Communauté Française de Belgique
Université de Liège - Gembloux Agro Bio-Tech

Multiscale approach of spray retention on superhydrophobic plant surfaces

Mathieu MASSINON

A dissertation presented for the degree of Doctor of Philosophy in Agricultural Sciences and Biological Engineering

Supervisor: Frédéric Lebeau
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To Margot, Antonin and Séverine

Mathieu Massinon (2016). *Multiscale approach of spray retention on superhydrophobic plant surfaces*. Université de Liège - Gembloux Agro-Bio Tech. 131 pages, 17 tables, 40 figures.

Abstract

The retention of most plant protection products on plants leaves is a key to their efficient use. In particular for monocots, problems observed in black-grass (*Alopecurus myosuroides* Huds.) weeding efficiency or the struggle against septoria in wheat may originate from insufficient retention of the active ingredients (a.i.) on this type of plants. Poor retention may even promote the emergence of resistance in the target population. Among the underlying factors related to these plants, some characteristics are detrimental to a good retention of a.i., namely their reduced leaves size, the superhydrophobicity of their leaf surfaces resulting from the presence of epicuticular waxes and hairs, as well as their erected architecture. Parameters related to the treatment, such as the spraying technique, the volume per hectare and the physico-chemical properties of the sprayed mixture are also involved and contribute to the variability of volumes of a.i. retained by each plant. The operating choices of a treatment must therefore be optimized according to the target properties in order to maximize retention and reduce variability in retained volumes by each plant or even leaf.

A mixture applied by agricultural nozzles impacts the plant in the form of droplets of various sizes, velocities and incidence angles. Two important phenomena determine the fate of each droplet: the possible adhesion to the surface as a function of the surface wetting regime and its possible fragmentation depending on the ratio of impact and surface energies. The combination of these two phenomena results in various types of impacts that unequally contribute to the overall retention by a plant. Spray application trials are often performed in the laboratory on small monocotyledon plant, such as barley at early growth stage, to test tracer or active ingredient retention for various formulations and additives. Unfortunately, results from such trials suffer from high variability rendering very laborious any identification of the overriding factors and the contribution of each underlying mechanism in the main process. An alternative approach is to focus on the physico-chemical properties of the formulation and of the leaf surface to characterise retention efficiency. Despite the efforts to develop predictive models of the fate of droplets based on physical and chemical properties, the complexity of leaf surfaces at different scales and diversity of formulation types still adversely affect the predictive quality of this type of approach. Moreover, the variability of retention existing between plants during a spray treatment remains poorly studied.

The main goal of this thesis is to develop a general methodology to improve the understanding of application methods of foliar pesticides and additives in terms of spray retention by leaf surfaces. This study attempts to link fundamental studies of the physics behind droplet impact with agronomic studies of spray application efficacy thank to its multiscale approach, from the droplet to the plant scale. It focused mainly on the most problematic targets for spray applications, *i.e.* small plants with predominantly vertical superhydrophobic leaves and contributes to answer the question of extension services about the reasons why black-grass (*Alopecurus myosuroides* Huds.) is so difficult-to-treat and

why herbicide resistance emerged in some populations. The multiscale approach chosen focuses primarily on the behaviour at impact of spray droplets on superhydrophobic target surfaces (natural and artificial). Secondly, the emphasis is put on the plant architecture in order to take into account the variability of leaf orientations resulting in a broad range of droplet incidence angle. Finally, numerical simulations were conducted using a virtual spray-plant interception model in order to study the variability of deposits that results from the application technique, the droplet impact behaviour and the plant architecture. For instance, one can understand why using anti-drift nozzles when treating small grass weed may still result in low treatment efficacy and environmental contamination using the proposed approach.

The first part focuses on the development of an experimental methodology based on high-speed imaging and image analysis relating accurately the behaviour of droplets at impact, specific to each formulation/surface combination for an agricultural spray, with their diameter and speed before impact. The originality of this methodology lies in the use of an artificial superhydrophobic surface, whose level of wettability is similar to a wheat leaf, and a moving agricultural nozzle to reflect the actual conditions of application. On a superhydrophobic surface, the Cassie-Baxter wetting regime is dominant, so different types of impacts are possible depending on the energy of the droplet, from direct adhesion at low impact energies, rebound at intermediate energies and up to fragmentation for high energies. This reference surface has proved to be a powerful tool for discriminating the effects of various spray additives thanks to its homogeneity allowing a high reproducibility of trials and to its very high level of hydrophobicity. The experimental methodology has been used to quantify the effect of a surfactant in relation with the spray application technology. Surfactants can alter the fate of the droplet impacts by the transition from the Cassie-Baxter wetting regime, favoring the rebound, to the Wenzel wetting regime promoting droplet adhesion. It has also been shown that various types of impact can coexist at similar impact energy levels and that the transitions between these impact outcomes can be described using probability density functions due to the intrinsic variability in droplet impact outcomes.

The second part of the thesis deals with the use of a logistic fitting of experimental impact probability histograms based on the Weber number of droplets. This histogram of observed droplet impact type frequencies is the core of the retention model. In a phase diragram of the droplet velocity as a function of its diameter, the histogram is built by discretizing the domain of droplet impact occurrence into classes on the basis of the droplet Weber number that reflects the ratio between its kinetic and surface energies. Limits between classes are set to follow a geometrical increase of their Weber number, what results in convenient evenly spaced classes in a log-log scale graph droplet velocity versus diameter. For an easy comparison between formulations and since the dynamic surface tension at the time frame of the impact of a droplet is not a readily available data, the static surface tension of the carrier media is used to calculate the droplets Weber number. In each energy class, the probability for each type of impact is calculated as the relative volume of each impact outcome in relation to the total volume impacting on the surface. The impact behaviour is compared at various tilt angles on a superhydrophobic slide and excised black-grass leaves. The main effects of the tilt of the surface are the reduction of the available surface area for droplet interception and a shift of the thresholds between types of impact towards lower energies classes since the normal component of the speed is reduced.

In the third part of the thesis, numerical simulations are performed in order to study the variability of deposits resulting from the application technique and from the droplet impact behaviour using the same plant model. A virtual nozzle produces droplets based on the Pearson system for random numbers. The jet is constructed from droplets drawn from the droplet spectra of agricultural nozzles of various spray qualities whose droplet size and speed were experimentally measured by an imaging technique called particle tracking velocimetry and sizing (PTVS). The droplet trajectories are computed to mimic the variability associated with the application method in the algorithm. The intersections between the droplet trajectories, assumed linear immediately near the target surface, and the three-dimensional representation of a scanned plant surface, consisting of a triangular mesh, is performed using a mathematical algorithm of intersection between straight lines and triangles in space. For each intercepted droplet, the model assigns an impact behaviour according the impact probability histogram taking into account the angle of incidence of the droplet. For a given plant architecture, increasing the average size of the droplets resulted in a decrease in the retention level, irrespective of the wettability scenario studied. The percentage retention in all the simulations varied from 7% to 97% of a theoretical scenario of full adhesion of droplets. The increase in droplet sizes led to an increase of the coefficient of variation of the simulations, reflecting the variability of deposits. Moreover, the level of variability is substantially similar irrespective of the formulation studied. The variability of deposits also increased with the reduction of volume per hectare applied. This effect is enhanced for the nozzles producing larger droplets because of the reduced number of droplets for an identical applied volume. The mean level of retention decreased linearly with the reduction in plant size and the variability increased according to the square root of total leaf surface area because the number of droplets intercepted decreased. Consequently, environmental benefit from the application of larger droplets in order to reduce the risk of drift resulted in a decrease of the mean retention and an increase of the variability of the dose retained by the foliage on the monocotyledon plant model. These two trends may result in underdosed plants (sublethal doses) that may reduce overall efficacy and even promote the emergence of resistance to the active ingredients. The use of an additive with fast spreading properties, *i.e.* with a low dynamic surface tension at time frame of droplet impact, should be prefered as it allows an increase in the retention efficiency of a treatment.

Finally, practical recommendations are proposed for difficult to treat plants and aimed at improving pesticide spray applications to reduce environmental and health concerns. Using a numerical and multiscale approach could guide the design of field trials to avoid testing completely ineffective methods and guide the industry in the development of new formulations or new application techniques. Further studies of the underlying mechanisms causing the variability in droplet impact outcomes could be achieved with the proposed methodology in order to be able to predict any new formulation/nozzle/species combination. Finally, a model of active ingredient biological efficacy could be combined with the proposed approach in order to deepen understanding of the response of droplets properties on treatment efficiency and efficacy.

Mathieu Massinon (2016). *Approche multi-échelles de la rétention des produits phytosanitaires sur plantes superhydrophobes*. Université de Liège - Gembloux Agro-Bio Tech. 131 pages, 17 tables, 40 figures.

Résumé

La rétention de la plupart des produits phytosanitaires sur les feuilles est un processus clé pour une utilisation efficace de ces derniers. En particulier sur monocotylédones, les problèmes observés de manque d'efficacité en désherbage du vulpin (*Alopecurus myosuroides* Huds.) ou de lutte contre septoriose du blé peuvent trouver leur origine dans une rétention insuffisante des matières actives et par conséquent, peuvent favoriser l'apparition de résistance au sein de la population ciblée. Une rétention insuffisante s'explique par des facteurs liés à la plante et au traitement. La taille réduite des feuilles, la nature superhydrophobe des surfaces foliaires résultant de la présence de cires épicuticulaires et de poils, ainsi que l'architecture dressée expliquent ce manque de rétention. Des paramètres liés au traitement, comme la technique de pulvérisation, le volume à l'hectare et les propriétés physicochimiques de la bouillie pulvérisée contribuent également à la variabilité des volumes de matières actives retenues par chaque plante. Les choix opératoires du traitement doivent dès lors être optimisés en fonction des propriétés de la cible afin de maximiser la rétention et réduire la variabilité des doses retenues par chaque plante voire de chaque feuille.

Un jet de pulvérisation appliquée par des buses agricoles arrive sur la plante sous forme de gouttes de divers diamètres, vitesses et angles d'incidence. Deux phénomènes importants conditionnent le devenir de chaque goutte: l'adhésion à la surface en fonction du régime de mouillage et la fragmentation en fonction du rapport des énergies d'impact et de surface. La combinaison de ces phénomènes résulte en divers types d'impacts qui contribuent inégalement à la rétention globale par la plante. Des tests de rétention sur plantes individuelles sont souvent effectués en laboratoire pour évaluer les effets des adjuvants sur l'efficacité du transfert des matières actives sur la cible. Malheureusement, les résultats de cette approche à l'échelle de la plante souffrent d'une variabilité élevée, rendant laborieuse toute identification des facteurs prépondérants et la compréhension des mécanismes sous-jacents dans le processus global. Une approche alternative est de se concentrer sur la propriétés physico-chimiques de la formulation et de la surface des feuilles pour caractériser l'efficacité de rétention. Malgré les efforts pour mettre au point des modèles prédictifs du devenir des gouttes sur base de propriétés physico-chimiques, la complexité des surfaces foliaires à différentes échelles et la diversité des types de formulations nuit encore à la qualité prédictive de ce type d'approche. En outre, la variabilité de la rétention liée à un traitement reste peu étudiée et les mécanismes sous-jacents non décrits.

