Characterisation of forest weed species and herbicide formulations to predict droplet adhesion and optimise spray retention

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Summary Simple laboratory measurements can be used to characterise forest weed species for wettability and herbicide formulations for their ability to be retained. The forest scrubweed species studied ranged from easy through to very difficult-to-wet. An empirical adhesion model was used to predict the effect of plant wettability, formulation and droplet size on adhesion, and illustrated the difficulty in optimising a single formulation and set of application parameters to provide efficacy across the weed species tested. Low volume aerial applications using relatively low VMD droplets and low surface tension formulations would appear the best option.

Keywords Leaf wettability, contact angle, DST, adhesion model.

INTRODUCTION

Aerial application of herbicides is an important tool widely used in forestry establishment in New Zealand, but there is a need to improve the efficacy of herbicides and reduce their use to improve the environmental sustainability of forest operations.

Spray retention and placement in the plant canopy have a crucial effect on the biological activity of herbicides. Simple laboratory measurements (e.g. contact angle and dynamic surface tension) and models can be used to predict initial spray adhesion on different plant surfaces and species (Forster *et al.* 2005), and indicate whether spray modification is likely to be beneficial for agrichemical sprays (Gaskin *et al.* 2005).

The objective of the current research was to: (1) characterise forest weed species for wettability using the contact angle measurement, (2) characterise herbicide spray formulations using dynamic surface tension measurements, (3) determine the interaction of plant wettability, formulation and droplet size on the predicted adhesion using empirical models.

MATERIALS AND METHODS

Plants Blackberry (*Rubus fruticosus* L.), bracken (*Pteridium esculentum* (G.Forst.) Cockayne), buddleia (*Buddleja davidii* Franch.), gorse (*Ulex europaeus* L.), pampas grass (*Cortaderia selloana* (Schult. & Schult.f.) Asch. & Graebn.)), Scotch broom (*Cytisus scoparius* L.) and radiata pine (*Pinus radiata* D.Don.) were raised outdoors in pots (4 L capacity) from seedlings.

Chemicals Metsulfuron (Escort™) and glyphosate (Green Glyphosate 510) were used at various rates alone and with various rates of an organosilicone surfactant (Break-Thru S 240) as shown in Table 2.

Contact angle measurements Droplets (2 µl) of an acetone + water solution (20% v/v acetone) were applied to the surfaces of freshly detached juvenile and mature foliage of each species. Replicate droplets (n = 21) were measured on at least three separate leaf or needle surfaces of each species. A KSV CAM 200 optical contact angle meter and Basler digital video camera were used to determine the static (equilibrium) contact angles.

Dynamic surface tension (DST) A Krüss bubble pressure tensiometer (BP2 MKII) was used to measure DST of formulations over a surface age time span of 15 to 1300 ms.

RESULTS AND DISCUSSION

Forest scrubweed wettability The contact angle test (20% acetone) is a simple method of quantifying the wettability of different plant species, at different ages and maturity. The current study determined the wettability of only the upper leaf surface, which is the primary surface presented to the spray from aerial application, except for the pine needles that are grouped in a three needle fascicle that twist, and for which the wettability of both surfaces was tested.

The wettability of broom, gorse, buddleia, radiata pine, blackberry, bracken and pampas grass was determined in late spring/early summer, followed by wettability tests in autumn and early spring on gorse, scotch broom, buddleia and radiata pine (Table 1). It can be seen that forest scrubweed species range from easy through to very difficult-to-wet (Table 1), where a low contact angle (<60°) indicates easy wetting, 60°–80° is moderate, 80°–100° is difficult and angles >120° are very difficult-to-wet (Gaskin *et al.* 2005).

Mature radiata pine needles were easy-to-wet, irrespective of the season (Table 1). However, juvenile foliage was difficult-to-wet in the early spring, progressing to easy-to-wet in autumn. The lower juvenile surface of radiata pine was moderate to difficult-to-wet while the lower mature foliage was easy to moderate-to-wet.

In early spring, broom has only juvenile foliage, which was very difficult-to-wet, while the stem was moderate to difficult-to-wet. In late spring/early summer, both the juvenile and mature foliage on broom was very difficult-to-wet while by autumn broom has lost its foliage and is stem only, which was easy-to-wet. (Table1).

Gorse needles ranged from moderate to difficult to-wet, depending on season, with all juvenile needles being difficult-to-wet, but becoming less difficult-to-wet with age (Table 1).

The juvenile foliage of buddleia was very difficult-to-wet in the early spring and became difficult-to-wet in late spring/early summer and autumn (Table 1). The wettability of the mature foliage changed considerably, depending on season. In early spring the mature foliage was very difficult-to-wet, while in late spring/early summer it was easy-to-wet. The foliage was all the same on buddleia in autumn.

