

## Spray droplet impaction outcomes for different plant species and spray formulations

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### Abstract

A track-sprayer combined with a high-speed camera were used to visualize and identify droplet impaction outcomes for three formulations (water, 0.1% LI 700® (lecithin, a mixture of soya oils, propionic acid and surfactants) in water and 0.1% Pulse® (non-ionic surfactant, trisiloxane ethoxylate) in water) on four plant species (bean (*Vicia faba* L.), avocado (*Persea americana* L.), barnyard grass (*Echinochloa crus-galli* L. P. Beauv.) and cabbage (*Brassica oleracea* L.)) selected to represent a wide range of leaf surface characters. Droplet sizes and velocities were measured by image analysis and a multiple hypothesis tracking algorithm. Impaction outcomes were categorized into adhesion, bounce, or shatter. The probability of each outcome was estimated from logistic regression models related to the dimensionless Weber number. This approach is in contrast to various deterministic threshold criteria for droplet bounce or shatter that have been used to model droplet impaction events on leaves. It also provides a simple visual and numerical presentation of the complexity of impaction processes, and the relative influence of leaf surface character versus formulation for droplets with different impaction energies.

**Keywords:** Droplet impaction, Adjuvants, Wettability, Leaf surface roughness, Leaf surface chemistry, Adhesion, Bounce, Shatter, Pinning

### 1. Introduction

Weed and pest control is important in crop production to maximize yield potential and quality. The spraying of agrochemicals remains the most common approach to achieve this outcome. However, a better understanding of the processes involved is required to maximize biological efficacy while minimizing adverse effects on the environment.

The spray application and efficacy of foliar pesticides depends on four processes, namely the deposition, retention, uptake and translocation of the actives in the applied formulation (Zabkiewicz, 2007). The retention of most plant protection products on plant leaves is a key to their efficient use. Retention efficiency can be between 10% to 100%, depending on the application technique and plant properties (Butler Ellis et al., 2004; Knoche, 1994). Several

factors contribute to the variability of spray retention by plants. These primarily include spray nozzle kind and size, the volume applied per hectare, and the formulation (Matthews, 2008; Spillman, 1984). Some plant characteristics can also lessen retention of spray by the foliage, namely plant and leaf size (Dorr et al., 2014; Massinon and Lebeau, 2013), vertical architecture (Massinon et al., 2015) and the low or variable wettability of their leaf surfaces (Gaskin et al., 2005). The spray parameters must therefore be tailored and optimized to maximize foliar retention and coverage.

Predominant parameters related to the droplet, viz. size and velocity, its direction relative to the surface, or the liquid surface tension and viscosity, play significant roles in the behaviour of droplets impacting onto dry and solid surfaces (Josserand and Thoroddsen, 2016; Rioboo et al., 2001; Yarin, 2006). Other factors, such as air inclusion or complex formulations (e.g. emulsions), may also affect outcomes (Miller and Butler Ellis, 2000; Holloway et al., 2000). As the droplet spreads on impact with the leaf surface, the liquid and surface properties affect the liquid flow and lead to various scenarios of droplet impact. If the droplet kinetic energy overcomes the capillary forces, the droplet shatters into smaller secondary droplets that are detached radially from the expanding lamella. When the kinetic energy of the droplet is partly dissipated by viscous forces and partly converted into surface energy, capillary forces promote the droplet receding of its area of contact. If the remaining energy is not dissipated during the receding stage, the droplet can bounce. Otherwise the droplet adheres.

From an agronomic perspective, droplets reflected from a leaf surface on impact are direct losses if not recaptured by the plant canopy. Surfactants are commonly included in spray formulations to improve the retention and spreading of droplets, especially when the target is difficult-to-wet (Gaskin et al., 2005). The droplet impact and spreading of surfactant-laden formulations is complicated and the possible mechanisms are still being debated (Gatne et al., 2009; Ivanova and Starov, 2011; Kovalchuk et al., 2016). The effects that leaf surface roughness and chemistry have on the liquid dynamic wetting, and subsequently on the droplet impaction outcomes such as adhesion, bounce or shatter, are still not fully defined. However, it is known that droplet adhesion decreases with increasing droplet impact velocity, diameter, leaf angle, formulation surface tension and leaf roughness factor (Forster et al., 2005; Nairn et al., 2013).

Laboratory retention trials can reveal the actual response of a plant system, when the spray formulation, nozzle, volume applied, plant species and growth stage are controlled, but they provide a limited understanding of the complexity involved since there are many competing physical and chemical processes. It is therefore difficult to attribute the effect of each particular factor to the spray retention outcomes. High-speed cameras have been used to visualize droplet impaction on leaf surfaces (Dong et al., 2015; Reichard et al., 1998; Wirth et al., 1991) and provide some insight into the physics of droplet impaction. However, most studies have used single droplet generators resulting in droplets impacting at, or below, terminal velocity (which is in the range of 0.5 - 3 m s<sup>-1</sup> for 160 µm - 750 µm droplets) at impaction. Thus, these studies do not illustrate all the possible droplet impact outcomes that would result from a broader range of droplet impact energies that are relevant for real applications.

The current study relied on conventional spray equipment with higher droplet velocities so that the full range of impaction outcomes could be obtained within a spray application treatment. The aim was to document the droplet impact outcomes for three spray formulations ranging in equilibrium surface tension from 22 to 72 mNm<sup>-1</sup> impacting a range of leaf types. A further objective was to estimate the probability of these outcomes as computed from logistic regression models related to the dimensionless Weber number. Here, the Weber number ( $We_n$ ) is defined as the dimensionless ratio between droplet kinetic energy in the direction normal to the surface and its surface energy according to  $We_n = \rho V_n^2 D / \sigma$ , where  $\rho$  is the liquid density,

$V_n$  is the droplet velocity normal to the impacted surface,  $D$  is the droplet diameter and  $\sigma$  is the formulation equilibrium surface tension.

## 2. Material and methods

### 2.1. Plants

Four species were chosen to cover a range of leaf wettabilities: bean (*Vicia faba* L.), avocado (*Persea americana* L.), barnyard grass (*Echinochloa crus-galli* L. P. Beauv.), and cabbage (*Brassica oleracea* L.). All plants, except avocado, were grown from seed in individual pots containing PPC<sub>NZ</sub>/Bloom potting mix (Daltons, NZ), and raised under controlled environment conditions with 70% relative humidity, watered daily each morning prior to use, and 12 h photoperiod at ca. 450  $\mu\text{mol m}^{-2} \text{s}^{-1}$  light intensity. Day/night temperatures were 20°C/15°C for bean and cabbage, and 23°C/15°C for barnyard grass. The plants were used at approximately four weeks of age. Avocado leaves were harvested from an adult tree grown in Rotorua (New Zealand) under natural conditions.

