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Pesticide Formulation and Delivery Systems:

35th Volume

Pesticide Formulations, Adjuvants, and Spray Characterization in 2014

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G. Robert Goss

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Foreword

THIS COMPILATION OF Selected Technical Papers, *STP1587, Pesticide Formulation and Delivery Systems: 35th Volume, Pesticide Formulations, Adjuvants, and Spray Characterization in 2014,* contains peer-reviewed papers presented at a symposium held October 7–9, 2014, in New Orleans, LA. The symposium was sponsored by ASTM International Committee E35 on Pesticides, Antimicrobials, and Alternative Control and Subcommittee E35.22 on Pesticide Formulations and Delivery Systems. The Symposium Chairperson was Alan Viets, BASF Corp., Cincinnati, OH, USA.

STP Editor:

G. Robert Goss
Oil-Dri Corp.
Chicago, IL, USA

Contents

Formulations

Adjuvants

Delivery Systems

Overview

The 35th Symposium on Pesticide Formulations and Delivery Systems was held in New Orleans, LA, on October 7–9, 2014. ASTM International Committee E35 on Pesticides, Antimicrobials, and Alternative Control was the sponsor. The symposium was organized under the auspices of E35.22, Pesticide Formulations and Delivery Systems. The symposium chair was Alan Viets. G. Robert Goss, Oil-Dri Corporation, Chicago, IL, was the editor of this publication.

This series of publications has been, and continues to be, one of the foremost publications on pesticide formulations and delivery systems. Without these selected technical publications (STPs), the intercommunication between professionals in the area would be limited. Control of pests is a very important aspect of feeding the world and this STP series contributes to that effort. Most contributions to this series of STPs include industry, government, and academia.

This STP addresses current topics on formulations, adjuvants, and delivery systems. Addressing formulations, the paper by Castelani, Antunes, and Leal addresses oil dispersions (OD) formulations. The paper by Guzmán, Martínez, and Montaño describes a novel method to use solvents as a snail attractant. And the paper by Gavlick, Wright, MacInnes, Hemminghaus, Webb, Yermolenka, and Su provides a new method to assess relative volatility of auxin herbicides. Adjuvants are often an invaluable aid to active ingredient performance. The paper by de Ruiter, Geuijen, and Hof describes an adjuvant to increase performance of abamectin. The paper by Zollinger, Howatt, Bernards, and Young discusses use of phosphate compounds to increase effectiveness of glyphosate and dicamba. Without a delivery system, pesticides could not function. Pesticides are often sprayed. Hoffmann, Fritz, and Yang discuss droplet size from a rotary atomizer, an important parameter for both effectiveness and drift potential. The paper by Fritz, Hoffmann, and Anderson discusses an experimental design and methodology to assess nozzle droplet size distribution.

The editor could not do this without the help of many others. In particular, thank you to my wife, Jenny; the ASTM E35.22 chair, Curt Elsik; committee E35; and my company, Oil-Dri Corp.

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Franci L. S. Leal[1]

Oil Dispersion Formulations: Stability Assessment and Field Trials

Citation

Castelani, P., Antunes, M. C. F., and Leal, F. L. S., "Oil Dispersion Formulations: Stability Assessment and Field Trials," *Pesticide Formulation and Delivery Systems: 35th Volume, ASTM STP1587*, G. R. Goss, Ed., ASTM International, West Conshohocken, PA, 2016, pp. 1–14, doi:10.1520/STP158720140129[2]

ABSTRACT

In the search for new agrochemicals with safe and improved agronomic efficacy in the field, oil dispersion (OD) formulations have been investigated intensively because they are expected to have a better performance on crops than ordinary formulations. This is because the oils and surfactants within the formulation play the role of adjuvants. Therefore, an OD formulation may show a better biological efficacy, making the addition of tank mix adjuvant (regularly used in association with systemic pesticides) optional. The main goal of this work was to develop a new insecticide OD formulation with active ingredients that would be produced as a suspoemulsion (SE), resulting in a better and easier way of formulating a commercial product. These formulations were developed with new surfactants and dispersants and were stabilized using different rheology modifiers, showing appropriate results in stability tests. Rheological assessments were also performed in order to understand system microstructure. The new insecticides' OD formulations also exhibited excellent performance in physical–chemical lab tests and were subjected to field trials with cotton crops at Primavera do Leste, Mato Grosso, Brazil, during the 2012–2013 season. The target insect evaluated in this study was the cotton boll weevil, *Anthonomus grandis Boh.* (Coleoptera: Curculionidae), which is

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[2] ASTM 35th Symposium on *Pesticide Formulation and Delivery System* on October 7–9, 2014 in New Orleans, LA.

primarily responsible for damage to Brazilian cotton. The results from using the new OD formulations showed an improved performance when compared to tank mixtures of the same insecticides. Dispersants and rheology modifiers used in this development are promising tools for future OD formulation technology.

Keywords
oil dispersion (OD) formulation, surfactants, insecticides, rheology modifiers, cotton, cotton boll weevil

Introduction

New oil dispersion (OD) formulations are of great interest because they can be considered "adjuvanted" suspension concentrates (SCs) (i.e., flowables that already contain oil-based adjuvants commonly added to tank mix products) [1]. Most oil-based tank mix adjuvants are primordial for improvement and guarantee of biological efficacy of SCs, which are known for not having the highest efficacy due to the fact that the active ingredients are suspended particles. In addition, ODs show another advantage, when compared with SCs, with regard to the hydrolysis of active ingredients, which is overcome in such an oil-based system.

On the other hand, the active ingredient must be insoluble in the oil phase (<200 ppm) to be suspended and to avoid crystal growth during long-term storage. Another issue is that ODs usually have a high viscosity at low shear rate to prevent sedimentation jeopardizing the self-emulsification process during dilution in water [2]. The great challenge in the development of OD formulations is to achieve shelf-life stability and desired behavior when diluted in water for spraying [3].

The common OD formulation process is very similar to that of an SC, with an initial mixture of the active ingredient, dispersants, and the oil phase being subjected to dispersion in a high-speed stirrer to break the solid agglomerates into smaller particles. However, unlike the SC process, with OD formulations, agents are not needed to wet the particles in the medium because oil usually has a lower surface tension than water. After dispersion, a grinding step reduces the particles to sizes from 1 to 5 μm. The suspension of small particles is a thermodynamically unfavorable energetic process and therefore generates a very unstable system. The dispersants stabilize the system and avoid increasing particle size and crystal growth [4].

During storage, gravitational forces cause sedimentation because the particles are denser than the oil phase. One way to overcome this effect is to balance the density of the dispersed phase and the oil phase, but this depends on the intrinsic properties of the active ingredient. A second way is to reduce particle size because gravitational force is proportional to the radius of the particle, and smaller particles are less likely to settle. A drawback of this approach is that milling to obtain a nanosuspension currently is a highly energetic and expensive industrial process. Consequently, the use of a rheology modifier or thickener is the preferred choice for preventing sedimentation phenomena [4].

Evaluating the stability of flowable formulations without any dilution requires carefully designed techniques that cause minimal disturbance to the dispersed system. Rheological measurements are dynamic tests where viscoelastic samples are subjected to oscillating stresses or strains. The dynamic tests provide data on viscosity and elasticity related to their time response. The gel network formed by the rheology modifier and added to the formulation must give sufficient elastic modulus (G') to overcome compression of the structure by gravitational forces [5].

After milling, besides adding rheology modifiers, emulsifiers may also be needed to improve the self-emulsification process of the oil phase when the product is diluted in water for spraying. This can be easily assessed by emulsion stability tests. Furthermore, after dilution in the tank mix, the OD formulation particles must also remain suspended in water, allowing a homogeneous spraying in the field. To evaluate the stability of this suspension in water, zeta potential measurements and suspensibility were tested.

The zeta potential is a key indicator of the stability of colloidal dispersions. The magnitude of the zeta potential indicates the degree of electrostatic repulsion among adjacent, similarly charged particles in a dispersion. Therefore, colloids with high zeta potential (negative or positive) are electrically stabilized, while colloids with low zeta potential tend to coagulate or flocculate [6].

Materials and Methods

Flowable formulations were prepared by distributing imidacloprid (Imidacloprid 98 %, Jiangsu Yangnong Chemical Group Co., Yangzhou, China) (up to 270 g/L); attapulgite (Attagel® 50, BASF Corporation, Iselin, NJ) (43 g/L); and dispersants (SURFOM® OD 8104, Oxiteno Industria e Comercio SA, São Paulo, Brazil) (220 g/L) in soybean methyl ester (SURFOM® EMS 2000, Oxiteno Industria e Comercio SA, São Paulo, Brazil) (252 g/L) at 10,000 rpm using a mixer for 10 min. This solution was transferred to a bead mill (MiniZeta, Netzsch Indústria e Comércio de Equipamentos de Moagem Ltda., Pomerode, Brazil) and milled until 50 % of the particles reached $\sim 5\,\mu$m diameter (d 0.5). The mill base was transferred to a beaker and a pyrethroid (Bifenthrin 96 % or Cypermethrin 94 %, Gharda Chemicals Limited, Mumbai, India) (up to 100 g/L), emulsifiers (SURFOM® CE 8056, Oxiteno Industria e Comercio SA, São Paulo, Brazil) (20 g/L), attapulgite (40 g/L), and another thickener (SURFOM® ESP 8105, Oxiteno Industria e Comercio SA, São Paulo, Brazil) (125 g/L) were added under vigorous mechanical agitation in an IKA® RW-20 (IKA Werke GmbH & Co., Staufen, Germany) for 30 minutes. If needed, soybean methyl ester was added to correct the active ingredients' concentration.

Emulsion stability tests were conducted according to Collaborative International Pesticides Analytical Council Methods (CIPAC MT) 36.3 and Associação Brasileira de Normas Técnicas-Normas (ABNT NBR) 13452 standards, [7,8] considering the dilution of the OD formulations in hard (342 ppm) and soft water (20 ppm), respectively. The spontaneous self-emulsification in water was assessed visually.

Viscosity measurements were made in a digital Brookfield viscosimeter (Model LVDV-II+, Brookfield Engineering Laboratories Inc., Middleboro, MA) according to the standard test method NBR 15683:2009 [9]. The measurements were carried out at 20°C and were repeated three times for each formulation.

Phase separation measurements were assessed visually. Samples were placed in a 10 mL volumetric flask for 15 days at 25°C, allowed to separate into phases, and evaluated for the percent volume in the upper phase. The upper phase was easily observed as a transparent oil phase, while the lower phase had a milky white/gray appearance.

Sedimentation measurements were assessed qualitatively as one of three categories: no sediment, soft sediment, and hard sediment. The test was conducted by manually inserting a glass rod into the flask and lowering it to the bottom. The technician estimated the sediment category based on the ease of lowering the glass rod. If the glass rod easily reached the bottom, no sediment had formed. If the technician noted some resistance from a precipitate, it was characterized as either soft or hard sediment depending on the degree of resistance. The measurement was performed only once with each sample because the insertion of the glass rod disrupted the sediment.

Particle size measurements for each of the formulations were carried out by adding the formulations to soybean methyl ester in a Mastersizer 2000 particle size analyzer (Malvern Instruments Ltd, Worcestershire, UK) until the suitable obscuration was reached (10–20 %). The measurements were repeated five times for each formulation, and the standard deviation of the results was ± 0.15 μm.

Rheology experiments were carried out using a Thermo Fisher Scientific Haake RheoStress 6000 (Haake, Karlsruhe, Germany), equipped with a cone-plate system (cone: C35/2° Ti sandblasted; plate: MP35 Ti sandblasted). Oscillatory sweep curves were done at 25°C, and the shear stress was oscillated from 0.01 to 50 Pa at a determined frequency (1 Hz) to measure the elastic modulus. Shear thinning behavior was also analyzed at 25°C, using the same equipment, by applying a shear rate from 0.01 to 100 s^{-1} and measuring shear stress.

Suspensibility was assessed according to ABNT NBR 13313:2007 standards [10], considering the dilution of the OD formulations in soft water (20 ppm).

The zeta potential measurements were carried out in a Zetasizer Nano ZS (Malvern Instruments Ltd, Worcestershire, UK) with the OD formulation diluted at 0.5 % v/v in 20 ppm water at 25°C. After dilution in water, the sample was allowed to rest. The colloidal particles of the sample (<500 nm) were separated from the larger particles by suction of the upper liquid and a measurement taken. The resulting pH of the solution was measured and not changed. These measurements were repeated three times; the standard deviation of the results was ± 0.4 mV.

The field trials were conducted in a cotton field in Primavera do Leste, Mato Grosso, Brazil, during September 2012 and March 2013 (summer season). The design of the experiments was that of random blocks with four replicates. The samples were applied three times: (A) in the beginning of the infestation; (B) five days after Treatment A (DATA); and (C) five days after Treatment B (DATB). The samples were applied using a CO2 backpack sprayer, with a volume of water equivalent to 150 L/ha. The target insect was the cotton boll weevil, *Anthonomus grandis Boh.* (Coleoptera: Curculionidae), and 20 cotton bolls per experimental unit were evaluated by counting the number of adult insects and noting the damage they had caused. The evaluations were done at 5 DATA, 5 DATB, 5 days after Treatment C (DATC), 10 DATC, and 14 DATC. The number of adults and their damage control efficiency was calculated using Henderson and Tilton's formula [11], considering the number of living insects.

Results and Discussion

The recent phase out of the insecticides endosulfan and methamidophos in the Brazilian market has forced many companies to develop new insecticide formulations to replace these popular pesticides that were used primarily to control insects in soybean and cotton crops. Neonicotinoid and pyrethroid are obvious choices among nonpatented pesticides.

Due to their physico-chemical properties, most pyrethroids usually are formulated as emulsifiable concentrates (ECs), while neonicotinoids are formed as SCs. To formulate a mixture of these active ingredients, the natural choice would be a suspoemulsion (SE). But even for skilled formulators, development of SEs is not an easy task as it is very time consuming. Oxiteno developed an OD technology where neonicotinoids can be suspended in the oil phase, while pyrethroids solubilize in it, making the formulation of different active ingredients with different solubilities in oil and water more feasible.

In this work, we developed a dispersant mixture for OD formulation in soybean methyl ester (SURFOM® OD 8104) that not only stabilized imidacloprid particles (up to 270 g/L) during and after the milling process but that also interacted with the attapulgite rheology modifier. This combination of dispersants and attapulgite resulted in a gel network structured system, preventing flocculation during the milling. To have the best stability in performance, the amount of dispersants was balanced with the amount of attapulgite and active ingredients.

After milling, a pyrethroid—bifenthrin or cypermethrin (up to 100 g/L)—was added, and the addition of SURFOM® CE 8056 emulsifiers was investigated in order to achieve a stable emulsion upon dilution in water. A stability test of the OD formulation with and without emulsifiers was conducted, and the results showed that emulsifiers were needed to achieve the best stability (Table 1).

Next, the addition of rheology modifiers was evaluated, varying the amount and the rheology modifiers themselves. The resulting formulations were subjected to accelerated stability tests for one month at 54°C. The results of phase separation are shown in Table 2.

Using these results, the lowest phase separation was obtained by combining SURFOM® ESP 8105, a rheology modifier specially developed for OD formulations, and the attapulgite that was added not only before the milling process but also after it. All samples showed no settling.

TABLE 1 Cream separation in emulsion stability tests with and without emulsifiers.

OD Formulation	Amount of Formulation Diluted in Water	Water Hardness (ppm)	Cream Separation After			
			1.0 h	2.0 h	4.0 h	24.0 h
Without Emulsifiers	1 %	20	0.3	0.25	0.25	0.2
	5 %	342	Ok	Ok	Ok	0.1
With Emulsifier, SURFOM® CE 8056	1 %	20	Ok	Ok	Ok	Ok
	5 %	342	Ok	Ok	Ok	Ok

With optimized dispersants, emulsifiers, and rheology modifiers, the final OD formulations for further stability tests and field trials were prepared as described in Fig. 1.

The results reported here were obtained for an imidacloprid 250 g/L and bifenthrin 50 g/L system. Stability of the formulations was investigated for short-term storage at room temperature (25°C) and in accelerated tests at high temperature (54°C).

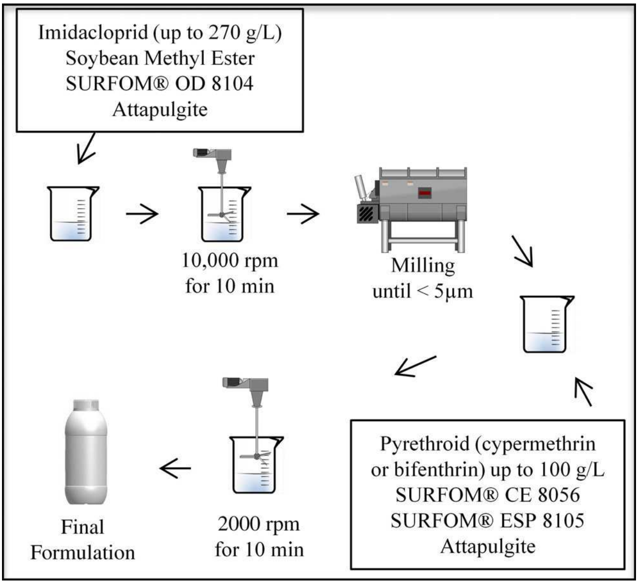
Particle size analysis was performed to evaluate flocculation because an increase in particle size may take place during storage. Crystal growth may also be observed with this analysis because such a phenomenon would change the particle size pattern; this is usually observed as an increase in the amount of the biggest particles [2]. Particle size analysis results are described in Table 3. For all formulations, the variation in particle size was less than the standard deviation of the measurements, indicating that no flocculation or crystal growth was occurring.

Another way to assess flocculation is by syneresis, which is the appearance of a liquid layer at the top of the suspension. Syneresis occurs with most flocculated and/or structured suspensions because the gravity force causes some contraction of the network of the suspended particles (either alone or combined with the thickener), which leads to some separation of the continuous phase that is entrapped among the droplets in the network [2]. A weak flocculation is reversible and, therefore, not an issue. From the results exhibited in Table 4, it is possible to conclude

TABLE 2 Phase separation of OD formulations of neonicotinoids and pyrethroids with different rheology modifiers after one month at 54°C.

Formulation	Thickener after Milling	Phase Separation
Imidacloprid 270 g/L + cypermethrin 100 g/L	125 g/L SURFOM® ESP 8105 + attapulgite	13.5 %
Imidacloprid 270 g/L + cypermethrin 100 g/L	100 g/L SURFOM® ESP 8105	32.1 %
Imidacloprid 270 g/L + cypermethrin 100 g/L	150 g/L SURFOM® ESP 8105	24.1 %
Imidacloprid 270 g/L + bifenthrin 100 g/L	100 g/L SURFOM® ESP 8105	27.8 %
Imidacloprid 270 g/L + bifenthrin 100 g/L	150 g/L SURFOM® ESP 8105	31.4 %

FIG. 1 Oil dispersion (OD) formulation process optimized with Oxiteno's products.



that, for an OD system, the formulation showed little syneresis. All samples showed no sedimentation, and they were easily rehomogenized by gentle shaking.

Another important parameter that must be investigated during stability is the viscosity (which should not change because an increase indicates flocculation and a decrease means that the system is breaking down). The results are displayed in Table 5 and show that the system gained little viscosity with time. A remarkable increase was noted only at 54°C for three months, which is a very harsh storage condition.

Some rheology tests were also performed to evaluate the microstructure of the system. Rheology modifiers produce a three-dimensional gel network in the

TABLE 3 Particle size measurements of imidacloprid 250 g/L and bifenthrin 50 g/L after different storage times at 25°C and 54°C.

Sample	D 0.1	D 0.5	D 0.9
Initial	1.153	5.858	14.052
1 month @ 25°C	1.361	6.552	14.055
3 months @ 25°C	1.502	6.980	14.996
3 months @ 54°C	1.285	7.255	15.977

Note: The first measurement ("initial") was the particle size measured just after the formulation was made (time = zero days). The D 0.1, 0.5, and 0.9 measurements were carried out in soybean methyl ester using a Mastersizer 2000 particle size analyzer.

TABLE 4 Phase separation of imidacloprid 250 g/L and bifenthrin 50 g/L after different storage times at 25°C and 54°C. The volume percentage of the upper phase was measured visually.

Sample	Phase Separation
1 month @ 25°C	2.2 %
1 month @ 54°C	4.0 %
3 months @ 25°C	3.0 %
3 months @ 54°C	6.0 %

continuous phase, resulting in a non-Newtonian fluid. When stored for a long time period (and subject to zero shear rate), these systems have very high viscosity. Therefore, the particles do not settle, but the formulation must present a shear thinning behavior. When some shear forces are applied to the bottle, the viscosity is reduced, which allows the OD to be poured out of the package [12]. **Fig. 2** and **Fig. 3** shows that the formulation has a suitable shear thinning behavior and that the variation during storage is acceptable. Again, the sample at 54°C after three months behaved differently, indicating flocculation (because the viscosity does not reach the initial values).

