Effect of target wettability on spray droplet adhesion, retention, spreading and coverage: artificial collectors versus plant surfaces

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Abstract This study demonstrated that natural foliage and artificial collectors range in surface wettability, affecting spray adhesion, retention, spreading and coverage. Therefore the choice of artificial collector or natural foliage depends on the scientific question. If the volume of spray available to the canopy, or spray accountancy, is to be determined then an artificial collector that will intercept and retain all of the spray is required. Careful consideration of collector is required to meet stated objectives. For example, water sensitive paper is an excellent aid to sprayer set-up, but does not distinguish differences between formulations. It also provides no indication of retention or coverage on the crop surface. All artificial collectors tested were poor indicators of adhesion and retention by, and spreading and coverage on, natural plant surfaces and should not be substituted for natural plant surfaces in field trials attempting to quantify spray retention and coverage on the crop surfaces.

Keywords artificial collectors, spray deposits, foliar retention, wettability.

INTRODUCTION

Artificial collectors are used to measure spray deposits, and drift, in field trials world-wide. Collection efficiency determines whether or not a droplet will intercept (impact) the target. The shape and dimension of a collector has long been established (May & Clifford 1967) to be of primary significance in collection efficiency, particularly for measuring driftable droplets (<100 µm).

The focus of this paper is the use of artificial or natural targets to quantify spray deposits on, or around, the target plant, rather than driftable droplets. The introduction of standards that define droplet size ranges produced by

different spray nozzles (e.g. ISO 10625) has resulted in international requirements, and local recommendations, for use of spray droplets >150 µm in diameter as a drift risk reduction tool for many spray applications. Whereas small, drifting droplets will be retained if they intercept the target, larger droplets, travelling at higher velocities, may bounce or shatter on interception, leading to low retention (Schou et al. 2012). High collection efficiency does not confer high spray retention. For droplets > 150 µm, wettability of the target (plant or collector), and spray formulation, are known to be important factors, not only for adhesion (Forster et al. 2005) and

retention (Gaskin et al. 2005), but also for plant surface coverage or spreading (J.J. Nairn, PPC_{NZ}, unpublished data). Differences in the wettability characteristics of commonly-used artificial collectors have rarely been considered, despite many evaluations of their collection efficiency (Hewitt 2010). The correlations between deposits (spray retention and coverage) on natural plant surfaces and artificial collectors have also rarely been examined.

The objectives of this paper were to (1) compare the surface wettability of leaf foliage from a range of species, along with artificial collectors commonly used in field trials, (2) demonstrate the effect of surface wettability on spray droplet adhesion and retention by, and spreading and coverage on, artificial collectors and leaf foliage, using different formulations, (3) determine the differences between artificial collectors, and therefore what their best use might be, and (4) determine whether artificial collectors can directly represent natural foliage in spray deposit studies.

MATERIALS AND METHODS

Surface wettability, spreading, adhesion and coverage

Three plants and four artificial collectors were included in the study. *Brassica oleracea* (cv. Matador; cabbage) seedlings were grown from seed in 9 cm-diameter pots for 4 weeks, to the 4-6 leaf stage, in a controlled environment (20/15°C day/night, 75% relative humidity, 12 h photoperiod, ca 500 µmol/m²/sec light). *Malus domestica* (cv. Galaxy; apple) leaves were taken from trees growing in the Scion Nursery, while *Vitis vinifera* L. (dark table grape) leaves were taken from a Rotorua backyard. The artificial collectors studied were Mylar sheet, water sensitive paper (WSP), steel plate and a plastic Petri dish.

The contact angle (CA) test is a simple method for quantifying the wettability of different surfaces (Gaskin et al. 2005). Droplets (2 µl) of an acetone+water solution (20% v/v acetone) were applied to the surfaces of freshly detached leaves or artificial collectors, mounted

on double-sided adhesive tape. Replicate droplets (n=21) were measured on at least three different leaf or artificial collector surfaces. A KSV CAM 200 optical contact angle meter and Basler digital video camera were used to determine the static (equilibrium) contact angles.

Nordox 75WG (750 g/kg cuprous oxide, Gro-Chem) was used alone at 37.5 g/100 litres or in the presence of Du-WettTM (an organosilicone superspreader adjuvant; Etec Crop Solutions Ltd.; 100 ml/100 litres) for the spread area experiments. The dynamic surface tension profile of cuprous oxide used alone at 37.5 g/100 litres (equilibrium surface tension of 75 mN/m does not differ substantially from water (72 mN/m equilibrium surface tension), and was therefore not included in the adhesion and coverage experiments to avoid blocking the nozzle. Water alone and plus 100 ml/100 litres Du-WettTM was used in the adhesion and coverage experiments.

