Weed Science

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Evaluation of potassium borate as a volatility-reducing agent for dicamba

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Research Article

Cite this article: Castner MC, Norsworthy JK, Roberts TL (2022) Evaluation of potassium borate as a volatility-reducing agent for dicamba. Weed Sci. **70**: 610–619. doi: 10.1017/wsc.2022.49

Received: 6 May 2022
Revised: 21 July 2022
Accepted: 2 September 2022
First published online: 13 September 2022

Associate Editor:
Prashant Jha, Iowa State University

Keywords:
Additive; off-target movement; volatilization

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Abstract

Dicamba was labeled in dicamba-resistant cotton (*Gossypium hirsutum* L.) and soybean [*Glycine max* (L.) Merr.] in 2017, resulting in a record number of off-target complaints. To address off-target movement via volatilization, experiments were conducted to evaluate the effectiveness of potassium tetraborate tetrahydrate (KBo) as a volatility-reducing agent (VRA) with dicamba. Low-tunnel experiments examined: (1) whether KBo functions as a dicamba VRA, (2) the relationship between KBo concentration and dicamba volatilization, (3) the effectiveness of KBo compared with potassium acetate as a VRA, and (4) the impact of KBo on dicamba volatilization with and without glufosinate. In a large-scale trial (0.4-ha plots), the effectiveness of KBo in reducing dicamba volatilization was quantified relative to a commercial dicamba application labeled for use in 2020. The addition of KBo to dicamba reduced volatility over dicamba alone and a dicamba plus potassium acetate premix. As KBo concentration increased in the dicamba spray solution, volatilization was exponentially reduced. Dicamba volatilization with the addition of KBo at 0.01 M was comparable to dicamba plus potassium acetate at 0.05 M. Potassium tetraborate tetrahydrate was more effective than potassium acetate at reducing volatility of a dicamba plus glufosinate mixture. In large-scale experiments over a 30-h period, the addition of KBo to a diglycolamine plus glyphosate mixture lowered dicamba volatilization 82% to 89% over the herbicide mixture alone. Overall, the addition of KBo to dicamba appears promising as a VRA compared with what is commercially available.

Introduction

Soybean [*Glycine max* (L.) Merr.] has historically been produced in proximity to corn (*Zea mays* L.), where in-crop applications of synthetic auxin herbicides are common in the latter and are an integral component of broadleaf weed control (Cao et al. 2011). Despite extensive use of 2,4-D, dicamba, and other related compounds in cereal crops, vapor drift has not been a major concern to sensitive soybean (Wax et al. 1969) until the registration of dicamba for use as a postemergence option in dicamba-resistant (DR) cotton and soybean in 2017 (Xtend® technology; Bayer Crop Science, St Louis, MO. Before the commercialization of dicamba-containing products for postemergence broadcast use for DR cotton (*Gossypium hirsutum* L.) and soybean, reports of damage to sensitive vegetation were rare (S Nichols, Arkansas State Plant Board, personal communication). Restricting dicamba usage to winter or early spring limits damage to sensitive species, specifically soybean, due to an absence of crop emergence and environmental conditions at application that favor lower volatility of the herbicide.

Belonging to the benzoic and phenoxy herbicide families, dicamba and 2,4-D, respectively, are now extensively used in some geographies for the management of herbicide-resistant weeds, particularly for management of Palmer amaranth [*Amaranthus palmeri* (S.) Watson] and waterhemp [*Amaranthus tuberculatus* (Moq.) Sauer] where multiple resistance to other herbicides is common (Heap 2021). An advantage of Enlist E3® (2,4-D resistant) cropping systems is utilization of glufosinate as a tank-mix partner with 2,4-D for difficult to control weed species (Anonymous 2021a). Currently, glufosinate is not labeled as a mixing partner with dicamba due to increased volatility of the latter herbicide (Anonymous 2021bc). In addition to providing growers with another herbicide site of action, the launch of DR technology also introduced off-target movement concerns from postemergence applications of low-volatile dicamba formulations such as XtendiMax® with VaporGrip® Technology (Bayer Crop Science), Engenia™ (BASF, Research Triangle Park, NC 27709), Tavium® (Syngenta, Greensboro, NC), and FeXapan® (DuPont Crop Protection, Wilmington, DE) to soybean and other sensitive vegetation. Although volatility is not the only concern regarding off-target movement of dicamba, it is believed to be a significant contributor to landscape damage to plants observed in some areas of the Midsouth (Behrens and Lueschen 1979; Mueller et al. 2013).

To reduce the potential for dicamba volatility, companies such as BASF and Monsanto (now Bayer CropScience) reformulated the herbicide. BASF registered the *N,N*-bis-(3-aminopropyl)methylamine salt of dicamba, and Monsanto combined the diglycolamine salt of dicamba with VaporGrip® (potassium acetate), a pH modifier, to lower the volatility of the herbicide by increasing spray solution pH (Hemminghaus et al. 2017; MacInnes 2017). Regarding dicamba volatility, both formulations offer improvements compared with previous formulations (Jones et al. 2019; MacInnes 2017; Mueller and Steckel 2019a; Westberg and Adams 2017). The labeled dicamba formulations utilize a larger salt molecule with greater bond strength to dicamba that discourages dissociation into the acid, which is the volatile form of the herbicide (Westberg and Adams 2017). However, according to (Sharkey et al. 2020), molecular weight is a poor indicator of dicamba volatilization; the number of hydrogen bonding sites is a better predictor. XtendiMax® with VaporGrip® Technology uses a larger salt than older dicamba formulations in addition to potassium acetate to scavenge protons if dissociation of the acid occurs in solution (Abraham 2018). Despite these attempts to reduce volatilization, complaints of off-target dicamba movement in 2017 until the present have plagued the launch of the Xtend® technology. With the most recent reregistration of XtendiMax® with VaporGrip® Technology and Engenia™ in 2020, both products require the use of a volatility-reducing agent (VRA) such as Sentris® (potassium carbonate) (Bayer Crop Science), VaporGrip® Xtra Agent, or other proprietary mixtures with potassium acetate as the primary active ingredient (Anonymous 2021b, 2021c).