Le principal objectif de cette thèse est de développer une méthodologie générale pour améliorer la compréhension de l'effet des techniques d'application des produits phytosantaires et des additifs en termes de rétention par le feuillage. Cette étude tente de faire le lien entre les études fondamentales de la physique de l'impact des gouttelettes et les études agronomiques d'efficacité des produits phytosanitaires grâce à son approche multi-échelles, de l'échelle de la goutte à l'échelle de la plante. Cette étude se porte principalement sur les cibles les plus problématiques, à savoir de petites plantes dressées et superhydrophobes et contribue à répondre à la question des services de vulgarisation sur les raisons pour lesquelles le vulpin (*Alopecurus myosuroides* Huds.) est si difficile à contrôler. L'approche multi-échelles choisie se focalise en premmier lieu sur le comportement des gouttes à l'impact sur surfaces superhydrophobes, tant naturelles qu'artificielles. En

second lieu, l'étude se porte à l'échelle de la plante afin de tenir compte de l'inclinaison variable des feuilles par rapport à la trajectoire des gouttes. Enfin, des simulations numériques ont été réalisées à l'aide d'un modèle virtuel d'interception des gouttes par la plante afin détudier la variabilité des dépôts résultant de la technique d'application et du comportement des gouttes à l'impact sur l'architecture d'une plante.

La première partie de la thèse se focalise sur la mise au point d'une méthodologie expérimentale par imagerie rapide reliant précisément le comportement des gouttes à l'impact, spécifique à chaque combinaison formulation/surface pour un jet agricole, avec leur diamètre et vitesse d'impact. L'originalité de cette méthodologie réside dans l'utilisation d'une surface superhydrophobe artificielle de mouillabilité similaire à celle d'une feuille de froment et d'une buse agricole en mouvement afin de refléter au mieux les conditions d'application réelles. Sur une surface superhydrophobe, dont le régime de mouillage est essentiellement celui de Cassie-Baxter, les différents types d'impacts se succèdent en fonction de l'énergie croissante de la goutte, passant de l'adhésion directe aux faibles énergies d'impact, au rebond aux énergies intermédiaires et à la fragmentation aux énergies les plus élevées. Le banc d'essai développé s'est avéré un outil performant permettant de discriminer les effets de différents adjuvants de pulvérisation grâce au niveau très élevé d'hydrophobicité et à l'homogénéité de sa surface. La méthodologie expérimentale a permis de quantifier l'effet d'adjuvants extemporanés tensio-actifs en lien avec la technique d'application. Les adjuvants tensio-actifs modifient le comportement des gouttes à l'impact par la transition d'un régime de mouillage de Cassie-Baxter, favorisant le rebond, vers un régime de Wenzel favorisant l'adhésion. Il a également été montré que différents types d'impact peuvent coexister à des niveaux d'énergie d'impact similaires en raison de l'hétérogénéité intrinsèque de la surface cible et que les transitions entre types d'impact peuvent être mise en évidence sous forme d'histogrammes.

La seconde partie de la thèse porte sur l'utilisation d'un modèle de régression logistique dont les paramètres sont ajustés aux probabilités d'occurence des divers types d'impact en fonction du nombre de Weber des gouttes. Cette probabilité expérimentale des divers types d'impact en fonction du nombre de Weber caractéristique est le cœur du modèle de rétention proposé dans cette thèse de doctorat. Dans une représentation graphique présentant la vitesse des gouttes en fonction de leur diamètre, l'histogramme de probabilité est construit en discrétisant le domaine en douze classes dont les limites sont calculées sur base du nombre de Weber de la goutte qui reflète le rapport entre son énergie cinétique et son énergie de surface. Par soucis de comparaison aisée entre formulations et puisque la tension de surface dynamique à l'échelle de temps de l'impact d'une goutte est une donnée difficilement accessible, la tension de surface de la phase porteuse des matières actives est été utilisée pour calculer le nombre de Weber. Les limites de classes sont fixées afin de suivre une progression géométrique du nombre de Weber, ce qui résulte en classes également espacées dans un diagramme de phase doublement logarithmique représentant la vitesse en fonction du diamètre de la goutte. Pour chaque classe d'énergie ainsi créée, la probabilité pour chaque type d'impact est calculée comme le volume relatif de chaque type d'impact par rapport au volume total observé sur la surface. Le comportement à l'impact est comparé à différents angles sur la surface artificielle superhydrophobe et sur des feuilles de vulpins excisées pour divers adjuvants. Les effets principaux de l'inclinaison de la feuille sont la réduction de l'aire de la surface disponible pour l'interception des gouttes et une translation des seuils entre types d'impact vers des classes d'énergies plus basses car la composante normale de la vitesse est réduite.

Dans la troisième partie de la thèse, des simulations numériques sont réalisées en utilisant un même modèle numérique tridimensionnel de plante pour étudier la variabilité des dépôts résultant de diverses techniques d'application et comportements des gouttelettes à l'impact. Une buse virtuelle est créée par un tirage aléatoire sur base du système de Pearson dans la population de gouttes issue de diverses qualités de jets agricoles dont la taille, la vitesse et l'orientation ont été éterminées expérimentalement par une technique d'imagerie de suivi des particules (Particle tracking velocimetry and sizing, PTVS). Cette méthode permet de reproduire la variabilité des diamètres, vitesses et trajectoires liée à la technique d'application au sein l'algorithme. Les intersections entre les trajectoires de gouttes, assumées linéaires immédiatement au-dessus de la surface cible, et la représentation tridimensionnelle de la surface d'une plante scannée, composée d'un maillage triangulaire, se réalise par un algorithme mathématique d'intersection entre des droites et des triangles dans l'espace. Pour chaque goutte interceptée, le modèle attribue un comportement à l'impact en fonction du modèle logistique en tenant compte de l'angle d'incidence de la goutte. Pour une architecture de plante donnée, l'augmentation de la taille moyenne des gouttes conduit à une diminution de la rétention, quel que soit le scénario de mouillabilité étudié. L'efficience du processus de rétention dans l'ensemble des simulations réalisées a varié de 7% à 97% d'un scénario théorique d'adhésion totale des gouttes. L'augmentation de la taille de gouttes mène à une augmentation de la variabilité de la rétention, le niveau de variabilité étant sensiblement similaire quelle que soit la formulation étudiée. La variabilité des dépôts augmente avec la réduction du volume par hectare appliqué. Cet effet étant plus marqué pour les buses produisant les plus grosses gouttes car le nombre de gouttes est réduit pour un même volume appliqué. La moyenne de la rétention diminue linéairement avec la réduction de la taille de la plante et sa variabilité (coefficient de variation) augmente selon la racine carrée de la surface foliaire car le nombre de gouttes interceptées se réduit. En conséquence, lla réduction du risque de dérive par l'application de grosses gouttes a résulté sur ce modèle de monocotylédone en une augmentation de la variabilité de la dose retenue par le feuillage. Cela conduit à des plantes sous-dosées, réduisant l'efficacité globale, et à favoriser l'émergence d'une résistance aux matières actives. L'utilisation d'un adjuvant aux propriétés d'étalement importantes, c'est-à-dire dont la tension de surface dynamique est faible aux échelles de temps de l'impact des gouttes, doit être préférée car elle induit une augmentation significative de l'efficacité de la rétention.

Finalement, des recommandations pratiques pour la technique d'application sont émises pour le traitement des plantes constituant des cibles difficiles. L'utilisation d'une approche numérique permettrait d'orienter la conception des essais de terrain afin d'éviter de tester des modalités totalement inefficaces. Elle a également la capacité de guider les industriels dans le développement de nouvelles formulations ou des nouvelles techniques d'application. D'autres études des mécanismes à l'origine de la variabilité des comportements à l'impact des gouttelettes pourraient être atteints avec le méthodologie proposée afin d'être en mesure de prédire toute nouvelle combinaison formulation/buse/espèce. Enfin, un modèle d'efficacité biologique des matières actives pourrait ête combiné avec l'approche proposée dans le but d'approfondir la compréhension de la réponse des propriétés des gouttelettes sur l'efficacité d'un traitement.

Preface

This dissertation is submitted for the degree of Doctor of Philosophy in Agricultural Sciences and Biological Engineering at the University of Liege. The research described in this document was undertaken at the Biosystems Engineering Department of the Gembloux Agro-Bio Tech Faculty.

Part of this work has been previously presented in the following scientific publications:

- **Massinon, M.** and Lebeau, F., 2012. Experimental method for the assessment of agricultural spray retention based on high-speed imaging of drop impact on a synthetic superhydrophobic surface. *Biosystems Engineering* 112:56-64 (http://hdl.handle.net/2268/114382).

- **Massinon, M.** and Lebeau, F., 2013. Review of physicochemical processes involved in agrochemical spray retention. *Biotechnology, Agronomy, Society and Environment* 17:494-504 (http://hdl.handle.net/2268/148678).

- **Massinon, M.**, Boukhalfa, H. and Lebeau, F., 2014. The effect of surface orientation on spray retention. *Precision Agriculture* 15:241-254 (http://hdl.handle.net/2268/161493).

- **Massinon, M.**, Dumont, B., De Cock, N., Ouled Taleb Salah, S. and Lebeau, F. (2015). Study of retention variability on an early growth stage herbaceous plant using a 3D virtual spraying model. *Crop Protection* 78:63-71 (http://hdl.handle.net/2268/185667).

Research collaborations also resulted in two publications not included in this dissertation:

- Zwertvaegher, I., Verhaeghe, M., Brusselman, E., Verboven, P., Lebeau, F., **Massinon, M.**, Nicolaï, B. and Nuyttens, D. (2014). The impact and retention of spray droplets on a horizontal hydrophobic surface. *Biosystems Engineering* 126:82-91 (http://hdl.handle.net/2268/171718).

- Boukhalfa, H., **Massinon, M.**, Belhamra, M. and Lebeau, F. (2014). Contribution of Spray Droplet Pinning Fragmentation to Canopy Retention. *Crop Protection* 56:91-97 (http://hdl.handle.net/2268/159488).

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Mathieu Massinon

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During four years, I was really pleased to assist Professor Marie-France Destain in educational tasks at in the Biosystems Engineering Department. I would like to thanks her for its relevant advices and remarks that have really improved this dissertation.

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Without the help of all these persons, this dissertation would never have come into existence.

