CHARACTERISING PLANT SURFACES FOR SPRAY ADHESION AND RETENTION

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ABSTRACT

A simple measurement of static contact angle of aqueous acetone droplets on surfaces has been developed for characterising leaf surfaces. It allows leaves to be compared and grouped by their surface "roughness factor" and it differentiates between easy, difficult and very difficult-to-wet species. This paper describes how the method has been used to survey a large number of plant species, including weeds and crops, fruit and foliage. High contact angles indicate difficult-to-wet surfaces. The quantitative measure of contact angle is a useful tool to predict spray droplet adhesion and rank plant surfaces for retention properties. It can also indicate whether surfactant addition is likely to be beneficial for agrochemical sprays targeted at fruit or foliage on different crops. Surfactants were most useful for improving spray droplet adhesion and retention on difficult-to-wet surfaces, but results varied with surface wettability, surfactant type and concentration, and with plant architecture.

Keywords: fruit, foliage, agrochemical sprays, surfactants, contact angle, wettability.

INTRODUCTION

The surfaces of plants are known to vary widely and can be classified from very easy through to very difficult-to-wet. The adhesion, retention and distribution of agrochemical sprays on plant surfaces are influenced by the target wettability (i.e. microscopic roughness). Micro-roughness can be due to surface contours, trichomes and waxes, and may be further altered by environmental factors such as dust and moisture deficit. Many attempts have been made to characterise plant surfaces in order to predict how spray formulations will adhere to and be retained on them. Contact angles have been used for a long time as an indicator of surface wettability, but droplet contact angles using actual spray formulations on a wide range of leaf surfaces do not show good correlation with adhesion (Forster et al. 1998). Pure water contact angles are inadequate to distinguish differences between difficult-to-wet species (Forster et al. 2001).

In the course of developing a universal spray droplet adhesion model, the static contact angle of a 20% acetone in water solution on a leaf was shown to be a simple and convenient measurement to account for the observed differences in adhesion between the surfaces. The correlation between percentage adhesion and contact angles was excellent ($R^2=0.97$) over a wide range of leaf surfaces (Forster & Zabkiewicz 2001). This method is now applied routinely in plant protection research to characterise the micro-roughness of surfaces and differentiate the wettability of species. It is a tool used to rank plant surfaces for adhesion properties, and to predict whether surfactant addition is likely to be beneficial for retention of sprays targeted at specific foliage or fruit. This paper demonstrates the practical use of the contact angle measurements.

METHODS

Contact angle measurements

Droplets (1 μ l) of an acetone+water solution (20% v/v acetone, with a surface tension of 41 mN/m) were applied to the surfaces of freshly detached leaves or fruit of the species

under test, mounted on double-sided adhesive tape. The static contact angle was calculated from the projected image of the droplet, obtained using a modified slide projector (Leitz). At least 20 replicate droplets were measured on at least three separate leaf or fruit surfaces of each species. All samples were taken from plants grown outdoors.

Determination of adhesion

The specific method for determining adhesion is described elsewhere (Stevens et al. 1993). In summary, ten droplets of each formulation were impacted onto each of five replicate leaves, taken from different plants, for each leaf surface studied. Droplet size, fall distance and leaf angle were 850 µm diameter, 400 mm and 22.5°, respectively. All treatments contained fluorescent dye and droplet adhesion was visualised under UV light. Adhesion is defined as the droplet sticking on first impact; if it bounces it is judged not to have adhered. Dock (*Rumex obtusifolius*), bean (*Vicia faba*) and pea (*Pisum sativum*) leaves were sampled from plants grown in a controlled environment, while grapes (*Vitis vinifera* cv. Semillon) were grown outdoors.

Retention studies

The retention data reported here have been determined over a number of laboratory and field trials using both a tracksprayer and commercial sprayers to deliver a wide range of pesticide spray formulations containing a dye tracer (tartrazine) to onion, grape, potato, kiwifruit, avocado and apple crops. Detailed methods are reported elsewhere (Gaskin et al 2004a,b). Retention is determined by washing dye off fruit and foliage samples to quantify spray recovery, i.e. spray deposits, by spectrophotometric methods. All deposit data reported here are normalised to an application rate of 1 kg/ha and are expressed relative to measured leaf or fruit surface area.

RESULTS AND DISCUSSION

Plant surface wettability

The contact angle test is applied as a simple method of quantifying the wettability of different species. A low contact angle (<60°) is indicative of easy wetting, up to 80° is regarded as moderate, measurements around 100° are regarded as difficult and angles over 120° are very difficult-to-wet (Table 1).