The wettability of blackberry, bracken and pampas grass was only measured in late spring/early summer. Pampas grass was very difficult-to-wet. The mature foliage of bracken was moderate to difficult-to-wet, while the juvenile foliage was very difficult-to-wet. The mature foliage of blackberry was easy-to-wet, while the juvenile foliage was difficult-to-wet (Table 1).

Herbicide formulation surface tension Surfactant structure and solution concentration affect the dynamic surface tension (DST) of a solution. DST has also been shown (de Ruiter *et al.* 1990) to correlate well with retention, and has since been included in an empirical retention model for arable crops (Forster *et al.* 2006). However, spray droplets from aerial applications will have time to reach equilibrium surface tension prior to impacting plant surfaces, unlike some spray droplets from ground sprayers, and therefore the equilibrium surface tension (ST) is required to predict adhesion and retention. The equilibrium surface tension of water, organosilicone surfactant, glyphosate and metsulfuron formulations are given in Table 2. The product glyphosate 510 contains an adjuvant that reduced the ST compared to water. Increasing the concentration of the glyphosate product decreased the surface tension of the solution (Table 2). However, the addition of organosilicone surfactant to the tank-mix further reduced the ST of the formulation.

Table 2. Equilibrium surface tension (ST) of formulations.

Formulation	a.i.% concentration	ST (mN m^{-1})
Water		72
Glyphosate	3	40.5
Glyphosate	6	37.9
Glyphosate+OS-S240[A, B]	2 + 0.5	24.3
Metsulfuron+ OS-S240[B]	0.0255 + 0.4	22.6
Metsulfuron+ OS-S240	0.408 + 4	22.8
OS-S240	0.5	23.1
OS-S240	2	22.5

[A] OS-S240 = organosilicone surfactant.
[B] Current standards.

Table 1. Wettability quantified by mean contact angle (°) of upper leaf surfaces for juvenile and mature leaves of forest weed species at different times of the year.

	Early Spring (September 2009)		Late Spring/Early Summer (Nov/Dec 2008)		Autumn (April 2009)	
Species	Juvenile foliage	Mature foliage	Juvenile foliage	Mature foliage	Juvenile foliage	Mature foliage
Pinus radiata	93 (7)[A]	54 (12)	75 (14)	54 (7)	53 (16)	48 (8)
Broom	180	85[B]	180	153 (11)	51 (13)[B]	
Gorse	102 (11)	90 (9)	105 (6)	107 (9)		74 (15)
Buddleia	143 (14)	157 (9)	119 (13)	65 (9)	97 (12)	
Blackberry	ND[C]	ND	98 (9)	57 (29)	ND	ND
Bracken	ND	ND	147 15)	87 (23)	ND	ND
Pampas grass	ND	ND	144 (8)	123 (26)	ND	ND

[A] SE; [B] Stem, not leaf, [C] ND = not done.

Effect of plant surface wettability, formulation ST and droplet size on droplet adhesion Adhesion has been defined as the ‘stickability’ of droplets on initial impact. Droplet adhesion is a consequence of dynamic interactions of the formulants within the spray during droplet flight and on impact (ST at impact), physical properties of the droplet (size and velocity), leaf surface wettability and leaf orientation. An empirical universal adhesion model (Forster *et al.* 2005) can be used to demonstrate the effect of plant surface wettability, formulation and droplet size on droplet adhesion. This information can then be used to prescribe optimal formulation ST and droplet sizes, while keeping in mind drift issues.

The size of droplets (VMD) from aerial spray applications using a range of nozzles, herbicide formulations and application volumes has been determined (J. Ray, Forest Research, unpublished data). The droplet sizes for glyphosate applied at different volumes ranging from 51 L ha^{-1} to 233 L ha^{-1} through D8 nozzles (D8-46) ranged from 502 µm to 1165 µm, depending on application rate and pressure.

Figure 1 (a–c) illustrates the predicted initial adhesion for 500 µm, 800 µm and 1000 µm droplets of different formulations with different surface tensions impacting plant surfaces ranging in wettability (Table 3). Adhesion increases with decreasing droplet size, decreasing surface tension, and as the target surface becomes easier to wet (Figure 1, a–c).

The model predicts no, or very low, adhesion of 1000 µm droplets to moderate through to very difficult-to-wet plant species, irrespective of the formulation ST (Figure 1a). Predicted adhesion to even the easiest-to-wet species, using the lowest ST formulation, is still only 30%.

The effect of formulation ST and species wettability is more evident with 800 µm spray droplets, although there is still no adhesion predicted to very difficult-to-wet species and at best 5% adhesion to difficult-to-wet species (Figure 1b). For the easier to-wet species it can be seen that as the surface tension of the formulation is reduced, so adhesion is predicted to increase, with the lowest ST formulation overcoming the effect of droplet size and leaf wettability with 67% and 84% adhesion predicted by moderately easy and easy-to-wet species, respectively, and 60% and 65% adhesion predicted to easy-to-wet species with formulations having STs of 37.9 and 40.5, respectively.