Nomenclature

Abbreviations

a.i. .... active ingredient

Bo .... Bond number, *dimensionless*

Ca .... Capillary number, *dimensionless*

CMC .... Critical micelle concentration, $mol \cdot l^{-1}$

CV .... Coefficient of variation, %

d .... Drop spreading diameter, m

$d^{\square}$ .... Dimensionless spread factor at a time t

D_0 .... Drop diameter before impact, m

DST .... Dynamic surface tension, $N \cdot m^{-1}$

E_K .... Drop kinetic energy, J

E_S .... Drop surface energy, J

Fr .... Froude number, *dimensionless*

h .... Drop height on the surface during impact, m

$h^{\square}$ .... Dimensionless drop height for a time t

La .... Laplace number, *dimensionless*

LAI .... Leaf area index, $leaf\ surface\ area \cdot soil\ area^{-1}$

Oh .... Ohnesorge number, *dimensionless*

r .... Roughness ratio, $true\ wetted\ area \cdot projected\ planar\ surface\ area^{-1}$

Re .... Reynolds number, *dimensionless*

SCA .... Static contact angle, $\circ$

t .... Time measured from the instant of impact, s

$t^{\square}$ .... Dimensionless spreading time

V .... Drop velocity, $m \cdot s^{-1}$

VMD .... Volume median diameter, μm

We .... Weber number, $dimensionless$

DV_{XX} .... XX% of the volume of spray is in droplets smaller than this value, μm

Symbols

σ .... Surface tension, $N \cdot m^{-1}$

θ .... Contact angle, $\circ$

μ .... Liquid viscosity, $Pa \cdot s$

ρ .... Liquid density, $kg \cdot m^{-3}$

Subscripts

c .... Critical

lg .... Liquid-gas

ls .... Liquid-solid

sg .... Solid-gas

0 .... State before impact

Y .... Young

W .... Wenzel

CB .... Cassie-Baxter

fin .... Final state

A .... Advancing

R .... Receding

Contents

CHAPTER 1

General introduction

"In crop protection the chemical weapon must be used as a stiletto, not a scythe"
A.W.A. Brown (1951).

1.1 Risk of herbicide resistance emergence

Spray application of herbicides is a fast, affordable and very effective action that became often the only way of controlling weeds in field crops. However, the use of herbicide as the sole weed management mean is questionable because of the adverse impacts of pesticide on environment and health. Moreover, the repetitive use of similar active ingredients along with the shift towards more intense cultivations and the early sowing of winter cereal crops (Moss, 2013) resulted in the emergence of herbicide resistance to one or several active ingredients in Northern Europe (Coelho, 2009; Powles and Shaner, 2001) due to the strong selection intensity of active ingredients (Richter et al., 2002; Neve and Powles, 2005). Herbicide resistance is an inherited physiological trait that leads to the selection of plants and/or plant populations able to survive herbicide treatments. The major weed problem in winter cereals in Europe is black-grass (*Alopecurus myosuroides* Huds.) (Heap, 2015; Keshtkar et al., 2015; Délye et al., 2011; Henriet and Maréchal, 2009). Black-grass is an annual weed propagated solely by seeds and its populations can build up very rapidly given favourable conditions. It becomes problematic if insufficiently controlled. For instance in England where the first cases of resistance were reported in 1982, it has been showed that the percentage of crop yield losses can reach up 50 % at 100 black-grass plants per square metre compared to weed free crop (Blair et al., 1999), the economic threshold of *Alopecurus myosuroides* being estimated at 12 plants/m^2 in England (Vizantinopoulos and Katranis, 1998). In order to reduce risk of yield losses, applying herbicide at lower infestation densities is common, *e.g.* applying pesticide at 1 plant per square metre density may be justified in high risks situations (Moss, 2013).

A reduced reliance to herbicide has been advised to reduce the risk of herbicide resistance (Chikowo et al., 2009). Integrated weed management (IWM) strategies has emerged as a solution to manage weed population without side effects on crop yield. IWM strategies include the rational use of herbicides or use of a combination of herbicides and cultural methods, such as crop rotation, adapted soil tillage, stale seedbed, adapted sowing dates, sowing densities and row widths, competitive cultivars, mechanical weeding, mixing crop, allelopathy, etc. (Chikowo et al., 2009). However, using solely non-chemical methods still give moderate and unpredictable levels of control at an individual field level (Lutman et al., 2013) and herbicides will still probably be used in sequence with other non-chemical methods to increase the overall level of control of problematic weeds. Consequently, further spray applications of active ingredients or biopesticides should be performed as best as possible.

1.2 Spray applications of herbicides

An optimised choice of the active ingredient and its dose, formulation, spray pressure, nozzle type and subsequent droplet size, water volumes and spray timings should be performed to maximise herbicide efficiency. Because the number of spraying occasions could be limited depending of weather conditions such as wind, rain and trafficability, timeliness of application is of key importance since correct timing enables efficacy to be maximised and therefore inputs to be minimised (Butler Ellis et al., 2007). Increasing works rates is therefore critical in the planning of applications strategies in relation with weed growth. For boom sprayers, work rates are mainly a function of forward speed, boom width and application volume (L/ha). Best Management Practices (TOPPS-LIFE project) advised to reduce the sprayer forward speed to limit the drift of pesticides and maximise boom stability. Secondly, boom widths are determined by the existing equipment and is therefore not a readily adaptable parameter. Thirdly, when spraying at reduced rates, the time taken to load and fill the sprayer as well as the number of trips between the loading area and the fields is reduced (Butler Ellis et al., 2007). Reducing the volumes applied will save water but also increase the concentration of active ingredient within droplets. A poor targeting of the spray mixture could therefore be more damageable for environment. To overcome the drift issues when reducing carrier volumes, farmers commonly make use of drift reduction nozzles that limit the proportion of spray volume in smaller droplet sizes (Figure 1.1), for instance by using technologies such as pre-orifice nozzles, low pressure nozzles or air induction nozzles. It is also possible to increase the mean droplet size by using larger nozzle calibres while increasing forward speed but this may have detrimental effects on boom stability or drift as seen previously and therefore it should be avoided. Because of the reduction in application volumes in combination with the use of larger droplets, each weed may receive variable dose of herbicide that could even be smaller than the required dose for killing the plant (sublethal dose) and could favour herbicide resistance emergence (Beckie, 2006; Neve and Powles, 2005). Increasing the work rates fulfils both an economic and environmental need. However, what effects these larger droplets have on the biological efficacy of products and the variability of herbicide doses, especially at reduced volumes, remains an open question.

1.3 Spray retention by plant leaves

The overall spraying process can be conceptually divided into four individual steps: deposition, retention, uptake and translocation (Zabkiewicz, 2007). For a common herbicide application, the efficiency range of each step is illustrated in Table 1.1. The ratio in amount of active substance received by the target site can reach 150 (from 0.24% up to 38%) between the worst and the better (optimised) scenario, highlighting the high variabil-

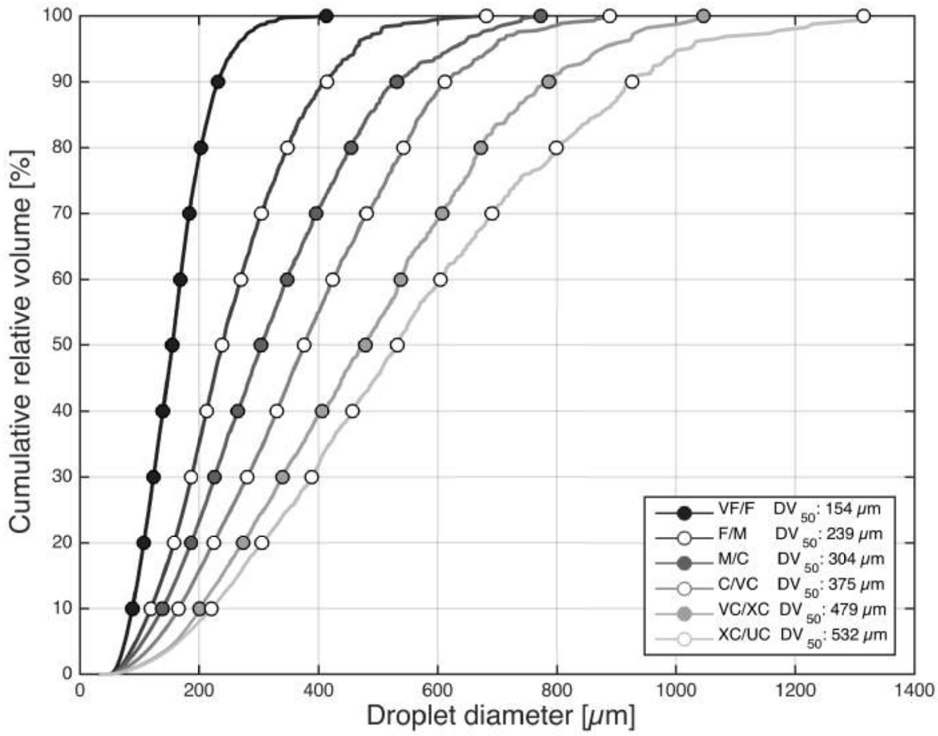


Figure 1.1: Cumulative droplet size distributions for 6 ISO reference flat-fan nozzles measured by shadowgraphy method according to De Cock et al. (2015): very fine (VF), fine (F), medium (M), coarse (C), very coarse (VC), extra coarse (XC) and ultra coarse (UC). These nozzles/pressure combinations are expected to be used as boundaries between classes in the ISO draft standard (ISO 25358) for classification of nozzle droplet size spectra.

ity in the final efficiency of a given treatment. While the droplet transport and drift as well as the retention have been extensively studied, the understanding of the relative importance of the various parameters involved in retention on a plant is still unsatisfactory. Spray retention on foliar surfaces is the overall capture of droplets by leaves and determines the amount of active ingredient on a plant. It is of key importance in the efficient uptake and biological activity of herbicides especially on leaves with difficult-to-wet surfaces covered with microcrystalline waxes (Barthlott et al., 1998; Taylor, 2011). Such an extreme wetting behaviour is called superhydrophobicity. For instance black-grass (*Alopecurus myosuroides* Huds.) plants at early growth stage at which the weeding is performed have such extreme detrimental wetting behaviours. Spray application techniques must therefore be adapted according to the target properties. There is consequently a need for methods allowing to study the effect of spray application techniques on retention and clarifying relationships between involved parameters.

Table 1.1: Representative spray application efficiency, system efficiency and off-target component loads for a herbicide application (Zabkiewicz, 2007).

