Adjuvant Effects on Evaporation Time and Wetted Area of Droplets on Waxy Leaves

L. Xu, H. Zhu, H. E. Ozkan, W. E. Bagley, R. C. Derksen, C. R. Krause

Abstract. *The use of an appropriate adjuvant for pesticide applications is a critical process to improve spray deposit characteristics on waxy leaves and to reduce off-target losses. After deposition and evaporation, residue patterns of 500 μm sessile droplets that incorporated four classes of adjuvants on five different waxy plants were investigated. Droplets were generated with a single-droplet generator and deposited on target leaves placed in an environmentally controlled chamber at 60% relative humidity and 25°C ambient temperature. Adjuvants tested were two oil-based types (crop oil concentrate, or COC; and modified seed oil, or MSO), a nonionic surfactant (NIS), and a mixture (oil surfactant blend, or OSB). Water-only droplets were also tested for comparative purposes. The five waxy plants were difficult to wet and had a water contact angle greater than 90°. The water-only droplets did not spread at all and formed extremely small wetted areas on the leaf surface. The addition of an adjuvant to the spray solution significantly reduced the contact angle and increased the wetted area, but the change or improvements varied with the plant species and adjuvant class. In general, MSO and NIS enhanced the droplet spread and maintained the droplet evaporation time on the waxy leaf surfaces. After evaporation, the residues formed patterns of "coffee rings". Droplets with oil-based adjuvants had more uniform residual distribution in the deposition patterns than droplets with the surfactant adjuvant. Results of this study demonstrated that selection of the appropriate class of adjuvants significantly improved deposit formation on waxy leaves, leading to more effectiveness of pesticides.*

Keywords. *Contact angle, Droplet spread, Oil-based adjuvant, Residual pattern, Spray coverage, Surfactant.*

Pesticide efficacy is often correlated with its spread area (wetted area) and evaporation time on a leaf surface, and it may be reduced if the active ingredients in droplets do not uniformly spread out and remain on the leaf surfaces, especially for the surfaces of difficult-to-wet plants. In addition, chemical residues may form large crystals that cannot remain on foliage after droplets dry. For systemic pesticides, longer wetted time of spray droplets increases the plant absorption and adhesive of active ingredients on leaves (Knoche and Bukovac, 1994; Knoche et al., 2000). The absorption of chemicals may stop after droplet evaporation on leaves (Ramsey et al., 2005). However, excessive retention of water droplets on leaves may accelerate germination of certain pathogens (Huber and Gillespie, 1992; Bradley et al., 2003).

Most plants have a thin epidermis and cuticular membrane that protects the plant from the outside environment (Wang and Liu, 2007; Koch and Ensikat, 2008). Various characteristics of the leaf surfaces of plants affect the performance of agrochemical sprays (Beattie and Marcell, 2002; Bhushan and Jung, 2008). Leaf wettability is one critical characteristic (Liu and Zabkiewicz, 1997; Beattie and Marcell, 2002; Liu, 2004). A leaf surface is considered easy to wet if the contact angle between the leaf surface and a droplet on the leaf is less than 90°. Easily wetted leaves with rough surfaces have smaller contact angles. However, difficult-to-wet leaves with rough surfaces have a contact angle greater than 90° (Cape, 1983; Bhushan and Jung, 2008). A surface is considered superhydrophobic if the droplet contact angle is greater than 150° (Bhushan and Jung, 2008).

Leaf surfaces with heavy cuticular waxes are found on difficult-to-wet plants, and these waxes are primary barriers against the deposition, retention, spreading, and penetration of droplets of agrochemical sprays. Adjuvants can overcome this barrier and enhance the deposition, spread, penetration, and uptake of pesticides (Gaskin et al., 2000; Hess and Foy, 2000; Kudsk and Mathiassen, 2007; Penner, 2000; Ramsey et al., 2005, 2006). They also can help chemicals remain in solution for longer periods in droplets and thereby improve the penetration and absorption of the pesticides into plants. The adjuvants used as humectants help prevent droplets of pesticides from drying quickly on leaf surfaces and similarly enhance performance (Ramsey et al., 2005).

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Spray adjuvants are usually categorized into two groups: activator adjuvants and special-purpose or utility adjuvants. Activator adjuvants can enhance the biological efficacy of the chemical (Hazen, 2000) and include surfactants, oils, and nitrogen-based fertilizers. Special-purpose adjuvants can modify the physical characteristics of the spray solution (Hazen, 2000) and include stabilizers, buffers, defoaming agents, deposition aids, and drift retardants.

Surfactants include nonionic, anionic, cationic, organosilicones, and silicones. They lower the surface tension of spray droplets on a leaf surface and consequently increase droplet coverage and foliar uptake (Hess and Foy, 2000; Liu, 2004; Wang and Liu, 2007; Ryckaert et al., 2007). The surfactant concentration can also influence the efficacy of agrochemical application. Increasing surfactant concentration from 0.01% to 1% will promote the foliar uptake of pesticides. However, for some surfactants, increased concentration can produce a negative effect on pesticide uptake when the concentration is above a critical value (Wang and Liu, 2007). The residues from droplets with alkyl polyoxyethylene surfactant formed residual patterns of "ring islands" at lower concentration and "solid rings" at higher concentrations on mildly hydrophilic substrates (Pierce et al., 2008). Similarly, a coffee droplet deposited on paper creates a "coffee ring" at post-evaporation because of the triple-phase line (pinned line) (Deegan et al., 1997).