Potassium tetraborate tetrahydrate (KBo) may serve as an alternative VRA for dicamba as well as providing the boron nutritional needs for DR cotton and soybean (Howard et al. 2000). Potassium borate is a weak acid buffer that raises the pH of the spray solution by scavenging protons, favoring the nonvolatile, deprotonated form of dicamba. Chemically, the higher pKa of potassium borate (9.15) in comparison to potassium acetate (4.76) allows greater buffering capabilities and therefore less production of dicamba acid. In solution, potassium borate converts to boric acid, a plant-available form of boron that can be used in foliar applications to alleviate boron deficiencies (Ali et al. 2011).

Because of the effectiveness of dicamba on difficult to control weeds, it is imperative that applications remain on target to protect the integrity and longevity of the technology. The objective for this series of experiments with KBo, was to determine whether the compound is a consistent and reliable VRA that would allow producers to continue using the DR technology in cotton and soybean while lowering the risk of damaging nearby sensitive vegetation by means of volatilization. Specifically, experiments examined: (1) whether KBo functions as a dicamba VRA, (2) the relationship between KBo concentration and dicamba volatilization, (3) the effectiveness of KBo compared with potassium acetate as a VRA, (4) the impact of KBo on dicamba volatilization with and without the addition of glufosinate, and (5) the effectiveness of KBo in reducing dicamba volatilization relative to a commercial dicamba application.

Materials and Methods

Common Methodology for Low Tunnel Experiments and Polyurethane Foam Tube/Filter Analysis

Experiments were conducted at the Milo J. Shult Agricultural Research and Education Center in Fayetteville, AR, on a Leaf silt loam (fine, mixed, active, thermic, Typic, Albaquults) with 34% sand, 53% silt, 13% clay, and 1.5% organic matter with a pH of 6.2 (Web Soil Survey, https://websoilsurvey.sc.egov.usda.gov/App/HomePage.htm). Each experiment was repeated, creating 2 site-years for the 2020 growing season. An indeterminate, medium/tall, 4.7 maturity group, glufosinate-resistant cultivar was planted ('CZ 4938LL', BASF Corporation) at 360,000 seeds ha^{-1} in 0.91-m-wide rows to serve as a dicamba-sensitive bioindicator for qualitative assessments. Before application of herbicide treatments, two flats (38 by 48 by 5.5 cm) were filled with soil (to approximately a 2.5-cm depth in the flat) that was collected from the top 5 cm of the soil profile at the trial location and sieved through a 10-mm screen (Oseland et al. 2020). The sieve removed large debris, creating a uniform and representative soil from the treated area. All flats of soil were moistened to saturation and then treated using a CO_2-pressurized sprayer calibrated to deliver an output of 140 L ha^{-1} using TTI110015 nozzles (TeeJet® Technologies, Springfield, IL). Applications occurred at least 1 km from the field to mitigate the potential for dicamba contamination through physical drift. To elicit greater dicamba symptomology on the bioindicator soybean, all treatments were mixed at a 1X rate and applied to each flat of soil four times to achieve a 4X rate, with a 1X being dicamba at 560 g ae ha^{-1} and glyphosate at 1,260 g ae ha^{-1}. The potassium salt of glyphosate (Roundup PowerMax® II, Bayer Crop Science) was added to the dicamba, because it is a labeled mixture, and the addition of glyphosate is known to increase dicamba volatilization potential (Mueller et al. 2019a, 2019b). In addition to using a greater dicamba rate to elicit auxin symptomology, all bioindicator soybean plants were at the highly sensitive V3 to V4 stage at application (Jones et al. 2019). Unless stated otherwise, each low tunnel experiment was structured as a single-factor randomized complete block design with three replications.

Low tunnels (1.5-m wide by 6-m long by 1.2-m tall) were constructed by bending and connecting four 1.25-cm-diameter polyvinyl chloride (PVC) cross sections of tubing with five 1.25-cm-diameter sections running lengthwise or parallel with soybean rows (Figure 1A and B). The tunnels were placed over two rows of soybean and completely covered the 6-m-long sides with 1.5-mil plastic (Painter's Plastic, Lowe's, Fayetteville, AR), leaving the tunnel open on the two 1.5-m sides. The plastic was secured to the lengthwise portion of the tunnel frame by placing soil onto the excess plastic located on the outside of the tunnel as well as applying tension and clamping (Irwin, Lowe's) the remaining plastic to the top of the open 1.5-m sides. The interior PVC tubing was secured to the soil with metal tent stakes to prevent shifting during windy conditions. A 9-m buffer separated replications lengthwise, and two soybean rows or approximately a 2-m barrier was used to divide tunnels widthwise.

For each low tunnel, a single treated flat was placed on either side of a 185 L min^{-1} air sampler (Hi-Q Environmental Products, San Diego, CA) located in the center of each low tunnel 3.1) m from edge of low tunnel) between two rows of soybean. Each low tunnel contained a total of two 4X-treated soil flats. The intake for the air sampler was located approximately 40 cm above the treated flats with a total of two treated flats per tunnel. Once all treated soil flats were placed in the appropriate tunnels, the air samplers were powered by generators outside the treated area (American Honda Motor, Torrance, CA). For each air sampler, dicamba was trapped on an embedded glass fiber filter paper measuring 102 mm in diameter followed in series by a 6 cm by 7.6 cm cylindric polyurethane foam (PUF) (Restek, Bellefonte, PA, cat. no.