The wettability of plant surfaces may change with age and maturity (Table 1). Little variation in contact angle is present in apples, either between species or between juvenile and mature foliage. Apple leaves are regarded as consistently easy-to-wet. In contrast, the foliage of eucalypt species is difficult-to-wet in the juvenile form, but mature leaves are much more readily wetted. Sprays targeting juvenile foliage will therefore benefit more from modification by surfactants to improve droplet adhesion on these leaves. Brassica are notoriously difficult to deposit sprays on, and both canola and cabbage exhibit typically high contact angles, for both juvenile and mature foliage. These contact angles tell us that sprays will adhere more easily to canola seedlings than to older plants, while there is little age effect evident on cabbage. Variegated thistle leaves will repel spray droplets more as they mature; better adhesion of herbicide sprays is more likely by targeting juvenile plants.

TABLE 1: Mean contact angle (°) and wettability of upper leaf surfaces for juvenile and mature leaves of seven plants.

Species	Juvenile leaf		Mature leaf	
	Contact angle	wettability	Contact angle	wettability
Apple cv. Braeburn	59.1 (7.2) ¹	easy	61.8 (7.3)	easy
Apple cv. Pacific Rose	60.8 (5.5)	easy	64.3 (7.1)	easy/mod.
<i>Eucalyptus nitens</i>	93.3 (2.2)	difficult	59.2 (4.2)	easy
<i>Eucalyptus cinerea</i>	115.5 (7.4)	difficult	67.5 (10.3)	moderate
Canola	110.2 (5.0)	difficult	132.0 (5.9)	very difficult
Cabbage cv. F1 Hybrid	119.2 (9.1)	very difficult	111.7 (5.8)	difficult
Variegated thistle	60.4 (10.0)	easy	77.0 (8.0)	moderate

¹SE

Effect of surface wettability on droplet adhesion

Droplet adhesion is the primary process in spray retention. The wettability of surfaces by water has a large effect on the initial adhesion of droplets (Table 2). Surfactants increase the adhesion of spray droplets onto plant surfaces by reducing their surface tension (Stevens et al. 1993). This effect is also demonstrated in Table 2, using a surfactant whose surface tension decreases with increasing concentration. Very easy-to-wet surfaces, such as dock, have no requirement for surfactants. As surface roughness (and contact angle) of leaves increase, the addition of surfactant, and in increasing amounts, improves droplet adhesion.

TABLE 2: Adhesion (%) of spray droplets with different levels of surfactant to the surface of leaves from different plant species.

Species	Contact angle	Leaf 'wettability'	Adhesion of spray droplets to leaf surfaces		
			water	0.1% surfactant	0.2% surfactant
Dock	45	very easy	100	100	100
Bean	55	easy	68	92	100
Grape	82	moderate	62	72	82
Pea	180	very difficult	0	0	52
LSD for all treatments (P=0.05)				10.7	

Adjuvant effects on spray retention by plant surfaces

When a droplet is impacted on a leaf, it may adhere, bounce, shatter, spread, redistribute or run-off. The total amount of spray retained by a leaf may be quite different from the initial adhesion of spray droplets. Retention is also affected by plant surface and canopy architecture, but contact angle measurements can give valuable information about the formulation requirements for different species. For example, a mancozeb spray containing a conventional nonylphenol (np) non-ionic surfactant is retained very differently by onion, grape and potato foliage (Table 3). Onion has a very-difficult-to-wet (contact angle 131°) upright leaf. It retains the least amount of the spray (dose per area) with the addition of three different surfactants, but benefits most from addition of superspreader surfactants that greatly reduce surface tension and are known to increase droplet adhesion on difficult-to-wet foliage (R.E. Gaskin, unpubl. data).

TABLE 3: Retention of three mancozeb spray formulations on three plant species with different contact angles.

Species	Contact angle ¹	Normalised spray retained by foliage (µg/cm ²)		
		+ np surfactant	+ superspreader	+ superspreader /sticker
onion	131	1.65 b ²	3.03 a	3.20 a
Grape cv. Cab. Sav.	93/132	3.90 a	3.70 a	3.90 a
potato	78/71	5.21 b	6.65 a	6.95 a

¹Upper/lower surfaces.
²Means within rows sharing common letters are not significantly different (P=0.05).

Grape foliage is moderately difficult-to-wet on the upper, and very-difficult-to-wet on the lower surface (Table 3). These leaves retain more dose per area than onions, but such foliage presents a dilemma for the grower. Sprays optimised for the upper leaf may not adhere to or cover the lower leaf surface and if optimised with surfactants to target the under-surface of leaves, spray is likely to be lost to run-off from the upper surface. In this case, the superspreader surfactants do not improve total retention on grape foliage, but they are known to improve spray distribution and coverage (Gaskin et al. 2000).