Oil-based adjuvants promote the penetration of chemical spray through a plant's waxy cuticle. The three types of oil-based adjuvants include crop oils, crop oil concentrates, and seed (vegetable) oil concentrates.

Although a wide variety of adjuvants have been reported to improve the performance of pesticides sprays, quantitative analyses are lacking on the relative effectiveness of different classes of adjuvants as spreaders and humectants. Knowledge of the interaction between the target plant and the adjuvant in the spray mixture is essential for successful pesticide application in agriculture. Yu et al. (2009a, 2009b) investigated droplet evaporation time and coverage area of pesticide droplets on hydrophobic and hydrophilic slides and on waxy and hairy leaves under controlled environmental conditions. They found that evaporation dynamics and post-evaporation deposit formations of pesticidal droplets on waxy and hairy (pubescent) leaf surfaces are greatly influenced by spray formulation, droplet size, and relative humidity. For droplets ranging in diameter from 246 to 886 μm exposed to an atmosphere of 30% to 90% relative humidity, addition of surfactant to the spray could increase the droplet coverage area 4.5 to 10.1 times on the hairy leaves and 3.4 to 4.1 times on the waxy leaves. However, only alkyl polyoxyethylene surfactant was investigated in those studies.

The objective of this research on four representative classes of adjuvants was to determine the relationships between these adjuvants and the contact angle, wetted area, evaporation time, and residual patterns of droplets after deposition on leaf surfaces of waxy plants.

Material and Methods

The spread and evaporation times of droplets were tested on waxy leaves of *Begonia sanguinea* (*B. sanguinea*), *Begonia echinosepala* var. elongatifolia (*B. echinosepala*), *Kalanchoe serrata* (*K. serrata*), *Pelargonium peltatum* (*P. peltatum*), and *Pelargonium stenopetalum* (*P. stenopetalum*). They were selected from the *Pelargonium* collection of the Ornamental Plant Germplasm Center (OPGC) in Columbus, Ohio. This collection provided an opportunity to select genetically related plant material with widely varying leaf phenotypes. Seedlings of each test species were transplanted into 4 L pots and grown in a greenhouse at a controlled ambient temperature of 25°C to 30°C. The plants were watered once a day to the point that the potting mix was saturated. Fertilizers were also applied to plants after transplanting. The abaxial surface of freshly cut leaf samples (2 cm × 2 cm) was secured onto a glass plate with double-sided adhesive tape and then tested in an environmentally controlled chamber described below. Leaf thickness varied with the plant species. A water droplet containing an adjuvant was deposited on the adaxial surface of leaf samples. Each treatment consisted of five samples representing five replications.

Adjuvants with five different formulations were mixed with distilled water separately to form five different spray solutions. They included two oil-based adjuvants (crop oil concentrate (COC) and modified seed oil (MSO)), a nonionic surfactant adjuvant (NIS), and a suspension of oil surfactant blend (OSB). The principal functioning agents of the surfactants and their formulated concentration with water are described in table 1. The adjuvants were formulated by Wilbur-Ellis Company (San Francisco, Cal.) and were homogenized in distilled water according to the manufacturer's recommendation (table 1). As a control, a treatment of droplets consisting of distilled water only was also included in the experiments.

Droplets were photographed at 40 magnifications from two perspectives in relation to the leaf surface: top view (fig. 1) and side view (fig. 2). Sequential images of a droplet taken from the top view were used to assess the spread and evaporation times of a droplet containing various adjuvants. The sequential images from the side view were used to determine the rate of changes in the contact angle of the droplet.

Table 1. Adjuvants and their concentrations in water used in the tests.

Adjuvant	Principal Functioning Agents	Concentration (% v/v)	Surface Tension (dynes/cm)
Crop oil concentrate (COC)	Paraffin base petroleum oil 83%; surfactant blend 17%.	1.040	34.6
Modified seed oil (MSO)	Methyl soyate, nonylphenol ethoxylate blend (surfactant content 15%).	0.521	35.4
Nonionic surfactant (NIS)	Alkylphenol ethoxylate, butyl alcohol, dimethylpolysiloxane 90%; constituents ineffective as spray adjuvant 10%.	0.250	31.8
Oil surfactant blend (OSB)	Ethylated seed oil; 3-(3-hydroxypropyl)-heptamethyltrisiloxane, ethoxylated acetate; polyoxyethylene dioleate; polyol alkyl thoxylate (surfactant content 40%).	0.130	29.0
Water only	--	--	72.8