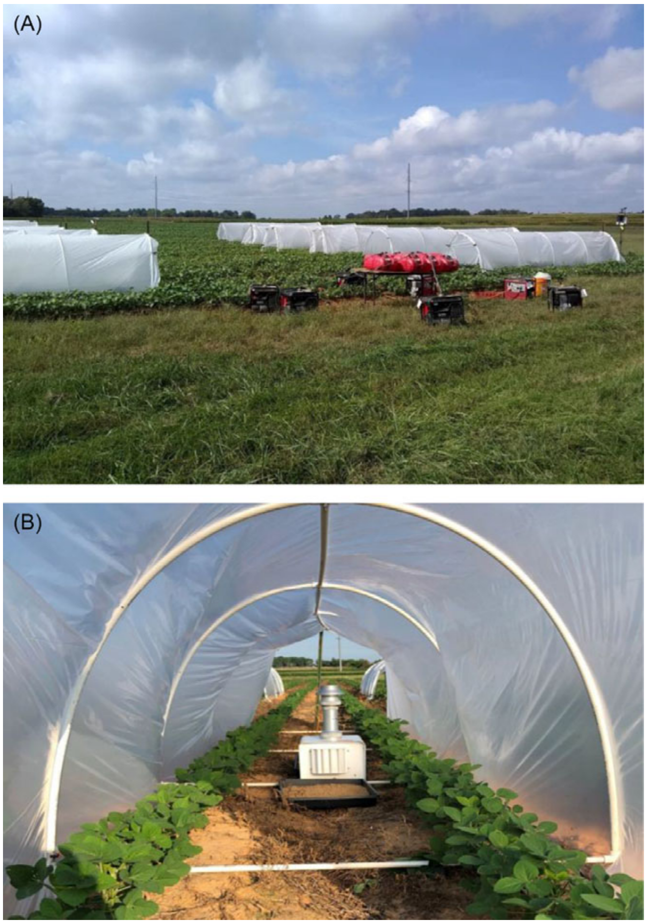

Figure 1. (A) Images of low tunnels and implementation of trial in the field, and (B) placement of air samplers and treated soil flats between two rows of bioindicator soybean located underneath a 1.5 m by 6 m by 1.2 m plastic-covered tunnel in Fayetteville, AR, in 2020.

22954). All low tunnels, flats, and air samplers (184 L min^{-1}) were removed from the field 48 h after trial initiation. A sample of the spray solution was collected before and after each application, and the pH of the solution measured.

For qualitative assessments, each row of bioindicator soybean under each low tunnel was divided into four quadrants (1.5 m of row) to evaluate visible injury and distance to 5% dicamba injury at 14, 21, and 28 d after treatment (DAT). Ratings collected from the quadrants allowed for assessment of maximum injury (most injured quadrant) as well as an average rating from all quadrants. Visible injury was rated on a scale of 0% to 100%, with 0% and 100% representing no injury observed and crop death, respectively. Distance to 5% dicamba injury was measured from the center of each low tunnel in the direction where greater dicamba symptomology was present, which typically was the downwind direction from the treated soil flats. Distance to 5% dicamba injury was chosen to quantify lateral movement of the herbicide because injury below 5% would be negligible or difficult to visually assess.

Polyurethane Foam Tube/Filter Sample Analysis

Following termination of the 48-h sampling period, the PUF and filter paper were collected, labeled appropriately, and immediately placed into coolers containing dry ice at −20 C and shipped to the Mississippi State Chemical Laboratory for dicamba residue analysis (Mississippi State University, Starkville, MS) (Riter et al. 2020; Soltani et al. 2020). Dicamba acid (221.04 g mol^{-1}) was extracted from each PUF and filter paper with 30 ml of methanol, which contained $^{13}C_6$-labeled dicamba (CAS no.: 1173023-06-7; Sigma Aldrich) as an internal standard. All PUF samples were homogenized with a SPEX SamplePrep Geno/Grinder® (OPS-Diagnostics, Lebanon, NJ). The supernatant was concentrated with a TurboVap to 1 ml, then filtered, evaporated, and solvent exchanged to an appropriate volume of 25% acetonitrile in water solution, so the samples were at a 50-fold concentration. For quality control, each sample included a blank matrix sample with no dicamba present and a spiked matrix sample that included a known concentration of dicamba. The dicamba-spiked matrix sample determined extraction efficiency for each sample, with a mean accuracy range of 70% to 120%. The limit of dicamba detection for PUFs and filters was 10 ng per PUF or filter paper.

Liquid Chromatography with Tandem Mass Spectrometry Conditions

Dicamba concentrated in PUFs and filter paper was quantitated using an Agilent 1290 liquid chromatograph combined with an Agilent 6460 C triple quadrupole mass spectrometer (Agilent Technologies, Santa Clara, CA) (Monsanto Company Method; Soltani et al. 2020). Chromatographic separation was performed using an Agilent Zorbax Eclipse Plus 100-mm column with a run time of 8 min and a 3-min post-run. The mobile phases utilized 0.1% formic acid in water for the aqueous phase (Solvent A) and 0.1% formic acid in acetonitrile for the organic phase (Solvent B). The flow rate was 0.3 ml min^{-1} with the subsequent solvent gradient system: 0 to 0.5 min of 25% B, 0.5 to 1 min of 50% B, and 1 to 4 min of 60% B. Ionization of dicamba was performed using electrospray ionization in negative mode with an auxiliary gas (N_2), source temperature of 200 C, and a gas flow rate of 10 L min^{-1}.

KBo Initial Experiment

An initial low tunnel experiment was conducted to evaluate KBo as a potential VRA because of its strong buffering nature (pKa = 9.15) and ability to scavenge hydrogen ions in acidic spray solutions. The experiment was designed to determine whether KBo was as effective as XtendiMax® with VaporGrip® Technology in reducing volatilization of dicamba when mixed with glyphosate. The concentration of KBo needed to effectively reduce dicamba volatility was unknown; therefore KBo was evaluated at 30 g L^{-1} of spray solution (140 L ha^{-1} spray volume), the maximum solubility of the additive in water at room temperature. Specific treatments evaluated were (1) DGA dicamba alone (Clarity®), (BASF Corporation), (2) DGA dicamba plus potassium acetate (XtendiMax® with VaporGrip® Technology), (3) DGA dicamba (Clarity®) plus KBo, and (4) a nontreated control. The potassium salt of glyphosate (Roundup PowerMax® II) was added to each dicamba-containing treatment at a rate of 1,260 g ae ha^{-1}. Two independent runs of the experiment were initiated on September 5, 2019, and repeated on September 12, 2019, at another site at the research center.

KBo Rate Titration

Following the success of the initial KBo studies, experiments were conducted to determine the effect of KBo concentration on dicamba volatility. KBo concentrations of 0, 0.00625, 0.0125, 0.025, 0.05, and 0.1 M were added to a 2-L spray mixture containing the diglycolamine salt of dicamba (Clarity®) at 560 g ae ha^{-1}

https://doi.org/10.1017/wsc.2022.49 Published online by Cambridge University Press

plus the potassium salt of glyphosate (Roundup PowerMax® II) at 1,260 g ae ha^{-1} and applied to the flats of soil in a spray volume of 140 L ha^{-1}. Two independent runs of the experiment were initiated on June 6, 2020, and July 21, 2020.