Elastic modulus (G') is a measure of the energy stored in a cycle of oscillation. A sufficiently high elastic modulus is necessary to overcome compression of the structure. Elastic modulus was determined using stress sweep measurements where the oscillation is fixed at 1 Hz. The viscoelastic parameters were obtained as a function of strain amplitude (**Fig. 4** and **Fig. 5**) [12]. All samples have elastic modulus (G') values of around 10 Pa in the linear region of the curves; the structure of the formulation began breaking down at stresses of around 1 Pa, which indicated that the system is very stable and does not change significantly with time and temperature.

The properties of the final formulation when diluted in water are also very important to evaluate how it will behave in a tank mixture. Therefore, the final

TABLE 5 Viscosity of imidacloprid 250 g/L and bifenthrin 50 g/L after different storage times at 25°C and 54°C. The measurements were carried out in a digital Brookfield viscosimeter LVDV-II+ at 20°C.

Sample	Viscosity (Brookfield, cP)
Initial	850
1 month @ 25°C	1000
1 month @ 54°C	1200
3 months @ 25°C	1140
3 months @ 54°C	1600

FIG. 2 Shear thinning behavior of imidacloprid 250 g/L and bifenthrin 50 g/L after different storage times at 25°C. The measurements were carried out using a rheometer equipped with a cone-plate system.

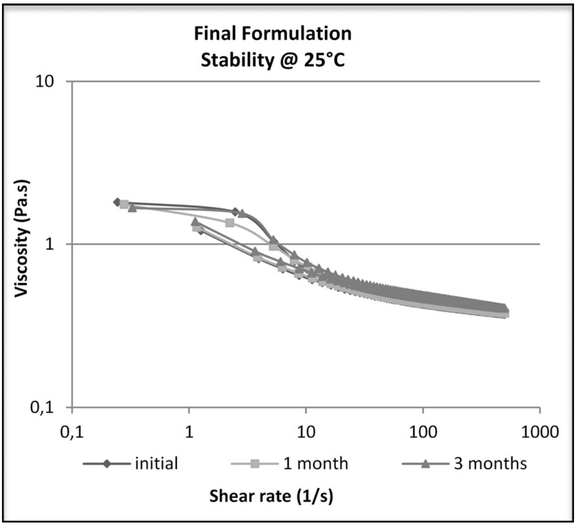


FIG. 3 Shear thinning behavior of imidacloprid 250 g/L and bifenthrin 50 g/L after storage different times at 54°C. The measurements were carried out using a rheometer equipped with a cone-plate system.

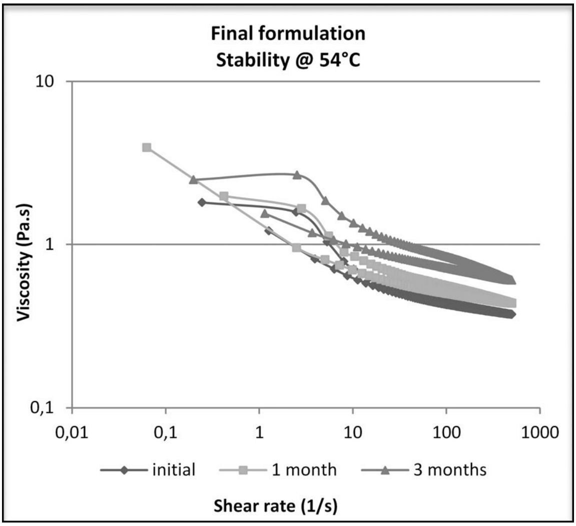


FIG. 4 Stress sweep oscillatory curves of imidacloprid 250 g/L and bifenthrin 50 g/L after different storage times at 25°C. The measurements were carried out using a rheometer equipped with a cone-plate system. The shear stress was oscillated from 0.01 to 50 Pa at a frequency of 1 Hz, and elastic modulus was measured.

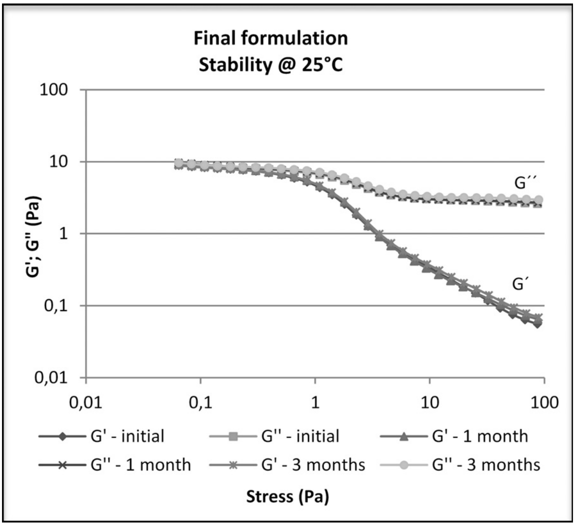
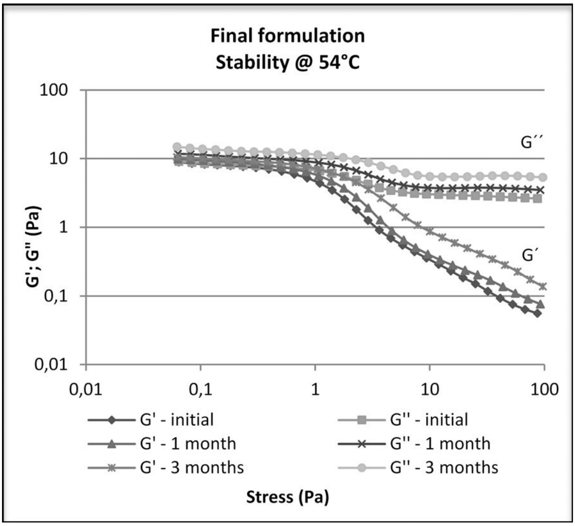


FIG. 5 Stress sweep oscillatory curves of imidacloprid 250 g/L and bifenthrin 50 g/L after different storage times at 54°C. The measurements were carried out using a rheometer equipped with a cone-plate system. The shear stress was oscillated from 0.01 to 50 Pa at a frequency of 1 Hz, and elastic modulus was measured.



formulation was evaluated with regard to self-emulsification. This was assessed visually and was shown to be very good for an OD formulation (Fig. 6).

Moreover, the zeta potential of the final formulation diluted in 20 ppm water was also measured to evaluate the stability of the suspended particles in the system. The result was −35.8 mV, at a pH of 8.6. This demonstrated that the system has good stability, reaching values above 30 mV in modulus—the potential at which dispersions are considered stable.

In addition, the final formulation and the samples stored at different times at 25°C and 54°C were also evaluated for suspension stability when diluted in water. The stability was measured by suspensibility. The suspensibility tests showed that all samples reached more than the 80 % level, which is the minimum desirable amount and indicates very good suspension stability (Table 6). Moreover, no agglomeration of particles was observed during this test.

To prove the biological efficacy of the OD formulation and to compare the performance of insecticide OD formulations versus other insecticide types and tank mixtures, the final formulations of imidacloprid 250 g/L and bifenthrin 50 g/L and imidacloprid 270 g/L and bifenthrin 100 g/L were subjected to field trials targeting boll weevils on cotton crops at Primavera do Leste, Mato Grosso, Brazil, during September 2012 and March 2013.

FIG. 6 Self-emulsification process of OD formulations of imidacloprid 250 g/L and bifenthrin 50 g/L upon dilution of 1.0 % in 20 ppm water: (A) shows a formulation under development, and (B) shows the final formulation.

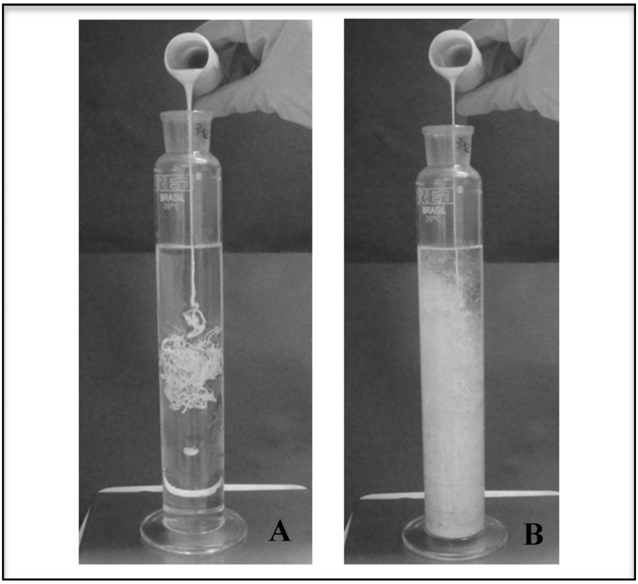


TABLE 6 Suspensibility of imidacloprid 250 g/L and bifenthrin 50 g/L after different times of storage at 25°C and 54°C. A level of 80 % is the minimum accepted by this test.

Sample	Suspensibility
Initial	92.5 %
1 month @ 25°C	92.5 %
3 months @ 25°C	92.9 %
3 months @ 54°C	85.9 %

The treatments described in Table 7 were applied three times: (A) in the beginning of the infestation; (B) five days after Treatment A; and (C) five days after Treatment B.

The evaluations in the field were carried out on 20 cotton bolls per experimental unit, counting the number of adults and noting the damage they caused. The evaluations were done at 5 DATA, 5 DATB, 5 DATC, 10 DATC, and 14 DATC. The number of adults and their damage control efficiency was calculated using Henderson and Tilton's formula [11]. The results are shown in Table 8 and Table 9.

From these results, it is possible to conclude that Treatment 6, which is the OD formulation of imidacloprid 250 g/L + bifenthrin 50 g/L at 0.4 L/ha, is the best. This was the only treatment that showed consistent results for adult population control efficiency. These results confirm that use of the new OD formulations is an improvement over tank mixtures of the same insecticides.

TABLE 7 Treatments sprayed in cotton fields.

Entry	Treatment	Dosage (L/ha)	Amount of Imidacloprid (g/ha)	Amount of Pyrethroid (g/ha)
1	OD: 270 g/L imidacloprid + 100 g/L bifenthrin	0.10	27	10
2	OD: 270 g/L imidacloprid + 100 g/L bifenthrin	0.15	36	15
3	OD: 270 g/L imidacloprid + 100 g/L bifenthrin	0.20	48	20
4	OD: 250 g/L imidacloprid + 50 g/L bifenthrin	0.20	50	10
5	OD: 250 g/L imidacloprid + 50 g/L bifenthrin	0.30	75	15
6	OD: 250 g/L imidacloprid + 50 g/L bifenthrin	0.40	100	20
7	Commercial 1: 100 g/L imidacloprid + 12.5 g/L beta-cyfluthrin	1.00	100	12.5
8	Commercial 2: 250 g/L imidacloprid + 50 g/L bifenthrin	0.40	100	20
9	Tank mix: imidacloprid WG 700 g/kg + bifenthrin EC 100 g/L	0.14 + 0.2	98	20

TABLE 8 Adult population control efficiency.

Treatment	5 DAT A	5 DAT B	5 DAT C	10 DAT C	14 DAT C
1	25.00	0.00	0.00	12.50	50.00
2	100.00	0.00	0.00	0.00	0.00
3	100.00	0.00	0.00	0.00	0.00
4	100.00	0.00	0.00	0.00	0.00
5	0.00	0.00	0.00	0.00	0.00
6	**75.00**	**100.00**	**75.00**	**45.83**	**50.00**
7	100.00	0.00	0.00	0.00	0.00
8	100.00	100.00	0.00	25.00	0.00
9	100.00	100.00	0.00	0.00	0.00

Note: Numbers in bold type show that the best results were achieved with Treatment 6.

TABLE 9 Cotton damage control efficiency.

Treatment	5 DAT A	5 DAT B	5 DAT C	10 DAT C	14 DAT C
1	0.38	55.82	38.88	9.62	0.00
2	25.63	48.40	36.15	18.75	6.07
3	40.77	53.06	50.52	0.00	0.00
4	0.00	32.69	39.70	0.00	0.00
5	0.00	50.30	53.43	13.46	0.00
6	**0.00**	**66.86**	**56.43**	**21.15**	**0.00**
7	0.00	58.82	36.57	0.00	0.00
8	8.46	39.25	41.79	13.46	0.00
9	7.80	44.84	41.86	4.88	0.00

Note: Numbers in bold type show that the best results were achieved with Treatment 6.

Conclusion

Insecticides with different physico-chemical properties, such as neonicotinoids and pyrethroids, were successfully combined into an OD type formulation. As a result, new products such as dispersants, emulsifiers, and rheology modifiers were developed for this type of formulation. Accelerated stability and rheology tests showed that OD formulations were stable with a long-term shelf life. In addition, dilution in water tests demonstrated the desirable performance of OD formulations for tank mixing and spraying. Field trials showed improved results regarding the biological performance of OD formulations versus tank mix products and other commercial mixtures. Dispersants, emulsifiers, and rheology modifiers were shown to be successful tools for use in OD formulation technology.

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Sustainable Solvents as Attractors in Snails

Citation

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ABSTRACT

Global crop losses due to pests have been estimated at more than 50 % of attainable crop output. Of this figure, insects cause 15 % of the crop destruction with an additional 10 % resulting from post-harvest pest infestations. Pesticides are used to avoid crop losses, but most of them are formulated with aromatic solvents. Aromatics, such as naphthalene or anthracene, are used as insect repellents. The repellency of aromatics could make insects move from one crop to another that is free of repellents, possibly resulting in a reduced pest control. For this is reason, it is very important to improve the current chemical control with adjuvants that act as attractants to the pests but also kill them. By their nature, sustainable solvents such as fatty acid methyl esters or fatty alcohols could act as attractors without having any volatile organic compounds (VOCs). In addition, the aromatic solvents in a formulation can evaporate in days or even hours, leaving insoluble the active and out of reach of the pest. Attack by mollusks causes large losses in agriculture and fish farming even with the use of pesticides. In this work, the attractant or repellent effect of some aromatic and sustainable solvents is tested using snails as an example related to pest control.

Keywords

snail, pest, damage, crop, sustainable, solvent

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[1] BASF Mexicana, Av. Lic. Angel Otero Rivero No.8, Industrias Tulpetlac, Estado de México, 55107

[2] ASTM 35th Symposium on *Pesticide Formulation and Delivery Systems* on October 7–9, 2014 in New Orleans, LA.

Introduction

Aromatic solvents are those having a basic benzene structure—usually coal tar types such as benzene, toluene, or xylene [1]—as well as the light aromatic solvents obtained from distillation of aromatic streams.

Agnique® sustainable solvents are obtained from natural sources with a low toxicity profile, are biodegradable, and have low or no volatile organic compound (VOC) content—such as fatty acid methyl esters, fatty alcohols, fatty acid dimethyl amides, lactates, and lactamides (**Table 1** and **Table 2**).

This work studied the attractant or repellent effect of some aromatic and sustainable solvents for controlling pests.

Pests and diseases have threatened crops since farming began. The damage that they cause can be economic (through losses in output, income, and investment) as well as psychological (manifested in shock or panic). The control of pests and diseases is a necessity for farmers and, as a rule, decisions regarding control are made by the individual farmer. However, the presence of a pest or disease on one farm poses a threat to adjacent farms and sometimes even to distant localities [2].

Estimates of global losses due to pests were made by Oerke, Dehne, Schonbeck, and Weber [3] for eight crops by region. The authors found that pest-induced losses affected more than 50 % of attainable crop output. Insects damaged 15 % of crops, pathogens and weeds another 13 % each, and post-harvest pest infestations another 10 % [2].

Pesticides are supposed to kill pests. Most of them are formulated with aromatic solvents even though it is known that some aromatics (such as naphthalene or anthracene) are used as insect repellents.

This repellency effect of the aromatics could make pests move away from where the pesticide is located and move toward a crop that is free of pesticide, resulting in a reduced pest control. In addition, aromatic solvents in formulations will

TABLE 1 Sustainable solvents.

Product	Chemistry	Abreviation
Agnique® ME 610	Methyl Caprylate-Caprate (C6-C10)	ME 610
Agnique ME 1298	Methyl Laurate (C12), 98 %	ME 1298
Agnique ME 1218	Methyl Coconate (C12-C18), Stripped	ME 1218
Agnique ME 181	Methyl Oleate (C18)	ME 181
Agnique ME 18RD	Methyl Rapeate (C18), Distilled	ME 18RD
Agnique ME 18R	Methyl Rapeate (C18)	ME 18R
Agnique ME 18SD	Methyl Soyate (C18), Distilled	ME 18SD
Agnique FOH 898	Octyl Alcohol, 98 %	FOH 898
Agnique AMD 810	Dimethyl Amide (C8-C10)	AMD 810
Agnique AE 3-2EH	2-Ethyl Hexyl Lactate	AE 3-2EH

TABLE 2 Aromatic solvents.

Chemistry	Abreviation
Xylene	Xylene
Solvent Naphtha 150	A 150
Solvent Naphtha 200	A 200

eventually evaporate within days or even in hours, leaving insoluble the active and out of reach of the pest.

Farmers look for formulations that stay on the crops as long as possible in order to reach the pest; sustainable solvents with low volatilization could help reach this goal.

On the other hand, attractant products are widely used in many applications—including the control of pests, and these products are made mostly with protein and fats. By their nature, sustainable solvents such as methyl esters or fatty alcohols could act as attractors without having any VOCs.

Mollusks cause large losses in agriculture and in fish farming. Damage results from their feeding on agricultural and horticultural crops as well as on native plants, thereby lowering crop yields and crop quality [4]. Mollusks scrape the epidermis of leaves, flowers, fruits, seeds, seedlings, young branches, and roots, making holes and edges and leaving a trail of mucus over the affected crop. They also can transmit pathogens to humans indirectly when humans consume contaminated vegetables and fruits. Mollusks transmit plant and livestock pathogens in their feces and displace native species of snails and slugs. Additionally, snails can disrupt agricultural operations when they group together in a behavior known as massing [4].

Chemical control of terrestrial snails and slugs involves the use of poisonous sprays, paints, irritating powders, and poisonous baits. However, arsenic spray compounds are ineffective because slugs and snails avoid these treatments. Copper-based sprays such as the Bordeaux mix are only efficient in concentrations that are toxic for plants. Other treatments—such as kerosene emulsion, chlordane, pyrethrins, DDT emulsion with kerosene, soap solutions, saline solutions, and sulphorous lime are good repellents but usually do not kill adult snails and slugs. In addition, most of these chemical products are toxic for humans and livestock.

Since its discovery as a molluscicide in 1934, metaldehyde has been the best chemical solution against terrestrial slugs and snails to date, but it is not 100 % effective. It is combined with calcium arsenate or sodium fluorosilicate to increase effectivity [5].

The brown garden snail, *Cornu aspersum* (formerly *Helix aspersa*), is the most common snail causing problems in California gardens [6]. This work tests the attractant or repellent effect of both aromatic and sustainable solvents on this pest (**Fig. 1**).

FIG.1 Brown garden snail.

Experiment Description

EXPERIMENT CONDITIONS

Each test (Table 3) was performed in an 18 in. by 11 in. by 4 in. tray filled with soil (Fig. 2); the soil was replaced after each test. The tray was delimited with copper pipes and colocated inside a vented 31 in. by 28 in. by 23 in. cabinet (Fig. 3).

The temperature was always controlled at 25°C but not the humidity. The cabinet vents were always open. In each test, some weeds or vegetables were

TABLE 3 Test Performed.

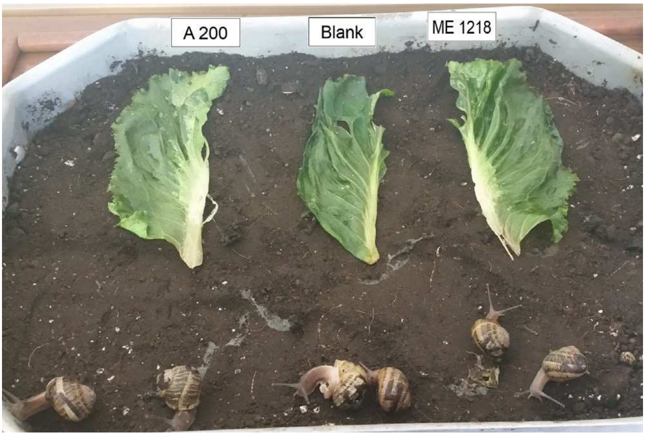
Test	Sustainable Solvent Tested	Aromatic Solvent Tested	Blank
1	ME 1218	A 200	Yes
2	ME 610	A 200	Yes
3	ME 1218, FOH 898	-	Yes
4	AMD 810, AE 3-2EH	-	Yes
5	FOH 898	A 200	Yes
6	AE 3-2EH	A200	Yes
7	-	Xylene, A 150, A 200	No
8	ME 18R, ME 18RD	-	Yes
9	ME 18SD	A 200	Yes
10	ME 1298	Xylene	Yes
11	ME 1218, ME 181	-	Yes

FIG. 2 Tray used for testing with soil, snails, and rosemary plants (Rosmarinus officinalis).

colocated in the tray in equivalent portions. To measure the snails' preferences, one weed or vegetable was added with 0.5 g of the aromatic solvent tested, another weed or vegetable was added with 0.5 g of a sustainable solvent, and another ("blank") had no addition of solvent (Fig. 4). Each test lasted 24 h, and the snails were observed periodically.