Table 1 shows the relative wettability of each species as defined by Gaskin et al. (2005). This technique is used to discriminate between leaf surface wetting based on the measurement of the static contact angle of 20% v/v acetone in water. 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. Contact angles were averaged over 21 measurements (2  $\mu\text{l}$  droplets) across 3 leaves each taken from different plants to minimise variations between individual plants and hysteresis in individual measurements. Leaf roughness and polarity, fundamental factors known to govern leaf surface wettability (Holloway, 1970), are assessed using the wetting tension-dielectric (WTD) technique (Nairn et al., 2011; Nairn and Forster, 2016) which is based on contact angle trends, using solutions with varying dielectric constant (used as a surrogate for polarity), measured on each leaf surface.

**Table 1:** Static contact angle (20% v/v acetone in water, +/- SD), leaf surface wettability, relative roughness and polarity determined according to Nairn and Forster, 2016.

Species	Static contact angle (°)	Wettability	Leaf surface roughness	Leaf surface polarity
Bean	60 (6.7)	easy	smooth	polar
Avocado	76 (8.9)	moderate	very smooth	non-polar
Cabbage	180 <sup>#</sup>	very difficult	rough	very non-polar
Barnyard grass	180 <sup>#</sup>	very difficult	very rough	relatively neutral

<sup>#</sup> The droplet is completely repulsed by the plant. Static contact angles with 50% v/v acetone in water are respectively of 114 +/- 7.1° and 126 +/- 7.1° for cabbage and barnyard grass.

### 2.2. Spray formulations

The three formulations used were: water, water plus LI 700® (lecithin, a mixture of soya oils, propionic acid and surfactants; Etec Crop Solutions Ltd, NZ) and water plus Pulse® (non-ionic surfactant, trisiloxane ethoxylate, Nufarm Ltd, NZ). Both adjuvants were used at 0.1% (w/v) in water. These were chosen to provide a representative range of solution properties

(chemistries and surface tensions). Agrichemical formulations can have equilibrium surface tension (EST) ranging from 72 mNm<sup>-1</sup> (no adjuvants), more typically around 40-50 mNm<sup>-1</sup>, and in the 20's for organosilicone formulations. The values for the EST and dynamic surface tension (DST) at 50 ms, determined using a Krüss bubble pressure tensiometer (BP2 MKII), are shown in Table 2 for each spray formulation. The DST values are provided as an insight of the variation of surface tension with time; an average time of 50 ms has been chosen as representative of flight times based on previous work (Dorr et al., 2016). Although the role of DST is evident in governing the time-dependent processes of droplet impact and film-spreading for surfactant-laden droplets, only EST has been used in this study. A fundamental contention remains on the scaling between droplet impact dynamics, liquid properties and wetting for surfactant solutions, which requires surfactant chemistry, ionic and molecular structure, adsorption-physiosorption rates and electrokinetics be considered (Gatne et al., 2009).

**Table 2:** Measured dynamic surface tension (DST) at 50 ms and equilibrium surface tension (EST; the value used in the current models) for the formulations used (mean of two analysis).

Spray formulation	Bulk surface tension (mNm <sup>-1</sup> )	
	DST	EST
Water	72	72
Water + 0.1% LI 700®	71	48
Water + 0.1% Pulse®	57	22

### 2.3. Tracksprayer impaction study

Sprays were applied using a calibrated moving head track-sprayer (PPC<sub>NZ</sub>, Rotorua, New Zealand) with a single flat fan XR11003VP nozzle (Sprayings Systems Co., Wheaton, USA) operating at 300 kPa (1.23 L min<sup>-1</sup>), traveling at an average speed of 1.7 m s<sup>-1</sup>, producing a range of droplet sizes. Respectively these were: water  $D_{v0.5} = 202 \mu\text{m}$ , relative span 1.28, initial velocity 20.1 m s<sup>-1</sup>; LI700  $D_{v0.5} = 241 \mu\text{m}$ , relative span 1.19, initial velocity 21.9 m s<sup>-1</sup>; Pulse  $D_{v0.5} = 221 \mu\text{m}$ , relative span 1.19, initial velocity 22.6 m s<sup>-1</sup> (Dorr et al., 2016). In the current study, the droplet size and velocity of each observed impacting droplet was measured just prior to impact as described below (sections 2.2.1 and 2.2.2). The nozzle height was set at 500 mm above the leaf sample. Leaf samples (approximately 2 mm x 10 mm) were taken from an excised leaf immediately before spraying and attached to a microscope glass slide with double-sided tape. Leaf samples were therefore taken from plants at normal turgor pressure, resulting in no modification of the leaf stiffness. The adaxial surfaces of new, fully expanded leaves were used in all cases. Leaf samples were carefully handled by their edges using tweezers to avoid any alteration of leaf surface properties. Ten replicate sprays were performed for each treatment with a new leaf sample randomly taken for each spray application.

### 2.4. High speed photography

The image acquisition setup used in this study has been previously described in Massinon and Lebeau (2012) and is summarized here. A high-speed camera (Y4 CMOS, Integrated Design Tools, Tallahassee, FL, USA) was used to visualize spray droplet impaction on the surface of leaf samples. The camera settings were adjusted to obtain well contrasted droplet images for accurate droplet sizing and the acquisition frequency was set at 20,000 images per

second to capture the droplet impaction event in detail. Exposure time was set to 14  $\mu\text{s}$  to provide an average background gray level around 200 for images. A zoom lens (12X zoom system, Navitar, Rochester, NY, USA) gave an  $8.93 \mu\text{m pixel}^{-1}$  spatial resolution, depth of field of about 2 mm and working distance of 341 mm to avoid wetting the lens. A LED lighting (19-LED Constellation, Integrated Design Tools, Tallahassee, FL, USA) with a beam angle of  $12.5^\circ$  placed 600 mm behind the lens provided both high illumination and uniform background to the contrasted shadow images. The pulsed lighting was synchronized with the image acquisition rate. A background noise correction was performed before tests with embedded camera software.

