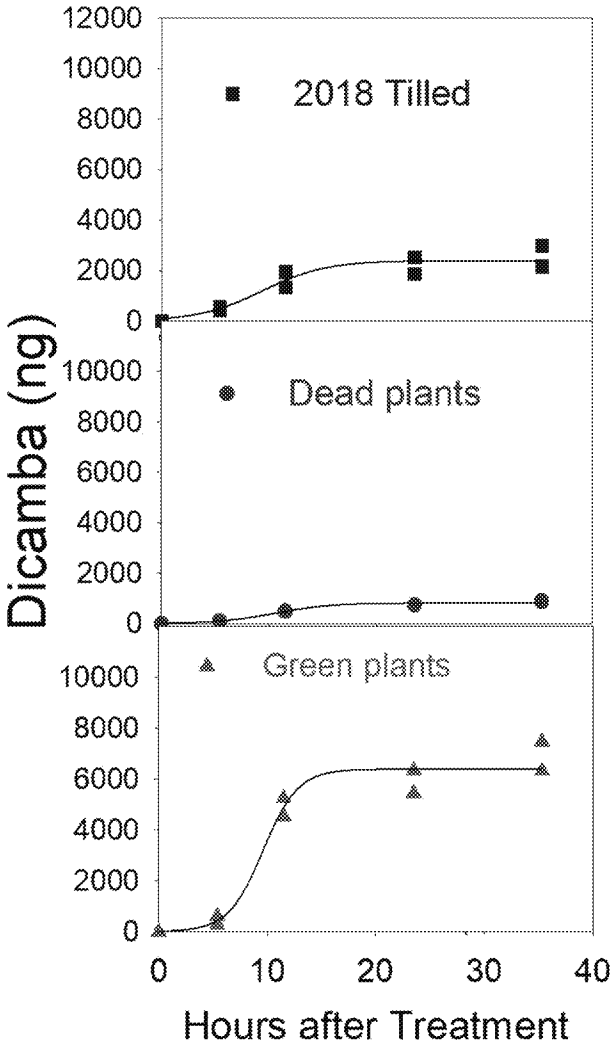

Figure 2. Dicamba emissions in 2018 as affected by surface condition and time after treatment (Hours after Treatment = HAT) presented as cumulative ng. Regression equation set to y =a/(1+exp(-(hours-c)/b)) insert from LES. Parameter a = maximum dicamba at asymptote, parameter c = time in hours to reach inflection point of curve where dicamba concentration is increasing at a slower rate. Regression parameters in Table 3.

Downloaded from https://www.cambridge.org/core. University of New England, on 24 Sep 2020 at 13:03:28, subject to the Cambridge Core terms of use, available at https://www.cambridge.org/core/terms. https://doi.org/10.1017/wet.2020.106

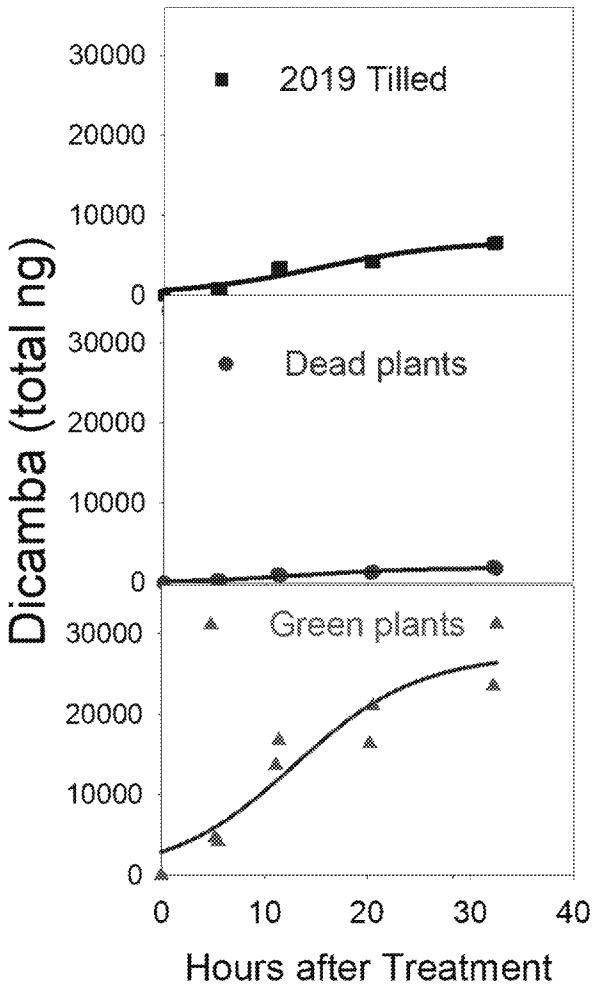

Figure 3. Dicamba emissions in 2019 as affected by surface condition and time after treatment (Hours after Treatment = HAT) presented as cumulative ng. Regression equation set to y = a/(1+exp(-(hours-c)/b)) insert from LES. Parameter a = maximum dicamba at asymptote, parameter c = time in hours to reach inflection point of curve where dicamba concentration is increasing at a slower rate. Regression parameters in Table 3.