FIG. 3 Cabinet used for the tests.

FIG. 4 Lettuce with addition of sustainable solvent (right), lettuce with aromatic solvent (left), and lettuce without addition of solvent (middle).



The study was based on snail vegetable preferences with the addition of both types of solvents and with the blank. The snails' preference was measured considering the following:

- To what location/vegetable they were attracted
- The location of the mucus trails
- Where they decided to hibernate
- From which weed or piece of vegetable they prefered to feed
- How much the weed or vegetable was damaged—partially or totally consumed (Fig. 5 and Fig. 6)

FIG. 5 Starting the test with pieces of lettuce undamaged, t = 0 h.

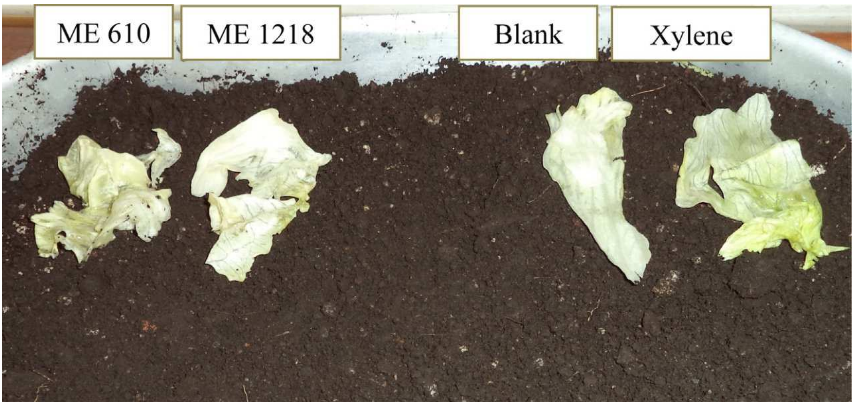
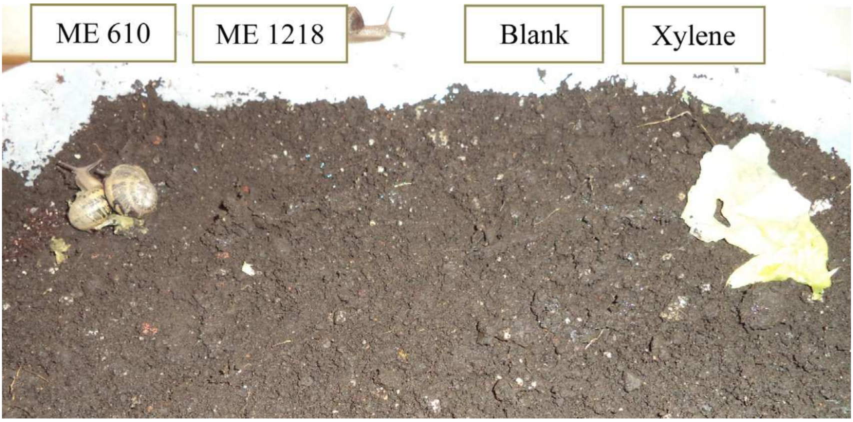


FIG. 6 Methyl ester treated lettuces and the blank were totally consumed. Xylene treated lettuce was undamaged, t = 24 h.



Summary of the Preferences and Percentage of Damages

In this summary, we presented the 11 tests made up of different combinations of aromatic and sustainable solvents chemistries (Table 4). For each test, the percentage

TABLE 4 Summary of the tests.

	Test										
Solvent Tested	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
Xylene							0 %			0 %	
Aromatic 150							0 %				
Aromatic 200	0 %	0 %			0 %	0 %	0 %		0 %		
C18 Methyl Oleate											**100 %**
C12-18 Methyl Ester	**100 %**		**100 %**								**100 %**
C12 Methyl Ester										0 %	
C6-10 Methyl Ester		0 %									
Distilled C18 Methyl Canolate								0 %			
C18 Methyl Canolate								**100 %**			
C18 Methyl Soyate									**100 %**		
C8 Fatty Alcohol			0 %		0 %						
C8-10 Dimethyl Amide				0 %							
2-ethyl Hexanol Lactate				0 %		5 %					
Blank	10 %	100 %	10 %	50 %	80 %	90 %		0 %	100 %	10 %	0 %

of damage to the vegetable with or without solvent is given from 0 % (no damage) to 100 % (totally consumed by the snails). Because each test was performed once, the result in each test is presented as is, not as statistic values.

According to the results, if the snail consumed 100 % of the vegetable with the sustainable solvent versus the blank or the one with an aromatic solvent, then the sustainable solvent is considered an attractor. If the snail consumed 0 % of the vegetable with an aromatic solvent, then it is considered a repellent.

Conclusions

The sustainable solvents such as methyl esters with long chains (C18) can act as attractors for snails based on their feeding and on the damage presented in the tests.

The tested aromatic solvents can act as a snail repellent; it was observed during the tests that, in all cases, snails avoided the plants or vegetables with the added aromatic solvents.

For methyl esters, the snails prefer the undistilled methyl esters over the distilled ones when both are put together. But in absence of undistilled methyl esters, the snails fed on the distilled esters.

It was shown that short chains of fatty alcohols and fatty acid dimethylamides, such as the C8–C10 chains, are not attractants for snails.

And finally, the formulations made with solvents that are sustainable by definition have the advantage of low toxicity profiles and biodegradability. The results of the present study also show that, in some cases, these sustainable solvent formulations can have an attractant effect for snails.

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A Method to Determine the Relative Volatility of Auxin Herbicide Formulations

Citation
Gavlick, W. K., Wright, D. R., MacInnes, A., Hemminghaus, J. W., Webb, J. K., Yermolenka, V. I., and Su, W., "A Method to Determine the Relative Volatility of Auxin Herbicide Formulations," *Pesticide Formulation and Delivery Systems: 35th Volume*, *ASTM STP1587*, G. R. Goss, Ed., ASTM International, West Conshohocken, PA, 2016, pp. 24–32, doi:10.1520/STP158720150006[2]

ABSTRACT

Auxins such as dicamba and 2,4-Dichlorophenoxyacetic acid (2,4-D) may volatilize when used as herbicides. In this work, a fast, straightforward method to determine the relative volatility of auxin formulations is presented. The method uses a sprayed soil substrate in a disposable closed dome system. For a 24-h period, air is drawn out of the closed dome and passed through a polyurethane foam (PUF) plug where any volatile auxin is trapped. The auxin is extracted from the PUF with methanol, and the resultant extract solution is analyzed for the auxin by liquid chromatography–mass spectrometry (either LC-MS or LC-MS\MS). The data are then used to determine the relative volatility of the formulations.

Keywords
volatility, auxin, dicamba, 2,4-Dichlorophenoxyacetic acid (2,4-D), formulations

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[1] Monsanto Company, 800 North Lindbergh Blvd., St. Louis, MO 63167

[2] ASTM 35th Symposium on *Pesticide Formulation and Delivery System* on October 7–9, 2014 in New Orleans, LA.

Introduction

The volatilities of dicamba and 2,4-Dichlorophenoxyacetic acid (2,4-D) have been known and studied [1,2] since the discovery of the compounds more than 60 years ago. A method to determine the relative volatility of formulations is needed to guide development and optimization work and to assess the impact of the addition of adjuvants. There are various bioassays found in the literature that can be performed in a greenhouse or growth chamber setting and used to evaluate the volatility of the formulation when applied to soil or plants [3–5]. These bioassays typically take one to three weeks after application of the herbicide to obtain a result and may not have the sensitivity to determine small differences in volatility. Being able to more quickly assess volatility and to detect smaller differences in that volatility would greatly speed up and improve the formulation development process.

The goal of this work was to develop a relatively fast, straightforward method to determine the relative volatility of auxin-containing herbicide formulations without using any plants. The key to this type of method is to set up a system in which the herbicide can be applied and then the volatile auxin trapped and quantified. There have been various approaches used to trap volatile herbicides. These include the use of sorbent tubes [6,7], scrubber solutions [8], and polyurethane foam (PUF) plugs [8,9]. The PUF approach has been used to trap volatile pesticides for more than 30 years as demonstrated by a U.S. Environmental Protection Agency (EPA) report from 1980 [10]. In the present work, PUFs were chosen to trap volatile dicamba and 2,4-D from formulations that had been sprayed on soil as part of a closed dome system.

Materials and Methods

The relative volatility of auxin-containing herbicide formulations was determined in a growth chamber under controlled environmental conditions through the use of a sprayed soil sample application and PUF-based auxin collection in a disposable closed dome system. A track sprayer in a fume hood was used to dose the soil with the auxin-containing formulation. The dosed soil was covered with a dome, placed into a growth chamber, and then air was drawn out of the closed dome and through the PUF for 24 h. Any auxin that was present in the air was trapped on the PUF. The auxin was then extracted from the PUF with methanol, and the resultant extract solution was analyzed for the auxin by liquid chromatography–mass spectrometry (LC-MS).

CLOSED DOME SYSTEM PREPARATION

Closed Dome Lid Preparation

A 7/8-in. (2.22 cm) diameter air outlet hole was cut into a disposable clear, plastic dome lid[3] with an arch punch on one end—two inches from the top of the dome—to allow for insertion of a glass air sampling PUF tube (**Fig. 1**). Another 7/8-in. (2.22 cm) air inlet hole was cut into the opposite end of the lid, two inches from the top.

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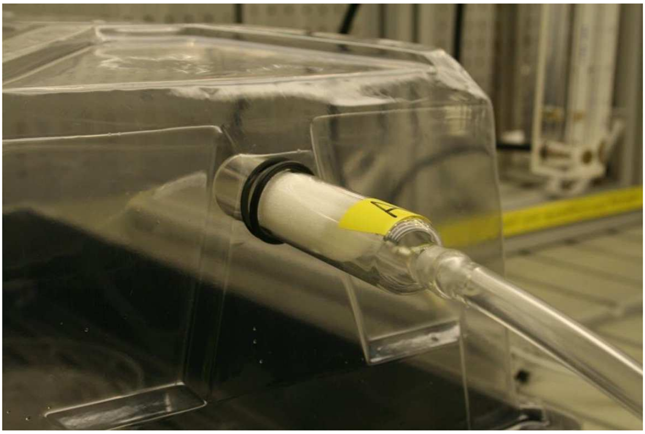
[3] Hummert part 14-3850-2; clear plastic; 6 in. H by 21 in. L by 11 in. W.

FIG. 1 Close-up view of polyurethane foam (PUF) in glass tube.



Closed Dome Tubing Preparation

A section of 1/4-in. (0.635 cm) inner diameter (ID) flexible air line tubing[4] with a quick disconnect fitting[5] on one end was secured onto the 3/16-in. (0.476 cm) tapered end of a glass air sampling tube[6] containing a PUF.[7] A Viton O ring[8] was placed over the larger open end of the glass tube, and the tube was inserted into the air outlet port in the dome lid, extending approximately one inch inside the dome. The glass tube was secured in place by inserting a second Viton O ring over the tube from inside the dome and pushing it against the dome wall toward the outer O ring (Fig. 1). The air inlet hole was plugged temporarily with a #3 rubber stopper.

Closed Dome Tray Bottom Preparation

A disposable flat plastic tray bottom[9] was filled with 1 liter of a 50 % Redi-Earth and 50 % US10 field soil mixture that was sifted with a 1/4-in. (0.635 cm) opening sieve screen. The noncompacted soil in the tray was leveled out to an approximate depth of 1 cm. A sample of the soil was tested for moisture content using a loss on drying (LOD) instrument.

Soil Dosing

To avoid contamination of its outer sides during spraying, the tray of soil was placed inside an empty tray bottom. The tray bottom containing the soil was sprayed with a test formulation that had been appropriately diluted (typically 1.2 %

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[4] Vincon part ABH02017.

[5] CPC part PLC1700412.

[6] SKC Inc. part 226-124G; 4 1/2 in. long with openings of 3/4 in. ID and 3/16 in. ID on opposite ends.

[7] SKC Inc. part P22692; polyurethane foam 76 mm long by 22 mm OD, which is cut to 30 mm L; approximately 1 in. from end of larger opening.

[8] Danco part 14; 15/16 in. OD by 3/4 in. ID.

[9] Hummert part 11-3050-1; F1020-no holes, 3 in. H by 20 in. L by 10 in. W.

dicamba acid, 2.4 % 2,4-D acid) at a rate of 10 gal per acre (GPA) (38 L per acre) using a track sprayer inside a fume hood with a 9501E nozzle tip 16 in. (40.6 cm) above the soil. After the spraying was complete, the tray was removed from the empty bottom. A humidity dome lid containing a PUF sampling tube with an air line apparatus in the outlet hole and a #3 rubber stopper in the inlet hole was then immediately placed over the tray of sprayed soil and secured along the edges and ends with metal binder clips. The tray was handled carefully to avoid shifting the sprayed soil (Fig. 2). All soil dosing and closed dome assemblies were completed before the domes were moved to the growth chamber.

Closed Dome Placement in Growth Chamber

The assembled closed dome was placed on a shelf inside the growth chamber (set at 35 °C, 40 % relative humidity (RH), 14-h day light cycle) and connected to a vacuum line (Fig. 3). The #3 stopper that was placed in the air inlet hole was then removed to allow air to flow through the dome and the PUF. The vacuum system consisted of a 12-port vacuum manifold with mass flow controllers and displays that allowed 12 closed domes to be used simultaneously. A vacuum pump was connected to the manifold and exhausted outside the growth chamber. The closed dome remained undisturbed in the growth chamber for 24 h with air drawn through it at a flow rate of two standard liters per minute (SLPM).

FIG. 2 Assembled closed dome system.

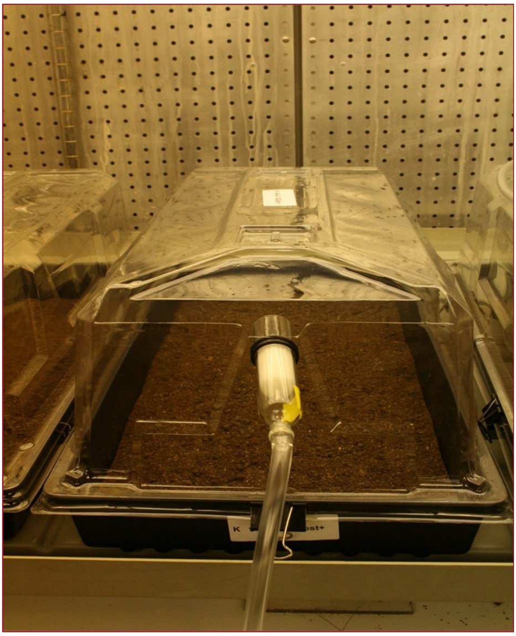
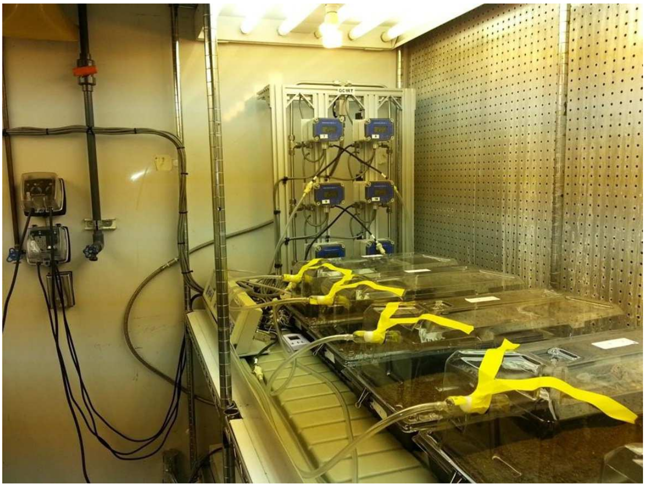


FIG. 3 Series of closed dome systems in a growth chamber.



Test Completion

After 24 h, the vacuum pump was turned off, and the closed dome was removed from the growth chamber with rubber stoppers placed in the air inlet holes to prevent the release of auxin vapors into the growth chamber. The glass PUF containing the sampling tube was removed and wrapped in aluminum foil.

Sample Analysis

The PUF was removed from the glass tube and placed into a 20 mL vial. Twenty milliliters of methanol were added to the vial, and the auxin was extracted from the PUF by repeatedly squeezing the PUF with a disposable pipet tip in an up and down motion. The resultant extract was analyzed by LC-MS[10] for extracts in the range of 0.002 to 2 ppm and by LC-MS/MS[11] for extracts in the range of 0.0005 to 0.2 ppm (0.5 to 200 ppb). The LC-MS method used a Waters Acquity UPLC HSS T3 (2.1 by 150 mm, 1.8 micron) column with a mobile phase gradient consisting of 0.1 % formic acid in water and 0.1 % formic acid in acetonitrile. The dicamba was quantitated at an m/z of 177, and the 2,4-D was quantitated at an m/z of 161 or 219. The 2,4-D ethylhexyl ester samples were hydrolyzed to 2,4-D acid by mixing the sample with an equivalent volume of 5 % v/v ammonium hydroxide and heating briefly to 50°C before the 2,4-D acid concentration was determined. The LC-MS/MS method used a Zorbax XDG-C8 (4.6 by 50 mm, 3.5 micron) column with a mobile phase gradient consisting of 0.1 % formic acid in water and 0.1 %

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[10] Waters Acquity UPLC with SQ detector.
[11] Agilent 1200 series HPLC with Applied Biosystems API 3200 MS/MS.

formic acid in acetonitrile. The dicamba was quantitated (Q) using Q1 at 218.811 and Q2 at 175.000 daltons.

Results and Discussion

KEY PARAMETERS

Various parameters that may impact volatility were identified in this assay. Dome cross contamination, soil moisture, pumping rate and consistency from each vacuum line, soil composition, PUF variability, sprayer consistency, and amount of soil were the most important parameters in terms of their impact on measured volatility. During the course of the work, various closed dome configurations and materials of construction were considered. Each of them exhibited cross contamination issues due to the difficulty in cleaning the closed domes. The cross contamination issue was resolved by using a disposable dome and tray. A soil moisture target of 20 % was set in an effort to minimize the impact of this variable. Although it was difficult to generate soil with the same moisture value, the soil moisture was measured by loss on drying (LOD) and recorded. If the LOD value varied outside a range of 12 % to 22 %, then the soil was not used. The pumping rate was set at a flow rate of 2 SLPM. In order to best control this rate, two vacuum pumps were used for each manifold system. The system was calibrated every six months to ensure the accuracy of the flow controllers. In order to minimize variability due to the soil composition, a one to one mixture of US10 field soil and Redi-Earth was used. Although different soil types may impact volatility, using this standard soil mixture helped reduce the impact of this variable. In order to minimize variability of the PUF, all PUFs were purchased from the same vendor. The speed and pressure of the track sprayer were calibrated to deliver 10 GPA when used with a 9501E nozzle tip 16 in. (40.6 cm) above the soil. This was held constant for all soil applications. The amount of soil was standardized to a depth of approximately 1 cm.

Polyurethane Foam Efficiency

To ensure that a single PUF was able to trap the volatile auxin, two PUFs were placed in series and then higher volatility formulations were tested in the closed dome system. For these higher volatility formulations, greater than 90 % of the volatile analyte was trapped by the first PUF. For lower volatility formulations, if 10 % was not trapped on the first PUF, it would not be detected on a second PUF because it would be below the detection limit of the analytical method. Thus, only one PUF was used.

CONTROL SAMPLE

Typically, 12 closed dome systems were placed into the growth chamber and used simultaneously. This allowed for at least three replicates when a total of four different formulations were tested. The data for the replicates were averaged and reported along with the standard error (SE). For dicamba-containing formulations, a sample of Clarity® (dicamba diglycolamine salt) was analyzed with each set to serve as a formulation control sample, and the results were normalized with respect to Clarity. By using Clarity as a control sample, the data from different data sets could be compared.