Leaf samples were positioned horizontally between the camera and the lighting source, in the camera focal plane, directly under the centre of the flat fan nozzle. A horizontal slit plate was placed 10 mm above the leaf samples to help with minimizing the image noise resulting from droplets out of the focal plane. The slit width was slightly smaller than the camera depth of field and the leaf sample width. In this configuration, droplet size and velocity could be measured immediately before impact (Figure 1).

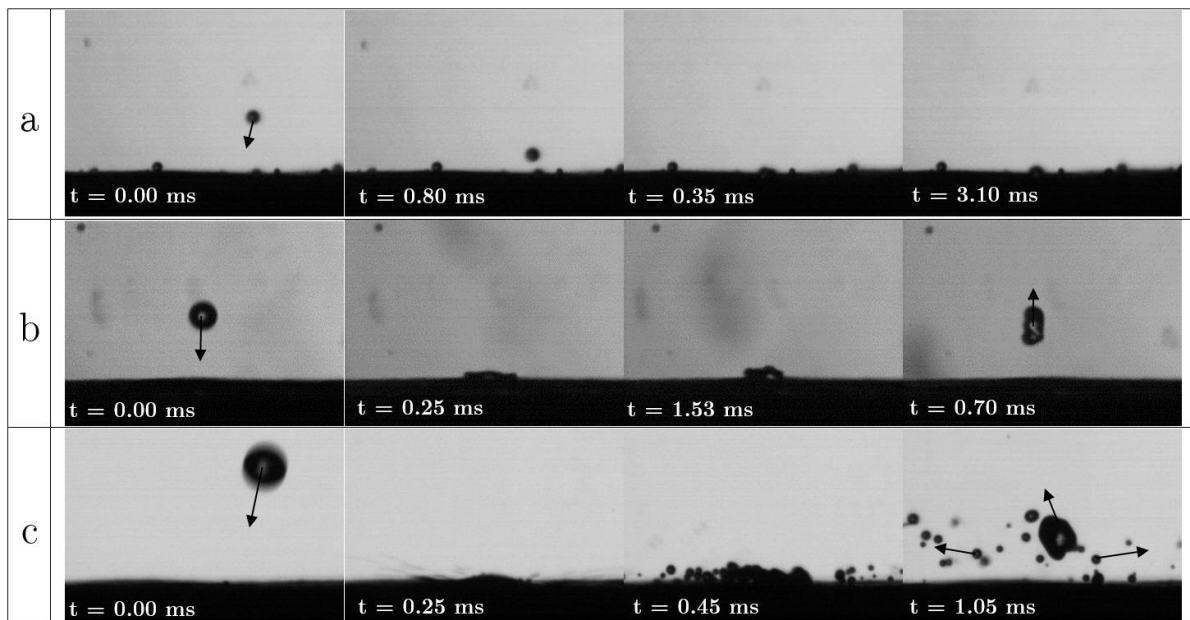


Figure 1: Representative examples of impaction sequences of water droplets on dry cabbage leaf surface: (a) adhesion [ $D = 111 \mu\text{m}$ ,  $V_n = 0.42 \text{ m s}^{-1}$ ,  $We_n = 0.27$ ]; (b) bounce [ $D = 236 \mu\text{m}$ ,  $V_n = 3.17 \text{ m s}^{-1}$ ,  $We_n = 33$ ] and (c) shatter [ $D = 357 \mu\text{m}$ ,  $V_n = 8.31 \text{ m s}^{-1}$ ,  $We_n = 342$ ].

## 2.5. Image analysis

The algorithm used to locate individual droplets on each image and accurately measure their diameter has been described in De Cock et al. (2016) and is summarised in Section 2.2.1 below. The droplet tracking algorithm (Section 2.2.2) used in this study has been adapted from Castanet et al. (2013) for a single moving agricultural spray nozzle to compute the velocity of each impacting droplets. Algorithms used in the following sections were run on a personal computer using Matlab (The MathWorks Company, Natick, MA, USA).

### *2.5.1. Droplet identification and sizing procedure*

The first operation consisted of cropping images to select the region above the plant surface showing droplets. A composite background, generated from the 80 percentile of each pixel intensity on a set of ten images, was then subtracted from each image. The gray level was then rescaled in such a way that 1% of pixels were saturated (i.e. equal to 0 or 255) to maximize image contrast, independently of the acquisition conditions that may vary slightly between replicates.

Next, a first location of the droplets was achieved by computing the light intensity gradient on the whole image using Sobel's filters. The highest intensity gradients generally corresponded to droplet boundaries that defined a surface considered as a droplet. Objects smaller than four pixels width and objects truncated by the edges of the image were rejected because of the weak measurement accuracy.

Centroid coordinates were computed for the retained objects, which were isolated in sub-images for subsequent droplet sizing to take into account the local image background for more accurate sizing. This sizing was performed using the Canny edge detector that determines droplet edges based on the maxima of the local gradient values. It provides a 1 pixel thin continuous envelope corresponding to highest values of local gradient maxima which was extended to the droplet edges. The droplet size immediately before impact was finally determined by computing the inner area defined by the detected edge and considering the droplet as a perfect sphere, which was generally fulfilled since droplets experience low aerodynamic deformation forces. This allowed the droplet sizing to have a sub-pixel resolution.

Despite the presence of the slit above the leaf sample, some droplets appeared out of focus on images. For each droplet, an in-focus parameter was then computed based on the fact that gradient intensity at droplet boundaries increases with particle degree of focus. Thresholds for in-focus droplet selection were determined by studying the evolution of the in-focus parameter and the error on particle size measurement from images containing uniform droplets with a known size at various distance of the object plane (De Cock et al., 2016). The threshold was chosen to permit an error less than 5% of the droplet diameter. Droplets that were very irregular in shape and those with a diameter under 30  $\mu\text{m}$  were rejected because of the higher uncertainty in the size measurement. The latter almost certainly adhere due to their very low Weber number and only contribute very weakly to the total impacting volume.

### *2.5.2. Tracking of droplet trajectories*

An algorithm based on a multiple hypothesis tracking method was used, which relies on generating a set of data-association hypotheses to account for all possible origins of every selected droplet. The algorithm searches within an area represented by a circle around the droplet on image  $n$ , for the same droplet on image  $n + 1$  with an equivalent diameter. The diameter of this circle of confidence is a function of the maximum expected displacement of the droplet within the time between two successive images. A relationship between droplet velocity and diameter (De Cock et al., 2016), after traveling a distance equal to the nozzle height above the target surface, is used here to define the diameter of the confidence circle. The diameter of the potential droplet on image  $n + 1$  ranges between 0.85 and 1.25 times the diameter of the droplet on image  $n$  to account for any droplet deformation and oscillation. Each droplet on image  $n$  starts a new track that is extended until no matching droplet is detected in the circle of confidence. The track is then terminated and the droplet is removed from being a potential candidate for another track formation. A track is defined in the algorithm as a matrix containing the diameters and the centroid coordinates for the tracked droplet appearing on successive images. The velocity of the droplet along the track matrix is then computed between each pair of images,  $n$  and  $n + 1$ , using the centroid positions and the time delay between

successive images. Finally, the diameter and velocity attributed to each droplet correspond to the mean of the velocities and diameters along the track matrix.