Molar Comparison of KBo and Potassium Acetate

An experiment was conducted to evaluate the effectiveness of KBo and potassium acetate as VRAs on a molar basis. The experiment was a randomized complete block with three replications in which treatments were a mixture DGA salt of dicamba plus K-salt of glyphosate alone, the mixture with KBo, and the mixture with potassium acetate. KBo and potassium acetate were evaluated at 0.02 and 0.05 M concentrations. Two independent runs of the experiment were initiated on July 13, 2020, and August 5, 2020.

Addition of KBo and Potassium Acetate to Dicamba plus Glufosinate

Despite glufosinate and dicamba not being labeled for mixture due to increased volatility concerns, experiments were conducted to determine whether the addition of potassium acetate, KBo, or the combination of VRAs could reduce volatility of a dicamba plus glufosinate mixture over that of no additional VRA. Treatments evaluated included a mixture of glufosinate at 656 g ai ha^{-1} plus the DGA salt of dicamba applied alone, with potassium acetate at 0.5 M, with KBo at 0.5 M, and with the combination of the two additives at 0.5 M. Two independent runs of the experiment were initiated on July 3, 2020, and August 13, 2020.

Large-Scale Experiment

Two large-scale dicamba volatility studies were conducted in 2020, one in Fayetteville, AR (July 7, 2020), at the Milo J. Shult Agricultural Research and Extension Center, and another near Newport, AR (July 7, 2020), at the Newport Extension Station. Each experiment consisted of two 61 m by 61 m treated areas (0.4 ha). The experiment in Fayetteville was conducted on a Leaf silt loam (fine, mixed, active, thermic, Typic, Albaquults) with 34% sand, 53% silt, 13% clay, and 1.5% organic matter with a pH of 6.2. The experiment near Newport was conducted on an Amagon silt loam (fine-silty, mixed, active, thermic, Typic, Endoaqualfs) with 39% sand, 58% silt, 13% clay, and 2.6% organic matter with a pH of 5.8. The experiment in Fayetteville was conducted on a non-crop area with 99% groundcover (weedy vegetation) at application. The test site near Newport was planted to Xtend® soybean on a 76-cm row spacing, with approximately 25% groundcover at application.

At both test sites, the two treatments evaluated were DGA dicamba (XtendiMax® with VaporGrip® Technology) at 560 g ae ha^{-1} plus the K-salt of glyphosate (Roundup PowerMax® II) with and without KBo at 0.1 M. Herbicide applications at both sites were made using a Bowman MudMaster (Bowman Agricultural Spray Equipment, Newport, AR) equipped with TTI11002 nozzles (TeeJet® Technologies) calibrated to deliver 140 L ha^{-1} at 6.5 kph. The pH of each spray solution was collected at the time of application. Approximately 400 m separated the two treatments at both sites.

The first treatment of the experiment (DGA dicamba with VaporGrip® plus the K-salt of glyphosate) in Fayetteville was initiated at 7:52 AM and was concluded by 7:54 AM. The second treatment with the addition of KBo at 0.1 M began at 8:18 AM and was completed at 8:20 AM. At the Newport location, the first treatment began at 10:00 AM and ended at 10:04 AM, with the second treatment applied from 10:39 AM to 10:43 AM. Three air samplers (same equipment and parameters as previously described for low-tunnel experiments) were placed approximately 2 m apart in the middle of each 0.4-ha treated area 30 min after application, and the dicamba concentration in the air was measured for a 30-h duration. Sampling intervals consisted of 0.5 to 6, 6 to 12, 12 to 24, and 24 to 30 h after treatment (HAT). Additionally, background air samples were collected at each sampling interval approximately 1 km from where the experiment was conducted. At the end of each sampling interval, PUF and filter paper were removed from each sampler and placed on dry ice (Newport) or immediately frozen at −20 C until completion of the experiment. Upon completion of sampling, samples were sent to the Mississippi State Chemistry Laboratory for quantification of dicamba.

Statistical Analyses

All injury data assumed a beta distribution and were subjected to ANOVA using PROC GLIMMIX in SAS v. 9.4 (SAS Institute, Cary, NC) (Gbur et al. 2012). Distance to 5% injury and total dicamba assumed a normal distribution and were subjected to ANOVA using JMP Pro 15 (SAS Institute). Run and herbicide treatment were included in the model as fixed effects. If run was not significant, it was considered as a random effect along with replication, and the two runs were combined, with the only fixed effect being the herbicide treatment. The only low tunnel experiment to have a significant run effect was the addition and combination of KBo and potassium acetate to dicamba plus glufosinate, with herbicide treatment as a fixed effect and replication as a random effect and each run analyzed separately. Means for average and maximum injury, distance to 5% injury, and total dicamba detected (ng) were separated using Fisher's protected LSD ($\alpha = 0.05$). For the large-scale volatility experiment, the amount of dicamba detected (ng) is reported (±SE) as an average across the three air samplers for each location.

Results and Discussion

KBo Initial Experiment

The two initial experiments solely focused on determining whether KBo demonstrated any volatility-reducing properties relative to DGA dicamba and XtendiMax® with VaporGrip® Technology (DGA dicamba plus an unknown concentration of potassium acetate). At 21 DAT, DGA dicamba plus potassium acetate was not different from DGA dicamba alone for average and maximum dicamba injury and lateral movement of the herbicide to sensitive soybean (Table 1), which is consistent with findings in other low tunnel experiments with these herbicides (Scott et al. 2018). However, Mueller and Steckel (2019a) found that the addition of VaporGrip® to DGA dicamba reduced dicamba volatility in humidome trials (Carbonari et al. 2022). Compared with DGA dicamba alone (2,030 ng), the total amount of dicamba detected from the PUFs and filter paper was less when potassium acetate was present in solution (1,272 ng).