METHOD PRECISION

The precision of the method was assessed by preparing 12 closed dome systems with Clarity (diluted to a 1.2 % dicamba acid concentration) and then testing them simultaneously. A mean value of 0.0735 ng/L was determined for the 12 systems with a standard deviation of 0.0190 ng/L, a standard error of 0.0055 ng/L, and a 95 % confidence interval of 0.0121 ng/L. Eq 1 was used to calculate the dicamba concentration values.

$$C = (S \times A)/(F \times M \times T) \tag{1}$$

where:

C = ng/L of analyte
S = mL of extraction solvent (20 mL methanol)
A = ng/mL of analyte in extract solution (as determined by LC-MS)
F = air flow rate in SLPM (2 SLPM)
M = 60 min. per h
T = hours of air flow (24 h)

DICAMBA FORMULATIONS

The relative volatilities of several dicamba formulations were assessed: a proprietary dicamba diglycolamine (DGA) salt containing formulation, Clarity (dicamba DGA salt containing formulation), and Banvel® (dicamba dimethylamine [DMA] salt containing formulation). Samples were diluted to a 1.2 % dicamba acid concentration. Fig. 4 demonstrates the normalized volatility of the formulations.

FIG. 4 Closed dome volatility results for dicamba formulations.

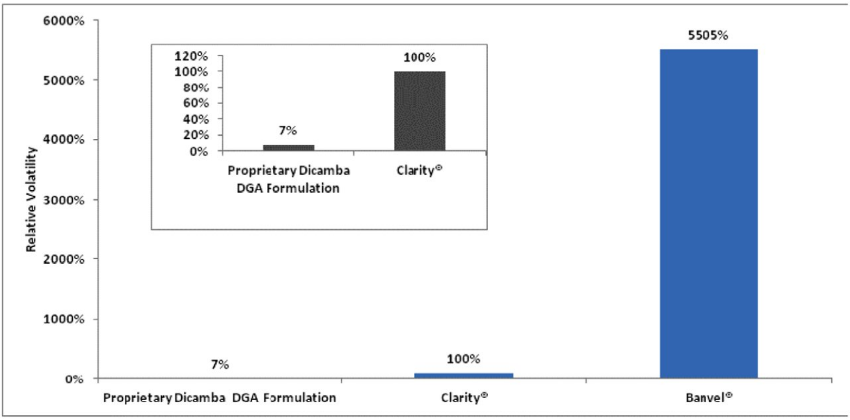
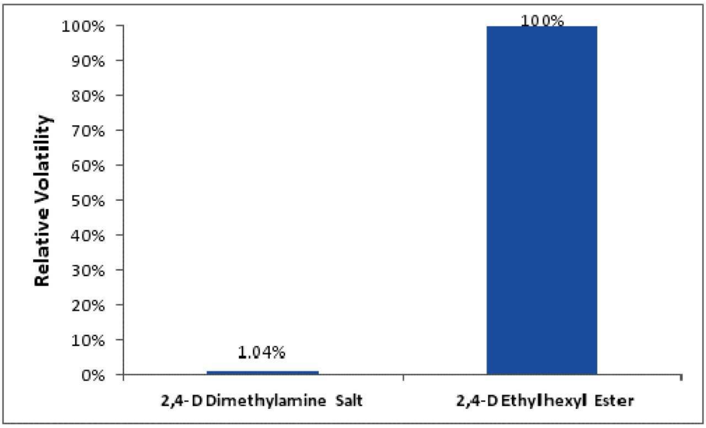


FIG. 5 Closed dome volatility results for 2,4-D samples.



SAMPLES OF 2,4-DICHLOROPHENOXYACETIC ACID

The relative volatilities of 2,4-D dimethylamine salt and 2,4-D ethylhexyl ester, diluted to a 2.4 % 2,4-D acid concentration, were assessed. Fig. 5 demonstrates the relative volatility of each of the two samples.

Conclusion

A closed dome-based method has been developed to determine the relative volatility of auxin-containing herbicide formulations. A description of how to set up the method has been presented along with example data for dicamba and 2,4-D. This method would serve as a valuable tool to determine the effect of formulation changes, adjuvant additions, and overall formulation optimization work with respect to the minimization of auxin volatility.

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Adjuvant Improves Performance of Abamectin Against Spider Mites in Cucumbers

Citation

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ABSTRACT

Spider mites (*Tetranychus urticae*) can attack a wide range of plants. Their infestation of cucumbers (*Cucumis sativus*) may create a serious problem for growers. Abamectin (VERTIMEC®) is one of the acaricides used for control of spider mites. Addition of an emulsifiable and esterified canola oil (Hasten NNP) to abamectin resulted in 90 % control of mites at 14 days after the third treatment. Without the adjuvant, control was 8 % on average. Analysis of the foliar absorbed abamectin demonstrated that the oil adjuvant increased the foliar uptake of abamectin 10-fold on average. Analysis of the abamectin present on and in the cucumber fruits demonstrated that the maximum residue limit (MRL) was not exceeded by the addition of the oil adjuvant. Addition of the adjuvant did not result in any phytotoxicity symptoms or in visible spray residues on the leaves. We believe that the oil adjuvant (Hasten NNP) substantially improves the robustness of abamectin performance against spider mites in cucumbers.

Keywords

abamectin, adjuvant, spider mite, *Tetranychus urticae*, maximum residue limit (MRL)

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Introduction

Greenhouse-grown cucumbers for the fresh market are an important crop for the Netherlands. In 2012, Dutch growers produced 410,000 tons [1]. Most of the production is exported, and approximately 20 % is consumed in the country itself [2]. The acaricide abamectin is used by cucumber growers against several pest organisms. One of the targets is the control of spider mites (*Tetranychus urticae*). A female spider mite lives 2–4 weeks and lays hundreds of eggs. This short reproduction time and the high level of offspring facilitates adaptation of the mites to acaricides [3]. Increased resistance of the spider mites to abamectin has been reported for the San Francisco Valley in the United States [4] and for the state of Pernambuco in Brazil [5]—areas where abamectin is used intensively. As a result, growers are using twice or three times the recommended rate of abamectin [6]. In this study, we investigated whether the addition of an appropriate adjuvant improves the performance of abamectin against spider mites. Because of the lipophilic character of abamectin, we selected an emulsifiable ethylated seed (canola) oil. This adjuvant type can improve the performance and the foliar uptake of abamectin [7].

Materials and Methods

EXPERIMENT 1: TRIAL PERIOD, JUNE 12, 2013–JULY 16, 2013

Plant Material

Cucumbers (cv. Sheila) were grown on hydroponic substrate (rockwool) in a greenhouse at temperatures between 20 and 26°C. Water plus nutrients was supplied via drip irrigation. Plants were spaced two plants/m^2. The tests were conducted at Botany BV, a research facility in Horst-Meterik in the Netherlands.

Artificial Infestation of Plants

The plants were artificially infested by introducing spider mites (*Tetranychus urticae*) from a commercial cultivation of strawberries, at crop BBCH development stages 51 or 61 (40–50 cm in height). Infestation took place by spreading *T. urticae* infested strawberry leaves over the trial plants. As soon as the strawberry leaves started to decay, adult mites migrated to the cucumber plants and there the deposition of eggs began. The artificial infestation was completed when eggs hatched and nymphs of *T. urticae* were present in the cucumber crop.

Treatments

The plants were treated with the acaricide abamectin (VERTIMEC Gold 18EC) with and without emulsifiable ethylated seed oil (Hasten NNP; abbreviation ESO; contents >60 % esterified canola oil and <40 % nonionic surfactants). Abamectin was applied at 12.5 ml and 25 ml VERTIMEC/100 l at a water volume of 1300 l/ha, which is equivalent to 2.9 and 5.8 g ai/ha. The label rate for the application investigated in this study is 5.8 g ai/ha. ESO concentration was 0.25 % (v/v). Only tap water was applied to plants not treated with abamectin. The treatment solutions were applied with a compressed-air backpack sprayer with a spray stick fitted with one hollow cone Birchmeier nozzle, size 1.3 mm.

Efficacy of Treatments

Efficacy was measured according to the European and Mediterranean Plant Protection Organization (EPPO) guideline "*Tetranychus urticae* on Vegetables" (PP 1/37(2)). At the start of the experiment, 30 fully grown and infected leaves were marked. For each assessment, leaf discs (2 cm in diameter) were taken from the marked leaves. The number of *T. urticae* mites (nymphs and adults) and eggs were counted with a binocular. The percentage control of *T. urticae* was calculated according to the Henderson and Tilton formula [8]. Visible leaf damage caused by *T. urticae* was assessed on a percentage area basis (whereby 0 % = no visible damage and 100 % = completely damaged leaf).

Abamectin Analysis in Leaves and Fruits

Leaves (10 fully grown leaves per plot with a total weight of ± 200 g) and fruits (10 mature cucumbers per plot) were harvested for analysis of abamectin contents. On the day of harvest, the leaves were washed twice with an abundant amount of acetone/water mixture (3 : 1 v/v) to remove abamectin from the leaf surface. By application of a known amount of abamectin treatment solution to leaves and immediate harvest, tests have shown that this mixture removes 100 % of any unabsorbed abamectin. Then the leaves were dried and subsequently ground. A sample of the ground material was extracted with a mix of dichloromethane, petroleum ether, and acetone by using an Ultra Turrax immersion blender. A sample of the extract was dried and then dissolved in methanol. The amount of abamectin in the methanol was analyzed by liquid chromatography–tandem mass spectrometry (LC–MS/MS). The harvested fruits were stored at 5°C for five days. The cucumbers were processed and analyzed as described for the leaves but without a washing procedure (Maximum Residue Limit [MRL] protocol).

Phytotoxicity and Visible Spray Residue

Phytotoxicity was monitored according to a scale from 0 to 100 % whereby 0 = no phytotoxicity and 100 = 100 % of the leaf surface shows phytotoxicity symptoms. Visible spray residue on the leaves was monitored according to a 1 to 10 scale whereby: 1–3 = totally unacceptable residue; 4–5 = unacceptable residue; 6–7 = just acceptable residue; 8–9 = totally acceptable residue; and 10 = no visible spray residue.

Experimental Design and Statistics

Each plot was 3 m long by 1.6 m wide, and there were 10 plants per plot. The plots were arranged according to a completely randomized block with four replicates. The plots were treated three times with a 7-days interval. The first treatment was on June 12, 2012. Abamectin efficacy, phytotoxicity, crop development, and visible spray residue were monitored before each treatment and on Day 7 and Day 14 after the third treatment. Leaves for analysis of abamectin were harvested 24 h after Treatments Nos. 1 and 3, and fruits for analysis of abamectin were harvested 72 h after Treatments Nos. 1 and 3.

The percent control and the crop damage data were subjected to analysis of variance using the Agricultural Research Manager (ARM) statistical package software (version 9.1.1; Gylling Data Management, Brookings, SD). After natural logarithmic transformation (ln) of the foliar uptake data, the data were subjected to analysis of variance using the Genstat statistical package (Release 15.3; Rothamsted Experimental Station). The means of treatments were compared according to Fisher's least significant difference (LSD) (0.05) test.

EXPERIMENT 2: TRIAL PERIOD, SEPTEMBER 20, 2013–OCTOBER 25, 2013

The protocol for this experiment was similar to that of Experiment 1; here, we only mention the differences. The plants were artificially infested by introducing spider mites (*Tetranychus urticae*) from roses. Abamectin was applied at one rate: 5.8 g ai/ha with and without ESO. In this test, we did not analyze abamectin residues. The effect of abamectin treatment on mite infestation was monitored by counting the mites (nymphs and adults) on 30 leaves per plot. Numbers of mites were used to classify the infestation according to a scale from $0 = $ no mites to $9 = >500$ mites per leaf. For example, a classification of 5 meant that the number of mites was between 100 and 150 mites per leaf. Classification data were used to calculate percentage control according to the Henderson and Tilton formula. The status of the plants was monitored before each of the three applications and 7, 14, and 21 days after the third treatment.

Results and Discussion

EFFICACY

Experiments 1 and 2 (Tables 1–3 and Tables 5–6, respectively) demonstrate that, without adjuvant, the recommended rate of abamectin for this application (5.8 g ai/ha) and half of the recommended rate (Tables 1–3) were not quite effective against the spider mites. In spite of that, there was a dose effect of abamectin alone based on control of nymphs plus adults (Table 1). With the recommended rate, the control of spider mite nymphs plus adults averaged over time in Experiment 1 was 10.5 %, and the average control based on the counting of eggs was 9 %. In Experiment 2, the control of spider mite nymphs plus adults averaged over time was 37.5 %. The activity of abamectin without adjuvant was higher in Experiment 2. This may be related to a different source of spider mites (see Materials and Methods section), or it may relate to the fact that the average population of mites at the start (on the day of the first treatment) was 10 per leaf in Experiment 1 and 5 per leaf in Experiment 2.

In Experiments 1 and 2, addition of ESO had a substantial (and in most time points) statistically significant effect on the performance of abamectin against spider

TABLE 1 Experiment 1—Effect of ESO on the performance of abamectin against *T. urticae* (nymphs plus adults).

	Control of *T. urticae* nymphs plus adults (%)			
Treatment	**7 DAT No. 1**[1]	**7 DAT No. 2**	**7 DAT No. 3**	**14 DAT No. 3**
Abamectin ½ rate[2]	3	5.7	1.5	0
Abamectin ½ rate + ESO[3]	14.2	83.0	91.5	94.7
Abamectin full rate[2]	4.2	19.6	18.9	0
Abamectin full rate + ESO	51.7	91.1	97.5	96.4
LSD(0.05)	25.9	13.2	15.3	4.8

[1] 7 days after treatment (DAT) No. 1.
[2] ½ rate is 2.9 g ai/ha; full rate is 5.8 g ai/ha.
[3] ESO concentration is 0.25 %.

mites (Tables 1, 2, and 5). At 14 days after the third treatment, ESO addition resulted in a >90 % control of nymphs plus adults (Tables 1 and 5). ESO addition resulted in a control of eggs >80 % at 14 days after treatment in Experiment 1 (Table 2). Averaged over time and taking the recommended rate of abamectin, ESO increased control of nymphs and adults in Experiment 1 from 10.5 % to 84.2 % (Table 1) and in Experiment 2 from 37.5 % to 77.5 % (Table 5). ESO increased average control of eggs in Experiment 1 from 9 % to 80.3 % (Table 2).

The results on crop damage caused by the spider mites followed the same patterns as observed with the control of the mites and egg populations (Tables 3 and 6). Averaged over time and using the recommended rate of abamectin, ESO reduced the crop damage from 37.9 % to 15.3 % in Experiment 1 and from 19.5 % to 6 % in Experiment 2. At later time points, the ESO effect was much more pronounced on crop damage, which reflects the substantial ESO effect on mite population growth.

In a third experiment (data not shown) conducted according to a protocol similar to that of Experiments 1 and 2, we verified that the ESO effect is not caused by a possible acaricide effect of ESO itself. There was no ESO effect on the spider mite

TABLE 2. Experiment 1—Effect of ESO on the performance of abamectin against *T. urticae* (eggs).

	Control of *T. urticae* eggs (%)			
Treatment	**7 DAT No. 1**[1]	**7 DAT No. 2**	**7 DAT No. 3**	**14 DAT No. 3**
Abamectin ½ rate[2]	27.8	14.6	10.3	0.4
Abamectin ½ rate + ESO[3]	48.7	70.8	84.4	83.8
Abamectin full rate[2]	12.6	12.0	11.2	0
Abamectin full rate + ESO	64.4	79.7	91.7	85.2
LSD(0.05)	29.1	24.5	19.7	18.6

[1] 7 days after treatment (DAT) No. 1.
[2] ½ rate is 2.9 g ai/ha; full rate is 5.8 g ai/ha.
[3] ESO concentration is 0.25 %.

TABLE 3 Experiment 1—Effect of ESO on the performance of abamectin against *T. urticae* (crop damage).

	Control of *T. urticae* crop damage (% area)			
Treatment	**7 DAT No. 1[1]**	**7 DAT No. 2**	**7 DAT No. 3**	**14 DAT No. 3**
Water	36.3	71.3	81.3	80
Abamectin ½ rate[2]	21.3	41.3	52.5	73.8
Abamectin ½ rate + ESO[3]	20	18.8	22.5	21.3
Abamectin full rate[2]	26.3	31.3	36.3	57.5
Abamectin full rate + ESO	17.5	13.8	15	15
LSD(0.05)	17.4	19.1	18.5	14.5

[1] 7 days after treatment (DAT) No. 1.
[2] ½ rate is 2.9 g ai/ha; full rate is 5.8 g ai/ha.
[3] ESO concentration is 0.25 %.

population. This means that the ESO effect can be ascribed to a better performance by abamectin.

ABAMECTIN IN THE LEAVES

Addition of ESO resulted in a much higher abamectin content in the leaves (Table 4). In leaves sampled 24 h after Treatment 1, the abamectin contents increased eight-fold and almost 20-fold at the half and full recommended rate of abamectin, respectively. In leaves sampled after Treatment 3, ESO increased the abamectin contents 8-fold and 6-fold at the half and full recommended rate of abamectin, respectively. Because spider mites puncture the plant cells on the underside of the leaves to feed [9] and taking into account the predominantly translaminar and limited systemic character of abamectin [10], it seems reasonable to conclude that increased abamectin content in the leaves resulted in the better abamectin performance in the presence of ESO.

TABLE 4 Experiment 1—Effect of ESO on the foliar uptake of abamectin by cucumber leaves.

	Foliar uptake of abamectin (mg ai/kg FW)[1]	
Treatment	**1 DAT No. 1**	**1 DAT No. 3**
Abamectin ½ rate[2]	0.01 a	0.02 a
Abamectin ½ rate + ESO[3]	0.08 b	0.16 b
Abamectin full rate[2]	0.02 c	0.06 a
Abamectin full rate + ESO	0.39 d	0.35 b

[1] The geometric means of the values were compared using Fisher's LSD (0.05) test, and the arithmetic means are presented. Means within one column and for the same factor followed by the same letter do not differ at the 5 % probability level.
[2] ½ rate is 2.9 g ai/ha; full rate is 5.8 g ai/ha.
[3] ESO concentration is 0.25 %.

TABLE 5 Experiment 2—Effect of ESO on the performance of abamectin against *T. urticae* (nymphs plus adults).

Treatment	Control of *T. urticae* nymphs plus adults (%)				
	7 DAT No. 1	7 DAT No. 2	7 DAT No. 3	14 DAT No. 3	21 DAT No. 3
Abamectin[1]	70	35	30.4	33.6	18.3
Abamectin[1] + ESO[2]	76.5	58.9	73.3	92.4	86.2
LSD(0.05)	35.1	39.9	34.7	25	34.5

[1] Abamectin rate 5.8 g ai/ha.
[2] ESO at 0.25 %.

The abamectin content 24 h after Treatment 3 is higher than the content 24 h after Treatment 1, with the exception of the recommended rate plus ESO. This may relate to abamectin that was absorbed after Treatments 1 and 2 still being present 24 h after Treatment 3. Taking into account the half-life time period of 2.4 days reported for abamectin degradation in cucumbers grown under field conditions [11], it is doubtful whether there is a strong accumulation of abamectin in the leaves under the test conditions of Experiment 1. However, we cannot exclude certain accumulation.

A higher abamectin content in the leaves may be caused by enhanced retention of the treatment solution by the leaves and by increased foliar uptake from an individual drop deposit. Visual assessment of the cucumber leaves after spraying gave the impression that the amount of treatment solution retained by the leaves is not affected much by inclusion of ESO. This means that increased foliar uptake of abamectin in the presence of ESO is most likely the important factor that explains the higher contents of abamectin in the leaves.

ABAMECTIN ANALYSIS WITH THE CUCUMBERS

With all of the cucumber samples (totally 32 samples from plants treated with abamectin in Experiment 1), the amount of abamectin did not exceed the detection limit of 0.01 mg/kg fresh weight of cucumbers. Because the MRL is 0.02 mg/kg [12],

TABLE 6 Experiment 2—Effect of ESO on the performance of abamectin against *T. urticae* (crop damage).

Treatment	Control of *T. urticae* crop damage (% area)				
	7 DAT No. 1	7 DAT No. 2	7 DAT No. 3	14 DAT No. 3	21 DAT No. 3
Water	3.8	13.3	37.7	59.9	70
Abamectin[1]	1.7	5	13.1	25.2	52.5
Abamectin[1] + ESO[2]	1.5	4.8	7.8	6.5	9.3
LSD(0.05)	1	4.6	23.3	27.3	31.5

[1] Abamectin rate 5.8 g ai/ha.
[2] ESO at 0.25 %.

we conclude that all treatments did not exceed the MRL. We think that the translaminar character of abamectin [10] explains this outcome.

PHYTOTOXICITY AND VISIBLE SPRAY RESIDUE

In Experiments 1 and 2, application of abamectin with and without ESO did not result in any phytotoxicity symptoms or in visible spray residues on the leaves (data not shown). Therefore, we conclude that the rate of abamectin (5.8 g ai/ha) recommended for cucumbers can be combined with the ESO Hasten at 0.25 % without deleterious effects on the cucumber plants.