The droplet (0.5 µl, 985 µm) spread areas for each formulation on each surface were photographed under UV illumination, processed in Photoshop CS3, and areas calculated using V++ for Windows image analysis software (mean of 20 determinations). To visualise droplet spread, Blankophor-P fluor (5 g/litre, Bayer NZ) was included in each formulation.

Adhesion and coverage were investigated using an impulse-jet droplet generator to produce monosized droplets with an average diameter of approximately 817 µm (ca 0.28 µl). The fall distance studied was 0.54 m, producing a droplet velocity at impact of approximately 2.48 m/s (below the terminal velocity of ca 3.3 m/s for this size of droplet). The detached leaves or artificial targets were oriented at 0° and 45° from the horizontal on plastic stages. Ten droplets (per formulation) were impacted (within a 40 × 27 mm area) on to each of ten replicate leaves or artificial collectors for each target angle and target surface studied. If the droplet stuck, then this was defined as adhesion; if it bounced (or shattered), regardless of distance, this was defined as no adhesion. In order to calculate the percentage coverage, the targets were photographed under UV illumination, and the percentage coverage

within the 40×27 mm area calculated, using Photoshop CS3 and V++ for Windows image analysis software.

Spread areas on kiwifruit leaves and canes

Actinidia chinensis (Hort16A) kiwifruit leaves and canes were taken from outdoor grown PPC_{NZ} potted plants. All leaves were used immediately after picking in March 2014. The formulations were as described above, with an additional concentration of Du-Wett included (50 ml/100 litres). The methods used to determine spread area were as described above.

Spray retention field studies

Post-harvest kiwifruit vines (*Actinidia chinensis*; Hort16A) were aerially sprayed with tartrazine tracer (10 g/litre) plus 0.15% Du-Wett, at 217 litres/ha, using a nozzle producing an average VMD of 250-300 μ m (Strand et al. 2012). Three types of artificial collectors were fixed 3 m above the ground and approximately 0.8 m above the canopy. The mean retention to the kiwifruit foliage, free Mylar (fixed at one end, but flapping in the vertical plane), fixed Mylar (horizontal plane) and ping pong balls (fixed) was measured as described by Strand et al. (2012).

Videos of spray retention

Brassica oleracea (cv. Matador; cabbage; grown as described above), *Actinidia chinensis* (Hort16A) kiwifruit leaves as described above, Mylar sheet and ping pong balls were sprayed with water or water plus Du-WettTM (150 ml/100 litres; 100 ml/100 litres for cabbage) using a hand-held spray bottle. All spray solutions contained Blankophor-P (10 g/litre, Bayer NZ) to enhance visualisation. The targets were sprayed under UV light and white light (3 $\times$ UV light sources, 1 $\times$ white/incandescent light source). Videos were captured using a Panasonic DMC-TZ20 digital camera, and edited using Easy Video Editor LoiLoScope 2.

Statistical analysis

Treatments were compared using analysis of variance (Statistix 9) and Fisher's Protected

LSD tests. Statistix 9 was used to calculate the correlation coefficients.

RESULTS AND DISCUSSION

Surface wettability, spreading, adhesion and coverage

The apple leaf surface, Mylar sheet and WSP were easy-to-wet (CA <60°; Table 1), the steel plate and plastic Petri dish were considered moderate (CA ranging 60°-80°), while grape was moderately difficult-to-wet (CA ranging 81°-99°) and cabbage was very difficult-to-wet (CA >120°).

The spread area test determines relative potential coverage differences between formulations should the spray be retained. Coverage is of particular importance for the efficacy of protectant pesticides, which include many fungicides and insecticides. When cuprous oxide was applied in water, spread areas ranged from 0.4 mm² on the very difficult-to-wet cabbage surface to 7.0 mm² on the very easy-to-wet Mylar surface (Table 1). In the presence of Du-WettTM, the greatest spreading was on the moderately difficult-to-wet grape leaf surface and the easy-to-wet apple leaf surface, with spreading being significantly less on all other surfaces, irrespective of whether they were easier or more difficult-to-wet.