The set of potential tracks is then filtered to select the most likely impacting droplets. i.e. to avoid selecting droplets with irregular trajectories (having significant change in velocity direction between successive images) resulting from incorrect droplet matching. Moreover, tracks that are too short, i.e. those containing only one element, are also rejected as well as tracks starting too low on the image or not ending close enough to the leaf surface. Droplets with a zero horizontal or vertical velocity between the beginning and the end of the track are removed since their probability is assumed to be too low. Finally, only tracks with a positive vertical velocity sign, i.e. a downward trajectory, are selected. The droplet sizing and tracking algorithm has been compared to a manual identification on images for some acquisitions to validate its performance. The next step consists of identifying and attributing an impact outcome to each tracked droplet, i.e. adhesion, bounce or shatter.

### *2.5.3. Droplet impact outcomes classification and logistic regression model for transitions between outcomes*

The droplet impact outcomes on a dry surface fall into three main classes, i.e. adhesion, bounce and shatter (Figure 1). This categorization is facilitated via a graphical user interface that assists in determining the behavior of each selected droplet through displaying images with superimposed trajectories from the previous step (Section 2.2.2). In this way, each droplet identified by the automated tracking procedure is viewed by an operator, who subsequently classify the droplet impact outcome and identify whether the leaf surface was previously wetted by another droplet or by a liquid film. Some remaining false-positive droplets that have been selected from the sizing algorithm or droplets impacting at leaf edges are rejected in this step. Adhesion (entire droplet “sticks” on impact) includes adhesion in both Cassie-Baxter (Cassie and Baxter, 1944) and Wenzel (Wenzel, 1936) regimes. Droplet shatter behaviour can also vary. For example, we could have made a distinction between complete shatter, where no liquid remains on the leaf after droplet impact, and partial shatter, where a variable amount of liquid remains on the leaf surface, called pinning (Boukhalfa et al., 2014; Rioboo et al., 2008). The pinning proportion significantly affects the spray retention by the whole plant (Dorr et al., 2016). However, in this study, these two kinds of shatter are not distinguished.

As spraying takes place, there are instances in which a thin liquid film is formed on the leaf surface, leading to droplet impact onto this liquid film. As with droplet impaction on a dry surface, outcomes include adhesion, when capillary forces dominate, or bounce. Alternatively, the impact could also cause the pre-existing film to splash away from the impaction point (Yarin, 2006). To avoid confusion between data for impaction on dry and wet surfaces, only the droplets impacting a dry surface were used in this study. Impaction events on a wet surface that were identified by the operator during the droplet impact outcome classification were therefore rejected (Table 5 and 6).

For droplet impaction on leaf surfaces, the transitions between impact outcomes are not sharp, with different impact behaviours coexisting at similar energy levels, as highlighted by the “transition region” proposed by Webb et al. (1999). In other words, for certain intervals of Weber numbers, two (or even three) outcomes are reasonably possible. Therefore, we sought a probabilistic description of the droplet impaction behaviour. In the context of surfactant-laden droplets impacting on leaf surfaces, previous researchers have attempted to present the adhesion/bounce/shatter outcomes in relation to Weber and Reynolds numbers (Webb et al., 1999), or in relation to sharp droplet adhesion/bounce and shatter thresholds (Dorr et al., 2016), to provide better insights into the impaction relationships. A further approach (Massinon et al., 2014) was to also incorporate constant Weber number curves in such velocity/droplet volume

scatter plots as guidelines to assist interpretation and interpolation options. We follow the latter approach here. Furthermore, in this study, logistic regressions are used to demonstrate the probability of each impact outcome depending on the impact energy. Hierarchical multinomial logistic regressions were performed with the impact classes as binary dependent variables, and the droplet Weber number as the independent variable (Zwertvaegher et al., 2014). Probability distributions for adhesion, bounce and shatter were determined for a range of Weber numbers using the *mnrfit* function of the Matlab statistical toolbox, which uses an iteratively weighted least squares algorithm to find the maximum likelihood estimates, according to the model (one predictor,  $We_n$ ):

$$P_k = \frac{1}{1 + e^{-\alpha_k - \beta_k We_n}} \quad (1)$$

where  $k$  is the type of impact outcome (adhesion or shatter),  $\alpha_k$  is the intercept of the  $k^{th}$  logit, and  $\beta_k$  is the regression coefficient of the  $k^{th}$  logit. Interactions between the multinomial categories were included in the analysis. The probability for bounce distribution was calculated for a range of Weber numbers by subtracting the probabilities of adhesion and shatter distributions from unity.

### 3. Results

The data acquired by the methods described above for four plant species and three formulations are presented in Figs 2-4. The actual experimental impaction outcomes are represented in Figs 2a-d, 3a-d and 4a-d, respectively, on the left-hand side, and the complementary logistic derivative probability profiles in the corresponding Figs 2e-h, 3e-h and 4e-h on the right. The latter were gathered into three main impact classes as described in Section 2.3 for the logistic regressions. Impact outcomes with some pinning features are distinguished in the actual experimental impaction graphs (Figs 2-4 left) for illustrative purposes.

In the current point data sets (Figs 2a-d, 3a-d and 4a-d), there is a common feature, an inflection in the slope of the scatter plot where the diameter is approximately 180  $\mu\text{m}$  and the velocity is 0.6  $\text{m s}^{-1}$ . All points below this inflection represent the smaller droplets that have reached terminal velocity and are very likely to adhere; above this region, the larger droplets impact at above terminal velocity and exhibit a range of behaviours. The data sets are arranged such that the upper four graphs on each page are for easy or moderately easy-to-wet species (bean and avocado), while the lower four are for difficult-to-wet species (cabbage and barnyard grass). This provides an interesting contrast in droplet impaction outcomes.