When KBo at a 0.1 M concentration was added to DGA dicamba, significant reductions to visible injury, distance to 5% injury, and total dicamba detected in air samples were observed (Table 1). In comparison to DGA dicamba alone, the addition of KBo to DGA dicamba reduced the amount of dicamba detected by 74%, whereas the DGA dicamba with potassium acetate had only a 37% reduction. Additionally, pH of the spray solution containing KBo was 8.65, whereas potassium acetate buffered solution was 4.8, and without a buffer the pH was 4.5 (Table 1). Mueller and

https://doi.org/10.1017/wsc.2022.49 Published online by Cambridge University Press

Table 1. Maximum and average injury to sensitive soybean, distance to 5% injury, and total dicamba detected at 21 d after dicamba treatment with an initial water source pH of 7.41 in 2019 at Fayetteville, AR.[a,b]

Additive[c]	Conc.	pH	Injury at 21 DAT Max.	Injury at 21 DAT Avg.	Distance to 5% injury	Total dicamba
	molar		——%——		m	ng
None	—	4.47	28 a	14 a	4.8 a	2,030 a
Potassium acetate	—	4.75	23 a	9 a	4.5 a	1,272 b
KBo	0.1	8.65	10 b	3 b	2.2 b	522 c

[a]Abbreviations: Conc., concentration; DAT, days after treatment; KBo, potassium tetraborate tetrahydrate; Max., maximum; Avg., average.
[b]Means within a column followed by the same letter are not different according to Fisher's protected LSD ($\alpha = 0.05$).
[c]Glyphosate at 1,260 g ae ha^{-1} added to all treatments.

Table 2. Maximum and average injury to sensitive soybean and distance to 5% injury 21 d after dicamba treatment with an initial water source pH of 7.72 in 2020 at Fayetteville, AR.[a,b]

Additive[c]	Conc.	pH	Injury at 21 DAT Max.	Injury at 21 DAT Avg.	Distance to 5% injury
	molar		——%——		m
None	—	4.52	37 a	19 a	3.5 a
KBo	0.00625	5.05	33 a	16 a	3.0 a
KBo	0.0125	5.40	17 b	6 b	1.7 b
KBo	0.025	6.08	8 c	2 b	0.7 c
KBo	0.05	7.84	4 c	1 b	0.2 c
KBo	0.1	8.66	1 c	0 b	0.0 c

[a]Abbreviations: Conc., concentration; DAT, days after treatment; KBo, potassium tetraborate tetrahydrate; Max, maximum; Avg., average.
[b]Means within a column followed by the same letter are not different according to Fisher's protected LSD ($\alpha = 0.05$).
[c]Glyphosate at 1,260 g ae ha^{-1} added to all treatments.

Steckel (2019b) and Striegel et al. (2020) witnessed similar results both with and without the addition of glyphosate to DGA dicamba and DGA dicamba plus VaporGrip® and noted that mixtures with glyphosate decrease spray solution pH. Regardless of weather conditions, a spray solution pH <5.0 is likely to increase dicamba volatility and be in violation of the herbicide label (Anonymous 2021b. An increase in approximately 4 pH units was observed with KBo and equates to a 10,000-fold decrease in hydrogen ions, creating a less acidic spray solution.

KBo Rate Titration

Based on the qualitative parameters evaluated (maximum injury, average injury, and distance to 5% visible injury) at 21 DAT, the addition of KBo to DGA dicamba plus glyphosate reduced maximum and average injury to sensitive soybean by decreasing volatility of the herbicide (Table 2). Maximum injury to soybean typically occurred in the middle quadrant closest to the treated soil flats from which dicamba volatilizes. Regarding maximum visible injury to soybean, the lowest concentration of KBo (0.00625 M) was not enough to reduce dicamba volatility compared with DGA dicamba plus glyphosate alone (33% and 37%, respectively), which served as a standard for comparison. In general, as KBo concentration increased, visible injury to soybean decreased, with maximum injury being only 1% when the DGA dicamba plus glyphosate spray solution contained KBo at 0.1 M. Displaying a similar trend to maximum and average visible injury to soybean, the distance traveled to 5% dicamba symptomology further reflected that an increasing concentration of KBo (0.0125 to 0.1 M) decreased the lateral movement of the herbicide. Similar to what was observed with visible injury, the highest concentration of KBo negated movement of dicamba concentrations sufficient to cause at least 5% injury in any quadrant.

The total dicamba detected from the PUFs and filter paper closely reflected the extent of injury observed in the plots (Figure 2). As KBo concentration in the spray solution increased, injury to soybean and the amount of detectable dicamba in the air likewise decreased. Furthermore, variability in dicamba detected within a treatment decreased as KBo concentration increased, an indication of less environmental influence on the volatilization of the herbicide in the presence of the VRA. In other research, it has been noted that the detection of dicamba can be quite variable because of differences in environmental conditions during experiments (Behrens and Lueschen 1979; Bish et al. 2021; Mueller et al. 2013, 2019a). Despite the absence of an established threshold for in-air concentrations of dicamba as it pertains to a specific degree of soybean injury, findings suggest KBo at 0.025 M or higher concentrations show dicamba volatilization is significantly reduced, likewise resulting in less risk for off-target soybean injury. Additionally, KBo concentrations of 0.025 to 0.1 M are sufficient to satisfy the foliar boron needs of cotton and soybean when deficiencies exist (Ali et al., 2011; Howard et al. 1998; Ross et al. 2006).

The pH of the spray solution became more alkaline as KBo concentration increased (Table 2). Chemically, dicamba is classified as a weak acid (pKa = 1.87) (Shaner 2014), and when mixed with glyphosate, the latter further acidifies the spray solution in favor of the conversion of dicamba anion to dicamba acid, the active, volatile form of the herbicide (Anonymous 2021b. Despite the acidic nature of the dicamba plus glyphosate mixture, the buffering properties of KBo at 0.025 to 0.1 M lead to boric acid formation (pKa = 9.15) sufficient to reduce volatility as a result of the increased pH when mixed with these herbicides, reducing

https://doi.org/10.1017/wsc.2022.49 Published online by Cambridge University Press