Spray efficacy processes	Process efficiency (%)	System efficiency (%)	Off target component (%)
Deposition	80-95	80-95	20-5
Retention	10-100	8-95	92-5
Uptake	30-80	2.4-76	97.6-24
Translocation	10-50	0.24-38	99.6-62

1.4 Spray application technique assessment methods

In the overall context of weed resistance management, efficacy problems may arise from the insufficient coverage, *i.e.* the number of droplets per target surface area, and the insufficient amount of active ingredient retained by the plant. The latter results from improper spray droplet impacts associated to the use of unoptimised application techniques and formulations. If the spray properties are not optimised, the droplets will bounce off the surface and be lost to the ground. Formulators improve the performance of their products using additives, especially surfactants that enhance wetting properties of the spray mixture by lowering its surface tension. The modification of liquid properties also acts on the deposition phase by the modification of the droplet generation process, but also uptake since mixture with very low surface tension may better penetrate the plant through leaf stomata. The spray application of plant protection products is therefore a complex system with many interconnected factors related either to the target or the droplet properties. Field trials have often been used in order to assess the performance of post-emergence herbicide efficacies (Knoche, 1994). Comprehensive spray retention trials are resource consuming since a vast array of possible formulations at each spray application would have to be tested against every species. This instructive approach, however, highlights only major trends without clear understanding of underlying mechanisms. When testing additives, it is also common to perform spray retention tests on individual plants in the laboratory (Holloway et al., 2000) in order to test additive effects on active ingredient efficacy. Unfortunately, results from such retention trials are hightly dependent of the droplet size distribution and plant material used, at the detriment of reproductibility. Furthermore, plant architecture and orientation variations between trials as well as droplet trajectories can also affect the statistical power of such an overall test which are therefore enable to discriminate tenious treatment variations. Current spray retention evaluation techniques are integrative, which means that they are still not fully satisfactory since they provide no insight of the physics behind droplet adhesion.

1.5 Modelling spray retention

To overcome repeatability issues of retention trials, a modelling approach has been recently used to better understand the complex mechanisms conditioning spray retention by plant. This approach is also driven by the need of formulators to be guided in their developments of new products and additives. First studies resulted in empirical models for droplet adhesion on leaf surface without description of the plant architecture (Forster et al., 2005). Another way rely on using coherent overarching simulation package including spray-canopy interactions models based on the intersection of droplet trajectory with a mathematical model of the leaf or the plant that attributes to each intercepted droplet an impact behaviour (Dorr et al., 2008). These complex models include good descriptions of droplet transport including the plant architecture but make the simplifying assumption that if a plant intercepts a droplet, it is always retained. This approach was improved using process-driven models for retention based on droplet impact studies (Dorr et al., 2014) and compared with droplet impaction studies based on high-speed imaging (Dorr et al., 2015). However, discrepancies with the model highlighted the need of a better description and prediction of droplet impact behaviours on leaf surfaces.

1.6 Objectives and outline of the thesis

This doctoral thesis will focus on the most problematic (or difficult-to-treat) targets encountered in spray application, *i.e.* small plants with predominant vertical leaf orientation and superhydrophobic leaf surfaces, such as black-grass (*Alopecurus myosuroides* Huds.), and aims at describing the reasons why some spray applications fail to control this difficult to treat weed through a better understanding of mechanisms involved in herbicide retention. The main objective of this doctoral thesis is to provide a screening tool able to predict spray retention by difficult-to-treat plants for determining optimal application parameters depending on the target properties. Since this study stands at the interface between fundamental studies of the physics behind droplet impact (microscopic scale) and agronomic studies of spray application efficacy (field scale), a multi-scale model is chosen to address these objectives. The approach results in a deeper understanding of the mechanisms involved in spray retention at the droplet scale and extrapolates droplet outcomes to the plant scale in order to predict the overall plant retention. This approach could reduce the high resource consumption of laboratory or fields retention trials and should at least be used prior to their design.

The following specific objectives are followed in this thesis:

1. Develop a flexible research tool able to identify and quantify the behaviour at impact of droplets produced by a single and moving agricultural hydraulic nozzle on a reference horizontal superhydrophobic surface (Chapter 3) that can highlight the effect of the various parameters involved in spray retention, i.e. droplet size and velocity, formulation surface tension and target surface wettability based on the state of the art of leaf wetting knowledge (Chapter 2);

2. Improve the understanding of droplet impacts on slanted superhydrophobic surface and propose a statistical representation of the spray droplet impact behaviours that takes into account the inherent variability in droplet impact outcomes on a given surface (Chapter 4);

3. Gather these informations in a numerical model of droplet interception in order to systematically study the effect of each parameter on the final spray retention at the plant scale and quantify the variability of retention between plants that could be used to select the optimal application technology parameters, *i.e.* nozzle type and size, applied volume per hectare and formulation properties (Chapter 6);

4. Propose practical recommendations about spray application of plant protection product on superhydrophobic species, especially on black-grass, that could be extended to other difficult-to-treat species. Spray recommendations include advices in the context of herbicide resistance management (Chapter 8).

In order to meet the fixed objectives, the dissertation will be structured as follows (Figure 1.2):

Chapter 2 reviews processes and parameters involved in applying post-emergence agrochemicals to leaf surfaces through macroscopic and microscopic points of views. The macroscopic aspects are related to the effect of spray operational parameters on the rentention by means of fields trials. Microscopic studies are related to interactions between droplet and target surface and mainly focus on surface wetting and droplet impaction behaviour on difficult-to-wet surfaces, or superhydrophobic surfaces.

Chapter 3 describes a dynamic spray application bench designed to gain a deeper understanding of the mechanisms involved in droplet impaction on artificial and natural surfaces. This dynamic test bench comprised a moving agricultural hydraulic nozzle, a sample holder, an high-speed camera with high magnification lenses and pulsed backlit system. A reference synthetic target surface has been chosen for its similar wettability level to monocots leaves. This artificial superhydrophobic surface reduces the variability related to the target surface state and enables studying the effect of operating choices on spray retention. It also allows ranking of application techniques and spray formulations and additives in reproducible conditions.

Chapter 4 investigates the effect of various surface angles on the fate of spray droplets during impact since it is a preponderant explanatory factor on the droplet impact outcome on stiff plant architecture. Using the test bench described in chapter 3, the effect of surface orientation is studied in comparison between the artificial superhydrophobic surface and excised black-grass leaves. This chapter also presents a statistical representation of the spray droplet impact probabilities depending on the droplet impact energy as basis for the subsequent modelling approach (chapter 6).

Chapter 5 aims at highlighting the potentialities of the experimental method proposed in the chapters 3 and 4. It is divided into 2 sections from 2 conference proceedings. The first part of the chapter describes the relevance of using this artificial surface is discussed in comparison with wheat leaves. Secondly, it is investigated if increased black-grass weeding efficiency by reduced volume per hectare observed during 2010 Arvalis field trials may be related to increased pesticide application method efficiency and it is possible to find an explanation in the theories of droplet impacts on difficult-to-wet targets.

Chapter 6 deals with the integration of all the previous experimental data into a numerical spray-plant interaction model. The model computes the interception of droplet trajectories with the 3D plant architecture and assigns an impact behaviour to droplets based on outcome probabilities depending on droplet impact energy and incidence angle. This model enables systematic parametric studies to understand and assess the importance of each factor on the final retention by the plant and the effect on the variability of deposits.

Chapter 7 proposes somes theoretical simulations using the model described in chapter 6. This chapter also presents logisitic fitting applied on droplet impact behaviour histograms (chapter 4) as basis for modelling spray retention. Results of this chapter are gathered from 3 conference proceedings. The first paper deals with the evaluation of the model. Evaluation is performed on barley plants by comparing the actual to the predicted retention as a function of the spray mixture for the same single nozzle. The model is parametrised to fit at best the situation. The second part focuses on the effect on spray retention resulting from a gradual and theoretical modification of the formulation wetting properties. The third conference proceeding focuses on the modification of the application technique and highlights the benefits of using reduced span sprays for enhancing retention and reducing its variability between plants.

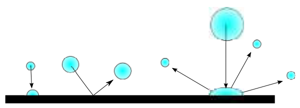
Chapter 8 describes the major conclusions of this doctoral thesis, proposes some interesting research perspectives and highlights some recommendations for improving spray application techniques and formulations.

Note that this dissertation is a paper based thesis compiling four papers published in international journals. Since each paper needs to be self-contained, this dissertation may contain repetitions. Relevant results published in conference proceedings have also been included.

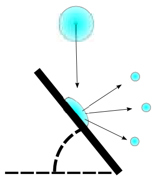
Chapter 1
General introduction

Chapter 2
State of the art of droplet impact behavior on leaf surfaces through microscopic and macroscopic scales

Chapter 3
Droplet impact behavior on an artificial superhydrophobic surface



Chapter 4
Effect of surface orientation on spray droplet impaction and logistic regression of droplet impact probabilities



Chapter 5
Comparison of the droplet impact behaviour between the artificial and leaf surfaces and assesment of herbicide efficiency on black-grass leaves

Chapter 6
Retention modelling at the plant scale

Chapter 7
Parameter sensitivity analysis

Chapter 8
Conclusions and recommendations

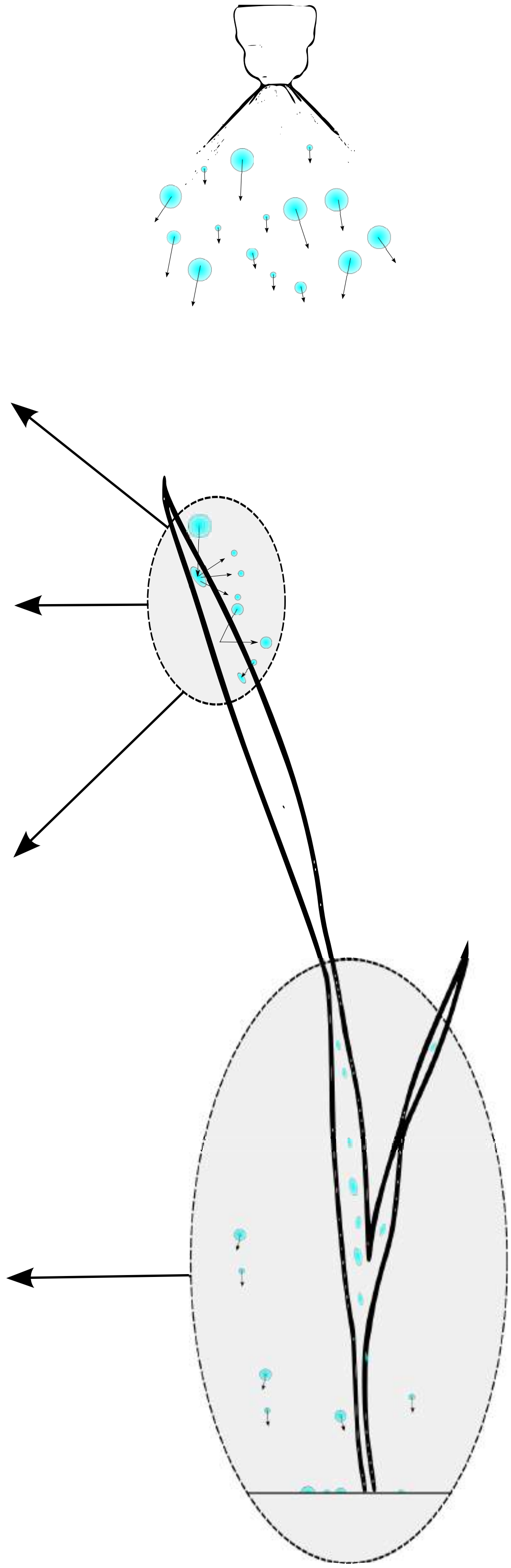


Figure 1.2: Outline of the thesis.