Potato leaves are the easiest-to-wet of the three species (Table 3) and least likely to require surfactant addition to optimise droplet adhesion. However, potato has a dense, layered canopy that requires redistribution of spray to target the inner foliage where disease develops. It retains 2-3 times greater dose per area than onion, and benefits from superspreader addition through improved redistribution of spray to the lower canopy (Gaskin et al. 2000). Canopy architecture is a major factor in spray retention (Gaskin et al. 2000) and must be taken into account, along with location of the intended target (e.g. pest, disease) and the plant surface wettability, to predict whether surfactant addition will be beneficial for an agrochemical spray.

Predicting relative retention on different surfaces

The leaves of an apple cultivar, both upper and lower, are easy-to-wet throughout a season, whereas the fruit are moderately difficult-to-wet (Table 4). Application of a total of 29 different sprays in two different studies confirms that foliage consistently retains 2-3 times more spray (dose/area) than fruit. Avocado leaves have an easily wetted upper surface, similar to apple, but a very difficult-to-wet lower surface (Table 4). The mean contact angle indicates avocado foliage will be a much more difficult target for spray adhesion than apple and the dose retained is 50% less than by apple. Avocado fruit has a similar contact angle to apple fruit and retention varies only by 10-30%. Crop architecture also contributes to differences in retention, as avocado fruit is shaded more by its foliage than are apples. Kiwifruit and avocado leaves have similar mean contact angles (ca. 100°, Table 4), but the differences between upper and lower surfaces of kiwifruit leaves are far less extreme, making it an easier target to optimise sprays for. The contact angle of kiwifruit (fruit) is not quantifiable due to the presence of large surface hairs that distort the measurement. Retention results indicate the wettability of fruit surfaces to be similar to leaves in this species, and easier to wet than either apple or avocado fruit.

TABLE 4: Mean normalised spray retained by the fruit or foliage ($\mu\text{g}/\text{cm}^2$) of three plant species at different times.

Species	Contact angle		No. of sprays ²	Spray retained by foliage ($\mu\text{g}/\text{cm}^2$)	
	Foliage ¹	Fruit		Foliage	Fruit
Apple (Nov)	64/64	100	11	3.07 (0.22) ⁴	1.38 (0.10)
Apple (Feb)	68/68	86	18	3.44 (0.30)	1.03 (0.08)
Avocado (July)	64/140	86	4	1.63 (0.14)	0.94 (0.14)
Kiwifruit (Apr)	79/120	na ³	10	1.87 (0.18)	1.61 (0.17)
Kiwifruit (May)	79/120	na ³	10	1.73 (0.20)	1.58 (0.14)

¹Upper/lower leaf surfaces.

²Total number of different spray formulations applied in each study.

³Unable to measure due to presence of macro surface hairs.

⁴(SE)

CONCLUSIONS

The simple method of measuring contact angles of acetone:water droplets on plant surfaces can be used to predict relative initial spray adhesion on different surfaces and species. This quantitative measure of micro-roughness is also used to rank surfaces for the more complex retention characteristics. Used together with canopy structure and target location, contact angle can indicate whether surfactant addition is likely to be beneficial for agrochemical sprays aimed at specific plant surfaces.

ACKNOWLEDGEMENTS

Thanks to Elliott Technologies Ltd and NZ Pipfruit Inc. for use of data generated in their projects, Sarah Skinner for contact angle measurements and Jerzy Zabkiewicz for helpful advice.

REFERENCES

- Forster WA, Zabkiewicz JA 2001. Improved method for leaf surface roughness characterisation. Proceedings of the 6th International Symposium on Adjuvants for Agrochemicals. Pp. 113-118.
- Forster WA, Kimberley MO, Zabkiewicz JA 2001. Pesticide spray droplet adhesion modeling. *Pesticide Formulations and Applications Systems* 21: 163-174.
- Forster WA, Kimberley MO, Zabkiewicz JA 1998. Spray droplet adhesion models – Evaluation of critical solution and leaf factors. Proceedings of the 5th International Symposium on Adjuvants for Agrochemicals. Pp. 55-60.
- Gaskin RE, Manktelow DWL, Elliott GS 2004a. Adjuvant prescriptions to lower water volumes and improve disease control in vineyards. Proceedings of the 7th International Symposium on Adjuvants for Agrochemicals. Pp. 236-241.
- Gaskin RE, Manktelow DWL, Skinner SJ, Elliott GS 2004b. Use of a superspreader adjuvant to reduce spray application volumes on avocados. *New Zealand Plant Protection* 57: 266-270.
- Gaskin RE, Elliott G, Steele KD 2000. Novel organosilicone adjuvants to reduce agrochemical spray volumes on row crops. *New Zealand Plant Protection* 53: 350-354.
- Stevens PJG, Kimberley MO, Murphy DS, Policello GA 1993. Adhesion of spray droplets to foliage: The role of dynamic surface tension and advantages of organosilicone surfactants. *Pesticide Science* 38: 237-245.