The practice of many growers mixing various active ingredients can create a risk when ESO is added to a mix that also includes abamectin. The foliar uptake of other "hard for the plant" active ingredients may be enhanced as well and, with inclusion of systemic active ingredients, one has to pay attention to the MRLs.

Our study demonstrates that the addition of an appropriate adjuvant to abamectin is an effective and pragmatic solution for overcoming the observed lower susceptibility of spider mites to abamectin. A lower frequency of abamectin applications may create a more definitive solution.

Conclusions

Emulsifiable ethylated seed oil (Hasten NNP) strongly improved the performance of abamectin against spider mites in cucumbers. The adjuvant substantially increased the abamectin contents in the leaves, and this explains the better performance. Addition of the adjuvant did not result in any phytotoxicity symptoms or in visible spray residues on the leaves and did not result in exceeding the MRL for cucumbers.

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Ammonium Sulfate and Dipotassium Phosphate as Water Conditioning Adjuvants

Citation

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ABSTRACT

Glyphosate and dicamba are weak acid herbicides that can bind with antagonistic salts in the spray carrier. Ammonium sulfate (AMS) is commonly used as an adjuvant with glyphosate to enhance activity and overcome antagonistic salts. Dicamba use in resistant soybean will restrict addition of AMS due to the potential to form the ammonium salt of dicamba, considered more volatile than the applied form of dicamba, thus increasing risk of injury to nearby susceptible crops. Dipotassium phosphate (DPP) as a substitute for AMS does not contain nitrogen. DPP can partially overcome antagonism from minerals in the spray solution but is ineffective in reducing dicamba antagonism of clethodim. The margin of separation is greater on species that are particularly responsive to AMS in hard water. In addition to water conditioning properties of sulfate, ammonium in AMS increases herbicide absorption and translocation. The positively charged potassium from DPP is a weak herbicide antagonist and, even at low amounts, may reduce herbicide efficacy. Because DPP may condition water through the phosphate anion, the compound is void of nitrogen, which may explain why DPP does not exhibit the same level of overcoming mineral and herbicide antagonism as AMS.

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Keywords
water conditioner, adjuvants, glyphosate, ammonium sulfate, dipotassium phosphate

Introduction

Glyphosate is hydrophilic, nonvolatile, nonphotodegraded, and is a weak acid compound as measured by the acid dissociation constant [1]. Various surfactants enhance phytotoxicity of formulated glyphosate [2–4]. Glyphosate is enhanced by ammonium through increased uptake across the leaf cuticle [5]. Glyphosate is antagonized by cationic salts in spray water [6,7]. Surfactants or oil adjuvants do not overcome cation antagonism, and oil adjuvants may further antagonize glyphosate activity [3]. Glyphosate labels and many other postemergence herbicide labels recommend adding dry ammonium sulfate (AMS) at 8.5 to 17 lb/100 gal of water to the spray solution prior to adding herbicides. Addition of AMS to the spray solution enhances herbicide phytotoxicity by overcoming the antagonistic effects of cationic salts in hard water [8–10]. The ammonium ion can outcompete the antagonistic cations, complexing with weak acid herbicides. The sulfate anions bind to antagonistic cations in the spray solution, the precipitate of which thereby prevents interference with herbicide absorption. Both processes contribute to water conditioning activity.

Soybean has been genetically transformed resulting in resistance to glyphosate and dicamba. Dicamba has been formulated as a diglycol amine (DGA) salt and a bis(3-aminopropyl)methyl amine salt (BAPMA) with each salt increasingly less volatile than the original dimethyl amine salt formulation [1]. Less volatile DGA and BAPMA of dicamba will be registered in dicamba resistant soybean to reduce risk of dicamba injury to susceptible crops. AMS will be restricted for use with dicamba in this soybean technology because the potential formation of the ammonium salt of dicamba has been considered more volatile than the marketed dicamba salt. Many adjuvants classified as water conditioners contain nitrogen and will be restricted from use. Dipotassium phosphate (DPP) has been introduced as a substitute for AMS. DPP does not contain nitrogen; however, the potassium does have the potential to form the potassium salt of dicamba, which also may be more volatile than the marketed dicamba formulation.

The objectives of this research were to compare water conditioning and overcoming herbicide antagonism from AMS, commercial adjuvants that contain AMS, and DPP at different rates.

Materials and Methods

Field experiments were conducted in 2014 in West Lafayette, IN; Macomb, IL; Fargo, ND; and Hillsboro, ND. Plant species used as assay species at each location were as follows:

- Indiana: Velvetleaf (*Abutilon theophrasti* Medik.) and common lambsquarters (*Chenopodium album L.*)
- Illinois: Velvetleaf, amaranth (*Amaranthus cruentus* L.), tall waterhemp (*Amaranthus rudis* Wood), sunflower (*Helianthus annuus L.*), sorghum (*sorghum bicolor*), and conventional corn (*Zea mays* L.)
- North Dakota (Fargo): Flax (*Linum usitatissimum* L.), redroot pigweed (*Amaranthus retroflexus L.*), wild mustard (*Sinapis arvensis L.*), Venice mallow (*Hibiscus trionum* L.), curly dock (*Rumex crispus L.*), tame buckwheat (*Fagopyrum esculentum* Moench), and wild buckwheat (*Polygonum convolvulus L.*)
- North Dakota (Hillsboro): Flax, amaranth, sunflower, barley (*Hordeum vulgare L.*), foxtail millet (*Setaria italica (L.) Beauv.*), and conventional corn

Each assay species used was either from the natural infestation or was planted in strips across the entire plot area to ensure uniform populations and uniform stages of plant growth at herbicide application. Velvetleaf is particularly susceptible to effective conditioning of hard water. However, velvetleaf does not occur naturally in North Dakota and was not planted at trial locations there.

Treatments were applied perpendicular to assay species to the center 2 m of the 3 m wide by 12 m long plots with a backpack-type plot sprayer delivering 79 to 93 L/ha at 138 kPa through Turbo TeeJet[5] 11001/110015 nozzles. Assay species were 10 to 60 cm tall at application.

Each experiment had a randomized complete block design (RCBD) with four replicates. Herbicide phytotoxicity was visually estimated on assay species 28 days after treatment (DAT) based on a scale of 0–100 %, with 0 equal to no plant damage, and 100 equal to complete plant death. The data were analyzed through analysis of variance in Statistical Analysis Systems (SAS) software.[6] Because some species either did not show treatment separation or were completely killed, data from species were included only when significant treatment differences occurred. F-test results were considered significant at $P \leq 0.05$, and separation of means calculated with an F-protected least significant difference test at $\alpha = 0.05$. The variance from all locations was similar, and all data were combined across locations.

GLYPHOSATE PLUS DICAMBA TREATMENTS

A commercial formulation of glyphosate-potassium salt containing 0.54 kg acid equivalent (or ae)/L (Roundup PowerMax®)[7] was applied at 48 g acid equivalent (or ae)/ha with dicamba-diglycolamine salt containing 0.48 kg acid equivalent (or ae)/L (Clarity®)[8] at 24 g/ha. Both herbicide rates were 40 % of the projected use rate of the combined commercial mixture. The low rates were used to accentuate

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[5] TeeJet TT11001 and TT11015 flat fan nozzles, Spraying Systems Co., P.O. Box 7900, N. Ave., Wheaton, IL 60788.

[6] Statistical Analysis Software 2003, version 9.1, SAS Institute Inc., 100 SAS Campus Dr., Cary, IL 87513.

[7] Monsanto Company, 800 N. Lindbergh Blvd., St. Louis, MO 63167.

[8] BASF, 26 Davis Drive, Research Triangle Park, NC 27709.

treatment differences. Nonionic surfactant (NIS) (R-11®)[9] was applied in all treatments at 0.25 % volume per volume (v/v). Glyphosate plus dicamba plus NIS was applied alone in distilled water and in water with 1000 ppm hardness for standards to compare the level of water conditioning from ammonium sulfate (AMS) and 50 % solid dipotassium phosphate (DPP). Water at 1000 ppm hardness was made by adding 13.45 g CaCl2 - 2 H2O plus 4.62 MgCl2 - 6 H2O in 11.36 L of water.

Glyphosate plus dicamba plus NIS was applied with dry soluble AMS at 3, 6, 9, 12, and 15 lb/100 gal of water or with DPP at 0.5, 1, 1.5, 2, and 2.5 % v/v. Glyphosate plus dicamba plus NIS was also applied with monocarbamide dihydrogensulfate (AMADS) at 0.5 % v/v and with five commercial water conditioner (WC) adjuvants: WC (Request®),[10] AMADS plus WC (Brimstone®)[9] at 1 % v/v, AMS + WC (Bronc Max® and Transport™)[9,11] at 1 % v/v, and AMS + NIS (Class Act NG™)[12] at 2.5 % v/v.

CLETHODIM PLUS DICAMBA TREATMENTS

A commercial formulation of clethodim containing 0.12 kg active ingredient (or ai)/L (Select Max)[13] was applied at 0.75 g/ha with dicamba-diglycolamine salt containing 0.48 kg/L (Clarity)[8] at 45 g/ha. The herbicide rates of clethodim and dicamba were within the use ranges in registered crops and were used to evaluate the ability of AMS and DPP to overcome dicamba antagonism of clethodim. Clethodim plus dicamba was applied with the following commercial adjuvants: NIS (R-11)[9] at 0.25 % v/v, petroleum oil concentrate (POC) (Herbimax)[14] at 2 Pt/A, high surfactant (methylated) oil concentrate (HSMOC) (Destiny HC)[12] at 1 Pt/A. These herbicide and adjuvant combinations were applied with dry soluble AMS at 9 lb/100 gal of water or with DPP at 2 % v/v. Monocarbamide dihydrogensulfate (AMADS) and five commercial WC adjuvants were also applied with clethodim and dicamba.

Results and Discussion

AMS was applied from 3 to 15 lb/100 gal of water, and DPP was applied from 0.5 to 2.5 % v/v (**Fig. 1**). Different rates of AMS can be compared to different rates of DPP based on various criteria:

- Criteria #1—Field use rates: AMS at 9 lb/100 gal of water compared to DPP at 2 % v/v, which are recommended use rates for each chemical.
- Criteria #2—AMS at 12 lb/100 gal of water compared to DPP at 2 % v/v. DPP is a liquid formulation containing 50 % DPP weight per weight (w/w) and 50 % DPP w/w. DPP has a density of 1.53 g/ml, which yields 6.378 lb DPP/gal. DPP at 2 % v/v equals 12.76 lb DPP/100 gal of water.

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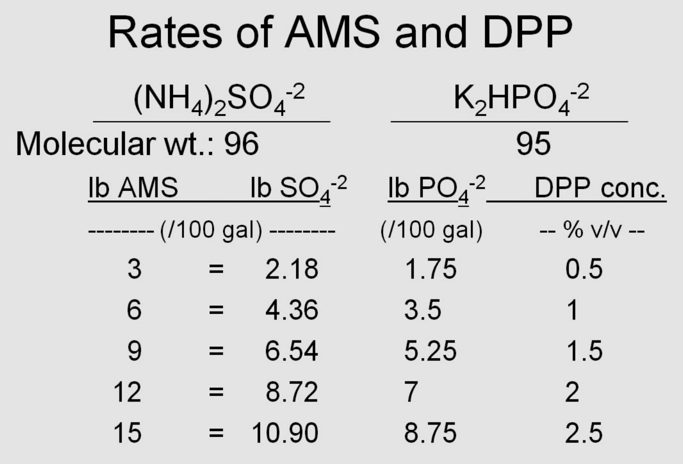
[9] Wilbur-Ellis, 345 California St., 27th Floor, San Francisco, CA 94104.
[10] Helena, 225 Schilling Blvd., Suite 300, Collierville, TN 38017.
[11] Precision Laboratories, 1429 S. Shields Dr., Waukegan, IL 60085.
[12] Winfield Solutions LLC, P.O. Box 64589, St. Paul, MN 55164.
[13] Valent U.S.A. Corporation, 1600 Riviera Ave. #200, Walnut Creek, CA 94596.
[14] Loveland Products Inc., 3005 Rocky Mountain Ave., Loveland, CO 80538.

FIG. 1 Rates of ammonium sulfate (AMS) and dipotassium phosphate (DPP) used in field research with corresponding amounts of sulfate and phosphate.



Rates of AMS and DPP

$(NH_4)_2SO_4^{-2}$			$K_2HPO_4^{-2}$	
Molecular wt.: 96			95	
lb AMS		lb SO_4^{-2}	lb PO_4^{-2}	DPP conc.
-------- (/100 gal) --------			(/100 gal)	-- % v/v --
3	=	2.18	1.75	0.5
6	=	4.36	3.5	1
9	=	6.54	5.25	1.5
12	=	8.72	7	2
15	=	10.90	8.75	2.5

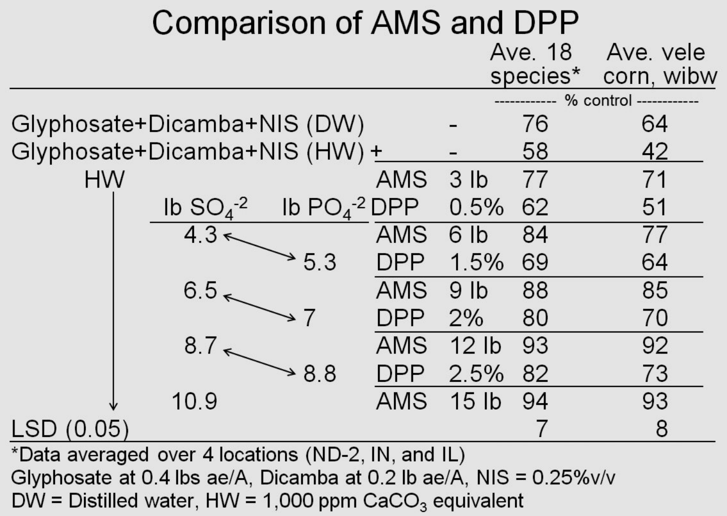
- Criteria #3—Amount of sulfate compared to phosphate. The molecular weights of sulfate and phosphate are 96 and 95, respectively. The amount of sulfate in AMS from 3 to 15 lb/100 gal of water and the amount of phosphate in DPP from 0.5 to 2.5 % v/v is shown in Fig. 1. The amount of sulfate in AMS at 9 lb/100 gal of water (6.54 lb) is similar to the amount of phosphate in DPP at 2 % v/v (7 lb). A different comparison shows the amount of sulfate in AMS at 12 lb/100 gal of water (8.72 lb) is similar to the amount of phosphate in DPP at 2.5 % v/v (8.75 lb).

Weed control, when AMS was used to condition water and overcome hard water antagonism, was greater compared to similar rates of DPP when data was averaged over 18 weed species (Fig. 2). There was a greater range in weed control between similar rates of AMS and DPP in velvetleaf, corn, and wild buckwheat, which are species that show a greater response to AMS. Velvetleaf and corn have been used as indicator species to AMS with previous water conditioning research [11,12]. Wild buckwheat also demonstrated a greater response to AMS compared to DPP.

DPP partially overcame mineral antagonism because weed control was greater from all rates of DPP than herbicides applied in hard water with no WC used, but values were lower than AMS in most similar rate comparisons (Fig. 2). Using Criteria 1, 2, and 3, weed control from DPP was significantly lower than AMS except when DPP was added at 2.5 % v/v and compared to AMS at 9 lb/100 gal of water, which provided 82 % and 88 % control, respectively.

Commercial AMS plus NIS adjuvant applied at 2.5 % v/v contains AMS at 8.5 lb/100 gal of water and overcame hard water antagonism similar to AMS at 8.5 lb/100 gal of water (91 % and 88 %) (Fig. 3). All other commercial adjuvants were

FIG. 2 Effect of ammonium sulfate and dipotassium phosphate on the efficacy of glyphosate plus dicamba. Glyphosate plus dicamba plus nonionic surfactant (NIS) applied in distilled water (DW) or 1000 parts per million (ppm) hard water (HW) with ammonium sulfate (AMS) or dipotassium phosphate (DPP) at different rates; vele = velvetleaf, wibw = wild buckwheat.



Comparison of AMS and DPP

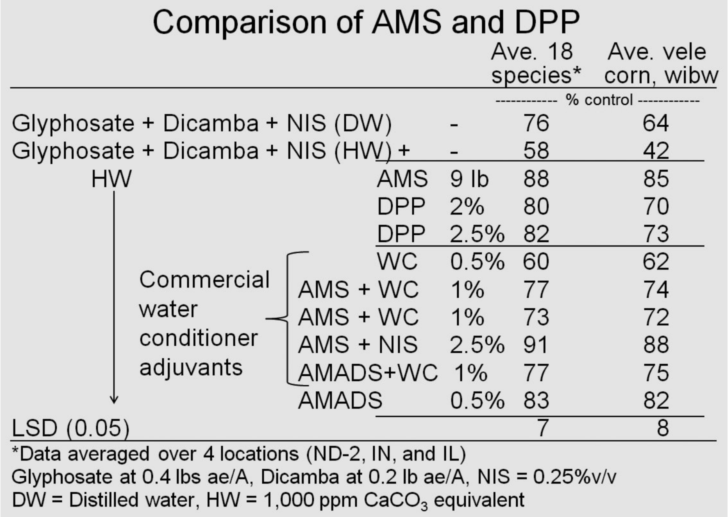
	lb SO_4^{-2}	lb PO_4^{-2}			Ave. 18 species*	Ave. vele corn, wibw
					% control	% control
Glyphosate+Dicamba+NIS (DW)				-	76	64
Glyphosate+Dicamba+NIS (HW) +				-	58	42
HW			AMS	3 lb	77	71
			DPP	0.5%	62	51
	4.3		AMS	6 lb	84	77
		5.3	DPP	1.5%	69	64
	6.5		AMS	9 lb	88	85
		7	DPP	2%	80	70
	8.7		AMS	12 lb	93	92
		8.8	DPP	2.5%	82	73
	10.9		AMS	15 lb	94	93
LSD (0.05)					7	8

*Data averaged over 4 locations (ND-2, IN, and IL)
Glyphosate at 0.4 lbs ae/A, Dicamba at 0.2 lb ae/A, NIS = 0.25%v/v
DW = Distilled water, HW = 1,000 ppm $CaCO_3$ equivalent

applied at lower rates and contained less AMS or AMS replacement adjuvants, which resulted in less weed control. AMADS, a component in many acidic AMS replacement adjuvants, applied at 1 % v/v was equal to AMS (83 and 88 %). Zollinger et al. [13] reported that sulfuric acid in AMADS forming sulfate, when reacting with water, overcame antagonistic salt antagonism of glyphosate. The conversion of urea to ammonia is null to slow in a dry environment. In the presence of water, urea can rapidly hydrolyze to form ammonia. The conversion of urea to ammonium and carbon dioxide is controlled by several factors including pH. A moist and high pH environment increases the rate of conversion but, in low pH, the conversion of urea to ammonia is slow. The sulfuric acid in AMADS decreases the spray solution pH to near 2. It can be assumed that the low pH significantly reduces the release of ammonium from urea in AMADS, but the ammonium formed from the slow conversion can enhance herbicide activity similar to the ammonium in AMS.

Dicamba antagonizes clethodim activity on grass species (Fig. 4). The antagonism is reduced but not overcome by adding NIS, POC, or HSMOC. Grass control is reduced by tank mixtures or by close interval application of most acetyl CoA carboxylase (ACCase) (Group 2) herbicides, with postemergence herbicides used for broadleaf weed control. Grass antagonism can be avoided by applying a higher rate of the grass herbicide or by applying the grass herbicide one or more days before or

FIG. 3 Effect of ammonium sulfate and dipotassium phosphate on the efficacy of glyphosate plus dicamba. Glyphosate plus dicamba plus nonionic surfactant (NIS) applied in distilled water (DW) or 1000 ppm hard water (HW) with ammonium sulfate (AMS), dipotassium phosphate (DPP), or commercial adjuvants added at different rates; vele = velvetleaf, wibw = wild buckwheat.