CHAPTER 2

Review of physicochemical processes involved in agrochemical spray retention

2.1 Chapter objectives and outline

This chapter reviews processes and parameters involved in applying post-emergence agrochemicals to leaf surfaces through macroscopic and microscopic points of views. The macroscopic aspects are related to the effect of spray operational parameters on retention by means of fields trials. Field trials provide the total response of spray application in specific situations but are limited to point out the main effects of each parameters on spray retention without any description of underlying mechanisms. Microscopic studies are related to the interactions between droplet and target surfaces. They provide an insight of the foundations of surface wetting and droplet impact behaviours on difficult-to-wet surfaces. This study highlights the importance to gain a better understanding of leaf wetting through an experimental method able to quantify the spray droplet impact in relation with spray and target parameters (chapter 3). With the objecive of modelling spray retention, it also emphases the importance of the plant architecture through the need of measuring accurately the plant architecture (chapter 6) and consequently the need of gaining a better understanding of droplet impacts on tilted surfaces (chapter 4).

2.2 Appended publication

Autors: Massinon, Mathieu and Lebeau, Frédéric
Year: 2013
Title: Review of physicochemical processes involved in agrochemical spray retention
Status: Published
Journal: Biotechnology, Agronomy, Society and Environment **17**:494-504
URL: http://hdl.handle.net/2268/148678

2.3 Abstract

This review provides a broad view of the processes and parameters involved in applying agrochemicals to the leaves of field crops. Treatment efficiency is assessed using macroscopic and microscopic approaches to investigate spray retention. With the macroscopic approach, aspects related to spray coarseness, carrier volume, leaf wettability, plant architecture, crop density and additives are addressed. Comparative studies have highlighted the wide variability in spray retention as a function of these parameters. They have failed, however, to describe the underlying physical relationships clearly enough to generalize the results. These relationships are better investigated using a microscopic approach, where drop impact behavior is established in relation to target surface and fluid properties. The wetting regime (either Wenzel or Cassie-Baxter) depends on the leaf surface microscopic roughness ratio (r) and chemical nature, fluid dynamic surface tension and drop impact energy. Adhesion, rebound and shattering have been observed successively with increasing impact energy. Transitions between impact outcomes are influenced by fluid rheology and the dynamic surface tension of the fluid. The effect of surface orientation remains poorly explored, but it seems to have a limited influence on retention. Recent fundamental studies on superhydrophobicity and wetting should help practitioners in their search for an ever more rational application of agrochemicals. They could also drive the development of new systematic retention testing methods.

2.4 Introduction

Crop protection is still achieved mainly by using pesticides. Most products are sprayed over the intended target surface as uniformly as possible, using hydraulic nozzles. The nozzles release sprays of drops of varying size and velocity into the air. Farmers can adjust the carrier volume applied by modifying nozzle kind or size, liquid pressure and sprayer travel speed. The use of adjuvants is also common in efforts to improve the active ingredient performance, which is within the control of formulators. Adjuvants include any materials used as compatibility agents, drift retardants, suspension aids, spray buffer or surfactants. The spray mixture is therefore highly complex and the interaction between drop and leaves can be greatly modified. The target itself introduces additional parameters, such as species, leaf orientation, canopy density, age, position on the leaf and weathering. Much work has been done on maximizing spraying efficiency by optimizing each step of the process (Wirth et al., 1991; Zabkiewicz, 2007). The aim of this work has been to adjust and apply the dose in order to ensure the required level of crop protection while minimizing wastage and pollution.

This paper deals with spray retention, which can be studied using two approaches. The first is the macroscopic approach, based on quantifying retention using an integrative measurement method for the whole plant or leaf. Input variables include nozzle type, formulation, adjuvant type and concentration, and target. The second is the microscopic approach, which focuses on the drop impact dynamic and investigates the interactions between the liquid and the surface (wetting) at drop scale. Although macroscopic studies are designed to select the most effective application method under realistic field conditions, microscopic studies can highlight the physics behind performance differences and elicit more detailed information of value for systematic developments. The paper reviews the whole retention process by plant surfaces, from both the macroscopic and microscopic points of view. The review should help practitioners achieve optimal spray retention and guide the development of new testing methods for optimizing biological efficacy.

2.5 Phenomenological or macroscopic view

Selecting an optimal application technology has been investigated in many retention studies. Usually, a tracer is added to the sprayed formulations and the retained content is measured after washing one leaf or the whole plant. Gravimetric methods and active ingredient dosage are also used (Wirth et al., 1991). Retention is expressed by the volume of spray solution retained per unit of plant dry weight or surface area, the results being statistically interpreted to highlight any significant differences (Byer et al., 2006; Butler Ellis et al., 2004; Furmidge, 1962).

2.5.1 Spray nozzle classification and carrier volume

In general, finer sprays result in better retention of foliar-applied herbicides for a constant carrier volume, whatever the drop size range investigated (Koch and Barthlott, 2009). This was shown, for example, on corn (Zea mays L.) (Feng et al., 2003) and green foxtail (Setaria viridis [L.] Beauv.) (Peng et al., 2005). The spray coarseness induced different responses, however, depending on the species. Retention is reduced by increasing spray coarseness when applied to the difficult-to-wet giant foxtail (Setaria faberi Herrm), but no influence was evident in the case of smooth pigweed (Amaranthus hybridus L.) (Wolf et al., 2000). The flat-fan nozzles resulted in higher retention than air-induction nozzles, and this efficacy gap grew with the dynamic surface tension (Butler Ellis et al., 2004). Reducing the carrier volume to below 100 $l.ha^{-1}$ reduces retention performance more often than a carrier volume above 400 $l.ha^{-1}$. On difficult-to-wet species, however, reducing carrier volume increases retention more often than on easy-to-wet plants (Knoche, 1994). The possible reasons for these differences are often related to plant properties.

2.5.2 Plant properties

Plant architecture and crop canopy

Regardless of spray drift, plant architecture and canopy density modify drop interception by leaves. There is a higher probability that a drop will hit a leaf in high plant density conditions with high density sprays. In a very dense canopy of wheat where the leaf area index (LAI) was high, retention was independent of liquids and nozzles tested, whereas for lower densities there appeared to be clear differences between formulation retention, whatever kind of nozzle tested (Butler Ellis et al., 2004). Leaf orientation varies with growth stage and species. A thin, vertical leaf, such as blackgrass (*Alopecurus myosuroides* HUDS.) at an early growth stage, is very difficult to treat because of the low LAI and the limited projected area available for drops. With such challenging targets, increasing the proportion of drops below $150\mu m$ enhanced the performance more consistently than for drops above $150\mu m$ (Knoche, 1994). With small drops there is a more homogeneous distribution of the active substance on the leaves because of the higher spray density. Fine drops are better retained by plants at impact, but they are also more sensitive to small air turbulences. They can penetrate deeper within the canopy and even reach leaf undersides. They are more sensitive to drift and evaporation, however, than larger drops. This indicates the importance of drop size and spray density in relation to crop canopy density. In addition to plant architecture, leaf wettability is a crucial parameter in explaining differences recorded in field retention trials.

Leaf wettability and contact angle

Leaves are often ranked according to their wettability. Leaf surfaces vary widely from easy-to-wet to very difficult-to-wet (Zabkiewicz, 2007). Wettability is a thermodynamic property of the solid-liquid-gas interface defined by the equilibrium contact angle θ. On ideal dry smooth surfaces, the equilibrium contact angle is given by Young's equation:

$$\cos(\theta_Y) = \frac{\sigma_{sg} - \sigma_{ls}}{\sigma_{lg}}$$

where σ_{sg}, σ_{ls} and σ_{lg} are the interfacial tensions (Nm^{-1}) at the boundaries of the liquid-solid-gas system. The static contact angle (SCA) is measured at the point where the liquid, solid and gas interfaces meet, known as the 'contact line'. The classical mechanism for liquid spreading on a solid surface depends on a disparity in the interfacial tensions at the contact line: if the solid/gas tension is greater than the sum of the two others, the drop spreads until the balance is restored. The SCA is then reached (Nikolov et al., 2002) and is independent of drop size (Quéré, 2005). It is sometimes referred to as 'apparent contact angle' because it is the macroscopic behavior of liquid/surface interactions. The more the drop spreads on the surface, the more the surface is wet by the liquid and the smaller the contact angle. The lower the surface tension, the faster the drop spreads. For SCAs ranging from 0° to 10°, surfaces are termed 'superhydrophilic'. Between 10° and 90°, they are known as 'hydrophilic'. For higher contact angles, they are termed 'hydrophobic', and when the angle exceeds $150 - 160°$, the surface is called 'superhydrophobic'. Leaf classification is important in order to predict effective retention and liquid behavior. This is very helpful for identifying appropriate application techniques and agrochemical requirements for species. Since agrochemical formulations are complex and often designed for maximum spread, it is sometimes difficult or impossible to measure any contact angles. The contact angle of pure water, however, is not always appropriate for differentiating between species (Gaskin et al., 2005). On very difficult-to-wet species, the water contact angle is too high and no significant differences can be highlighted. It was therefore proposed to use a 20 % v/v acetone in water solution to reduce surface tension. The wettability of leaf surfaces depends on species, variety, growth stage, leaf position, growth conditions and environmental factors, hence the retention variations observed in field trials. Overall, leaf wettability can change with age and maturity, but no trend has been identified, although wheat leaves become less hydrophobic with age (Butler Ellis et al., 2004). Wettability modifications could originate from fouling and sandblasting from wind-borne particles of leaves, indoor-grown leaves being more hydrophobic. When performing laboratory tests using indoor-grown plants, therefore, the findings cannot be directly extrapolated to field, although the leaves are able to regenerate their waxes after a few days. Leaf surface properties (e.g., wettability, as affected by dew, rain, sandblasting or dust) before the day of treatment should be integrated into the results analysis or used to help decide on the optimum time of treatment.

2.5.3 Additives

The difficult-to-wet leaf issue is often addressed using additives. Surfactants promote drop spreading on surfaces by reducing surface tension and the advancing and receding contact angles (section 3.2 and 3.3). Their effects depend on concentration, leaf surface properties and application volumes (Gaskin and Murray, 1997). Overall, the use of surfactant increases retention by plants, which increases pesticide efficiency. The beneficial effect grows with surfactant concentration (Wirth et al., 1991) until a concentration threshold is reached above which there will be no further retention improvement (Furmidge, 1962). Easy-to-wet species exhibit no variation in retention because they are made wet by water (high surface tension). The differences in retention between surfactants are closely correlated to the dynamic surface tension (DST) of the spray mixture; DST refers to surface tension variation over time. If the surfactant adsorption time is greater than the drop impact, the surfactant effect can be greatly reduced or even negated. This will be discussed further in section 2.6.4.