The model predicts that for 500 µm droplets all of the formulations, except water, will provide excellent adhesion to easy through to moderately difficult-to-wet species (Figure 1c; 83–100%). Even water droplets adhere relatively well to easy and moderately

Table 3. Contact angles (CA) used as examples in adhesion model.

Wettability	CA	Species (foliage)
Easy	54	Radiata (mature)
Easy/moderate	65	Buddleia (mature)
Moderate	75	Radiata (juvenile)
Moderate/difficult	87	Bracken (mature)
Difficult	105	Gorse (juvenile)
Very difficult	144	Pampas (juvenile)

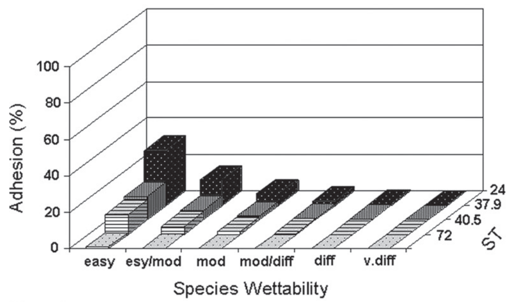

Figure 1a.

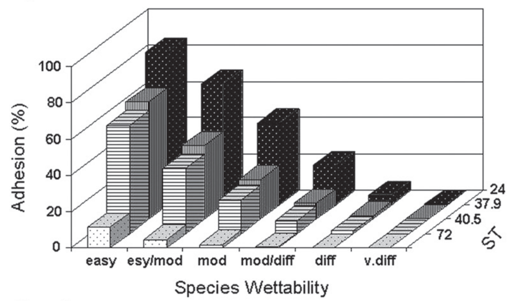

Figure 1b.

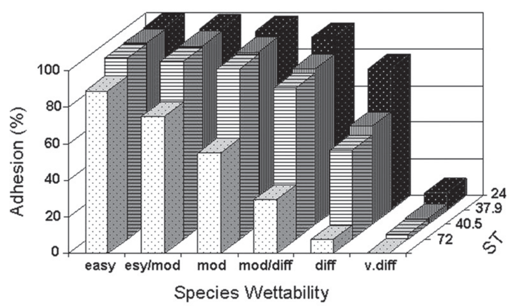

Figure 1c.

Figure 1. Effect of plant surface wettability (CA) and formulation (ST) on the predicted adhesion of (a) 1000 µm droplets, (b) 800 µm droplets and (c) 500 µm droplets impacting horizontal foliage.

easy-to-wet species. It is predicted that there would be 77% adhesion of 500 µm droplets to difficult-to-wet species using the lowest ST formulation, but that formulation cannot overcome droplet size and leaf wettability effects on very difficult-to-wet species.

Implications of adhesion processes for spray retention Retention is the overall capture by plant surfaces of droplets either on initial or subsequent impact. Spray retention can only be modified by varying application (e.g. droplet size) and formulation (e.g. DST) parameters, as target wettability is dependent on species, growth stage and environment. Although calculated adhesion may be low, retention can be higher due to re-capture of bouncing or shattered droplets. Shatter is more likely the larger the droplet, the higher the velocity and the lower the surface tension of the formulation (Mercer *et al.* 2010). Shatter leading to higher retention is more likely to occur in aerial application of herbicides when the VMD is high, compared to ground application of herbicides using a much lower VMD droplet size. As the volume applied aerially is reduced, so the VMD reduces, and shatter is less likely to be a secondary mechanism for retention. It can be inferred from the trends shown in Figure 1 (a-c) that high volume aerial application using low surface tension formulations and smaller VMD droplets would lead to run-off on the moderate through to easy-to-wet weeds. However, a large VMD is more likely in high volume aerial spray applications, with retention to difficult and very difficult-to-wet species saved from being negligible only by the high volume and recapture of shattered droplets. Run-off is unlikely with very low spray application volumes. However, to achieve high levels of spray retention to difficult and very difficult-to-wet species (and minimise loss to the ground) with low volume aerial spray applications, adjuvants that can significantly reduce the surface tension of the formulation are imperative, while in order to avoid spray drift there is a limit on how small the droplet size can be. Therefore, low volume aerial applications using relatively low VMD droplets and very low surface tension formulations would appear the best option to optimise aerial spray applications to a community of weed species covering a range of wettabilities. The use of increasing adjuvant concentration, while reducing application volume, to maintain efficacy against the difficult and very difficult-to-wet species gorse and broom is illustrated by Gaskin *et al*. (2010).

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