Comparison of AMS and DPP

			Ave. 18 species*	Ave. vele corn, wibw
			% control	
Glyphosate + Dicamba + NIS (DW)		-	76	64
Glyphosate + Dicamba + NIS (HW) +		-	58	42
HW	AMS	9 lb	88	85
	DPP	2%	80	70
	DPP	2.5%	82	73
Commercial water conditioner adjuvants	WC	0.5%	60	62
	AMS + WC	1%	77	74
	AMS + WC	1%	73	72
	AMS + NIS	2.5%	91	88
	AMADS+WC	1%	77	75
	AMADS	0.5%	83	82
LSD (0.05)			7	8

*Data averaged over 4 locations (ND-2, IN, and IL)
Glyphosate at 0.4 lbs ae/A, Dicamba at 0.2 lb ae/A, NIS = 0.25%v/v
DW = Distilled water, HW = 1,000 ppm $CaCO_3$ equivalent

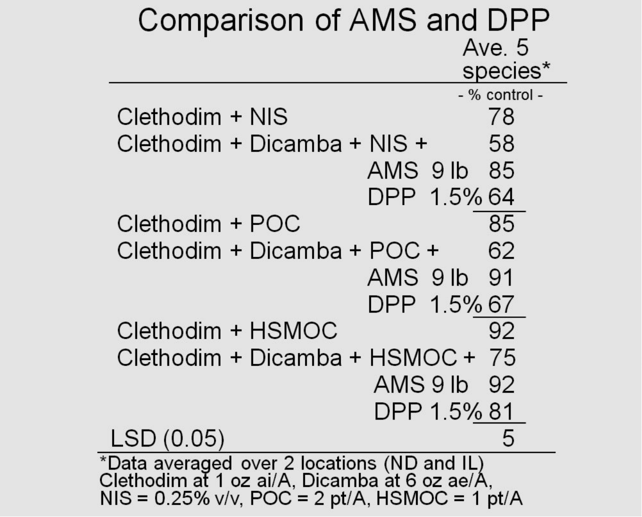
seven days after the broadleaf control herbicide. These results show that AMS can overcome dicamba antagonism of clethodim and can provide a higher level of grass control when applied with NIS and oil adjuvants. DPP at 2 % v/v had a negligible effect in overcoming dicamba antagonism and was not significantly different with POC. These data show the high level of response of corn and other grass assay species to the conditioning activity of any treatment containing AMS.

AMS plus NIS adjuvant applied at 2.5 % v/v enhanced herbicides' activity to provide a level of grass control similar to AMS at 8.5 lb/100 gal of water (90 % and 86 %) (Fig. 5). AMADS and most other commercial adjuvants improved weed control near the level of AMS.

The results of these studies conducted over a wide geographic region and across a wide spectrum of plant species show AMS as an effective water conditioner for hard water and chemical antagonism of herbicides. DPP also conditions water but not at the same level as AMS. Data averaged across 18 plant species show DPP to be limited in water conditioning, but the margin of separation is even greater on species that are particularly responsive to AMS. Velvetleaf, corn, and wild buckwheat were good indicators of antagonism and show the conditioning ability of AMS compared to DPP.

Rates of the commercial mixture of glyphosate and dicamba may be 1 and 0.5 lb/A, respectively. High rates of both herbicides may overcome the reduction in

FIG. 4 Effect of ammonium sulfate and dipotassium phosphate on the efficacy of clethodim. Clethodim plus dicamba plus ammonium sulfate (AMS) at 9 lb/100 gal of water or dipotassium phosphate (DPP) at 2 % v/v applied with nonionic surfactant (NIS), petroleum oil concentrate (POC), or high surfactant methylated oil concentrate (HSMOC) adjuvants.



Comparison of AMS and DPP

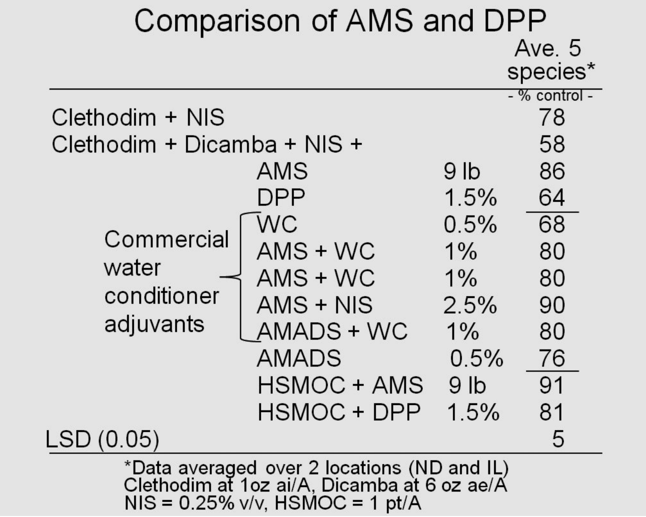
	Ave. 5 species*
	- % control -
Clethodim + NIS	78
Clethodim + Dicamba + NIS +	58
AMS 9 lb	85
DPP 1.5%	64
Clethodim + POC	85
Clethodim + Dicamba + POC +	62
AMS 9 lb	91
DPP 1.5%	67
Clethodim + HSMOC	92
Clethodim + Dicamba + HSMOC +	75
AMS 9 lb	92
DPP 1.5%	81
LSD (0.05)	5

*Data averaged over 2 locations (ND and IL)
Clethodim at 1 oz ai/A, Dicamba at 6 oz ae/A,
NIS = 0.25% v/v, POC = 2 pt/A, HSMOC = 1 pt/A

water conditioning from DPP, but utilizing this concept will not optimize herbicides used in dicamba resistant soybean technology. Lack of herbicide optimization may result in reduced weed control from weeds taller than recommended and weeds marginally controlled. The progeny of weeds that escape herbicide phytotoxicity may contribute to development of herbicide resistance.

DPP can partially, and AMS can completely, overcome herbicide antagonism from minerals in water and from herbicides in tank mixture. The herbicide moiety to condition water is from the sulfate and phosphate. The positively charged potassium and ammonium ions also affect herbicide activity. Potassium was shown by Nalewaja and Matysiak [14] to be a weak antagonist of herbicide activity. The potassium in DPP may not accumulate in a large amount, but the antagonism from any added potassium may contribute to less herbicide activity. Several researchers have demonstrated ammonium to be highly active in increasing herbicide absorption and translocation [15–17]. Gronwald et al. [16] proposed a model whereby absorption of most all weak acid herbicides is increased from ammonium. After absorption into the cell wall, ammonium is transported across the plasma membrane into the cytoplast and converted to ammonia for protein synthesis. The free proton is transported back across the plasma membrane into the cell wall via an ATPase enzyme creating a pH gradient: cytoplasm = pH 7, cell wall = pH 5. The more acidic pH in the cell wall

FIG. 5 Effect of ammonium sulfate and dipotassium phosphate on the efficacy of clethodim plus dicamba. Clethodim plus dicamba plus ammonium sulfate (AMS), dipotassium phosphate (DPP) with nonionic surfactant (NIS) or high surfactant methylated oil concentrate (HSMOC) adjuvants, or with commercial adjuvants at various rates; AMADS = monocarbamide dihydrogensulfate, WC = non-AMS water conditioner.



Comparison of AMS and DPP

			Ave. 5 species* - % control -
Clethodim + NIS			78
Clethodim + Dicamba + NIS +			58
	AMS	9 lb	86
	DPP	1.5%	64
Commercial water conditioner adjuvants	WC	0.5%	68
	AMS + WC	1%	80
	AMS + WC	1%	80
	AMS + NIS	2.5%	90
	AMADS + WC	1%	80
	AMADS	0.5%	76
	HSMOC + AMS	9 lb	91
	HSMOC + DPP	1.5%	81
LSD (0.05)			5

*Data averaged over 2 locations (ND and IL)
Clethodim at 1oz ai/A, Dicamba at 6 oz ae/A
NIS = 0.25% v/v, HSMOC = 1 pt/A

causes weak acid herbicide conversion into the acid form, which is more readily transported across the plasma membrane. Inside the cytoplasm, the herbicide is then converted back to the ionic form causing ion trapping of weak acid herbicide molecules and translocation throughout the plant. This model explains the AMS enhancement of weak acid herbicides. Because DPP is void of nitrogen, this may also explain why DPP does not exhibit the same ability to overcome mineral and herbicide antagonism as does AMS.

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Effects of Spray Adjuvants on Spray Droplet Size from a Rotary Atomizer

Citation

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ABSTRACT

Rotary atomizers are used in a number of aerial applications, such as forest pest spraying and mosquito control sprays. These types of atomizers have a rotating cage at speeds of 2,000 to 10,000 revolutions per minute (rpm) through which a spray is emitted and atomized. Many applicators routinely add spray adjuvants to change the droplet size, reduce drift potential, or to reduce evaporative effects of a particular spray solution; therefore, six commonly used classes of spray adjuvants were evaluated to determine their effects on droplet size. If an applicator's only concern was minimizing spray drift, the applicator could choose a polymer or high surfactant oil concentrate for helicopter speeds and a polymer for fixed-wing applications. For applicators working under hot, dry conditions where evaporation is a concern, choosing an oil-based adjuvant to help get better coverage by creating smaller droplets that do not evaporate would be recommended. Understanding the role the different adjuvant types play in the final droplet size of the spray is key to successfully setting up and making applications with rotary atomizers.

Keywords

droplet size, rotary atomizer, spray adjuvants

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Introduction

Rotary atomizers are best known for their uniform droplet spectra compared to conventional high-pressure nozzles, and they are commonly used in forestry and vector control spray applications as well as in some row crop applications [1,2]. These nozzles are designed to rotate at 2,000 to 10,000 revolutions per minute (rpm), and the spray is emitted radially through a mesh or a perforated cylinder [3]. Droplet size of the rotary atomizer can be changed through modifications in spray pressure and flow rate [4,5], but it is primarily influenced by the rotational speed [5]. Formulation types and physical properties such as viscosity and surface tension also play a critical role in determining the spray droplet size spectrum [6–9].

Teske et al. [2] developed a drop size distribution database for two rotary atomizers under various tank mix, flow rate, airspeed, and blade angle conditions based on wind tunnel measurements. Their test results confirm that the main factor affecting droplet size is the rotation rate of the atomizer. At higher flow rates and lower airspeeds, rotation rates were slower and the sprays were therefore coarser. Higher airspeeds caused more air shear across the atomizer, which produced finer sprays. Flow rate by itself did not have a large effect on atomization. However, tank mix had a large impact on droplet size. The tank mixes with low dynamic surface tension (water with a seed oil) produced the finest sprays, the tank mixes with high extensional viscosity (water with a polyacrylamide) produced the coarsest sprays, with water alone being the intermediate between the other two.

More recently, Fritz et al. [10] examined the influence of both adjuvant type (modified vegetable oil, methylated seed oil, and polymer) and airspeed (53.6, 62.6, and 71.5 m/s) on droplet size in the presence of a formulated glyphosate product using a Micronair AU5000 rotary atomizer (Micronair, Bromyard, Herefordshire, UK). The oil-based adjuvant solutions decreased $D_{v0.1}$, $D_{v0.5}$, and $D_{v0.9}$ values relative to the other solutions tested (water-only, glyphosate-only, and glyphosate plus a polymer). The glyphosate-only and glyphosate plus a polymer yielded similar results, but the polymeric solution had the largest droplet sizes across the airspeeds tested. This translates to fewer fine droplets with the water-only, glyphosate-only, and glyphosate plus polymer solutions than with the oil-based adjuvant solutions. Although this is contrary to what is typically seen with standard hydraulic nozzles, it agrees with what was seen by Teske et al. [2].

Given the limited droplet size data for aerial rotary atomizers published in the literature, the objective of this study was to evaluate the effects of six different classes of spray adjuvants on droplet size at different airspeeds and at rotational speeds for a rotary atomizer.

Materials and Methods

To meet the objectives of this research, a series of spray trials was conducted in a high-speed wind tunnel to determine spray droplet size under aerial application conditions with a rotary atomizer and several spray solutions that included an active fungicide—with and without additional spray adjuvants. The specific test methods and spray treatments are detailed in the following sections.

FORMULATIONS

Droplet size testing was conducted for seven different spray solutions. All solutions consisted of a fungicide (pyraclostrobin: (carbamic acid, [2-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy]methyl]phenyl]methoxy-, methyl ester, 23.6 %) (Headline® [HL], BASF, Research Triangle Park, NC), with six of the treatments containing additional spray adjuvants (see Table 1 and Appendix for additional details on each adjuvant used). An additional treatment of water-only was also included as a baseline. Treatment number, notation, and mixing rates for each spray solution are given in Table 1.

ROTARY ATOMIZER TREATMENTS

Each spray solution was tested for droplet size using a Micronair AU5000 rotary atomizer (Micronair, Bromyard, Herefordshire, UK). Airspeeds of 31.3 m/s (70 mph) and 58.1 m/s (130 mph) were selected for testing as representative of typical rotary-wing and fixed-wing operational airspeeds. A Micronair Variable Restrictor Unit (VRU), which regulates the flow rate, with a #2 VRU setting was used with a spray pressure of 206 kPa (30 psi). This setting resulted in a flow rate of 0.6 L/min. Targeted rotational velocities for airspeeds tested were approximately 2500, 5000, and 8000 rpm, representing minimum, median, and maximum ranges of the AU5000, respectively. Although these rotational velocities were obtainable at 58.1 m/s, at the lower airspeed (31.3 m/s), the maximum blade angle setting resulted in a rotational speed of 5,450 rpm; therefore, the 8000 rpm

TABLE 1 Treatment numbers with Headline® added at the rate of 357 mL with spray adjuvant types and mixing rates for 18.9 L (5 gal) of spray solution.

Treatment Number	Treatment Key	Commercial Name of Adjuvant	Adjuvant Type and Mixing Rate (Volume of Adjuvant Added)
1	HL	n/a	None
2	HL + PP	Control[1]	Petroleum polymer (PP) (2.97 ml)
3	HL + HSOC	High Load[2]	High surfactant oil concentrate (HSOC) (475.2 ml)
4	HL + COC	R.O.C.[2]	Crop oil concentrate (COC) (475.2 ml)
5	HL + O/S	Syl-Tac[2]	Oil/surfactant blend (O/S) (118.8 ml)
6	HL + IE	In-Place[2]	Invert emulsion (IE) (118 ml, premixed w/ HL)
7	HL + ME	Crosshair[2]	Micro emulsion (ME) (118.8 ml)
8	Water	n/a	0

[1] GarrCo Products Inc., Converse, IN.

[2] Wilbur-Ellis Company, San Francisco, CA.

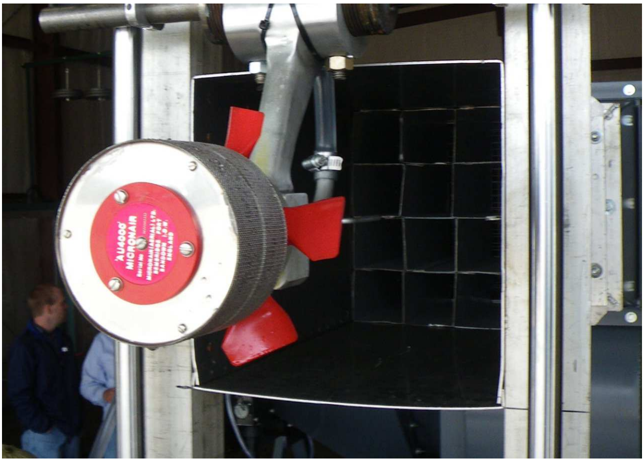
treatment was not included at this airspeed. Rotational velocities for all treatments were measured with the spray activated using a tachometer (Extech Mini Laser Photo Tachometer Counter Model 461920, Extech, Nashua, NH). Measured rotational velocities are presented in the Results section.

U.S. DEPARTMENT OF AGRICULTURE TESTING FACILITY

All droplet size testing was conducted at the U.S. Department of Agriculture–Agricultural Research Service (USDA-ARS), Aerial Application Technology Research Unit's spray atomization research facility. A 164 kW diesel-engine-driven forward-curve centrifugal fan (1.27 m diameter), with a tapered exit approximately 2.4 m long that exhausted through a 30.5 by 30.5 cm outlet, was used to generate the high-speed airstream across the nozzle, simulating aerial application conditions. A series of 2.5 cm diameter by 61 cm long tubes were positioned upstream of the outlet to straighten airflow near the nozzle. Engine speed and inlet duct louvers were used to change airspeed, which was measured near the outlet section using a pitot tube and aircraft airspeed indicator. The rotary nozzle was mounted on a boom section positioned such that the nozzle was situated in the center (horizontally) of the wind tunnel exit (Fig. 1). Pressure to the spray tank was controlled by a pressure regulator, and spray pressure at the nozzle was measured using an electronic pressure gauge (PX409-100GUSB, Omega Engineering, Stamford, CT) that was positioned within 20 cm (8 in.) of the nozzle outlet.

All droplet size measurements were made using a Sympatec HELOS laser diffraction system with the manufacturer-denoted R6 lens, which had a dynamic

FIG. 1 Rotary atomizer positioned at the exit of the USDA-ARS high speed wind tunnel facility.



size range from 0.5/9–1750 μm in 32 bins. The Sympatec was located 45.7 cm downwind-stream of the nozzle and positioned such that the measurement zone was aligned vertically with the center of the rotary nozzle. A minimum of three replicated measurements were made at each treatment point with additional replicates added, if needed, to ensure that standard deviations were within 10 % of the means for each parameter reported. The droplet size metrics recorded included the $D_{V0.1}$, $D_{V0.5}$, and $D_{V0.9}$ (ASABE Standards S327.3, 2012) as well as $\% < 100\ \mu$m and $\% < 200\ \mu$m (percent of spray volume comprised of droplets with diameters of less than 100 and 200 μm, respectively). Summary statistics and means separations were calculated using JMP (JMP®, SAS Institute, 2013). Main effects (airspeed, rotational speed, and treatment) and all cross effects were tested using a full-factorial least squares model with treatment as a nominal variable and with airspeed and rotational speed as continuous variables using the JMP Fit Model platform. Means separation tests were conducted using a least squares means model and Tukey's honest significant difference (HSD) test ($\alpha = 0.05$).

Results

Researchers have shown that adding active ingredients, such as HL, lowers surface tension as compared to water [9,10], thereby creating smaller droplets, as was seen in this study. When evaluating the different effects and results presented in Table 2, one must keep in mind that spray atomization data is highly repeatable and can have variances of less than 1–2 % among replications. Therefore, there are many times when there are significant differences among treatments where numerical differences may be as little 2–3 μm. Small numerical differences such as these would be undetectable under field spray conditions where the inter-replication variances are 10–20 % and likely would not result in any biological differences. Also, changes in droplet size are neither "bad" nor "good." The purpose of this work was to provide users with atomization data so that they could set up and operate the rotary nozzle to perform in their desired manner.

All main effects and cross terms were significant ($P < 0.0001$), justifying separating out means. Across all data, as airspeed and rotational speed increased, droplet size decreased with $\%\text{Vol} < 100\ \mu$m increasing. Means separations were conducted among adjuvant treatments for each rotational speed within each airspeed range (Table 2). The effects of the spray adjuvants and rotational speed are discussed separately for the two airspeeds. Fritz et al. [11] provided a detailed description of how, at fixed-wing airspeeds, spray droplets are created by the nozzle and then subjected to secondary atomization forces caused by the spray droplet impacting the high-speed air and further shattering. The secondary atomization forces are marginal at rotary-wing speeds. Using water as a baseline, the effects of adding the different products to the spray mix were evaluated under the different airspeed and nozzle rotational velocities (Table 2).

TABLE 2 Droplet size data and means separations (Tukey's HSD, α = 0.5) for airspeeds and rotational velocities tested. Shown rotational velocities are as measured with spray active.

	Trt	30.3 m/s (70 mph)		58.1 m/s (130 mph)		
		2700 rpm[*]	5450 rpm	2400 rpm	5000 rpm	8200 rpm
$D_{V0.1}$	HL	67.6 C	37.8 B	43.1 A	31.1 AB	20.5 B
	HL + PP	71.9 A	40 A	32.5 C	31.8 A	22.6 A
	HL + HSOC	68.9 C	36.9 BC	39.9 B	29.7 E	20 C
	HL + COC	61.4 F	30.3 E	41.5 AB	27.9 G	19 E
	HL + OS	63.3 E	33.4 D	41.7 AB	28.8 F	19.6 D
	HL + IE	64.8 D	34.8 D	41.6 AB	30.2 DE	20 C
	HL + ME	64.2 DE	34 D	42 AB	30.3 CDE	20.1 C
	Water	70.4 B	40.2 A	34.7 C	30.5 BCD	18.1 F
$D_{V0.5}$	HL	180.8 B	109.9 ABC	109.6 B	74.3 BC	48.5 C
	HL + PP	179.9 B	105.3 BC	116.2 A	76.1 B	50.5 B
	HL + HSOC	194.1 A	110.4 AB	106.2 C	73.5 BCD	47.7 CD
	HL + COC	172 D	88.9 E	102.4 D	68.2 E	43.7 E
	HL + OS	180.9 B	102.7 CD	105 CD	71.4 D	45.9 D
	HL + IE	177.8 BC	103 CD	103.7 CD	72.2 CD	47.7 CD
	HL + ME	174.9 CD	97.5 D	104.6 CD	72.6 CD	48.4 C
	Water	192 A	114.9 A	110.1 B	83.3 A	53.1 A
$D_{V0.9}$	HL	293.6 B	176.7 AB	180.8 D	130.9 B	93.5 B
	HL + PP	320.2 A	175.9 AB	225.7 A	141.5 A	100.3 A
	HL + HSOC	317.5 A	171.3 BC	179.3 DE	131.5 B	93.4 B
	HL + COC	285 C	155.1 E	170.7 F	121 D	87.2 C
	HL + OS	294.3 B	166 BCD	175.7 DEF	125.1 C	90.1 BC
	HL + IE	289.6 BC	171.4 BC	173.7 F	126.1 C	91.8 B
	HL + ME	286.7 C	161.2 DE	174.7 EF	127.3 C	92.6 B
	Water	321 A	182.4 A	198 B	143.5 A	101.6 A
%Vol < 100um	HL	22 C	43.4 DEF	43.2 CD	72.2 D	92.6 B
	HL + PP	21.6 CD	46.8 CDE	42.2 CD	69.1 E	89.9 C
	HL + HSOC	20.8 D	42.7 EF	45.7 B	72.6 CD	92.6 B
	HL + COC	25.2 A	57.2 A	48.1 A	78.4 A	95 A
	HL + OS	23.7 B	48.3 BCD	46.3 B	75.2 B	93.6 B
	HL + IE	23.3 B	48.1 BC	47.2 AB	74.5 BC	93.3 B
	HL + ME	23.8 B	51.7 B	46.6 AB	74 BCD	93.1 B
	Water	19.1 E	38.4 F	43.9 C	63.6 F	89.3 C

[*] Means followed by the same letter within each rotational speed column and droplet size parameter are not significantly different.