Additives also affect jet break-up. Smaller drops are produced by reducing the surface tension and viscosity of the sprayed formulation. Thus, the volume median diameter (VMD) is modified, as are the leaf impact conditions. Although smaller drops are favorable for retention, they are more prone to drift. Liquid DST has to be considered in spray formation because surface tension governs break-up type. Surfactants can produce drops that include air, which reduces drop liquid density and affects drop transport (Butler Ellis et al., 1997) and behavior at impact. Much information about the physics of drop formation is available (Sirignano and Mehring, 2000). Finally, liquid properties affect drop formation, trajectory and impact on the target. An optimum approach between formulation and application technique has to be found in order to maximize retention while minimizing drift.

2.5.4 Discussion on phenomenological studies

Macroscopic studies are conducted to gain a better understanding of a complex process, performing tests in specific and variable conditions. They successfully identify some general trends and the main variables involved in spray retention by leaves. Since many variables change between trials, it is not easy to generalize the findings. These studies are very educational and have provided the impetus to improve spray efficiency, but a thorough understanding of each mechanism involved in this complex process is needed. Therefore, the physics at drop scale has to be understood because retention is determined mainly by the fate of all drops sprayed. Drop generators have often been proposed for systematic studies on the effect of physiochemical parameters on retention (Forster et al., 2005; Lake, 1977; Reichard et al., 1998; Webb et al., 1999). Using such apparatuses, however, has reinforced the perception of spray retention on leaves as a two-state process. A drop may either adhere to or bounce off the target because these apparatuses shift the focus mainly to the effect of drop size. Since drops are released into the air without initial velocity, impact always occurs at or below terminal velocity, depending on release height. Adhesion is then assimilated to retention. Shattering has seldom been observed because of insufficient drop energy at impact. The development of affordable high-speed cameras and the use of dimensional analysis to simplify the relationship between variables (Lake and Marchant, 1983) encouraged many studies to be conducted on the dynamic of drop impact. Some of the current techniques for studying retention use real agricultural nozzles and generate all impact outcomes likely in practical conditions (Massinon and Lebeau, 2012b).

The points addressed in section 2.5 will therefore be discussed from the microscopic perspective in section 2.6. Leaf surfaces are described in section 2.6.1, the various wetting models developed are presented in section 2.6.2, the resulting impact regimes in section 2.6.3 and the effect of liquid properties on drop impact in section 2.6.4.

2.6 Microscopic perspective

2.6.1 Leaf surfaces and superhydrophobicity

The wetting and subsequent drop impact behavior is determined mainly by the structure of the outermost layers of plant surfaces. Superhydrophobic leaves are the most challenging targets to treat, especially at early growth stages. Superhydrophobicity characterizes hydrophobic materials when their specific surface is increased beyond a certain roughness value. A study of the lotus effect and self-cleaning surfaces has emphasized the importance of the micro-structure and even of the nano-structure of the surface on wetting (Koch and Barthlott, 2009). The outermost layer of the epidermis contains a cuticle that creates the structure of folds and subcuticular inserts which are covered by epicuticular waxes. This coating helps prevent leaf colonization by bacterial pathogens and controls plant humidity. The epicuticular waxes are crystalline; their size ranges from 0.2 to 100μm and there is a wide diversity of morphological types, including films, crusts, tubules, platelets, rodlets and transversely ridged rodlets (Barthlott et al., 1998). These characteristics give leaf surfaces extreme water repellency.

2.6.2 Wetting models for rough surfaces

The contact angle measured on real surfaces does not obey Young's equation, which is valid only for ideal smooth surfaces. For superhydrophobic surfaces, where the apparent contact angle is often greater than 150°, two extreme situations can occur. They are described in two models based on Young's equation. In the first situation, an increase in the surface area due to the micro-texture enhances the hydrophobicity of the material compared with Young's ideal model. The liquid fills the rough grooves completely. The drop replaces the air trapped in the surface roughness and fits into the microstructure of the material. This situation is referred to as non-composite, homogeneous, sticking or pinning wetting regime and is described by the Wenzel regime (Wenzel, 1936):

$$\cos(\theta_W) = r \cdot \cos(\theta_Y)$$

where r is the ratio of the true wetted area to the projected planar surface area (always greater than unity), θ_W is the apparent angle and θ_Y is the Young angle. The second situation describes the wetting of rougher (porous) surfaces where air pockets are trapped in the surface texture beneath the liquid. The drop contacts only the top of the surface asperities. This situation is described by the Cassie-Baxter regime (Cassie and Baxter, 1944):

$$\cos(\theta_{CB}) = -1 + f \cdot [\cos(\theta_Y) + 1]$$

where f is the fraction of the solid/liquid interface (the liquid contacts the solid only through the top of the asperities on a fraction f) and $\cos(\theta_{CB})$ is the apparent contact angle.

A transition between the two situations is possible and depends on how the drop comes into contact with the surface (gently deposited or impacted) (He et al., 2003), the ratio of drop size to roughness scale (Bartolo et al., 2006; Marmur, 2008; Reyssat et al., 2006), topography parameters and pattern density (Callies and Quéré, 2005). If the pattern density is very low, the drop reaches the Wenzel state because there is not enough contacting surface to sustain the liquid, which sinks into the surface texture. This can occur by increasing the impact velocity for a surface that exhibits a Cassie-Baxter state at lower speeds. This is referred to as pinning and is caused by a high contact angle hysteresis. Using these models, section 2.6.3 describes the impact outcomes.

2.6.3 Drop impact outcomes of single drop

Since drops are released above the crop, impact velocities depend on drop size. The varying impact outcomes therefore depend on leaf wettability and roughness. Drop impact on a dry solid surface, however, can be divided into four successive phases (kinematic, spreading, relaxation and equilibrium phase), based on the dimensionless spread factor $d^* = d \cdot D_0^{-1}$, where D_0 is the drop diameter before impact and d^* is the spread diameter after a time t (Rioboo et al., 2002). Dimensionless height $h^* = h \cdot D_0^{-1}$ is also useful for characterizing impact outcome (Crooks et al., 2001). Dimensionless parameters enable a comparison to be made between drops of various sizes.

The kinematic phase is the initial phase of impact. The bottom of the drop is stopped at impact, but the upper part of the drop is still moving. The drop takes a truncated shape (initially spherical), the wetted spot increases and the dimensionless height decreases over time. The bottom of the drop begins to spread out on the surface as a thin film. The spreading is triggered by a shock wave created at impact because of liquid compression (Rein, 1993). Inertial forces dominate during this first phase and the spread factor increases with the square root of dimensionless time $t^* = t \cdot V \cdot D_0^{-1}$, where V is the drop velocity at impact. Before impact, a drop contains a certain amount of kinetic energy:

$$E_{K0} = \frac{\rho \pi D_0^3 V^2}{12}$$

where ρ is the fluid density ($kg.m^{-3}$). Some of the kinetic energy is converted into surface energy as a result of drop deformation. The initial surface energy is computed as:

$$E_{S0} = \rho \pi D_0^2$$

where ρ is the surface tension of the liquid ($N.m^{-1}$). This phase ends at approximately $t^* = 0.1$. Wettability has no influence, neither do the viscous forces.

In the second phase, the liquid lamella (spreading disk) is spread on the surface. The lamella is bordered by a rim caused by surface tension. The contact line moves radially in the direction of the gas (Šikalo et al., 2005b). The contact angle established during this phase is called the 'advancing contact angle' θ_A. Spreading increases and the contact line acceleration decreases towards the end of the spreading phase. This is because of the dissipation of the drop's kinetic and surface energy by viscous processes into additional surface energy (Rein, 1993). The maximum spread diameter is smaller and reached earlier when viscosity is increased. This trend is identical for impact velocity. For determining the maximum spread diameter and the time taken to reach it, most approaches apply the laws of energy conservation to the spreading lamella (Moreira et al., 2011; Mundo et al., 1995; Rein, 1993), assuming the event is adiabatic:

$$E_{K0} + E_{S0} = E_{Kfin} + E_{Sfin} + E_{diss}$$

where E_K is the drop's kinetic energy (J), E_S is its surface energy (J), E_{diss} is the energy dissipated by viscous effects (J) and subscript 0 denotes the state before impact and fin the final state. The final state is taken at the maximum spread diameter.

When dissipation overcomes the inertial energy, spreading stops and the drop reaches its maximal spreading diameter. The contact angle then decreases, becoming the 'receding contact angle', and the contact line begins to recoil on an already wetted surface (relaxation phase). The recoil is initiated by the dominating surface forces, with the liquid trying to restore the drop shape that minimizes the free surface energy. The contact angle is therefore smaller during the recoil phase. The difference between the advancing and receding contact angles is called 'contact angle hysteresis' and greatly influences impact outcome (Quéré, 2005). Hysteresis depends on surface roughness. If hysteresis is high and viscous forces dissipate the kinetic energy, the drop adheres to the surface. Drop oscillations dissipate the remaining energy at impact. If kinetic energy remains after viscous dissipation, the drop may splash or shatter. Splashing is the result of the drop disintegrating into two or more secondary drops after landing on the surface. It occurs because of the instability of the spreading lamella and depends on surface roughness. Finally, the equilibrium or wetting phase ends the impact outcome. If hysteresis is low and the advancing contact angle is high, a total rebound can occur, depending on impact velocity.