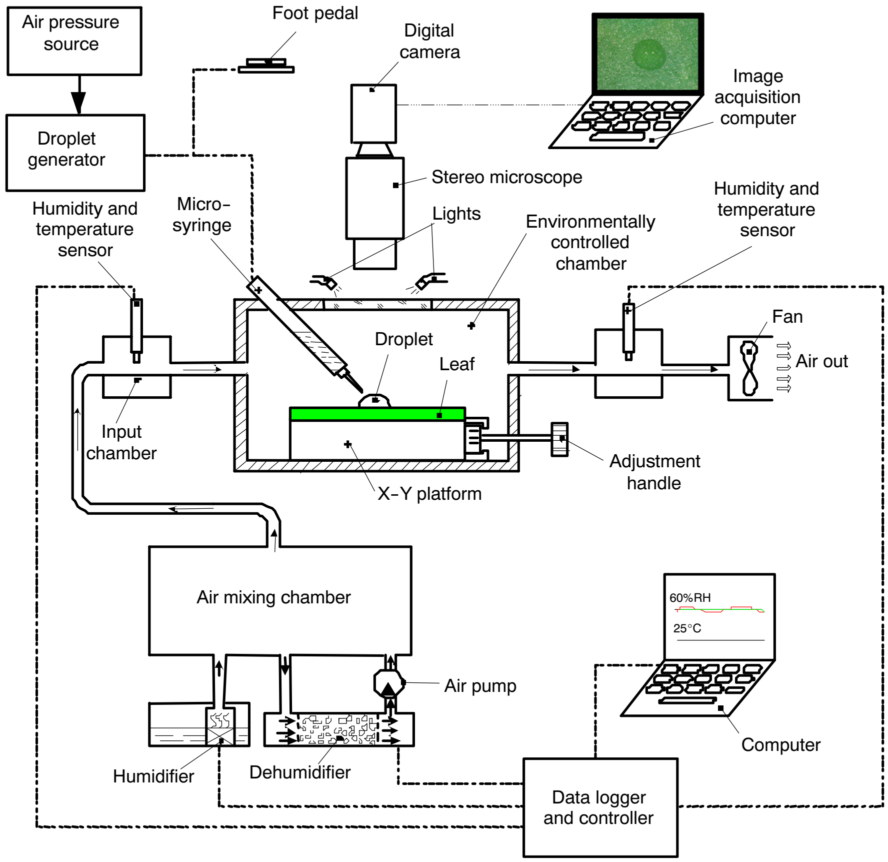


Figure 1. Experimental system to determine droplet evaporation and spreading on waxy leaves in an environmentally controlled chamber.

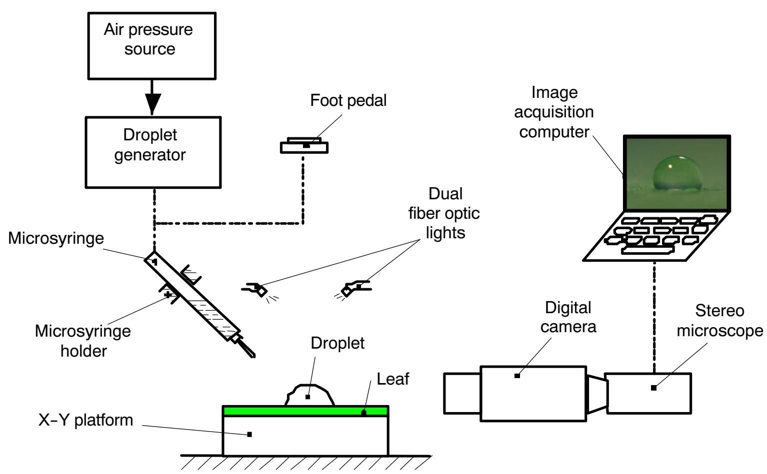


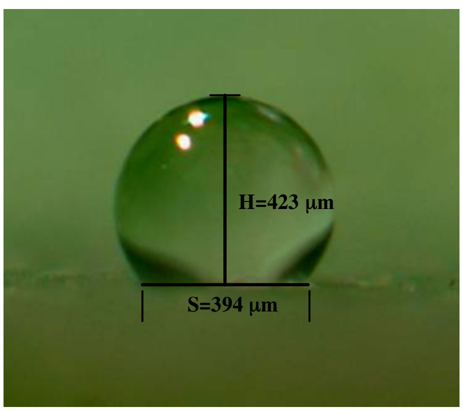
Figure 2. Experimental system to determine contact angle of droplets on waxy leaves.