The addition of Du-WettTM increased the spreading of water plus cuprous oxide by > 5-fold on Mylar and up to 109 times on cabbage. The exception was WSP, where there was no significant difference in spreading with the addition of the adjuvant. Because WSP absorbs solution it does not show formulation differences. The present observations confirm that WSP cannot be used to indicate the differences that might be expected between formulations, in terms of spread area or coverage. While there was a negative correlation between the target contact angle and the spread area of cuprous oxide applied in water only (Pearson's $r = -0.8895$, $P=0.0073$), when Du-WettTM was included in the formulation, there was no correlation between contact angle and spread area (Pearson's $r = 0.3370$, $P=0.4598$). This effect has been previously observed on both

Table 1 Spread area (mm²), adhesion (%) and coverage (%) of two formulations on a range of natural leaves and artificial surfaces, along with their mean contact angle, CA (°). Means within the Spread area, Adhesion and Coverage columns followed by different letters are significantly different at $P \leq 0.05$.

			Spread	Adhesion		Coverage	
Target	CA	Formulation ¹	area ²	0°	45°	0°	45°
Natural leaves							
Apple	55	Water	2.0 ^{ef}	97 ^{ab}	95 ^b	3.3 ^{ijkl}	4.5 ^{hij}
		+ DW	62.7 ^a	100 ^a	97 ^{ab}	31.9 ^c	36.5 ^b
Grape	87	Water	1.3 ^f	85 ^c	70 ^d	2.9 ^{kl}	3.7 ^{ijk}
		+ DW	65.4 ^a	100 ^a	95 ^b	40.2 ^b	45.4 ^a
Cabbage	143	Water	0.4 ^f	0 ^f	0 ^f	0.1 ⁿ	0 ⁿ
		+ DW	39.4 ^b	9 ^c	0 ^f	17.6 ^{de}	1.2 ^m
Artificial collectors							
Mylar	10	Water	7.0 ^d	100 ^a	100 ^a	3.6 ^{ijk}	4.2 ^{hij}
		+ DW	39.2 ^b	100 ^a	100 ^a	7.0 ^g	14.0 ^f
WSP	36	Water	3.5 ^{ef}	100 ^a	100 ^a	3.9 ^{hijk}	4.0 ^{hijk}
		+ DW	4.8 ^e	100 ^a	100 ^a	4.7 ^{hi}	5.2 ^h
Steel Plate	61	Water	1.9 ^{ef}	100 ^a	100 ^a	2.4 ^l	2.4 ^l
		+ DW	35.3 ^c	100 ^a	100 ^a	16.5 ^{ef}	17.7 ^{de}
Petri dish	74	Water	0.6 ^f	100 ^a	100 ^a	1.0 ^m	1.1 ^m
		+ DW	42.6 ^b	100 ^a	100 ^a	15.1 ^f	19.9 ^d

¹DW=Du-Wett™.

²For the spread area experiments, cuprous oxide alone and cuprous oxide + Du-Wett™ were studied.

foliage (e.g. Holloway 1994) and artificial surfaces (Stoebe et al. 1996), using a range of adjuvants. The interaction between the surface chemistry and formulation has been shown to influence spreading (J.J. Nairn, PPC_{NZ}, unpublished data). The best that could be inferred, using the artificial collectors tested, excluding WSP, is that inclusion of Du-Wett™ would be expected to increase the spread area on foliage compared to water. However, if different adjuvant formulations were to be compared, the order of increased spreading on one surface wouldn't necessarily correlate to the order of spreading on other surfaces, again due to the chemical interactions at the solid-liquid interface (Stoebe et al. 1996).

When a spray droplet is intercepted by a leaf, it may adhere on initial contact (adhesion), bounce or shatter. Although these rebounding or shattering droplets within the applied spray may be recaptured elsewhere in the target-plant canopy, initial adhesion is a primary process

involved in spray retention (Nairn et al. 2014). Adhesion is influenced by target wettability, with least adhesion observed on the very difficult-to-wet cabbage leaf surface, followed by the moderately difficult-to-wet grape leaf surface (Table 1). The easy-to-wet apple surface had a slightly lower observed adhesion compared to the moderate wettability surfaces of the steel plate and Petri dish. This is hypothesised to be due to the comparatively complex nature of the apple leaf surface (e.g. leaf veins). Although Du-Wett™ significantly increased adhesion to the horizontal cabbage leaf, compared to water alone, adhesion remained low (9%), and this reduced to 0% with an impact angle of 45°. The presence of Du-Wett™ significantly increased adhesion to the grape leaf surface (from 85% to 100% on a horizontal grape leaf and from 70% to 95% at a leaf angle of 45°). There was effectively no recapture of bouncing or shattering droplets when water was applied alone to cabbage (Table 1). Although only 9% of

the water plus Du-Wett™ formulation adhered on initial impact to the horizontal cabbage leaf surface, it is worth noting that the coverage (17%) was greater than when water alone was applied to all other surfaces, even though 100% of droplets adhered to most of those surfaces.