A map of impact behavior according to surface roughness and impact velocity was built from experimental investigations on artificial superhydrophobic surfaces (Figure 2.1) (Rioboo et al., 2008). For low Wenzel roughness, a drop of low kinetic energy is deposited in a Wenzel state. By gradually increasing its kinetic energy, the drop is fragmented. Depending on impact energy, a single satellite drop (referred to as 'partial rebound') or several satellite drops (referred to as 'pinning fragmentation') can leave the surface, whereas the rest of the drop adheres to the impact point. For intermediate Wenzel roughness, low velocity drops adhere in a Cassie-Baxter regime. With increasing speed, the drop bounces completely. If impact pressure is great enough or liquid surface tension low enough, the liquid can penetrate the surface roughness, modifying the wettability regime from Cassie-Baxter to Wenzel. Thus, sticking, partial rebound or pinning fragmentation can be observed. Finally, for high Wenzel roughness, a drop can adhere in a Cassie-Baxter regime, rebound or splash completely, depending on impact velocity. If it splashes, all the liquid is shattered into numerous satellite drops and leaves the surface. Drop

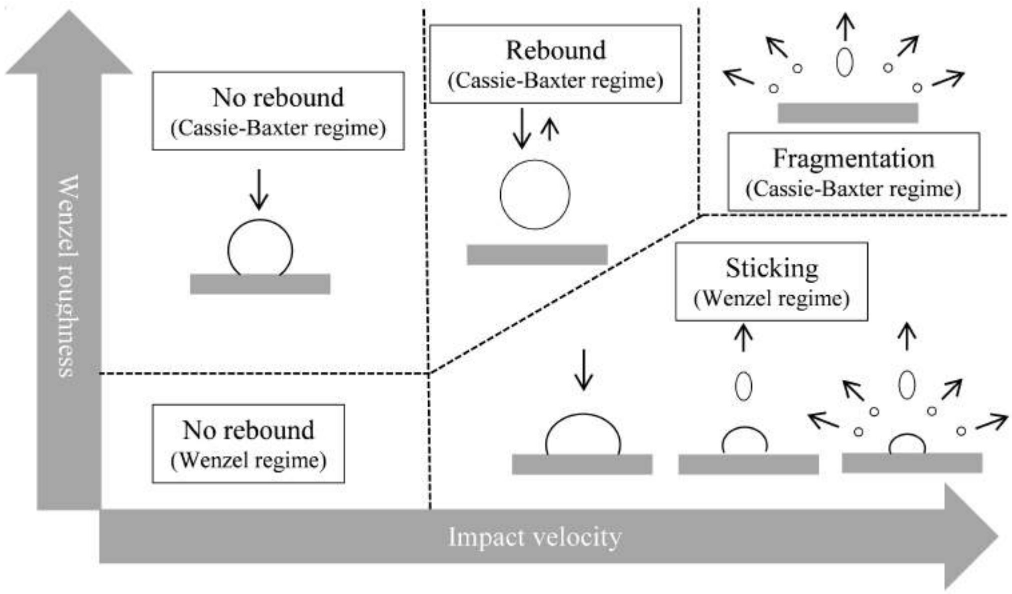


Figure 2.1: Possible impact outcomes of a drop hitting a superhydrophobic surface, depending on Wenzel roughness and drop impact velocity (Rioboo et al., 2008; Massinon and Lebeau, 2012b).

impact involves many forces that can be grouped in dimensionless numbers (Table 2.1), characterizing the relative magnitude of the forces acting on the drop. Dimensional analysis is usually used to simplify the relationships between the variables involved (Lake and Marchant, 1983) and to build threshold criteria for establishing boundaries between impact and for forecasting impact behavior on the basis of drop properties before impact and surface properties. More information about threshold criteria can be found in Mundo et al. (1995), Range and Feuillebois (1998), Cossali et al. (2005), Yarin (2006) and Moreira et al. (2010). The effects of drop impact on an angled leaf surface still need to be clarified, although much work has been done (Wirth et al., 1991; Forster et al., 2005; Bird et al., 2009; Massinon et al., 2014). The main effects related to increase in leaf angle are:

– a reduction in the projected area available for spray drops, and therefore a reduction in the number of impacts per unit area of leaf;

– a reduction in the normal velocity component a impact.

Table 2.1: Most relevant dimensionless numbers used in the analysis of drop/solid surface interactions (Moreira et al., 2011).

Dimensionless number	Definition	Relationships
Weber number Inertial/surface tension forces	$We = \frac{\rho V^2 D_0}{\sigma}$	
Reynolds number Inertial/viscous forces	$Re = \frac{\rho V D_0}{\mu}$	
Capillary number Viscous/surface tension forces	$Ca = \frac{\mu V}{\sigma}$	
Froude number Inertial forces/gravitational forces	$Fr = \frac{V}{(dD_0)^{0.5}}$	
Ohnesorge number Viscous/surface tension forces	$Oh = \frac{\mu}{(\rho \sigma D_0)^{0.5}}$	$Oh = \frac{We^{0.5}}{Re}$
Laplace number Surface tension forces/momentum transport (dissipation)	$La = \frac{\rho \sigma D_0}{\mu^2}$	$La = \frac{Re^{0.5}}{We} = \frac{We}{Ca^2} = \frac{Re}{Ca} = Oh^{-2}$
Bond number Body (gravitational)/surface tension forces	$Bo = \frac{\rho g D_0^2}{\sigma}$	$Bo = \frac{We}{Fr}$

Rebound occurs if the drop does not have enough kinetic energy to undergo a transition from a Cassie-Baxter to Wenzel wetting regime by expelling the air trapped in the surface roughness. Overall, a reduction in the normal velocity component by an increase in leaf angle leads to partial and total rebound (Yarin, 2006). The use of the normal velocity component has been proposed for computing the dimensionless number: for low impact angles ($< 35°$) , the Weber number at which the rebound occurs is constant if the normal velocity component is used in computing the Weber number. The drop can also slip, depending on impact angle, liquid and surface properties and impact energy (Šikalo et al., 2005a).

2.6.4 Effect of liquid properties on drop impact

Surface tension. In the first two phases of drop impact, the equilibrium surface tension has a negligible effect on the spread factor because these phases are dominated by inertial and viscous forces (Crooks et al., 2001). If the drop contains molecules of surfactant, the recoil phase is subdued. Overall, two outcomes are possible: either the drop splashes because of an excess of kinetic energy (high Weber number), or it remains spread if the viscous dissipations are large enough. However, the rebound is not always eliminated by surfactants, for reasons given below. Immediately before impact, a drop is spherical and surface tension has reached the equilibrium value. During drop deformation, the surface area of the liquid/gas interface increases quickly (< 2 ms). Surfactant molecules of the bulk solution migrate to the surface to fill the gaps by adsorption. If the surfactant concentration is below the critical micelle concentration (CMC), three mechanisms for surfactant distribution along the liquid/gas interface have been proposed (Zhang and Basaran, 1997). First, there is a dilution of the surfactant due to the creation of a new surface area. Second, there is a convection of the surfactants towards the contact line that accumulate at the moving front during spreading, increasing the maximum spread diameter and inhibiting the recoil phase. This effect, however, was not reported by Crooks et al. (2001). Third, there is a repopulation of the interface by the surfactants. It is the drop hydrodynamics, therefore, that control the surfactant concentration in bulk solution. If the surfactant concentration is above the CMC, a demicellisation occurs, keeping the surfactant concentration constant in the bulk solution and supplying surfactant molecules for the new surface created during impact. If the demicellisation time rate is higher than the transport and adsorption of free molecules to the surface, the accumulation of surfactant molecules by convection at the moving edge is overcome and surface tension is dramatically reduced. Since the timescales of the initial phases of drop impact are very short, the adsorption rate and concentration of surfactants in the drop play an important role in the fate of an impacting drop by modifying the dynamic surface tension. In order to guarantee continued spreading, the surfactant adsorption rate at the contact line must exceed the diluting effect of area expansion (Venzmer, 2011). Overall, the reduction of surface tension by surfactants increases spreading and reduces recoil. Depending on the kinetic of surfactant adsorption and surface energy, a drop can still rebound off the surface (Mourougou-Candoni et al., 1997). In addition, lower surface tension favors splashing. Although the first phase of drop impact is governed mainly by inertial energy, especially when the DST is high, a description of the drop spreading mechanism could be useful in improving the overall understanding of pesticide efficiency. Three mechanisms can promote spreading:

- reducing the liquid/gas tension by the adsorption of surfactants at this interface,
- reducing the solid/liquid tension by the adsorption of surfactant molecules on the substrate,
- by increasing the solid/gas tension when surfactants are adsorbed in front of the moving contact line (Starov et al., 2010; Ivanova and Starov, 2011).

The adsorption of surfactant molecules on a bare hydrophobic surface in front of the contact line is a spontaneous process. Since that process leads to an increase in the local solid/gas interfacial tension, the adsorption goes via a potential barrier, which is the change in local free energy caused by the jump of a single surfactant molecule from the liquid/gas interface on the surface. Organosilicone (trisiloxane) surfactants promote rapid spreading of the drop even on (super) hydrophobic substrates. They are frequently used in the composition of agrochemicals. The reasons for superspreading, however, are not fully understood and various explanations have been proposed. Nikolov et al. (2002) suggested that superspreading could be driven by Marangoni flows, whereby the expansion of the contact line stretches the drop surface area, reducing local surfactant concentration. The surface tension at the edge of the spreading drop is then higher than that in the center, creating a surface tension gradient. The Marangoni stresses drive the liquid from the lower to the higher surfactant concentration, leading to drop spreading. This contradicts the classic wetting described in section 2.6.3, where spreading requires low surface tension in the drop. Other possible reasons for controverted superspreading have been discussed by Venzmer (2011).

Viscosity. Spraying viscous products is not common in pesticide application because of pumping problems. Viscosity could, however, have a beneficial effect on spray retention. An increase in shear viscosity reduces a drop's maximum spreading diameter (Clanet et al., 2004) and reduces the tendency to bounce on dry surfaces (Caviezel et al., 2008). Viscosity exhausts the energy stored in the drop by deformation, but this effect is offset by high surface tension. The splashing of a viscous liquid drop differs in that it develops slowly and fragmentation is reduced.

More recently, it has been shown that the use of polymer additives enhances spray deposition and retention on a plant surface. A small amount of flexible polymer added to the aqueous phase can inhibit drop rebound by increasing elongational viscosity (Bergeron, 2003). The surface tension and shear viscosity of the solution are not affected by these polymers. Stretching such solutions unfolds and deforms the polymer molecules, which drains drop energy. Splashing is reduced because the elongational viscosity stabilizes the capillary instabilities responsible for fragmentation. Polymer solutions also have a great influence on atomization by stabilizing the perturbations that drive jet break-up (Mun et al., 1999). Adding polymers to spray solution increases the VMD, reduces the proportion of fine drops and improves treatment efficacy (Jones et al., 2007). The use of such additives therefore also reduces the drift potential of the application.

2.6.5 Discussion on microscopic studies

The numerous studies on the dynamic of single drop impact reveal the complexity of the process and the influence of many factors on the fate of a single drop. These studies are needed to understand the mechanisms that are relevant for retention, but involve sprays with various energy drops. In this context, some aspects should also be addressed in retention studies. For instance, drop impact behavior is affected by the accumulation of a liquid film on leaf surface (Rein, 1993; Roisman et al., 2006; Yarin, 2006; Kalantari and Tropea, 2007; Moreira et al., 2010), although this is now rarely observed in field application because of the ever lower volumes per hectare applied (below 150 $l\ ha^{-1}$), the small drop sizes, the spray boom displacement, the granulometric drop sorting during the fall, the leaf wettability and the canopy architecture. Furthermore, secondary drops produced by drop disintegration can be directly lost on the soil or be captured by the same or another leaf in a dense canopy. The amount of product remaining on the leaf surface after a drop impact in Wenzel wetting state has still to be assessedto gain a better correlation between impact behavior and retention. Finally, hydrophobic defects caused by fouling, sandblasting and/or epicuticular compounds, as well as leaf elasticity dissipating the drop kinetic energy by leaf bending for large drops and reducing the likelihood of bounce (Forster et al., 2005), increase the variability in trials.