The equipment used to observe the top view of droplets included a droplet dispenser, an environmentally controlled chamber, and an image acquisition component (fig. 1). The droplet dispenser was a droplet generator (model 2405, EFD, Inc., East Providence, R.I.) mounted with a 3 mL barrel-piston microsyringe and a needle with a chamfered tip. The environmentally controlled chamber included a humidifier, a dehumidifier, two humidity and temperature sensors, an air mixing chamber to condition the air at 25°C and 60% RH prior to its entry into the chamber, a micro datalogger, and a portable computer. A target object (leaf sample) was placed on a movable platform inside the environmentally controlled chamber. The image acquisition component included a stereoscopic microscope (model SZX12, Olympus Corp., Tokyo, Japan), a vertically mounted Insight Firewire Color Mosaic digital camera (model 18.2, Diagnostic Instruments, Inc., Sterling Heights, Mich.), and an image acquisition computer, as previously reported by Zhu et al. (2008). Conditions for observations and photographing the side view of droplets were essentially similar, except the stereoscopic microscope with the camera was oriented horizontally to view droplets on leaves that were exposed outside the environmentally controlled chamber (fig. 2).

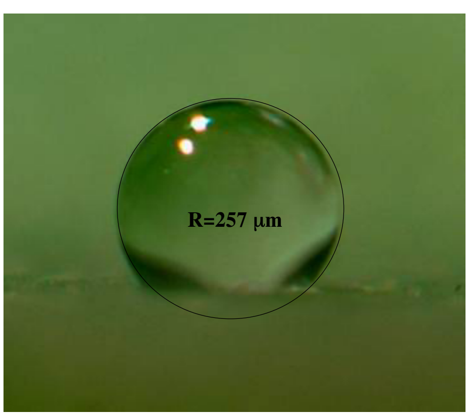
The contact angle of a water droplet on a leaf surface was used to determine the wettability of the leaf. A leaf was considered "wettable" if the water contact angle was less than 90° and "non-wettable" if the water contact angle was greater than 90° (Cape, 1983; Bhushan and Jung, 2008). The contact angle of a droplet on leaf surfaces is commonly measured by the tangent method (Zisman, 1964). This method assumes that the droplet is deposited on a flat smooth surface. However, leaf surfaces, especially those of dicots, are usually somewhat wrinkled. Thus, it is difficult to precisely determine the point of intersection between the droplet contact profile and the leaf surface. Consequently, the measurement of contact angle of droplets on leaves with the tangent method will result in significant errors.

In this study, a supposition was made that the shape deformation of droplets on the leaf surfaces by gravity could be ignored. The shape of the droplet on the leaf surface was considered to be a segment of a sphere (figs. 3a and 3b). The contact angle (θ) was determined with the following equation by measuring the contact width (*S*) of the droplet on the leaf surface and the height (*H*) of the droplet (fig. 4):

$$\theta = 90° - \arctan\left(\frac{S}{4H} - \frac{H}{S}\right) \text{for } R \le H \text{ and } R > H \quad (1)$$



(a)



(b)

Figure 3. A 500 µm water-only droplet deposited on a leaf surface of K. serrata with a contact angle of 130°: (a) measurement of contact length (S = 394 µm) and height of the droplet (H = 423 µm) on the leaf surface, (b) calculated radius of the sphere (R = 257 µm) that coincided with the outline of the droplet.

where θ is greater than or equal to 90° when $R \le H$ and smaller than 90° when $R > H$, and *R* is the radius of the sphere, which is calculated with the following equation:

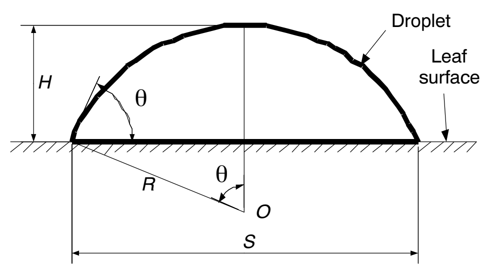
$$R = \frac{S^2}{8H} + \frac{H}{2} \quad (2)$$

For example, the measured values of *S* and *H* for a 423 µm droplet were 394 µm and 423 µm (fig. 3a), respectively. The radius (*R*) of the sphere was calculated as 257 µm and coincided with the outline of the droplet (fig. 3b). In this case, the resulting contact angle was then calculated as 130°.

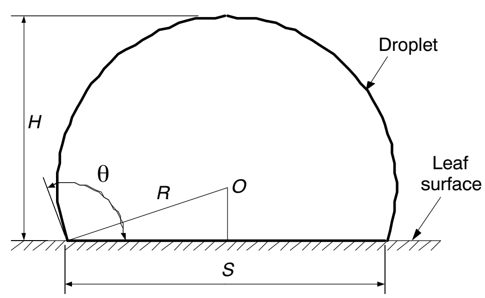
The "wetted area", defined as the maximal contact area of a droplet on a leaf surface after deposition, was used to describe the droplet spread capability. It was determined by tracing the marked outline of the deposit contact area on the leaf surface using the polygonal hand-trace feature of Image-Pro Plus software (version 6.1, Media Cybernetics, Bethesda, Md.).

After a droplet was deposited on a leaf surface, sequential photographic images at 2 s intervals were used to determine the time required for droplet spread and evaporation. The first image was photographed as soon as the droplet was deposited on the leaf surface, and the last image was photographed when the droplet completely evaporated. Thus, the time required for droplet evaporation was the product of the number of sequential images and the time interval.