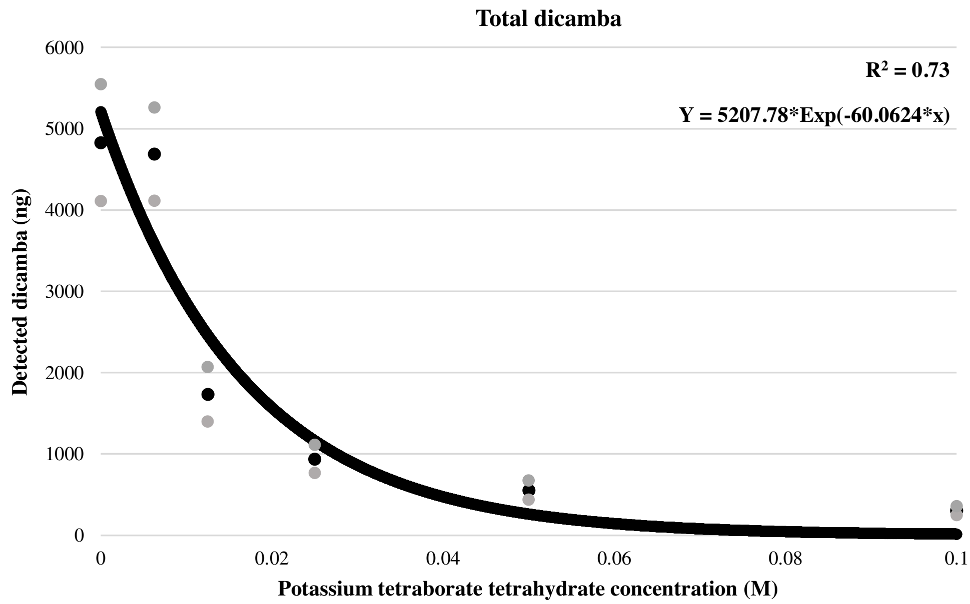

Figure 2. Exponential 2p curve ((*a**Exp(*rate), *a* = scale, *b* = growth rate) fit to potassium tetraborate tetrahydrate (KBo) concentration and total dicamba recovered from polyurethane foam and filter paper from the two KBo rate titration experiments conducted in 2020; R^2 value displays the percentage of variability explained by the fit of the line. Black dots in the middle represent mean recovered dicamba of the respective KBo concentration, and gray dots above and below the mean represent the SE.

protonation of the dicamba anion, which may have a considerable influence on volatility (Behrens and Lueschen 1979; Meuller and Steckel 2019a). However, the functionality of VRAs is still not well understood. The VRA potassium acetate, the active ingredient in VaporGrip® technology, does not considerably raise the pH of the spray solution at the concentration present in XtendiMax® with VaporGrip® Technology (Mueller and Steckel 2019b). However, potassium acetate does likely scavenge ions in solution that are responsible for the conversion to dicamba acid (Abraham 2018). Conversely, KBo has the capacity to buffer pH as well as potentially scavenge ions in the spray solution. Ion scavenging and buffering of a spray solution are both mechanisms that could be used to reduce formation of dicamba acid and ultimately volatility.

Molar Comparison of KBo and Potassium Acetate

The primary objective of the molar comparison of KBo and potassium acetate was to evaluate the effectiveness of the two VRAs at equivalent concentrations. One mole of potassium acetate weighs 98.14 g, and 1 mole of KBo weighs 305.5 g. On a mass basis, KBo is approximately three times heavier than potassium acetate but contains an additional potassium per mole. Overall, higher concentrations of each VRA likewise result in reduced volatilization of dicamba (Table 3). However, at the 0.01 M concentration, KBo prevented more dicamba volatility in comparison to potassium acetate based on average and maximum injury to soybean, which was comparable to DGA dicamba with no additive. At the 0.05 M concentration, both VRAs reduced the amount of injury and lateral movement over DGA dicamba with no additive. KBo at 0.05 M outperformed potassium acetate for average visible injury to soybean at the same concentration but was comparable with respect to maximum visible injury.

With the concentrations of VRAs used in these experiments, spray solution pH appears to be a major influencer of dicamba volatility on the basis that additives with a similar pH have comparable levels of visible damage to soybean. Concerning total dicamba detected, KBo has a numerical advantage over potassium acetate at each concentration but is not statistically different. The dicamba amount detected in air was almost 1,000 ng less with the addition of KBo at 0.01 M than DGA dicamba with no additive and approximately 300 ng less than potassium acetate at 0.01 M. However, the lack of significance may be due to variation in lower concentrations of the additives, similar to what was documented in the rate titration experiment (Figure 2). At a 0.05 M concentration, both additives were able to reduce detectable dicamba volatility compared with the DGA dicamba plus glyphosate standard. Over large acreage, the advantage of KBo with respect to detectable dicamba in air may become more apparent compared with dicamba containing potassium acetate as a VRA.

Addition and Combination of Potassium Borate and Potassium Acetate to Glufosinate

The pH of the DGA dicamba plus glufosinate standard treatment for comparison was more neutral than what has been observed with mixtures of DGA dicamba plus glyphosate, with the first run having a solution pH of 6.75 and the second run a pH of 7.07, with an initial water source pH of 7.8 and 7.6, respectively (Table 4). However, in the case of substituting glufosinate for glyphosate as a tank-mix partner, the increase in pH did not appear to lessen visible injury to soybean or the amount of detectable dicamba in the air. The current theory is that the ammonium salt formulated with glufosinate to balance the charge of the herbicide is responsible for increased dicamba volatility via ammonia production. The increased volatilization when mixed with glufosinate likely contributes to the inability to register the mixture for use in DR crops. In each run, the addition of each VRA increased pH, with KBo appearing to increase pH over the standard as well as potassium acetate alone. Additionally, the combination of the two VRAs did not alter the pH far from KBo alone.

In the first run of the experiment, DGA dicamba plus glufosinate had maximum and average injury of 53% and 47%,

Table 3. Maximum and average injury to sensitive soybean, distance to 5% injury, and total dicamba detected at 21 d after dicamba treatment with an initial water source pH of 7.51 in 2020 at Fayetteville, AR.[a,b]

			Injury at 21 DAT			
Additive[c]	Conc.	pH	Max.	Avg.	Dist. to 5% injury	Total dicamba
	molar		——%——		m	ng
None	—	4.48	52 a	23 a	6.0 a	1,698 a
KBo	0.01	5.71	38 bc	15 b	4.8 bc	736 ab
Potassium acetate	0.01	4.77	47 ab	17 ab	5.6 ab	1,040 ab
KBo	0.05	8.30	21 d	6 c	3.6 d	453 b
Potassium acetate	0.05	5.11	30 cd	13 b	4.2 cd	647 b

[a]Abbreviations: Conc., concentration; DAT, days after treatment; Dist., distance; KBo, potassium tetraborate tetrahydrate; Max, maximum; Avg., average.
[b]Means within a column followed by the same letter are not different according to Fisher's protected LSD (α = 0.05).
[c]Glyphosate at 1,260 g ae ha^{-1} added to all treatments.