In the current study, the experimentally derived data sets are used to plot the probability of each impaction process versus the normal Weber number as shown in Figs 2e-h, 3e-h and 4e-h. This approach makes it much easier to visualise the experimental data for the respective adhesion, bounce and shatter processes. In effect, a vertical line from any point on the  $x$ -axis intersecting through the respective adhesion, bounce or shatter lines, will provide a probability of the proportion of outcomes in each such category. This representation is particularly useful in showing the behaviour of each formulation on different species (species effects) or different formulations on the same species (formulation effects). Parameters for the logistic regression models are available in Table 3.



Table 3: Parameters of the logistic regression model (Matlab, *mnrfit* ) for the impact outcomes adhesion and shatter for bean, avocado, cabbage and barnyard grass.

Species	Parameters	Formulations		
		Water	LI 700	Pulse
<b>Bean</b>	$\alpha_a$	9.4890	6.5687	5.3964
	$\beta_a$	-0.0702	-0.0405	-0.0102
	$\alpha_s$	-102.5661	-102.5661	-102.5661
	$\beta_s$	2.8571e-16	4.9036e-16	4.1894e-16
<b>Avocado</b>	$\alpha_a$	11.5835	7.5390	7.0532
	$\beta_a$	-0.0524	-0.0272	-0.0098
	$\alpha_s$	-102.5661	-102.5661	-102.5661
	$\beta_s$	8.3139e-15	2.0035e-15	9.4106e-16
<b>Cabbage</b>	$\alpha_a$	-1.3754	0.5836	3.7177
	$\beta_a$	-0.3804	-0.0649	-0.1713
	$\alpha_s$	4.3029	3.3768	1.5892
	$\beta_s$	-0.0635	-0.0425	-0.0213
<b>Barnyard Grass</b>	$\alpha_a$	-0.1155	0.8490	3.9227
	$\beta_a$	-0.3804	-0.0491	-0.0292
	$\alpha_s$	3.8343	2.5461	4.9054
	$\beta_s$	-0.0831	-0.0168	-0.0330

Table 4 shows the deviances for the logistic regressions from the *mnrfit* Matlab function as an indicator of the quality-of-fit. The higher deviances are related to the two difficult-to-wet leaf surfaces, while the deviances are lower for easy-to-wet leaves. The explanation lies in the fact that droplets are divided into 3 classes (adhesion, bounce and shatter) for difficult-to-wet species and into 2 classes (adhesion and shatter) for easy-to-wet species. There is therefore a higher number of droplets per class for easy-to-wet species. This indicates the need to capture more impaction events on such complex leaf surfaces where a coexistence of three different impact outcomes is observed on certain Weber number ranges. We leave this improvement for future work.

The number of droplets measured during the experiments for each species is given in Table 5. This number varies from 159 to 479 and highlights the variability of deposits within this small probe volume. Impaction events on a wet surface that were identified by the operator during the droplet impact outcome classification were rejected. Table 6 shows the number of droplets used to compute logistic regressions. The variability in droplet sampling contributes to the higher computed deviances since there are fewer droplets per class.

Table 4: Deviance of the multinomial logistic regressions as an indicator of goodness-of-fit. The smaller the deviance, the better the quality of the fit.

<b>Species</b>	<b>Formulations</b>		
	<b>Water</b>	<b>LI 700</b>	<b>Pulse</b>
<b>Bean</b>	13	14	18
<b>Avocado</b>	7	23	13
<b>Cabbage</b>	226	311	97
<b>Barnyard Grass</b>	248	216	60

Table 5: Number of droplets measured by the acquisition setup.

<b>Species</b>	<b>Formulations</b>		
	<b>Water</b>	<b>LI 700</b>	<b>Pulse</b>
<b>Bean</b>	373	239	252
<b>Avocado</b>	479	478	407
<b>Cabbage</b>	246	220	223
<b>Barnyard Grass</b>	186	159	160

Table 6: Number of droplets used to compute the logistic regressions.

<b>Species</b>	<b>Formulations</b>		
	<b>Water</b>	<b>LI 700</b>	<b>Pulse</b>
<b>Bean</b>	314	191	192
<b>Avocado</b>	322	309	209
<b>Cabbage</b>	246	220	223
<b>Barnyard Grass</b>	186	159	160