Sessile droplets of 500 µm diameter were selected for the test. With this diameter, the droplet generator was able to consistently reproduce constant-size droplets and the size was small enough to avoid shape deformation that might compromise the contact angle measurement. During this study, the relative humidity and the temperature in the environmentally controlled chamber were set at 60% and 25°C, respectively. Each treatment was repeated five times.



(a) $\theta \le 90°$ (or $H \le R$)



(b) $\theta > 90°$ (or $H > R$)

Figure 4. Geometry to determine the contact angle (θ) of a droplet on leaf surfaces when (a) θ ≤ 90° (or *H* ≤ *R*), and (b) θ > 90° (or *H* > *R*).

Data from replicated samples were analyzed with Duncan's multiple range test using ProStat version 3.8 (Poly Software International, Inc., Pearl River, N.Y.). All differences among treatments were determined at the 0.05 level of significance. An integrated index (λ) was used to characterize the droplet spread and evaporation and was defined as the product of the wetted area (*A*) and the evaporation time (*T*) of a droplet on a leaf surface: $\lambda = T \cdot A$.

Results and Discussion

Contact Angle

Contact angles of 500 μm droplets formulated with COC, MSO, NIS, or OSB adjuvant or with a water-only solution on waxy leaves of five test species (*K. serrata*, *P. peltatum*, *B. sanguinea*, *B. echinosepala*, and *P. stenopetalum*) are shown in table 2. The contact angles of all water-only droplets were greater than 90°, indicating that the leaf surfaces of all five test species were non-wettable or difficult to wet. Contact angles of the water-only droplets among the test species were also significantly different. Among the five test species, water-only droplets on leaves of *B. echinosepala* had the lowest contact angle (average 91.2°), and the droplets on leaves of *K. serrata* had the highest contact angle (average 122.1°). When adjuvants were added to the solution, the contact angles decreased substantially as a result of lowered surface tension of the droplets (tables 1 and 2).

Among the four adjuvants tested, MSO reduced the contact angles of droplets on waxy leaves the most and COC the least. These two oil-based adjuvants presented marked differences in decreasing contact angles. Compared to the contact angles of a water-only droplet on *K. serrata*, *B. echinosepala*, *P. peltatum*, *B. sanguinea*, and *P. stenopetalum*, the contact angles of the droplets with MSO were decreased by 79.3%, 57.1%, 56.9%, 54.9%, and 52.9%, respectively. Interestingly, the contact angles of droplets with any of the four adjuvants on *K. serrata* were reduced the most among the five species. Furthermore, the contact angle of the water droplet on *K. serrata* was the highest among the five species.

Droplet Residual Pattern

Figure 5 shows various residual patterns after droplets completely evaporated on the surfaces of *B. sanguinea* leaf with four classes of adjuvants with five replicated samples at 60% relative humidity and 25°C. A "coffee ring" was formed on the leaf surface after evaporation, although the shape of each residual pattern was different, such as solid ring, broken ring, or islands. The residual patterns of droplets with NIS were either a narrow solid or broken ring, but wider rings or islands appeared with oil-based adjuvants (COC and MSO) and the mixture of oil and surfactant (OSB). Solutions with oil-based adjuvants had a higher surface tension, which modified the droplet spread by reducing the capillary flow of the droplets. Thus, the residuals of droplets with COC, MSO, or OSB covered relatively larger areas with more small islands or broken rings than droplets with NIS (fig. 5). In addition, residuals that cover larger areas effectively improve the uniformity of spray deposition on leaves. A lower concentration of nonionic adjuvant might allow small islands of residuals to be distributed in the wetted area (Pierce et al., 2008). However, these droplets still might not spread if the concentration is too low. In the commercial market, droplets of some pesticide concentrates that are formulated with surfactants do not readily spread, in part due to insufficient surfactant concentration in the formulations (Yu et al., 2009a, 2009b).

Wetted Area

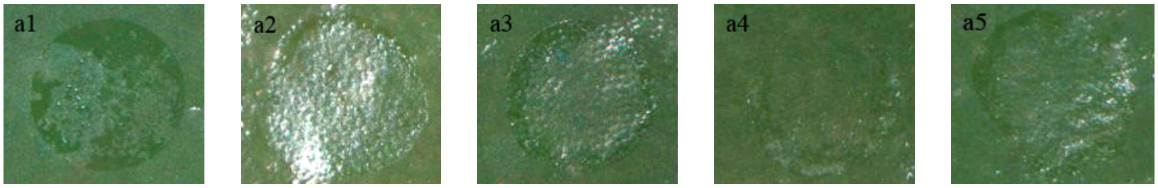
The average wetted area of 500 μm water droplets on the test species ranged from 0.114 to 0.275 mm^2 (table 3). The wetted areas of water droplets without adjuvants on *K. serrata* were the smallest among the test species. The wetted areas of water droplets increased significantly when adjuvants were added to the solution. In most cases, the effectiveness of the MSO and NIS adjuvants to spread droplets was significantly better than that of the COC and OSB adjuvants. The performances of the two oil-based adjuvants (MSO and COC) on the spread characteristics of droplets were also greatly different. The MSO adjuvant was more effective on droplet spread than COC, even though the concentration of COC was twice that of MSO. The suspension of OSB surfactant was the least effective on droplet spread on all five plant species. One reason for this may be that the recommended concentration of this adjuvant in the spray solution was insufficient. MSO is generated from renewable resources, being a kind of modified seed (vegetable) oil. On the contrary, COC is a paraffin-based petroleum oil. Hence, oil-based adjuvants made from the seed (vegetable) oil might have greater spreading capabilities than the adjuvants made from petroleum oil.