Downloaded from https://www.cambridge.org/core. University of New England, on 24 Sep 2020 at 13:03:28, subject to the Cambridge Core terms of use, available at https://www.cambridge.org/core/terms. https://doi.org/10.1017/wet.2020.106

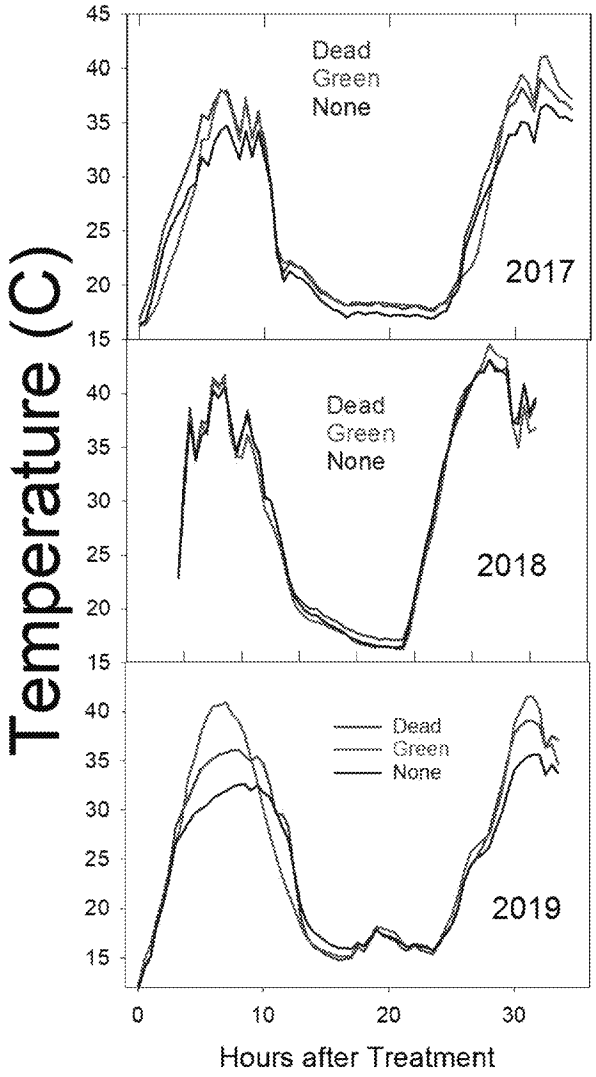

Figure 4. Temperature at soil surface for each surface condition in 2017, 2018, 2019

Downloaded from https://www.cambridge.org/core. University of New England, on 24 Sep 2020 at 13:03:28, subject to the Cambridge Core terms of use, available at https://www.cambridge.org/core/terms. https://doi.org/10.1017/wet.2020.106

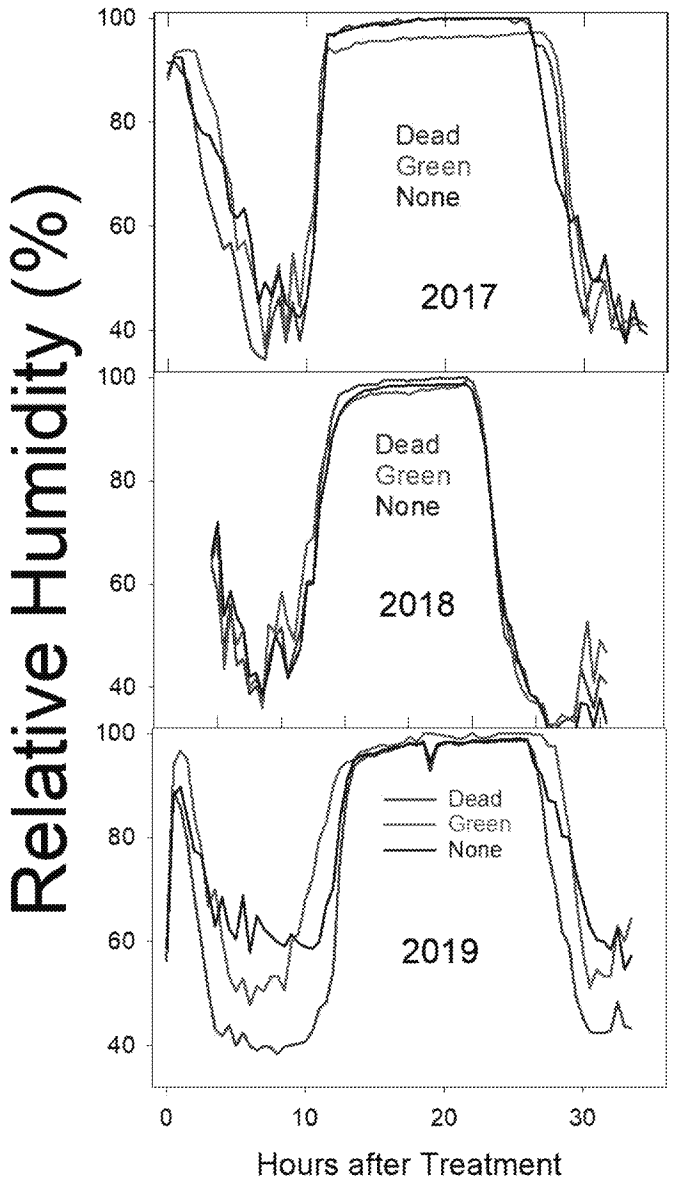

Figure 5. Relative humidity at soil surface for each surface condition in 2017, 2018 and 2019.

Downloaded from https://www.cambridge.org/core. University of New England, on 24 Sep 2020 at 13:03:28, subject to the Cambridge Core terms of use, available at https://www.cambridge.org/core/terms. https://doi.org/10.1017/wet.2020.106