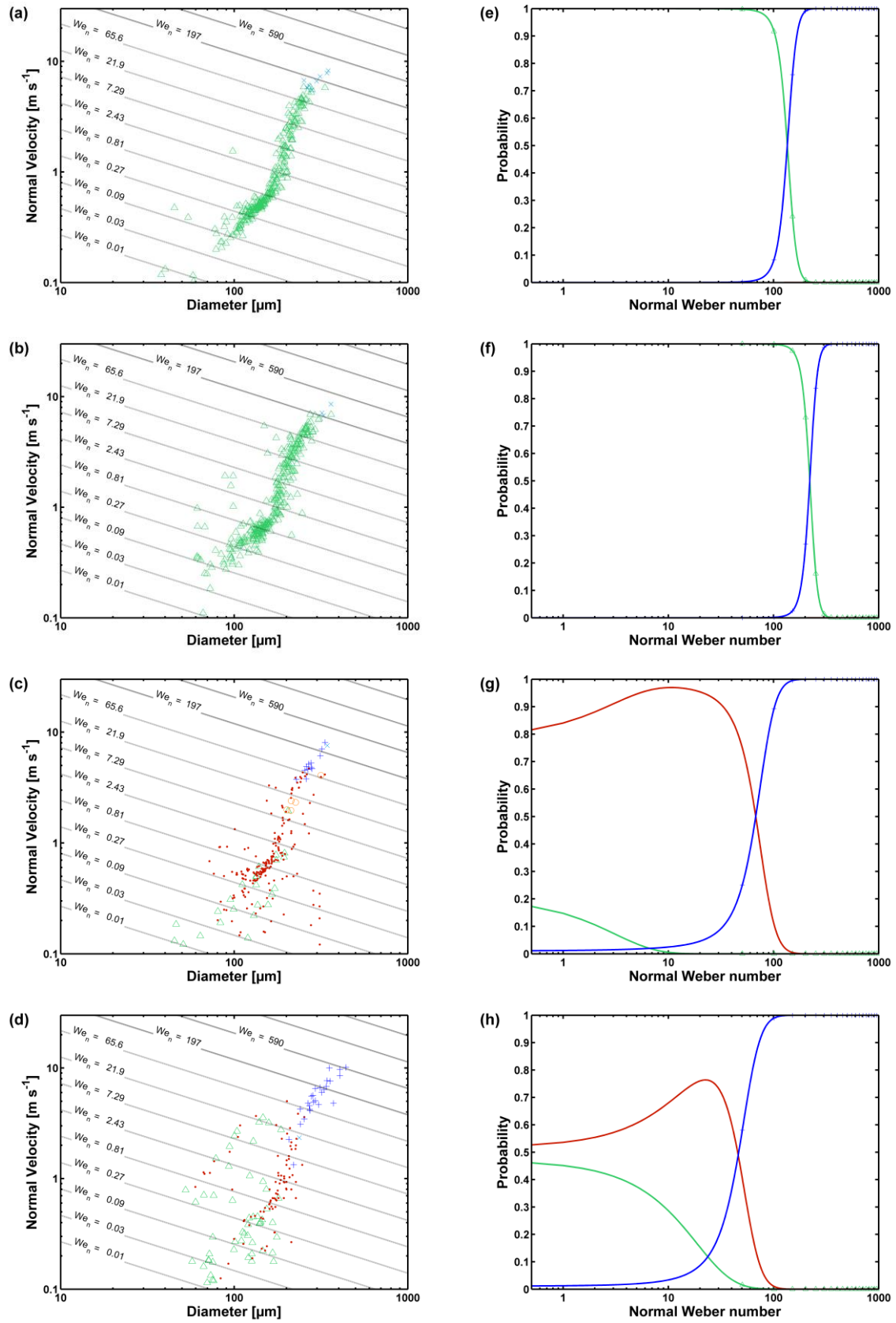


Figure 2: Spray impaction results with pure water: Bean (a and e), Avocado (b and f), Cabbage (c and g) and Barnyard (d and h). Observed impact outcomes at various individual droplet sizes and impact velocities (a-d). Adhesion ( $\Delta$ ), bounce ( $\bullet$ ), pinning bounce ( $\circ$ ), complete shatter ( $+$ ) and pinning shatter ( $\times$ ). Straight lines correspond to constant normal Weber numbers. Multinomial logistic regressions (e-h) show the probability versus the normal Weber number of each impact outcome in three classes: adhesion (green), bounce (red) and shatter (blue).

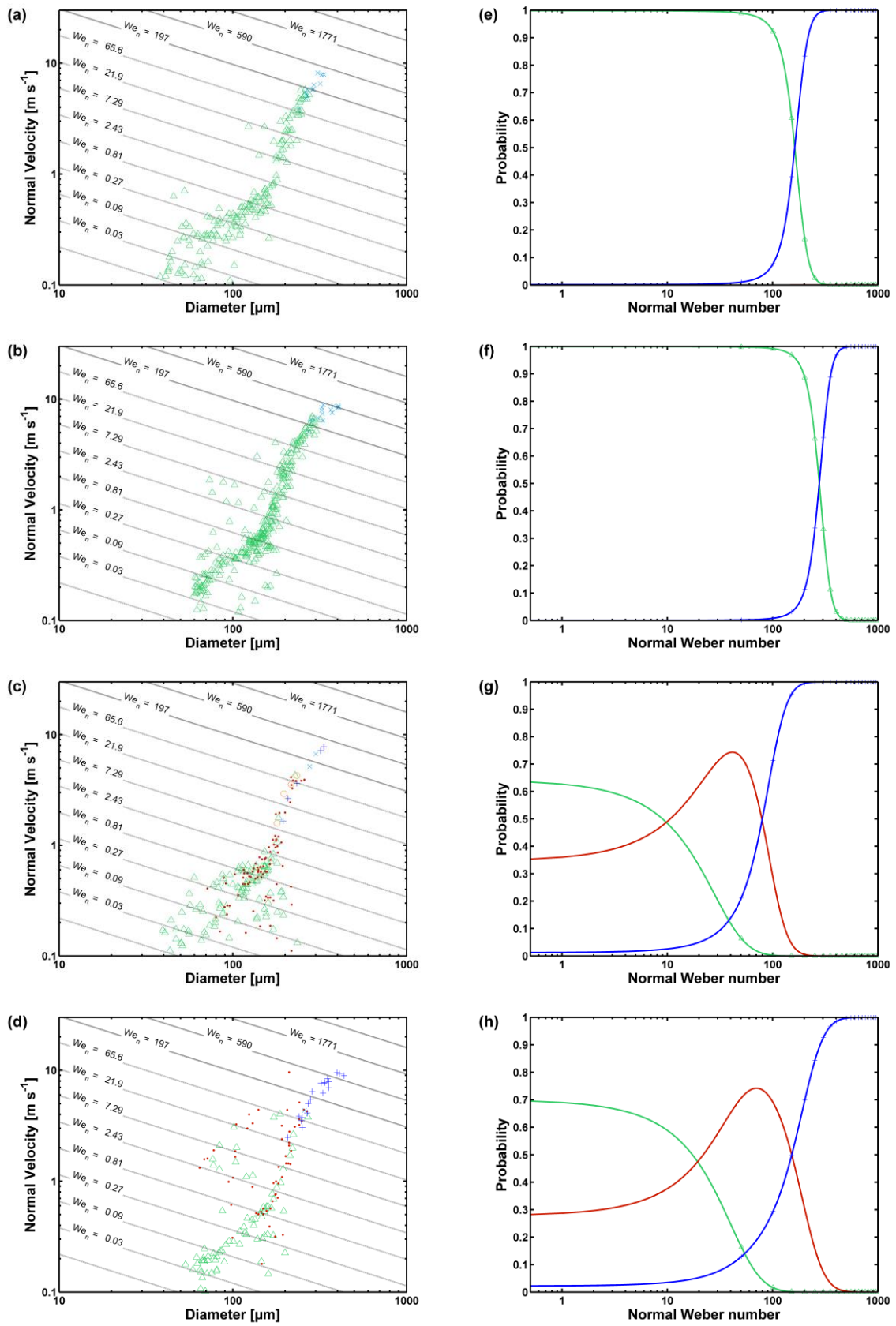


Figure 3: Same as Figure 2 for water plus LI 700® 0.1% v/v.