After a droplet adheres (on initial or subsequent impact), it may spread, redistribute or run-off. The formulation and plant species providing the largest spread area also provided the largest percentage coverage (Table 1), when the spray was completely retained. Overall there was a very high correlation (Pearson's $r = 0.9281$, $P = 0.0000$ for angle = 0° ; $r = 0.8642$, $P = 0.0003$ for angle = 45°) between spread area and % coverage, Mylar being the outlier with a lower % coverage than would be expected from the spread area results. Rather than spreading into a thin film after impact with the Mylar, the droplet spread slightly with the leading edge retaining a drip-like volume of liquid.

When examining only percentage coverage, the plant-species and artificial collectors performed similarly for the water only treatment, with the exception of the cabbage leaf, with coverage values for the horizontal collection ranging from 0.1 (cabbage) to 3.3 (apple) and 1.0 (Petri dish) to 3.9 (WSP). This relationship altered once Du-Wett™ was added to the formulation. Water + Du-Wett™ provided greater coverage even on the difficult-to-wet cabbage leaf (17.6%) compared to the artificial collectors, where the steel plate provided the greatest coverage at 16.5% with the same formulation.

The largest notable difference between the natural and artificial targets resides in the percent adhesion. Both formulations gave 100% adhesion to all of artificial collectors, but this was not the case for the natural targets (Table 1).

The use of WSP in orchard spraying

The spreading of cuprous oxide applied in water, and in the presence of two concentrations of Du-Wett™ (0.05% and 0.1%), on WSP, Hort16A kiwifruit leaves and Hort16A kiwifruit canes is shown in Figure 1. There was comparatively little difference in the spreading of cuprous

Figure 1 The spread area of cuprous oxide with different concentrations of Du-Wett™ on water sensitive paper (WSP), Hort16A kiwifruit leaves (adaxial surface) and Hort16A kiwifruit canes.

oxide alone on the three surfaces, and there was little increase in spread area on WSP with increasing concentration of Du-Wett™. In contrast, increasing the concentration of Du-Wett™ substantially increased spreading on both leaves and canes, with the spreading on canes significantly higher than the spreading on leaves for all Du-Wett™ treatments.

It is clear that WSP tells us nothing about differences between formulations or how formulations might affect spreading or coverage on different plant species (Table 1), or as illustrated here, on the canes versus the leaves of kiwifruit plants.

Figure 2 illustrates the differences between the wettability of WSP and very difficult-to-wet cabbage foliage. While the water spray reached the very difficult-to-wet target, as evidenced by the WSP (Figure 2a, 86% coverage), very little was actually retained by the cabbage leaf (< 1% coverage). In contrast, when water + 0.1% Du-Wett™ was sprayed using one-third of the volume (Figure 2b) used for the water alone spray, a substantial amount of spray was retained by the cabbage seedling. The spray covered about 80% of the cabbage leaf, but only 45% of the WSP.

Orchardists (e.g. kiwifruit, winegrowers) who spray their own crops or their spray contractors are advised to use WSP to “assess foliar spray coverage” (e.g. Manktelow et al. 2011). WSP is an

Figure 2 Spray applications of (a) water and (b) water + 0.1% Du-Wett™ at one-third of the volume of water, on very difficult-to-wet cabbage seedlings with WSP attached.

excellent tool to assist growers in sprayer setup to confirm that spray droplets are delivered to (intercept) the spraying target. This is the first step in effective spray application. Visualisation of spray droplets on WSP provides a qualitative indication of the quantity of spray (droplets) delivered to the target and relative droplet sizes when application volumes are below runoff (compare the WSP in Figure 2a with that in Figure 2b where one-third of the volume had been applied). While WSP provides rapid feedback for sprayer set-up, this artificial collector gives no indication as to whether the spray formulation will provide good retention, coverage or efficacy on the target plant surface.

Spray retention

Spray retention is defined here as the overall capture, by plant surfaces or collectors, of spray droplets either on initial or subsequent droplet impact, and after any run-off has occurred, i.e. it is the total amount of spray remaining on the surface immediately after dry-down. Differences in contact angles (surface wettability) and the effect of target angle on both spray interception and adhesion help to explain the relative differences in spray retention between the artificial targets (free Mylar, horizontal Mylar or ping pong ball) and kiwifruit foliage (Figure 3).