Table 4. Maximum and average injury to sensitive soybean, distance to 5% injury, and total dicamba detected at 21 d after dicamba plus glufosinate treatment with an initial water source pH of 7.8 and 7.6 for the first and second site-year, respectively, in 2020 at Fayetteville, AR.[a,b]

			Injury at 21 DAT			
Additive[c]	Conc.	pH	Max.	Avg.	Dist. to 5% injury[a]	Total dicamba[a]
	molar		——%——		m	ng
None[d]	—	6.75	53 a	47 a	5.4 a	15,442 a
Potassium acetate	0.05	7.17	35 b	15 b	3.7 a	1,898 b
KBo	0.05	9.16	10 c	3 c	1.4 b	640 c
Potassium acetate plus KBo	0.05	9.12	3 c	1 c	0.7 b	294 c
None[e]	–	7.07	45 a	39 a	6.3 a	10,845 a
Potassium acetate	0.05	7.30	27 b	12 b	3.6 b	5,927 b
KBo	0.05	9.08	7 c	3 c	0.7 c	759 c
Potassium acetate plus KBo	0.05	9.04	5 c	2 c	1.12 c	2,378 c

[a]Abbreviations: Conc., concentration; DAT, days after treatment; Dist., distance; KBo, potassium tetraborate tetrahydrate; Max, maximum; Avg., average.
[b]Means within a column followed by the same letter are not different according to Fisher's protected LSD (α = 0.05). Site-years are separated due to statistical differences.
[c]Glufosinate at 656 g ai ha− 1 added to all treatments.
[d]First site-year.
[e]Second site-year.

respectively (Table 4). Typically, the average soybean injury is lower due to several of the eight quadrants under each low tunnel displaying minimal injury. Although the objective was not to compare DGA dicamba plus glyphosate to DGA dicamba plus glufosinate, the damage caused by the mixture with glufosinate was more uniform across the treated area, indicating there was more lateral movement of the herbicide. More consistent soybean injury throughout the plots is likely a result of more detectable dicamba in the air than the typical range observed with DGA dicamba plus glyphosate (approximately 2,000 to 6,000 ng compared with 15,442 and 10,845 ng detected in the first and second runs with glufosinate, respectively). The addition of glufosinate to dicamba is known to increase dicamba volatilization (Oakley et al. 2020). More uniform damage could also be seen in the second run, though not to the extent of the initial run despite similar weather conditions for the duration of each experiment. Despite the degree of injury being less in the second run of the experiment, KBo outperformed potassium acetate at the 0.05 M concentration for each run. In the first run, KBo at 0.05 M, had maximum and average injury of 10% and 3%, respectively, 25 and 12 percentage point decreases in visible injury. The second run exhibited the same statistical separation but had 20 and 9 percentage point decreases in maximum and average visible injury, respectively, from potassium acetate to KBo. Regarding DGA dicamba plus glufosinate, combining the two VRAs did not offer an advantage over KBo alone for all the qualitative and quantitative parameters evaluated.

Large-Scale Experiment

Fayetteville

DGA dicamba with no KBo had a pH of 4.66 and a cumulative dicamba detection over a 30-h period of 5,812 ng (Table 5). Most dicamba volatilization occurred within the first 12 h after initiation (4,749 ng), with 1,063 ng of dicamba lost over the subsequent 18-h period. Air sampling was terminated at 30 h because of upcoming rain events, but dicamba detection in air has been measured for 96 HAT (Mueller et al. 2013). Once again, the addition of KBo increased spray solution to an alkaline pH and limited the total dicamba detected in a 30-h duration to 655 ng. The addition of KBo to XtendiMax® with VaporGrip® plus glyphosate reduced dicamba volatility 89% over the 30-h sampling period.

Newport

The pH of each spray solution in Newport was similar to the samples collected in Fayetteville, with the KBo increasing the pH of the spray solution to 8.51, whereas in its absence the spray solution had a pH of 4.42 (Table 5). The initial volatility from 0.5 to 12 HAT was lower than what was documented in Fayetteville on the same date, most likely because the weedy groundcover in Fayetteville covered approximately 100% of the sprayed area, whereas the soybean canopy at Newport was estimated to provide 75% groundcover. Both Mueller and Steckel (2021) and Carbonari et al. (2020) documented lower levels of dicamba volatility from dead plant tissue

https://doi.org/10.1017/wsc.2022.49 Published online by Cambridge University Press

Table 5. Cumulative dicamba emissions from large-scale experiments conducted in Fayetteville and Newport, AR, in 2020.

Location	Additive[a]	pH	Sampling interval	Cumulative dicamba
			h	ng
Fayetteville[b]	None	4.66	0.5–6	2,302
			6–12	2,363
			12–24	5,168
			24–30	5,812
	KBo	8.69	0.5–6	40
			6–12	255
			12–24	300
			24–30	655
Newport[c]	None	4.42	0.5–6	285
			6–12	1,317
			12–24	1,986
			24–30	2,434
	KBo	8.51	0.5–6	66
			6–12	163
			12–24	309
			24–30	427

[a]Abbreviations: KBo, potassium tetraborate tetrahydrate.
[b]Fayetteville groundcover: 99%.
[c]Newport groundcover: 25%.