EFFECT OF SPRAY ADJUVANTS FOR 30.3 M/S AIRSPEEDS

At the rotational speed (2700 rpm), the HL, HL + PP, and HL + HSOC tended to have $D_{V0.1}$ and $D_{V0.9}$ values similar to that of water, while the other solutions tended to be lower. However, all solutions had lower $D_{V0.5}$ values than water. HL, HL + PP, and HL + HSOC all had similar %Vol $< 100\,\mu$m to water, while all other solutions had significantly greater percent fines than water. When the rotational speed was increased from 2700 to 5450 rpm, the $D_{V0.1}$ and $D_{V0.9}$ trends remained the same; however, the HL + IE spray solution $D_{V0.9}$ was not significantly different than that of the HL + HSOC solution. The $D_{V0.5}$ values followed the $D_{V0.1}$ trends, with HL, HL + PP, and HL + values similar to that of water, while the other solutions tended to be lower. All solutions had %Vol $< 100\,\mu$m values that were significantly lower than water, with HL and HL + HSOC being the closest to water-only. Generally, at the rotary wing airspeed, the addition of HL resulted in less than 10 % change in $D_{V0.1}$, $D_{V0.5}$, and $D_{V0.9}$ and only increased the %Vol $< 100\,\mu$m by 3 %. The addition of the PP and HSOC resulted in very little change in all parameters compared to the HL only, while the other adjuvants tended to reduce $D_{V0.5}$ and increase the %Vol $< 100\,\mu$m, which could lead to slightly more spray drift. However, it should be noted that, for all treatment points run for this work, all sprays would be classified as very fine based on the $D_{V0.1}$ data and on the aerial reference nozzle very fine to fine cutoff for $D_{V0.1}$ of 84 μm.

EFFECT OF SPRAY ADJUVANTS FOR 58.1 M/S AIRSPEEDS

At 2400 rpm, HL + PP decreased $D_{V0.1}$ and increased $D_{V0.9}$ (**Table 2**). This result was similar to previously reported work [10] and is thought to be caused by an increase in the number of larger droplets that are ejected radially from the nozzle into the airstream, which then experience secondary breakup when entering the high-speed airstream. The other adjuvants generally decreased $D_{V0.1}$, $D_{V0.5}$, and $D_{V0.9}$ as compared to the HL-only solution. At 5000 and 8200 rpm, the addition of the polymer (HL + PP) increased $D_{V0.1}$ and $D_{V0.5}$, as compared to the HL-only solution, but only by 0.7–2.1 μm. When the other five adjuvants were added to HL, $D_{V0.1}$ and $D_{V0.5}$ decreased. The HL + PP created significantly larger $D_{V0.9}$ values (6.8–10.6 μm) as compared to HL-only.

Similar to that found in the previous work [10], the COC tended to result in the smallest overall spray droplet size across all treatment and rotational speeds, with the exception of the $D_{V0.1}$ at 58.1 m/s and 2400 rpm. The %Vol $< 100\,\mu$m is generally considered to represent the portion of the spray released from the aircraft that is most susceptible to drifting. The polymer resulted in decreases in %Vol $< 100\,\mu$m of 1–4 %, as compared to HL-only solutions, while the other adjuvants resulted in increased %Vol $< 100\,\mu$m.

Discussion

For these tests, a fungicide was used to represent an actual spray solution that is applied using rotary atomizers by aerial applicators. Many applicators routinely add spray adjuvants to change the droplet size, reduce drift potential, or to reduce evaporative effects of a particular spray solution; therefore, six commonly used classes of spray adjuvants were evaluated to determine their effects on droplet size.

Although there were statistically significant differences between the fungicide-only solution and the fungicide + adjuvant solutions, numerical differences in droplet size were generally less than 10 % among the different solutions, or about 1.5 μm. If an applicator's only concern was minimizing spray drift, he could choose a polymer or high surfactant oil concentrate for helicopter speeds and a polymer for fixed-wing applications. An applicator working under hot, dry conditions where evaporation is a concern might choose an oil-based adjuvant to help obtain better coverage by creating smaller droplets that do not evaporate. Also apparent from the results presented here is that rotary atomizers generally produce lower overall droplet-sized sprays than those seen with typical hydraulic nozzles, which are generally operated as medium or coarser sprays. Rotary atomizers would then generally be used for applying iniquitous materials overall on larger areas with larger buffers, specifically fungicides (as tested in this work). Understanding the role the different adjuvant types play in the final droplet size of the spray is key to successfully setting up and making applications with rotary atomizers.

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Appendix

Petroleum polymer:

- Polyacrylamide polyvinyl polymer complex 1.3 %
- Constituents ineffective as spray adjuvants 98.7 %

High surfactant oil concentrate:

- Paraffin base oil, sorbitol fatty acid alkoxylates, alkyl ethoxylates 98 %
- Constituents ineffective as spray adjuvants 2 %

Crop oil concentrate:

- Paraffin base petroleum oil 83 %
- Surfactant blend 17 %

Oil/surfactant blend:

- Ethylated seed oil; 3-(3-hydroxypropyl)-heptamethyltrisiloxane, ethoxylated acetate; polyoxyethylene dioleate; polyol alkyl ethoxylate 100 %

Invert emulsion:

- Modified vegetable oil, aliphatic mineral oil, amine salts of organic acids, aromatic acid 100 %

Micro emulsion:

- Modified vegetable oils, amine salts of organic acids, organic acid 100 %

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Response Surface Method for Evaluation of the Performance of Agricultural Application Spray Nozzles

Citation

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ABSTRACT

Droplet size, as one of the critical factors that influences spray performance and drift, must be considered when selecting spray nozzles and operational setups. Characterizing a spray nozzle for droplet size is typically completed by evaluating only a select few nozzle types, sizes, and spray pressures, which typically do not provide detailed droplet size information for the entire operational space. This research proposes a structured, experimental design that allows for the development of computational models for droplet size based on any combination of a nozzle's potential operational settings. Ten nozzles with two operational settings (orifice and pressure) and one with three (orifice, pressure, and tip) were evaluated using a response surface experimental design. All models showed high levels of fit to independently collected droplet size data. The computational models were integrated into a spreadsheet-based user interface that allows convenient droplet size predictions for a given nozzle setup. The developed models also allowed for a detailed analysis of each nozzle's entire operational space thereby providing users with a screening tool based on

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desired droplet size classification. The use of the proposed experimental design provides for efficient nozzle evaluations that can be used to determined droplet size and classification for any combination of operational settings.

Keywords
spray nozzle, droplet size, droplet size model

Introduction

When making any agrochemical spray application, the primary concerns are ensuring maximum biological efficacy while minimizing any off-target movement and adverse environmental impact or other non-target biological harm. One of the principal factors to consider when setting up any sprayer prior to an application is droplet size, which has long been recognized as one of the primary parameters influencing overall spray deposition, efficacy, and drift [1,2]. Although there are a number of other factors that affect spray deposition and drift, droplet size is one of the easiest to modify to fit the needs of a given application scenario. Generally, the larger the nozzle orifice, the larger the droplet size spectrum, and the higher the spray pressure, the lower the droplet size spectrum [3]. Other factors can also influence droplet sizing including the use of air-assistance [4], different nozzle structures [5], and spray formulation [6]. Understanding how these factors interact and can be applied to improve agrochemical applications and reduce damage due to spray drift is one of the driving forces behind the U.S. Environmental Protection Agency's (EPA) drift reduction technology (DRT) program [7]. However, the program does not provide a list of operational points that should be tested for a given nozzle or product; rather, it states that any DRT rating is valid only for the test conditions for which the technology was tested [7]. In the case of nozzles with varying orifice sizes, tip types, and spray pressures, evaluating every potential combination of these factors to determine a DRT rating can be cost prohibitive. Aerial application platforms present the additional factors of airspeed and nozzle orientation angle, which further increase the potential number of operational settings. As a more efficient method for evaluating the potential number of aerial nozzle operational settings for any given nozzle type, Kirk [8] applied a response surface method experimental design that provided a coded set of treatment combinations of the four factors (orifice size, spray pressure, airspeed, and nozzle orientation). This limited set of 27 experimental data points allowed for the development of a second-order, multifactor regression equation to predict droplet size based on user-defined inputs of the four parameters determined by the range of operational conditions possible with a particular nozzle. To date, there is no indication in the available literature of a structured approach of this type applied to ground application nozzles, though the authors have heard anecdotal comments within the community of agricultural spray application technology that at least one laboratory uses a similar method.

Beyond the experimental design applied to droplet size testing of agrochemical sprays, the methods and droplet size measurement instruments used have an influence on the numerical droplet size data. Although a discussion of all of these factors is beyond the scope of this manuscript, simply stated the type of instrument used [9] and how it is used [10,11] can cause numerical results to differ. However, through standardization of instrument type and setup as well as other experimental methods (primarily standardized distance among nozzle and measurement zone and concurrent airflow to create uniform droplet velocities through the measurement zone), potential measurement biases can be minimized [12] and numerical results between multiple laboratories made equal [13].

The objective of this study was to develop and evaluate a structured experimental design method for evaluating spray droplet size associated with agricultural ground sprayer nozzles.

Materials and Methods

A series of ground sprayer nozzles were evaluated for droplet size following a set of structured response surface experimental designs. The resulting data were fit to mathematical prediction models, which were tested against independently measured data points for goodness of fit. The final ground nozzle models were incorporated into an easily navigable user interface that allows for the selection of operational settings for which droplet size and classification are returned. The following sections provide greater detail on measurement methods and data analysis.

RESPONSE SURFACE METHOD EXPERIMENTAL DESIGN

Ten of the nozzles tested allowed only for adjustments to spray pressure and orifice size. One nozzle tested had an additional setting that allowed for changes to spray stream deflection angle via a series of differing tip angles. With all nozzles tested, spray pressure was set as a continuous factor across the range of 138–414 kPa (20–60 psi). The same 110° flat fan style nozzles (Table 1) tested as part of a recent three-lab round robin [13] were used for this study. Although the orifice size range of these nozzles was limited in the nozzle kit used in the round robin tests to orifices from 2.5 to 5, most of these nozzles offer orifice sizes beyond #5. All the methods and models presented in this work can easily be extended to incorporate all available orifice sizes, and extended spray pressures, beyond those tested herein. The CP-65T-S (CP Products, Wichita Falls, TX) has a rotatable set of turrets that allow for orifice size selection (3, 4, 5, 6, 8, or 10) as well as tip number (3, 7.5, or 10). It should be noted that, although experimental designs of certain classes of response surface designs can be found in literature as coded tables to guide treatment selections, with custom response surface design, some form of statistical software is needed to properly define the test points upon which the final response surface

TABLE 1 Nozzle type, manufacturer, and naming convention for ground nozzles tested.

Nozzle (Naming Convention)	Manufacturer
Air Induction Extended Range (AIXR)	TeeJet (Wheaton, IL)
TurboTeeJet (TT)	
TurboTeeJet Induction (TTI)	
TurboTwinJet (TTJ60)	
Extended Range (XRC)	
Guardian (G)	Hypro (New Brighton, MN)
Guardian Air (GA)	
UltraLow Drift (ULD)	
AirMix (AM)	GreenLeaf Technologies (Covington, LA)
TurboDrop Venturi (TDXL)	

model is based. All experimental designs and data processing for this work were completed using JMP® (Version 11.1.1, SAS Institute, 2013).

For all nozzles, orifice size was set in the model as a discrete factor with four levels for the flat fans (2.5, 3, 4, and 5) and with six levels for the CP-65T-S (3, 4, 5, 6, 8, and 10). Additionally, the spray tip was set as a discrete level with three factors (3, 7.5, and 10) for the CP-65T-S. All flat fan nozzles had the same set of 11 treatments, while the CP-65T-S required 14 treatments. The final developed models are only applicable across the range of parameters tested and cannot be extended beyond. All treatments are presented in Table 2. Note that, with both treatment lists, there are one or two treatments that are identical (Runs 3 & 4, 6 & 7 for the flat fan nozzles and Runs 6 & 7 for the CP-65T-S). These are specified by the experimental design and are typically in the center of the operational space. For both treatment sets, these runs were separated by another treatment and not run as a continuous set of replications. In addition to the treatment points listed, an additional six operational points within the operational parameter of the nozzle that were different from those used to build the model were conducted for each nozzle. These six data points were used to test the resulting model's goodness of fit.

DROPLET SIZE MEASUREMENTS

Droplet sizing measurements were conducted at the U.S. Department of Agriculture (USDA), Agricultural Research Service (ARS) Aerial Application Technology Research Unit's (AATRU) laboratory located in College Station, TX. Nozzles were positioned in a low-speed wind tunnel (1.2 by 1.2 m^2 by 9.8 m long) with the nozzle positioned 2.4 m upstream of the tunnel exit. The nozzle was positioned such that the exiting spray sheet was parallel to the tunnel floor in the direction of the surrounding air stream. Spray solution (water + 0.25 % v/v of 90 % nonionic surfactant) was fed from 19 L stainless steel pressure tanks that were pressurized using an air compressor. A pressure regulator was used to change pressure, which was measured using an electronic pressure gauge (PX409-100GUSB, Omega Engineering,

TABLE 2 Custom response surface experimental design designated treatment combinations.

All Flat Fan Nozzles			CP-65T-S Nozzle			
Run No.	Orifice	Pressure (kPa)	Run No.	Orifice	Tip	Pressure (kPa)
1	2.5	138	1	4	3	138
2	2.5	414	2	4	10	138
3	3	276	3	8	7.5	138
4	3	276	4	10	3	138
5	4	138	5	3	7.5	276
6	4	276	6	5	7.5	276
7	4	276	7	5	7.5	276
8	4	414	8	8	3	276
9	5	138	9	8	7.5	276
10	5	276	10	10	10	276
11	5	414	11	4	3	414
			12	4	10	414
			13	8	7.5	414
			14	10	3	414

Stamford, CT) positioned within 20 cm of the nozzle outlet. The tunnel was operated such that the air velocity at the nozzle was 6.7 m/s. A Symptec HELOS laser diffraction system (operated with the manufacturer denoted R7 lens, dynamic size range of 0.5–3500 μm across 32 bins) was positioned downstream of the nozzle such that the area of measurement was 30.5 cm from the exit of the nozzle. Both the concurrent air stream velocity and the measurement distance, determined from a previous work [12] to minimize spatial sampling error, are now standard methods at several droplet size laboratories [13]. Evaluation of each treatment (**Table 2**) consisted of a series of replicated measurements, each of which was one full vertical traverse of the spray plume (at a rate of 6.4 cm/s). Sufficient replications were made to ensure that the standard deviations of $D_{V0.1}$, $D_{V0.5}$, and $D_{V0.9}$ [14] were within ± 5 % of the means (minimum of three replications). Additionally, the percent volume of the spray contained in droplets of diameter 100 μm (%Vol $<$ 100 μm) was also recorded [14].

DROPLET SIZE CLASSIFICATION

The reference nozzles, as specified by ASABE S572.1 spray classification standard [15], were evaluated for droplet size as part of this work. The reference nozzles used were a set obtained from Spray Systems Co. (Wheaton, IL) and were flowrated to meet the levels specified in the standard. Prior to testing, these nozzles were flowrated at the AATRU laboratory to confirm they met the standard. Droplet size measurements were taken for each nozzle at the reference pressures specified (450, 300, 200, 250, 200, and 150 kPa for the 11001, 11003, 11006, 8008, 6510, and 6515 nozzles, respectively) [15].

DATA PROCESSING

All data processing was conducted using JMP. The droplet size data ($D_{V0.1}$, $D_{V0.5}$, $D_{V0.9}$, $\%V < 100\ \mu m$, and $\%V < 200\ \mu m$) were entered into JMP as the response variables for each treatment. A standard least squares analysis was used to fit a model to a second-order response relationship with factors X_1 (orifice size) and X_2 (spray pressure) for nozzles; these two can be varied (Eq 1). The CP-65T-S nozzle has the additional factor X_3 (tip size), which was included in its prediction equation (Eq 2).

$$
\begin{aligned}
Y = {} & A + B\left(\frac{X_1 - C_{sub1}}{C_{div1}}\right) + C\left(\frac{X_2 - C_{sub2}}{C_{div2}}\right) + D\left(\frac{X_1 - C_{sub1}}{C_{div1}}\right)\left(\frac{X_2 - C_{sub2}}{C_{div2}}\right) \\
& + E\left(\frac{X_1 - C_{sub1}}{C_{div1}}\right)^2 + F\left(\frac{X_2 - C_{sub2}}{C_{div2}}\right)^2
\end{aligned}
\tag{1}
$$

where:

Y = atomization parameter to be predicted based on input combination of X_1 through X_2 (i.e., DV0.1, DV0.5, etc.)

X_1 = orifice size (unitless, specific orifice number for each nozzle)

X_2 = spray pressure (psi for model input user interface)

C_{subi} = constant subtraction term used to adjust each X_1 from input value to value between (−1 and 1) (unitless and unique for each nozzle)

C_{divi} = constant dividend term used to adjust each X_1 from input value to value between (−1 and 1) (unitless and unique for each nozzle)

A to F = constant coefficients for each term of the prediction expression (unitless and unique for each nozzle)

$$
\begin{aligned}
Y = {} & A + B\left(\frac{X_1 - C_{sub1}}{C_{div1}}\right) + C\left(\frac{X_2 - C_{sub2}}{C_{div2}}\right) + D\left(\frac{X_1 - C_{sub1}}{C_{div1}}\right)\left(\frac{X_2 - C_{sub2}}{C_{div2}}\right) \\
& + E\left(\frac{X_1 - C_{sub1}}{C_{div1}}\right)^2 + F\left(\frac{X_2 - C_{sub2}}{C_{div2}}\right)^2 + G\left(\frac{X_3 - C_{sub3}}{C_{div3}}\right) \\
& + H\left(\frac{X_1 - C_{sub1}}{C_{div1}}\right)\left(\frac{X_3 - C_{sub3}}{C_{div3}}\right) + I\left(\frac{X_2 - C_{sub2}}{C_{div1}}\right)\left(\frac{X_3 - C_{sub3}}{C_{div3}}\right) \\
& + J\left(\frac{X_3 - C_{sub3}}{C_{div3}}\right)^2
\end{aligned}
\tag{2}
$$

where all variables are as previously defined with the addition of:

X_3 = tip size (unitless, specific by manufacturer)

A to J = constant coefficients for each term of the prediction expression (unitless and unique for each nozzle).

Results

Pressure and orifice were significant effects for all flat fan nozzles ($\alpha = 0.5$); however, not all interaction terms were significant. Despite this inconsistency, all major and interaction terms were used to develop the final models. Similarly for the CP-65T-S, pressure, orifice, and tip were all significant, although many of the interaction terms were not. Again, all terms were included in the final model. For all models, the data used to develop the models had high levels of fit, with R^2 values ranging from 0.92 to 0.99 for all droplet size and velocity parameters. With respect to the independent points, all models showed high levels of fit with R^2 values ranging from 0.89 to 0.99 across all droplet size parameters, with the exception of the TTI $D_{V0.9}$ data, which had an R^2 of 0.5 due to two points that varied by $\sim$200 μm (predicted 1455 and 1414 μm versus actual 1261 and 1266 μm). The final model, still valid, reflects the level of variation seen with the $D_{V0.9}$ data for this particular nozzle. Given that a nozzle's droplet size classification depends only on $D_{V0.1}$ and $D_{V0.5}$, nozzle setups to meet product label guidance and to minimize drift are not affected. Droplet size classifications followed the method outlined by the ASABE Standard S572.1 [14]. Droplet size data (the mean plus one standard as specified by the standard) from these nozzles, as measured as part of this work, are presented in Table 3.