Compared to water-only droplets, droplets with MSO and NIS increased the wetted area on *K. serrata* leaves by 675% and 639%, respectively. In general, adjuvants significantly increased the wetted areas on *K. serrata* and *B. echinosepala*. The wetted areas of droplets with MSO adjuvant on *K. serrata* were 28.6% larger than that on *B. echinosepala*. Conversely, the wetted area of droplets with OSB adjuvant on *K. serrata* was 41.3% lower than that on *B. echinosepala*.

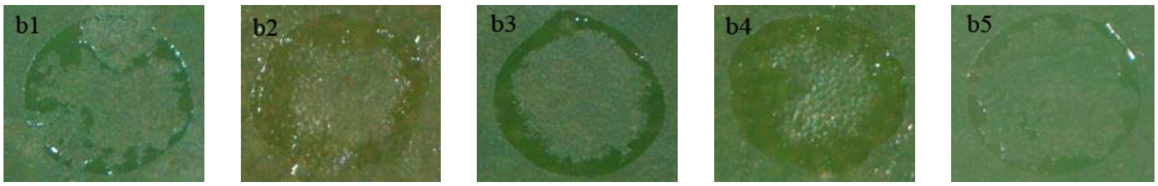
The wetted areas per droplet volume for the 500 μm droplets with and without the four adjuvants on the five test species are shown in figure 6. The average wetted area per droplet volume on the leaves of test species ranged from 7.2 to 9.0 mm^2/mm^3 with COC, from 7.5 to 13.5 mm^2/mm^3 with MSO, from 8.0 to 12.9 mm^2/mm^3 with NIS, from 4.8 to 8.2 mm^2/mm^3 with OSB, and from 1.7 to 4.2 mm^2/mm^3 with

Table 2. Contact angle (°) of 500 μm droplets with and without adjuvants on five different waxy plants. Standard deviations are in parentheses. Within a column, means followed by different letters are significantly different ($p < 0.05$).

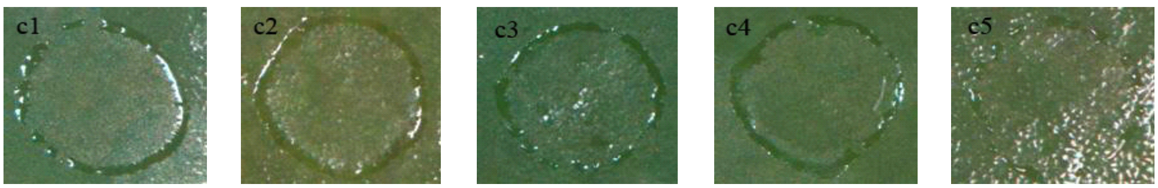
Adjuvant	*K. serrata*	*P. peltatum*	*B. sanguinea*	*B. echinosepala*	*P. stenopetalum*
COC	37.4 (2.8) b	57.7 (7.3) b	58.2 (3.7) b	43.2 (11.3) b	53.9 (4.9) b
MSO	25.3 (3.5)c	42.9 (6.5) c	49.7 (1.8) c	39.1 (8.2) b	46.5 (6.9) b
NIS	33.9 (6.3) b	48.6 (8.0) bc	54.2 (3.3) bc	45.2 (8.9) b	50.9(4.6) b
OSB	37.7 (6.2) b	43.5 (6.8) c	51.5 (4.0) c	43.5 (7.7) b	50.6 (9.5) b
Water only	122.1 (11.3) a	99.6 (2.5) a	110.2 (4.5) a	91.2 (15.3) a	98.8 (6.4) a



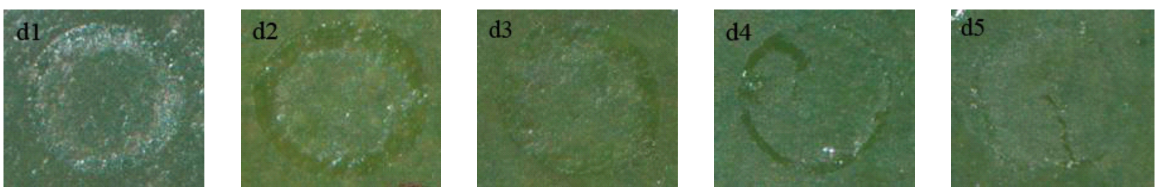
(a) COC



(b) MSO



(c) NIS



(d) OSB

Figure 5. Residual patterns of 500 µm droplets post-evaporation on the leaf of *K. serrata* with four classes of adjuvants, (a) crop oil concentrate (COC), (b) modified seed oil (MSO), (c) nonionic surfactant (NIS), and (d) oil surfactant blend (OSB), with five replicated samples, at 60% relative humidity and 25°C.