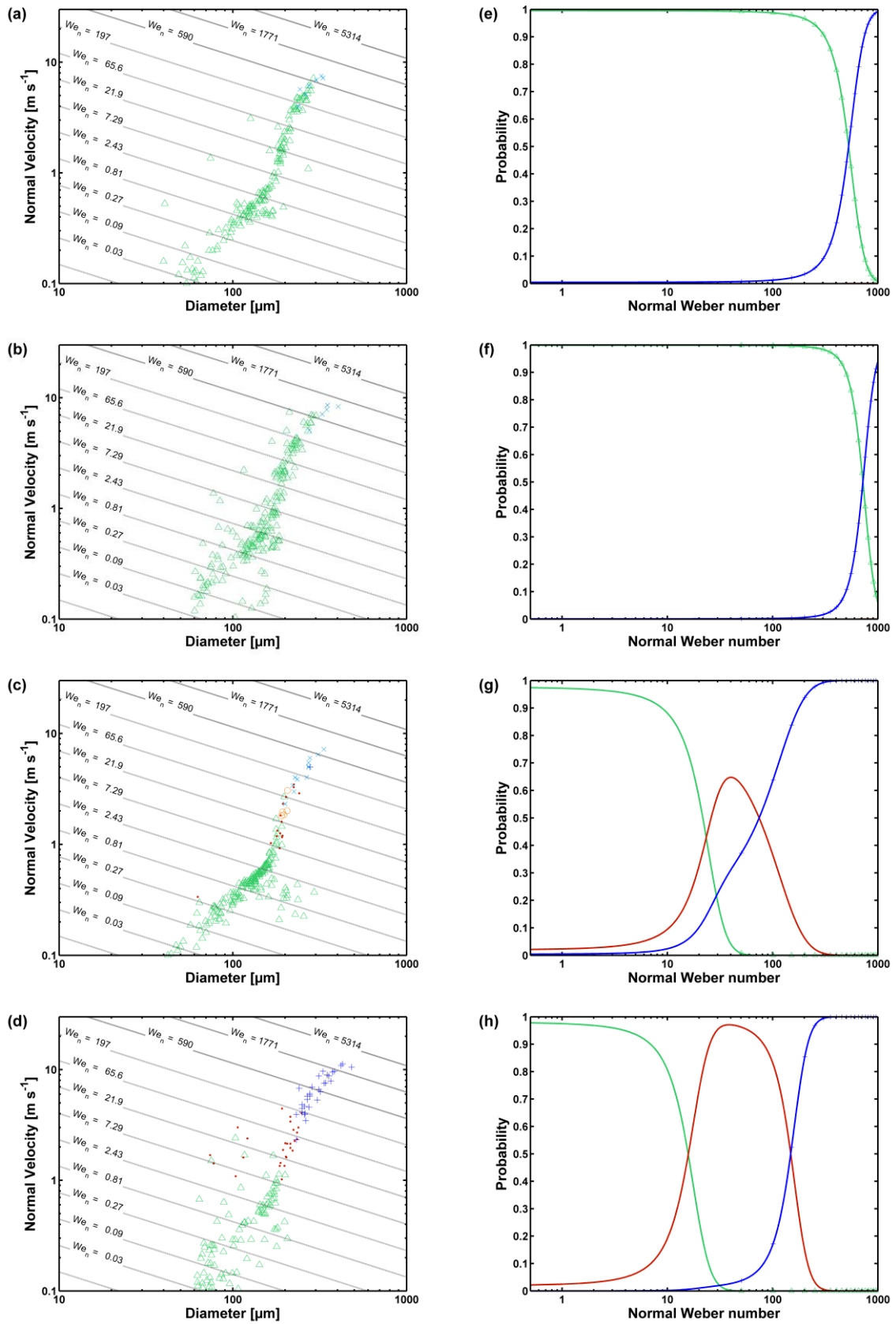


Figure 4: Same as Figure 2 and 3 for water plus Pulse@ 0.1% v/v.

## 4. Discussion

### 4.1. Easier-to-wet species

In the case of water on bean and avocado (Fig. 2e, f), the probability curves are very similar, with the predominant outcome being adhesion, followed by shatter at higher Weber values (for larger droplet sizes and higher impact velocities). On these easy and moderately easy-to-wet species, droplet bouncing does not occur. Almost identical trends are observed for the LI 700® and Pulse® formulations (Figs. 4e, f). The absence of bounce for impaction on easy-to-wet species is consistent with the results of Dorr et al. (2015), who observed that droplets either adhere or shatter on cotton (which is even more easy-to-wet than either bean or avocado).

Although the overall behaviour is very similar between formulations on easy-to-wet species, there is a consistent trend for the intersection of the adhesion/shatter probabilities to move to a slightly higher Weber number for avocado compared to bean (Figs. 2e vs 2f; 3e vs 3f; 4e vs 4f). Since in each pair the formulation is the same, this effect must be attributed to leaf surface character (or the interaction between formulation and leaf surface character). Recent work has determined that while bean is more wettable than avocado (eg., the contact angle for bean with 20% acetone in water is lower than that for avocado), avocado has the smoother surface (Nairn and Forster, 2016). Thus, for easy-to-wet species, the onset of shatter appears to be determined by a complex competition between surface roughness, which tends to increase the likelihood of shatter, and chemistry with polarity that tends to decrease the likelihood of shatter, complicated further by chemical interactions between the surface and the adjuvants.

For bean and avocado, there is only a slight formulation effect in that the adhesion/shatter crossover point moves to a slightly higher Weber value with decreasing DST. This illustrates that the addition of a surfactant can increase the probability of adhesion for larger droplets impacting at higher velocities, even on these easier-to-wet species.

### 4.2. More difficult-to-wet species

While the shatter probability curves look similar for each of the difficult-to-wet species leaves, with shatter dominating (i.e. > 50% probability) at lower Weber number values compared with the easy-to-wet leaves, overall the probability profiles are strikingly different from the much easier-to-wet species. There are clear cut species differences. In the case of water impacting cabbage and barnyard grass (Fig. 2g, h), the probability profiles for adhesion and bounce are quite different from each other. In contrast to the more easy-to-wet species (Fig. 2e, f), droplets bounce on these difficult-to-wet species, leading to a much lower probability of adhesion.

Barnyard grass leaf surface is much rougher than cabbage (Table 1). In the absence of a surfactant (Fig. 2g, h), bounce dominates adhesion at lower Weber values, while shatter dominates over the bounce process at higher Weber number values. While the two species are both very difficult to wet, water droplet bounce is much more likely (and therefore adhesion much less likely) on impact with the very non-polar cabbage surface (Fig. 2g), compared to the relatively neutral barnyard grass leaf surface (Fig. 2h).