The free Mylar retained slightly more spray than the foliage, while the fixed, horizontally-oriented Mylar retained about 2.5 times more

Figure 3 Retention (mean $\mu\text{g}/\text{cm}^2 \pm \text{SEM}$; normalised to 1 kg/ha application) of aerially applied spray (water plus 0.15% Du-Wett™; 217 litres/ha; nozzle VMD 250-300 μm) to kiwifruit foliage and three artificial collectors. Error bars denote SEM ($n=3$).

spray than the free Mylar, but still substantially less than the ping pong ball. Other authors have also found that ping-pong balls retained significantly more spray than Mylar (Richardson et al. 1989). It is well established that run-off can occur on easy-to-wet surfaces, when using high spray volumes and/or low surface tension sprays (Bruns & Nalewaja 1998). Laboratory video evidence, taken during the current study, of water alone applied to Mylar illustrated that the water droplets quickly coalesced forming a film of liquid that can run off the surface. This effect

was even more pronounced when Du-Wett™ was included in the water, which lowered the liquid surface tension, and/or when the Mylar sheet was at an angle or not fixed. While a low volume of spray was applied in the field, the low retention to the free Mylar is explained by run-off from the vigorously flapping surface (due to turbulence induced by the helicopter), as well as lower spray interception compared to the horizontally fixed Mylar. It is hypothesised, based on the laboratory spray videos, that spray loss through run-off still occurred for the horizontally placed Mylar.

When used in the field (Figure 3) at low spray volumes, the ping pong ball retained the greatest quantity of spray. The ping-pong ball is an excellent three dimensional capture surface and is able to capture droplets moving in all three directions due to turbulence, unlike the free Mylar or the horizontal Mylar. Although the ping-pong ball's surface was difficult to wet ($CA = 101^\circ$), at a microscopic view it appeared as a hairy mat on the surface (results not shown) and therefore the spray retention was higher (Nairn et al. 2013). Laboratory video evidence suggests that there is good retention to the ball when sprayed with fine water droplets, and that when Du-Wett™ is included in the formulation, the spray flows around the ping pong ball, adhering to its sides, but not reaching a run-off state. However, it is noted that at excessively high volumes (including large water droplets) run-off will occur.

Thompson et al. (1997) compared herbicide deposits, from aerial spray applications, on excised natural foliage with those on 2-dimensional and 3-dimensional artificial collectors, and also found that none of the artificial collector types tested accurately or consistently estimated true foliar deposit. However, the authors did not investigate potential reasons for their results.

The different retention results collected in the field (Figure 3) are, in part, explained by combining what is known about contact angle (wettability), adhesion, percentage coverage and orientation of the collector. Target orientation has an effect on spray collection efficiency, and in this field trial the kiwifruit had an atypical vertical orientation, with potentially less spray

interception than the artificial collectors, including the free Mylar. The differences between the artificial collection results is explained by the contact angle of the Mylar surface (very low, indicating a very easy-to-wet surface leading to run-off) and the dimensionality of the collector (2-dimensional Mylar versus 3-dimensional ping-pong ball). The ping-pong ball demonstrated the quantity of spray that reached the kiwifruit foliage zone, but the free Mylar better represented what was found on the foliage itself.

CONCLUSIONS

If the objective of measuring spray collection is to determine the volume of spray available to the canopy, then an artificial collector is required that will reliably intercept all of the spray regardless of spray volume (collector orientation and effective area should be considered) and once intercepted, will retain all the spray. Spray volume and droplet size need to be factored into these considerations. Given the high risk for run-off, Mylar, with its low CA, is a poor choice of collector.

If the objective of measuring spray collection is to determine the spray deposits retained on the foliage itself and coverage of the foliage, or other parts of the plant canopy, then only the plant species as a collector can provide that information. An artificial collector cannot be used as a one-to-one replacement for foliage, or other parts of the plant canopy, to determine retention of the spray on the foliage. Likewise, no artificial collector can truly show percentage coverage of the spray on the foliage. Only using the plant species itself can provide this information. However, recovery of spray or tracer deposits from natural plant surfaces is usually more difficult and more expensive than from artificial targets and is complicated by difficulties in accurately quantifying the surface area of the natural targets. For these reasons much of the research into spray application and deposits has made use of artificial targets, but as shown here, the limitations imposed by these mean that they may provide only information on the zones where the spray reached and not spray retention

or percentage coverage. Based on the results presented here, retention to, spreading on and coverage of natural foliage cannot be predicted with an artificial collector.

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