MODELING RESULTS

Coefficients for all models are presented in Tables A1–A12 in the Appendix. These coefficients are included so that the user can incorporate them into custom applications. To help explain how the models can be used, an example using the coefficient values for an AIXR 110° flat fan nozzle (Table A2) to calculate $D_{V0.1}$ based on Eq 1 is presented; X_1 represents the orifice size and X_2 represents the pressure. The appropriate subtraction (C_{sub}) and division (C_{div}) values from Table A1 must also be used. To calculate the $D_{V0.1}$ value of a #4 orifice size and a spray pressure of 25 psi (English pressure units must be used with these coefficients), the equation based on Eq 1 would be:

$$Y = 186.86 - 2.14\left(\frac{4-3.75}{1.25}\right) - 43.43\left(\frac{25-40}{20}\right) + 4.99\left(\frac{4-3.75}{1.25}\right)\left(\frac{25-40}{20}\right) - 9.26\left(\frac{4-3.75}{1.25}\right)^2 + 21.52\left(\frac{25-40}{20}\right)^2 \quad (3)$$

The result from Eq 3 is 229 μm for $D_{V0.1.}$ This process would be quite laborious if one had to make multiple calculations. Therefore, as part of this research, all nozzle

TABLE 3 ASABE S572.1 reference nozzle data means (plus one standard deviation) used for droplet size classifications (DSC) in this study.

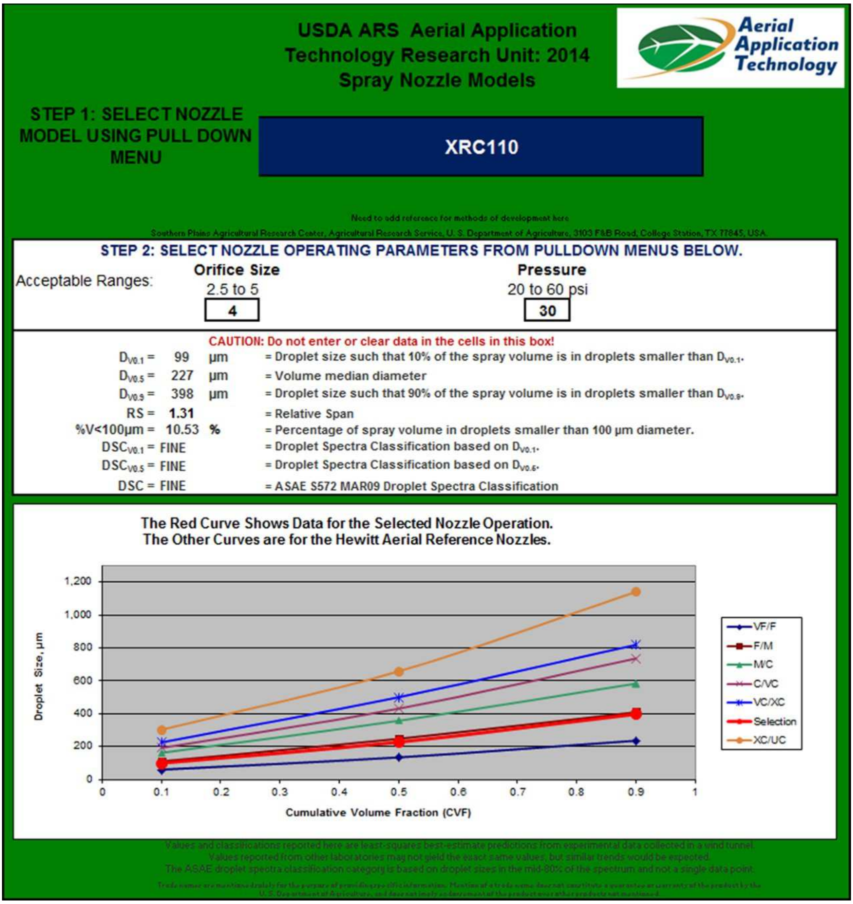
Nozzle	DSC	$D_{V0.1}$	$D_{V0.5}$	$D_{V0.9}$
11001	VF/F	60	134	236
11003	VF/M	110	248	409
11006	M/C	162	358	584
8008	C/VC	192	431	737
6510	VC/XC	226	501	820
6515	XC/UC	303	659	1142

models were integrated into a Microsoft Excel®-based user interface that allows the user to select orifice and pressure (and tip in the case of the CP-65T-S) for which droplet size and class information is returned. Droplet size parameters given include $D_{V0.1}$, $D_{V0.5}$, $D_{V0.9}$, relative span (RS), and %Vol < 100 μm (Fig. 1). Also shown are the DSC based on the $D_{V0.1}$ and $D_{V0.5}$ as well as the final DSC (the finer of the $D_{V0.1}$ and $D_{V0.5}$ DSC ratings) (Fig. 1). The user interface for the CP-65T-S contains an additional input for tip size. Interested readers should contact the corresponding author for a copy of these spreadsheets.

DROPLET CLASSIFICATIONS

These types of models provide the ability to look at the entire range of potential operational setting combinations and to explore a given nozzle's potential size

FIG. 1 User interface for ground sprayer droplet size models.



USDA ARS Aerial Application Technology Research Unit: 2014 Spray Nozzle Models

STEP 1: SELECT NOZZLE MODEL USING PULL DOWN MENU

XRC110

Need to add reference for methods of development here

Southern Plains Agricultural Research Center, Agricultural Research Service, U. S. Department of Agriculture, 3103 F&B Road, College Station, TX 77845, USA

STEP 2: SELECT NOZZLE OPERATING PARAMETERS FROM PULLDOWN MENUS BELOW.

	Orifice Size	Pressure
Acceptable Ranges:	2.5 to 5	20 to 60 psi
	4	30

CAUTION: Do not enter or clear data in the cells in this box!

$D_{V0.1}$ = 99 µm = Droplet size such that 10% of the spray volume is in droplets smaller than $D_{V0.1}$.
$D_{V0.5}$ = 227 µm = Volume median diameter
$D_{V0.9}$ = 398 µm = Droplet size such that 90% of the spray volume is in droplets smaller than $D_{V0.9}$.
RS = 1.31 = Relative Span
%V<100µm = 10.53 % = Percentage of spray volume in droplets smaller than 100 µm diameter.
$DSC_{V0.1}$ = FINE = Droplet Spectra Classification based on $D_{V0.1}$.
$DSC_{V0.5}$ = FINE = Droplet Spectra Classification based on $D_{V0.5}$.
DSC = FINE = ASAE S572 MAR09 Droplet Spectra Classification

The Red Curve Shows Data for the Selected Nozzle Operation.
The Other Curves are for the Hewitt Aerial Reference Nozzles.

Values and classifications reported here are least-squares best-estimate predictions from experimental data collected in a wind tunnel.
Values reported from other laboratories may not yield the exact same values, but similar trends would be expected.
The ASAE droplet spectra classification category is based on droplet sizes in the mid-80% of the spectrum and not a single data point.

Trade names are mentioned solely for the purpose of providing specific information. Mention of a trade name does not constitute a guarantee or warranty of the product by the U. S. Department of Agriculture, and does not imply endorsement of the product over other products not mentioned.

classifications across the entire range. To this end, a custom FORTRAN (Simply FORTRAN Ver. 2.15, Approximatrix LLC) code was used to calculate droplet size and classification for each nozzle for each orifice size and for all pressures from 138–414 kPa in 7 kPa (1 psi) increments. This clearly demonstrated the efficiency of using response surface models. The models were used to predict 1104 combinations of orifice size and pressure for each of the ten flat fan nozzles, and 4968 combinations of orifice size, pressure, and tip for the CP-65T-S nozzle using models developed from the 11 and 14 treatment points conducted for the flat fan and CP nozzles, respectively. This approach significantly reduced data collection costs.

The percentage of total operational points within each size class was then determined (Table 4). Referring to Table 4, an applicator that requires a specific class of spray for a particular application can quickly narrow down their nozzle choice. For example, if a fine spray was desired, the only real choice is the XRC nozzle; whereas, if a medium spray were desired, the most obvious nozzles choices are the TT, TTJ60, G, or GA nozzles, though both the AIXR and CP-65T-S have the ability to produce a medium spray. Similar choices can be deduced for coarse through ultra-coarse sprays. Once the nozzle selection is made, the applicator would go to the model to determine the specific operational parameters that produced the desired droplet size classification.

Additional Nozzle Data

In addition to the aforementioned nozzle test, a high (CP-65T-SH) and low (CP-65T-SL) flowrate version of the CP-65T were each evaluated and droplet sizing models developed, as well as a new series of pre-orifice flat fan nozzles (Extreme

TABLE 4 Droplet size classification breakdown.*

	Percentage of Total Operational Space in Each Class						
Nozzle	**VF**	**F**	**M**	**C**	**VC**	**XC**	**UC**
AIXR	0	0	17	49	26	8	0
TT	0	0	62	29	9	0	0
TTI	0	0	0	0	0	10	90
TTJ60	0	0	63	30	7	0	0
XRC	0	94	6	0	0	0	0
G	0	0	87	13	0	0	0
GA	0	0	44	37	18	1	0
ULD	0	0	0	2	18	78	2
AM	0	0	3	57	29	11	0
TDXL	0	0	0	26	32	40	2
CP-65T-S	0	1	14	5	8	17	55

*By percentage of operating points within each class for all nozzle and pressure (7 kPa increments) combinations.

Drop flat fans, CP Products, Wichita Falls, TX). The model parameter data for the CP-65T-SL and CP-65T-SH are given in Tables A13 and A14. These experimental flat fans incorporate a pre-orifice that limits the flowrate. Fan angles of 20, 40, 80, and 110 degrees with orifice sizes from 4 to 30 were tested at pressures of 207 and 414 kPa (30 and 60 psi) following the same testing protocols as all the other nozzles. The inclusion of the pre-orifice with the Extreme Drop flat fans resulted in the proposed response surface model method not being applicable and, as such, the results are not included in this work. Interested parties should consult the manufacturer for additional droplet size information (http://www.cpproductsinc.com/site).

Conclusions

This work focused on developing and executing a structured, experimental design to characterize nozzles types across their entire breadth of potential operational settings. The majority of the nozzles evaluated for this work only allowed for changes in orifice size and spray pressure. A typical evaluation examining every orifice size for a range of pressures would require many more treatments to be tested than the proposed response surface design proposed. For example, for the AIXR nozzle tested as part of this work, examining each of the four orifices across five pressures (each 69 kPa [10 psi] from 138 to 414 kPa [20 to 40 psi]) would require 20 treatments. For the full set of AIXR nozzles available (seven orifices in total: 015, 02, 025, 03, 04, 05, and 06), 42 treatments would be required across the same pressure ranges, and this number would increase significantly if finer increments in pressure were of interest. In contrast, using the response surface design method, either range of orifices only requires 11 treatment points. The number of treatments would increase dramatically if an additional factor beyond orifice size and pressure were added. As an example, the tip setting on the CP-65T-S potentially results in a dramatic increase in the number of treatments required. Examining this nozzle across the same five pressures for each of the three tip and orifice sizes would require 90 treatment points—versus the 14 required using the response surface method.

With the response surface design, the statistical analysis accounts for the dynamic response of the interactions among the operational parameters of the nozzle. This approach provided a mathematical model that can be used to calculate the droplet size parameter of interest at any combination of pressure, orifice, and other factors within the ranges tested. Applying a response surface experimental design to the evaluation of agricultural ground sprayer nozzles allowed for a structured approach that can be used to efficiently and accurately assess droplet size data across all possible operational combinations of a given nozzle. This structured design can be extended to include additional factors such as tip size (as shown with the CP-65T-S), which offers an even more efficient approach to characterizing the nozzle.

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Appendix

TABLE A1 Subtraction and division Terms (Eq 1) used to convert factor inputs to model coded inputs (−1 to 1).

Nozzle	X_1–Orifice		X_2–Pressure		X_3–Tip	
	C_{sub1}	C_{div1}	C_{sub2}	C_{div2}	C_{sub3}	C_{div3}
AIXR	3.75	1.25	40	20	-	-
TT	3.75	1.25	40	20	-	-
TTI	3.75	1.25	40	20	-	-
TTJ60	3.75	1.25	40	20	-	-
XRC	3.75	1.25	40	20	-	-
G	3.75	1.25	40	20	-	-
GA	3.75	1.25	40	20	-	-
ULD	3.75	1.25	40	20	-	-
AM	3.75	1.25	40	20	-	-
TDXL	3.75	1.25	40	20	-	-
CP-65T-S	6.5	3.5	40	20	6.5	3.5

TABLE A2 AIXR 110° flat fan model coefficients.

	Coefficient Term					
	A	B	C	D	E	F
$D_{V0.1}$	186.857666	−2.141355	−43.430722	4.999156	−9.258550	21.518239
$D_{V0.5}$	408.386128	1.858619	−81.459618	11.280110	−13.656868	35.969246
$D_{V0.9}$	672.137413	7.152585	−115.684864	20.854627	−13.585139	37.659420
$\%V < 100\ \mu m$	1.776921	0.019356	1.119161	−0.030073	0.350139	−0.240219

TABLE A3 TT 110° flat fan model coefficients.

	Coefficient Term					
	A	B	C	D	E	F
$D_{V0.1}$	158.909307	10.927811	−37.770254	−6.059518	−5.055425	9.157194
$D_{V0.5}$	370.564172	38.377240	−65.304099	−10.041020	−15.534802	8.848510
$D_{V0.9}$	696.805591	93.831995	−57.971145	−8.031996	−27.538529	3.028421
$\%V < 100\ \mu m$	2.864702	−0.475723	2.039715	−0.295302	0.193652	0.413956

TABLE A4 TTI 110° flat fan model coefficients.

	Coefficient Term					
	A	B	C	D	E	F
$D_{V0.1}$	367.882623	0.892705	−91.748713	−5.195976	−4.156105	36.345126
$D_{V0.5}$	759.002725	27.947961	−155.338840	−5.725735	−18.517715	67.473790
$D_{V0.9}$	1282.598836	85.108596	−196.190055	−13.729178	−113.630129	76.137412
$\%V < 100\ \mu m$	0.067318	0.005382	0.087636	0.009550	−0.003018	0.022649

TABLE A5 TTJ60 110° flat fan model coefficients.

	Coefficient Term					
	A	B	C	D	E	F
$D_{V0.1}$	145.246112	−10.427129	−40.615864	5.677127	7.241036	15.223070
$D_{V0.5}$	342.830338	−10.971998	−72.197515	8.705230	11.621690	22.656990
$D_{V0.9}$	632.826697	−2.622763	−122.365368	24.536360	21.700037	45.950184
$\%V < 100\ \mu m$	3.585129	0.543682	2.245031	0.179902	−0.298441	0.006130

TABLE A6 XRC 110° flat fan model coefficients.

	Coefficient Term					
	A	B	C	D	E	F
$D_{V0.1}$	87.744261	7.929437	−15.167748	−0.905450	0.837115	8.727871
$D_{V0.5}$	204.194349	22.017800	−30.062504	−0.840768	3.447238	12.993453
$D_{V0.9}$	360.444819	38.637309	−48.694656	−0.609331	4.994876	19.841678
$\%V < 100\ \mu m$	13.524614	−2.488191	4.348836	−0.932334	−0.038835	−1.660599

TABLE A7 G 110° flat fan model coefficients.

	Coefficient Term					
	A	B	C	D	E	F
$D_{V0.1}$	135.193344	21.166945	−26.256715	−0.096776	−7.524691	19.610261
$D_{V0.5}$	311.318957	49.174906	−47.648485	6.430603	−8.234130	33.351813
$D_{V0.9}$	540.443536	87.529431	−63.024156	21.709002	−2.918092	42.219360
$\%V < 100\ \mu m$	4.856227	−1.984129	2.195528	−0.884044	0.931328	−1.242028

TABLE A8 GA 110° flat fan model coefficients.

	Coefficient Term					
	A	B	C	D	E	F
$D_{V0.1}$	171.560032	8.082316	−44.807954	−1.011524	−2.017567	16.603260
$D_{V0.5}$	374.951097	23.643913	−77.793794	−3.665592	−7.341631	29.239784
$D_{V0.9}$	618.909680	49.864710	−109.278290	−6.923158	−23.902969	46.688191
$\%V < 100\ \mu m$	2.138531	−0.267927	1.709441	−0.328920	0.129705	0.131045

TABLE A9 ULD 110° flat fan model coefficients.

	Coefficient Term					
	A	B	C	D	E	F
$D_{V0.1}$	293.811425	20.595440	−43.622794	4.741908	−28.339008	10.322404
$D_{V0.5}$	582.079530	42.447989	−73.754588	5.186316	−48.367545	11.671590
$D_{V0.9}$	939.699076	70.778427	−97.692500	−2.308333	−83.112629	2.942116
$\%V < 100\ \mu m$	0.269866	−0.132498	0.258492	−0.074699	0.162873	−0.011043

TABLE A10 AM 110° flat fan model coefficients.

	Coefficient Term					
	A	B	C	D	E	F
$D_{V0.1}$	192.594548	6.037716	−41.423886	1.104956	0.560213	19.122770
$D_{V0.5}$	411.532754	14.727862	−80.211434	1.048180	2.353885	36.360636
$D_{V0.9}$	666.608910	36.365173	−112.929581	−0.003783	12.985045	43.515525
$\%V < 100\ \mu m$	1.650643	−0.136516	0.815343	−0.094091	0.000312	−0.200841

TABLE A11 TDXL 110° flat fan model coefficients.

	Coefficient Term					
	A	B	C	D	E	F
$D_{V0.1}$	217.966033	21.195835	−62.434583	2.215417	9.495370	29.409948
$D_{V0.5}$	475.772805	54.000460	−110.134419	−0.607050	9.931418	46.711912
$D_{V0.9}$	796.514961	95.742801	−159.816189	−9.796338	−11.651315	58.000024
%V < 100 μm	0.940521	−0.280811	0.764210	−0.265115	−0.004770	−0.058273

TABLE A12 CP-65T-S model coefficients.

	Coefficient Term				
	A	B	CP-65T-S	D	E
$D_{V0.1}$	229.5551475	−94.6827094	−195.026984	38.43798495	47.4111506
$D_{V0.5}$	522.0524868	−157.784822	−346.674974	54.48768836	81.08704189
$D_{V0.9}$	917.5866693	−204.89335	−466.58928	34.82939548	91.82459
%V < 100 μm	0.656689505	0.937129512	1.175219768	1.266150063	0.042163744

	Coefficient Term				
	F	G	H	I	J
$D_{V0.1}$	93.39824629	110.7249975	−17.770906	−57.599836	50.77490474
$D_{V0.5}$	161.4926551	192.8927311	−20.8464029	−85.2442398	80.24109428
$D_{V0.9}$	245.5797751	283.0717439	−49.0633284	−115.386975	93.70760103
%V < 100 μm	0.399882849	−0.70819211	−0.31124536	−0.83324753	0.053520873

TABLE A13 CP-65T-SH model coefficients.

	Coefficient Term				
	A	B	C	D	E
$D_{V0.1}$	279.3077	−86.2651	−24.2616	71.70021	33.77179
$D_{V0.5}$	735.0922	−150.288	−147.515	265.4635	146.3665
$D_{V0.9}$	1466.793	−168.524	−388.567	437.2144	254.2077
%V < 100 μm	0.730561	0.528569	0.169971	−0.3834	−0.22356

	Coefficient Term				
	F	G	H	I	J
$D_{V0.1}$	−30.3411	45.26585	6.865889	−13.7155	84.39625
$D_{V0.5}$	−57.456	125.4189	6.653231	−37.7141	233.9731
$D_{V0.9}$	−34.8951	207.6479	−16.0521	−44.042	344.0663
%V < 100 μm	0.135546	−0.3665	0.132715	−0.10546	−0.196

TABLE A14 CP-65T-SL model coefficients.

	Coefficient Term				
	A	B	C	D	E
$D_{V0.1}$	257.2376	−125.897	95.18029	85.7495	−68.0109
$D_{V0.5}$	549.8099	−234.637	170.4291	178.7951	−143.871
$D_{V0.9}$	909.2309	−300.551	174.2312	270.5277	−228.379
%V $<$ 100 μm	2.148438	2.010929	−1.56019	−3.30682	4.268621

	Coefficient Term				
	F	G	H	I	J
$D_{V0.1}$	−28.0981	−84.8859	30.00582	−8.64648	−57.0496
$D_{V0.5}$	−54.2773	−156.791	52.13276	−13.7927	−101.937
$D_{V0.9}$	−62.7137	−202.289	55.72397	−0.15052	−124.53
%V $<$ 100 μm	1.232485	0.077194	−0.67812	−1.89216	−0.37009

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