The influence of these formulations is much more pronounced on the difficult-to-wet leaves compared to the easier-to-wet leaves, and in agreement to prior publications (Bruns and Nalewaja, 1998; de Ruiter et al., 1990; Hall et al., 1997). The addition of a surfactant, which changes the chemistry as well as lowering the surface tension, causes an increase in the probability of adhesion, especially with Pulse® (lowest DST), and reduces the probability of bounce at the lower Weber values (Figs 4g, h versus water alone in Figs 2g, h). The probability of bounce with the LI 700® and Pulse® formulations differs between cabbage and barnyard grass at intermediate Weber values (Figs. 3g, h and 4g, h). This behaviour demonstrates that there is not simply an adhesion/shatter boundary, but also an adhesion/bounce, and

bounce/shatter threshold, as illustrated in earlier literature (Forster et al., 2010) and confirming predictions using process-driven models for adhesion/bounce, and shatter (Dorr et al., 2015). Thus for surfactant-laden droplets impacting on difficult-to-wet species, a range of complex impaction scenarios can occur with all three processes being reasonably possible at some Weber numbers (for example, for Pulse® on cabbage with Weber numbers close to  $We_n = 12$ , each outcome is at least 20% likely to occur).

It could be speculated that while surface roughness dominates the shatter process, surface chemistry and the interaction between surface chemistry and formulation chemistry also plays a role in the adhesion/bounce mechanism. The coexistence of adhesion and bounce for similar impact energy levels, highlighted by the gradual transition between these two impact outcomes at low Weber numbers, could be due to differences in plant surface morphology (the presence of veins/ridges/trichomes) and the relative length scale between the surface roughness and to the droplet size. The smaller droplets of the spray are therefore more sensitive to the local variations of the surface micro topography on impact. The interactions occurring on addition of surfactants therefore become very complex.

#### 4.3. Additional considerations

Some further finer details need to be explained. Although not represented in the probability graphs, examination of the scatter point graphs reveals the presence of a further identified process, that of droplet pinning. This occurs when a small proportion of solution is retained at the impingement point, while the remainder of the spray droplet either bounces or shatters away (Boukhalfa et al., 2014). All of the shatter events occurring on the two easiest-to-wet, smooth leaf surfaces (bean and avocado) involve pinning, irrespective of formulation (Figs. 2, 3, 4, a and b). On difficult-to-wet cabbage, pinning is minimal when water droplets shatter (Fig. 2c), but increases on addition of LI 700® (Fig. 3c), and dominates in the shatter process in the presence of Pulse® (Fig. 4c). Complete shatter dominates on barnyard grass leaf surfaces, irrespective of formulation (Figs. 2, 3, 4d), with effectively no pinning to this extremely rough surface.

A similar scenario exists for pinning with rebounding droplets. Complete rebound dominates with water droplets impacting cabbage (Fig. 2c), with pinning from rebounding droplets increasing on addition of LI 700® (Fig. 3c) although complete rebound still dominates. Pinning from rebounding droplets increases still further on addition of Pulse® (Fig. 4c). Again, there is effectively no pinning from rebounding droplets after impact with the extremely rough barnyard leaf surface. These results would indicate that contact with the surface proper is necessary for pinning to occur (Rioboo et al., 2008).

A further factor influencing the impaction outcomes is whether the droplets make contact with a dry leaf surface, or an area where there is a liquid film from previous retention or spreading of droplets. This issue is only relevant for bean and avocado, which are the easier-to-wet species. The data corresponding to impaction on a pre-wetted surface were not included on the graphs in Figures 2-4. However, we observed that the proportion of droplets impacting a pre-wetted surface increases with decreasing surface tension on both species, with the higher proportion in each case observed on avocado (the smoother, non-polar surface). This is consistent with the greater spread area of droplets on avocado compared to bean (Nairn and Forster, 2016). Adhesion was the dominant outcome of droplets impacting the pre-wetted surface of bean, irrespective of formulation. This was also the case for droplets of water and LI 700® impacting the pre-wetted surface of avocado, while some rebound did occur in the case of droplets with Pulse®.

Whether or not a droplet bounces on impact with a liquid film is dependent on droplet size, velocity and film thickness (Yarin, 2006). Low DST surfactants promote spreading and consequently increases the probability of droplets impacting a film and bouncing. A thick film

promotes adhesion (the liquids merge), while a high kinetic energy (higher Weber value) promotes splashing of the pre-existing liquid film. A very small proportion of splash was observed in all cases on bean and avocado. These behaviours were not observed on the more difficult-to-wet species, cabbage and barnyard grass.

In conclusion, this empirical study of droplet impact outcomes illustrates clearly the variability due to droplet impaction energies, versus species and formulations, resulting in adhesion, bounce, shatter and pinning of droplets. Furthermore, the spray impaction behaviour has been characterised using a logistic regression model and these outputs plotted versus droplet Weber numbers (proportional to droplet kinetic energy at impact). This graphical representation demonstrates the interactions among species, formulations and droplet kinetic energies (represented by Weber values). The current data will be used in future to validate or improve current process-driven models (such as that outlined in Dorr et al. 2016) for the droplet impaction processes and their influence on retention by plants.

Our probabilistic framework is in contrast to various deterministic threshold criteria for droplet bounce (Attane et al., 2007; Mao et al., 1997) or shatter (Mundo et al., 1995; Riboux and Gordillo, 2014; Rein and Delplanque, 2008) that have been used to model droplet impaction event on leaves (Dorr et al. 2014; 2015; Mercer et al., 2010). A feature of these threshold criteria is that, for a given set of input parameters, only one outcome is predicted to occur. The reality of droplet impaction on leaf surfaces is that the complex surface morphology leads to a spectrum of outcomes, which provides an argument in favour of our probabilistic approach.

As expected, droplets impacting upon easy-to-wet and difficult-to-wet leaf surfaces behave quite differently. Specifically, there are predominantly two outcomes on easy-to-wet leaf surfaces, namely adhesion or shatter (at lower or higher Weber values, respectively). In contrast, impaction on difficult-to-wet surfaces produces three possible outcomes, namely adhesion, bounce or shatter (depending on the Weber number), modified by formulation properties. Furthermore, for some combinations of difficult-to-wet leaf surfaces and formulations, all three outcomes are reasonably likely to occur over an interval of Weber numbers.

Secondary outcomes observed in this study include partial droplet pinning with all formulations on easy-to-wet species. Pinning is less likely on difficult-to-wet cabbage, and virtually non-existent on the very rough, difficult-to-wet barnyard leaf surface. A more detailed study of pinning in the context of spray droplets impacting on leaf surfaces is worth pursuing.

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