Table 3. Wetted area (mm^2) of 500 µm droplets with and without adjuvants on five different waxy plants. Standard deviations are in parentheses. Within a column, means followed by different letters are significantly different ($p < 0.05$).

Adjuvant	*K. serrata*	*P. peltatum*	*B. sanguinea*	*B. echinosepala*	*P. stenopetalum*
COC	0.509 (0.044) b	0.491 (0.072) b	0.524 (0.052) b	0.591 (0.224) a	0.471 (0.164) a
MSO	0.884 (0.272) a	0.812 (0.292) a	0.621 (0.062) a	0.687 (0.176) a	0.491 (0.090) a
NIS	0.842 (0.329) a	0.641 (0.081) ab	0.601 (0.050) ab	0.734 (0.133) a	0.526 (0.088) a
OSB	0.316 (0.052) bc	0.461 (0.042) b	0.439 (0.092) c	0.538 (0.183) a	0.321 (0.067) b
Water only	0.114 (0.009) c	0.190 (0.019) c	0.189 (0.036) d	0.275 (0.039) b	0.185 (0.025) c

water only. Generally, droplets with adjuvants increased the wetted area per droplet volume, but the degree of increase varied with the class of adjuvants. MSO and NIS has greater average wetted area per droplet volume on the test species than COC and OSB. Hence, to achieve optimum droplet spread and to maximize spray application efficiency, the choice of an adjuvant must also consider the plant species.

Evaporation Time

The evaporation time of 500 µm droplets prepared with one of the four adjuvants or with a water-only solution on the test species are presented in table 4. In contrast to the wetted area, the evaporation time did not vary greatly with any one of the four adjuvants. The evaporation time of droplets on the five test species ranged from 103.6 to 198.0 s and from 144.8 to 282.4 s with and without the addition of adjuvants, respectively. Compared to the water-only droplets, the average evaporation time with the COC, NIS, MSO, and OSB adjuvants on the tested species decreased by only 18.5%, 22.8%, 28.2%, and 30.6%, respectively. Thus, adding adjuvants into sprays only slightly accelerated the droplet evaporation time after its deposition on leaves. However, droplets with larger wetted areas had faster evaporation times on waxy leaves than droplets with smaller wetted areas. Among the four adjuvants, the evaporation time of droplets prepared with COC was the slowest, and droplets prepared with OSB evaporated the fastest. More importantly, because the concentration of COC was the highest and the concentration of OSB the lowest, the solution with a lower concentration also might be less effective in droplet spread (table 3) and in resisting evaporation (table 4).

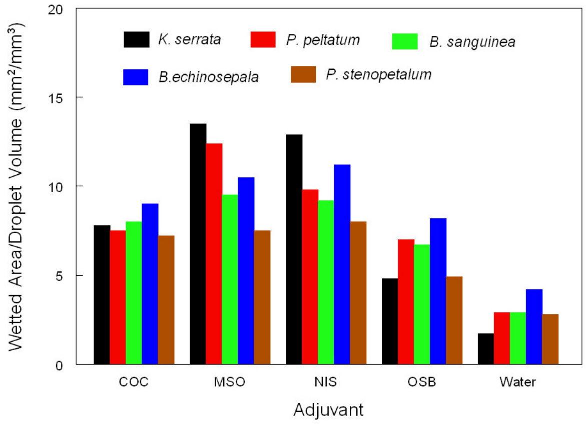


Figure 6. Wetted area per droplet volume of 500 µm droplets with and without adjuvants on five different waxy plants.

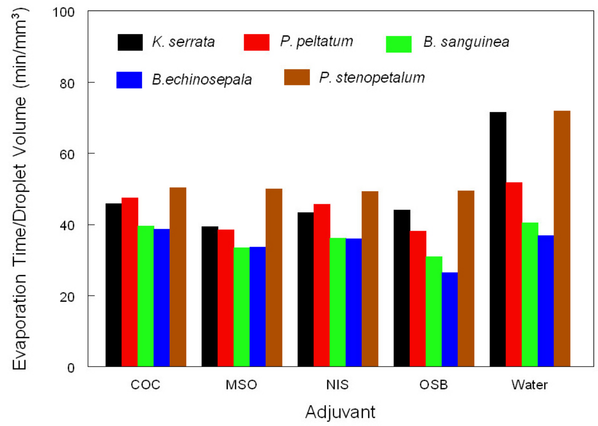


Figure 7. Evaporation time per droplet volume of 500 µm droplets with and without adjuvants on five different waxy plants.

Table 4. Evaporation time (s) of 500 µm droplets with and without adjuvants on five different waxy plants. Standard deviations are in parentheses. Within a column, means followed by different letters are significantly different ($p < 0.05$).