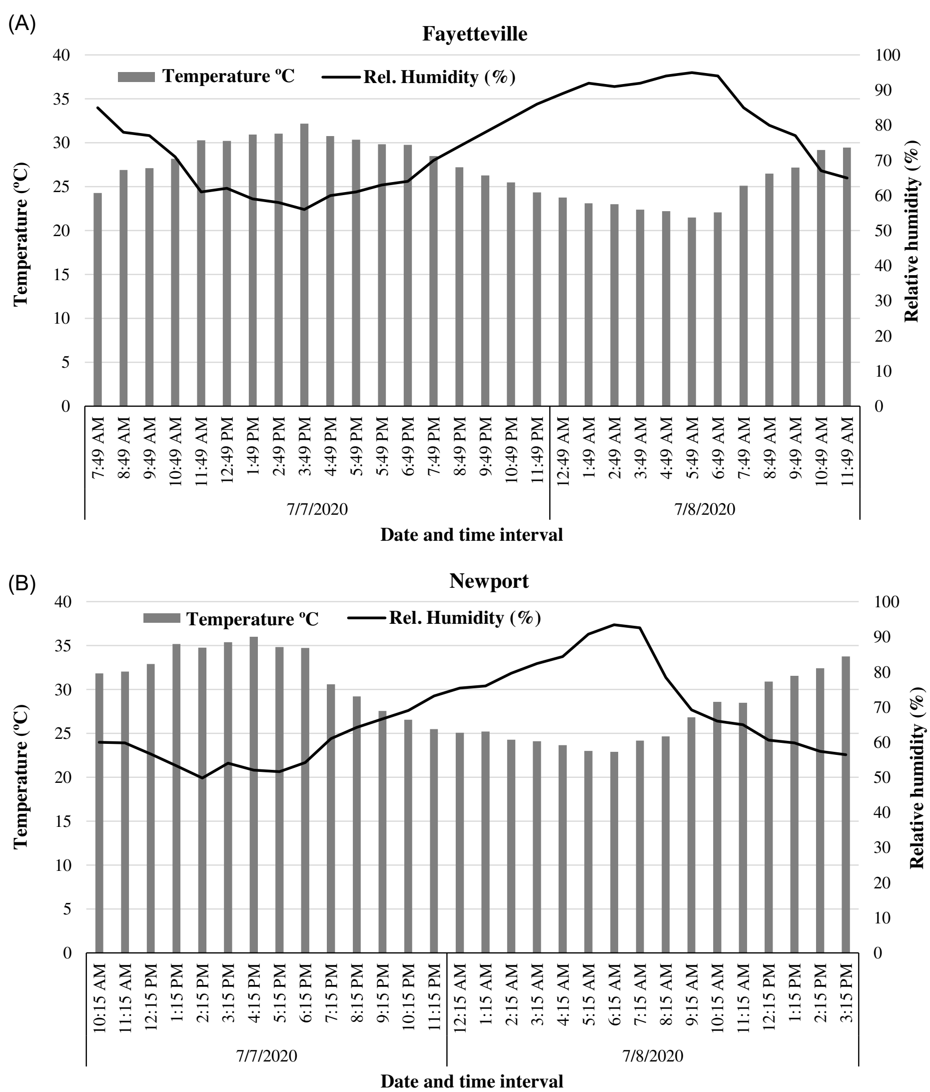

Figure 3. Temperature and relative humidity following herbicide application in 2020 at the locations in (A) Fayetteville and (B) Newport, AR, from July 7, 2020, through July 8, 2020 (30 h after application).

https://doi.org/10.1017/wsc.2022.49 Published online by Cambridge University Press

and dry soil than from green (living) plant tissue. In addition to groundcover, the presence of dew on soybean leaf tissue has been found to increase the volatility of dicamba (Henry et al. 2021). Despite differences in groundcover, KBo performed well as a VRA, lowering the detection of dicamba in air by 82% compared with the spray solution without the added KBo. Overall, weather data were comparable across locations and coincided with the amount of dicamba volatility detected in the first 12 h of the experiment, when higher temperatures and lower relative humidity were measured (Figure 3A and B). It is well documented that high temperatures coupled with low relative humidity are conducive for dicamba volatility, especially as temperatures rise above 30 C (Behrens and Lueschen 1979; Egan and Mortensen 2012; Mueller and Steckel 2019a). When averaging the cumulative dicamba detected in the two experiments, an almost 8-fold decrease in detectable dicamba was achieved.

Additional research is needed to quantify the relationship between in-air dicamba concentration and injury to sensitive species, as well as to understand the impact of environmental conditions at and surrounding a postemergence dicamba application. However, research conducted in 2019 and 2020 indicates that KBo consistently reduces dicamba volatilization in small-scale low tunnel and larger field-scale trials.

Practical Implications

The full launch of the Xtend® technology in 2017 undoubtedly led to a record number of complaints associated with extensive landscape damage to sensitive soybean from off-target movement of dicamba, specifically in areas where the adoption of DR crops was greater (Bish and Bradley 2017; Bish et al. 2020; Bradley 2017; Hager 2017; Oseland 2020; Steckel 2017). Although there are many avenues by which herbicides move off-target and injure nearby vegetation, most of the injury to soybean from labeled applications of dicamba is suspected to be the result of secondary movement via volatilization or particle suspension within temperature inversions, which likely explains the landscape nature of the damage (Bish et al. 2019).

Ultimately the results from this series of experiments lead to the conclusion that KBo functions as a consistent VRA when mixed with DGA dicamba, potentially reducing the opportunity for dicamba to volatilize and impact adjacent crops as well as sensitive vegetation present in lawns, gardens, and orchards. Additionally, reducing the amount of dicamba present in air would allow for better environmental stewardship by retaining the herbicide at the intended target area.

Substantial reductions in dicamba volatility with the addition of KBo have been observed in both small- and large-scale experiments, showing promising potential for commercialization of the nutritional material as a VRA. The conversion of KBo into boric acid once in the spray solution has the capability to amend deficiencies in both cotton and soybean (Ali et al. 2011; Howard et al. 1998; Ross et al. 2006) at the rates needed to sufficiently reduce dicamba volatility. However, further research is needed to conclude that multiple postemergence foliar applications of dicamba plus KBo will not cause significant phytotoxic injury or induce a boron toxicity to cotton or soybean. Furthermore, supplementary weed control experiments are needed to ensure that the combination of KBo and dicamba or dicamba, glyphosate, and KBo does not reduce efficacy, as some herbicides (Flint and Barrett 1989; Ou et al. 2018), compounds, or commercial additives (Roskamp et al. 2013) are known to antagonize the activity of dicamba. Phytotoxic activity of glyphosate is known to be reduced from the presence of divalent cations found in hard-water sources (Thelen et al. 2017). However, no reductions in weed control with various combinations of KBo, dicamba, and glyphosate have been documented for broadleaf or grass weed species (MCC and JKN, unpublished data).

The next phase for the commercialization of KBo is to continue conducting experiments evaluating large-scale volatility, nutritional capabilities, efficacy on key cotton and soybean weed species, economic analysis, and crop response to single and sequential applications. In addition to the aforementioned experiments, combining KBo with other VRAs, such as potassium carbonate or potassium acetate, may offer added advantages compared with those achieved with any VRA alone.

Acknowledgments. Facilities and equipment for this research were provided by the University of Arkansas System Division of Agriculture. No conflicts of interest have been declared.

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