Adjuvant	*K. serrata*	*P. peltatum*	*B. sanguinea*	*B. echinosepala*	*P. stenopetalum*
COC	180.0 (4.0) b	186.4 (29.3) b	155.2 (16.4) a	152.0 (7.3) a	198.0 (33.0) b
MSO	154.8 (17.2) c	150.8 (17.8) c	131.2 (7.3) bc	132.4 (13.3) b	196.4 (15.2) b
NIS	170.0 (16.4) bc	179.2 (24.1) bc	142.0 (6.8) ab	140.8(5.4) ab	193.6 (31.1) b
OSB	173.2 (15.1) bc	149.6 (10.8) c	121.6 (5.0) c	103.6 (10.5) c	194.0 (36.7) b
Water only	280.8 (19.2) a	203.2 (33.5) a	158.4 (5.0) a	144.8 (16.3) ab	282.4 (50.0) a

Table 5. Integrated index (λ, s·mm^2) of 500 µm droplets with and without adjuvants on five different waxy plants.

Adjuvant	*K. serrata*	*P. peltatum*	*B. sanguinea*	*B. echinosepala*	*P. stenopetalum*
COC	91.6	91.5	81.3	89.8	93.3
MSO	136.8	122.4	81.5	91.0	96.4
NIS	143.1	114.9	85.3	103.3	101.8
OSB	54.7	69.0	53.4	55.7	62.3
Water only	32.0	38.6	29.9	39.8	52.2

Plant species also slightly influenced the evaporation time. The evaporation time for the two begonia varieties (*B. sanguinea* and *B. echinosepala*) was significantly lower than for the other test species. Compared to the water-only droplets, the average evaporation time with four adjuvants was slowest on *P. stenopetalum* and fastest on *B. echinosepala*. On *K. serrata*, the average evaporation time of droplets with the four adjuvants was 28.2% slower than on *B. echinosepala*, even though their average wetted areas were similar.

The evaporation time per droplet volume of 500 µm droplets with and without four adjuvants on leaves of the five test species are shown in figure 7. Addition of adjuvants into sprays increased the droplet evaporation time per droplet volume, but the portion of increase did not coincide with the adjuvant class.

The integrated index (λ) of 500 µm droplets with and without the four different adjuvants varied with the adjuvant class and plant species (table 5). Droplets with the nonionic surfactant (NIS) and the oil-based MSO adjuvant had greater λ values due to higher droplet spreading and lower evaporation times on waxy plants, especially on *K. serrata*. For example, the difference in the average λ value between *K. serrata* and *B. sanguinea* with the same NIS adjuvant reached 40.4%. The OSB adjuvant had considerably lower λ values than the other adjuvants. The λ values for water-only droplets were much lower than the values for droplets with adjuvants, although the water-only droplets had slower evaporation times.

Due to the increased wetted area with adjuvants, the application efficiency and efficacy of pesticides should increase considerably and would greatly benefit waxy plants with water contact angles larger than 90°. The addition of an appropriate adjuvant to the spray solution is a practical and readily available option to applicators to improve the application efficiency of pesticides. Results from this study show that droplets containing adjuvants, such as oil-based adjuvants, nonionic surfactants, and oil and surfactant blends, performed better as a consequence of improved spreading capacity and slower droplet evaporation, especially on waxy plants. In general, the oil-based MSO adjuvant and the nonionic surfactant (NIS) were more effective in spreading the droplet contact area. Droplets that had lower contact angles on leaves would have greater wetted areas and spread capacity and slower evaporation time.

Conclusions

Spray solutions incorporating COC, MSO, NIS, or OSB adjuvants with water greatly reduced the contact angle of spray droplets on waxy leaves of all five plant species, and the reduction varied with the class of adjuvant and the plant species. Among the four adjuvants tested, MSO reduced the contact angles of droplets on waxy leaves the most and COC the least.

Adjuvants in spray solutions also significantly increased the wetted areas on leaves of the test species. The effectiveness of MSO and NIS on droplet spread was significantly greater than that of the other two adjuvants (COC and OSB). Adjuvants increased the droplet spread more on *K. serrata* and *B. echinosepala* than on the other three tested species. Compared to the water-only solution, MSO and NIS increased the wetted areas of 500 μm droplets on *K. serrata* leaves by 675% and 639%, respectively.

The spreading performances of the two oil-based adjuvants (MSO and COC) on waxy leaves were significantly different. Droplets with the seed oil based MSO had much stronger spreading performance than droplets with the petroleum oil based COC.

Evaporation time of droplets on leaves of different species did not change greatly with the adjuvant class. With adjuvants, the 500 μm droplets had evaporation times ranging from 103.6 to 198.0 s. Without adjuvants, the range was 144.8 to 282.4 s.

The residual patterns on leaf surfaces formed a "coffee ring" after evaporation of droplets with adjuvants of any class. The residual patterns of droplets with COC, MSO, and OSB covered relatively larger areas with more small islands or broken rings than droplets with NIS.

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