Microscopic studies provide no information on the biological efficiency of pesticides, but provide physical reasons for differences in retention. They could,however, help in the design of more discriminating field experiments and efficient actuators (nozzles, spot spraying) to meet the objectives of precision spraying.

2.7 Conclusion

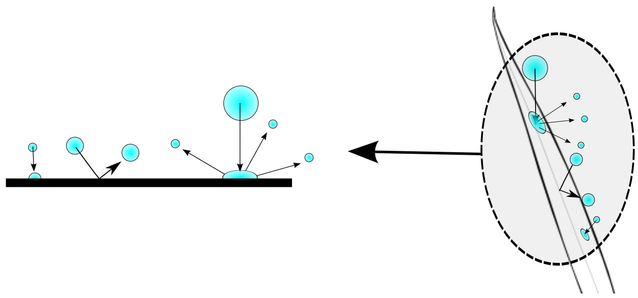
Retention is a key factor in spraying efficiency. In order to reduce environmental contamination, it has to be perfectly understood and mastered. The physicochemical properties of spray mixtures and their application techniques need to be optimized for a given leaf application, integrating an optimum time of spraying. Losses caused by drop rebound and disintegration have to be limited or avoided although their negative effects can be reduced or absent in very dense canopies.

Depending on species (growth stage and surface wettability), an optimal drop impact energy should be found to limit undesirable effects. This can be achieved by adjusting drop size and velocity distributions by choosing the best combination between nozzle, pressure and spray mixture properties (such as surface tension and viscosity) that alter both drop impact and spray formation. The use of surfactants with very low DST for reducing drop rebound and promoting spreading is well known. The use of non-Newtonian additives to exhaust drop impact energy is, however, less common although the promising perspectives of Bergeron (2003). Actuators such as rotary atomizers or splash plate nozzles generating sharper drop size distribution centered on the required VMD should also be considered for optimizing spray retention. As already done for spray characterization, the development of methods that could measure and/or predict the efficiency of any given application technique in terms of spray impact would be very useful for users and researchers. Some progress has been made using high-speed imaging, a synthetic superhydrophobic surface and agricultural sprays, leading to all the impact outcomes encountered in field (Massinon and Lebeau, 2012b). The development of recipes and tank mix adjuvants can be optimized using such methods for maximizing spray retention by leaves. These methods should ultimately be able to provide the spray volume proportions for each impact type and be related to retention using macroscopic approaches.

Further research is also needed on clarifying some aspects, such as leaf orientation, surface elasticity and polymer additives.

CHAPTER 3

A spray application bench for studying droplet impaction behaviours on surfaces with high-speed imaging



"In the land of splashes, what scientist knows as Inertia and Surface Tension are the sculptors in liquids, and fashion from them delicate shapes none the less beautiful because they are too ephemeral for any eye but that of the high-speed camera."
Adapted from Edgerton & Killian (1954).

3.1 Chapter objectives and outline

This chapter 3 describes the design of a dynamic test bench based on high-speed imaging, high magnification lenses and a pulsed backlit system comprising light-emitting diodes (LED) for studying spray droplet impact behaviour. The use of high-speed imaging is required since agricultural spray droplet impact dynamics occurs within 5 ms. Most studies use droplet-on-demand generators for providing droplets with a controlled size and velocity (Forster et al., 2005; Reichard et al., 1998). However, such device produce droplets with low initial velocities ($\approx\ 2-3m.s^{-1}$) unlike hydraulic nozzles. Consequently, droplets will never impact a target surface with velocities around 10 $m.s^{-1}$ and will not lead to high energy impact behaviour where droplet fragmentation occurs. In this chapter, a reference synthetic target surface has been chosen for its low wettability similar to the grass leaves and was set horizontally. Droplets were produced using a single flat-fan nozzle XR11003VK (Spraying Systems Co, Wheaton, IL, USA) mounted on a height-adjustable boom sprayer. two sets of experiments were conducted: Firstly, three spray pressures were tested 0.2, 0.3 and 0.4 MPa with distilled water. in the second experiment, the effect of liquid surface tension was investigated using three concentrations of a non-ionic surfactant: 0.025, 0.05 and 0.1% V/V in distilled water at a spray pressure of 0.3 MPa. The artificial surface reduces the variability related to the target surface state and enables studying the effect of operating parameters on spray retention. It also allows the ranking of application techniques and spray additives in reproducible conditions thanks to its uniform and very low level of wettability. Experiments were performed to examine how the measuring system can be used to assess spray operating parameters and point out advantages and limitations of the proposed method. This chapter also highlights how the efficiency of a spray application could be explained with a deeper understanding of the droplet impact behaviour at a lower scale.

3.2 Appended publication

Autors: Massinon, Mathieu and Lebeau, Frédéric
Year: 2012
Title: Experimental method for the assessment of agricultural spray retention based on high-speed imaging of drop impact on a synthetic superhydrophobic surface
Status: Published
Journal: Biosystems Engineering **112**:56-64
URL: http://hdl.handle.net/2268/114382

3.3 Abstract

Spray retention is a critical stage in pesticide application since non-retained drops results in reduced efficacy, economic loss and environmental contamination. Current methods of retention assessment are based either on field experiments or laboratory studies. The former are usually performed on whole plants under realistic spray application conditions but offer no insight into the physics behind the process whilst the latter mainly focus on drop impact physics but are usually restricted to unrealistically low drop speeds. The aim of the paper is to devise an experimental method to investigate retention at drop scale level as a function of operational parameters but under controlled realistic conditions. A device based on high-speed video was developed to study retention on a synthetic superhydrophobic surface for a moving agricultural nozzle. The sizes and velocities of drops generated were measured immediately before impact using image analysis. Impact class proportions were established and transition boundaries between impact outcomes were quantified using Weber number. Two contrasting experiments were performed to investigate the ability of method to detect small parametric changes. The insignificant changes in spray pattern that occur from pressure changes, did not significantly affect impact class boundaries, but changed the proportion of drops in each class because of size and velocity variations. The use of a surfactant reduced the volume mean diameter of the spray, increased impact speed and changed the impact class boundaries. The method should allow a precise parametric investigation of spray retention in laboratory and close to field conditions.

3.4 Introduction

Pesticide application efficiency improvement is required for health, safety, environmental and cost considerations. Zabkiewicz (2007) divided the measurement of the spray application process in 4 individual stages, namely deposition, defined as the amount deposited in the target area; retention, the fraction of drops captured by plant; uptake, the fraction of the retained material taken up into plant foliage and translocation, the amount of absorbed material translocated from absorption site. Depending on the scenario, it was estimated that the efficiency of the deposition process was in the 80 to 95 % range whilst the retention process was in the 10 to 100% range, resulting in a combined worst case efficiency of 8%. Much research has therefore been devoted to minimise these losses, either by improvements in spray technology or the physicochemical properties of the pesticide formulation, the objective being to decrease the amount of chemical applied per unit area whilst ensuring that the dose of chemical required for control reaches the target. Some spray application studies focus on deposition and retention as a whole at plant scale. Butler Ellis et al. (2004) examined the effect of liquid properties and application technology on spray retention in a range of situations representative of practical pesticide application. Retention on whole plants was strongly influenced both by plant growth and plant canopy. Changes in pesticide application method from conventional flat-fan to air induction nozzle had a detrimental effect. Leaf surface was influenced by age and growing conditions with indoor grown plants being more difficult-to-wet than outdoor grown plants due to leaf surface abrasion. Lower dynamic surface tension (DST) of the spray mixture improved retention, especially when using an air induction nozzle on difficult-to-wet leaves. These results show that retention process is governed by numerous factors: drop size and velocity, physicochemical properties of spray formulation, spatial distribution within the canopy and target surface properties. This approach provided an integrated estimate of the deposition and retention but failed to develop a fundamental understanding of the physics behind the processes. Some research has focussed on the retention phase at the drop scale. Drop impact was then studied using imaging devices and drop generators (Yang et al., 1991). This approach was used by Forster et al. (2005) to devise a statistical model based on extensive experimental work to predict the adhesion/bounce transition. The parameters or combination of parameters used were the product of velocity and drop diameter, leaf angle, leaf surface and formulation surface tension. Shattering is not usually observed in these studies. Monodisperse drops were produced, using either on demand or continuous drop generators (Reichard et al., 1998). On demand droplet generators are restricted to generating drops at their terminal velocities at best and a single drop is produced at a time. Continuous drop generators have the advantage to produce higher speed drops but they are however limited in size by the orifice diameter and aerodynamic interactions with the surrounding air (Sirignano and Mehring, 2000). While an overall approach to measurement can highlight the effects of nozzle drop size spectra, measurements at drop scale fail to produce drop size and velocity distributions representative of agricultural nozzles. However, both approaches highlight the major influence of leaf wettability on the retention process. Wettability refers to the drop behaviour on the leaf surface. The diversity of plant and their surface structures led a wide range of wetting, from superhydrophilic to superhydrophobic (Koch and Barthlott, 2009). Gaskin et al. (2005) proposed a method to rank plant surfaces using acetone-water contact angle measurements. Easy-to-wet leaves retain most of the drops while difficult-to-wet ones, such as blackgrass or wheat, are difficult to treat. More particularly, the hydrophobic behaviour of leaves usually originates from their waxy cuticles. If the leaf coating is composed of hydrophobic crystal waxes that generate small-scale roughness, this may result in superhydrophobicity (Taylor, 2011). Unfortunately, because of the variability of superhydrophobic natural leaf surfaces, retention studies face reproducibility limitations. When comparisons of small operational variations such as changes in pressure or adjuvants are conducted, serious limitations on sensitivity may result. Manufacturers are interested in clarifying the relationship between pesticide application methods and the physicochemical properties of the pesticide formulation and spray retention to guide their technical developments. To support this objective, a theoretical review that links drop dynamics and impact outcome for superhydrophobic surfaces is presented. Using this theoretical basis, an assessment method is proposed to analyse the physics of drop retention at the drop scale under controlled and realistic conditions. A synthetic superhydrophobic surface is used to perform tests on a well-controlled target representative of difficult-to-wet leaves. Experiments performed at different operating pressures and surfactant concentrations were used to assess the performance of the method.

3.5 Theoretical background

Drop impact on superhydrophobic surfaces is considered in this section as the foundation for further work. The aim is to deliver the connections between drop properties, wettability and impact behaviours on a superhydrophobic surface.

A drop hitting a surface exhibits different behaviours depending on drop size and velocity, liquid and surface properties. However, each impact begins with the same steps. The drop then spreads until it reaches its maximum spreading diameter. Different options are possible depending on the surface wetting regime and the drop energy during impact.

Two models describe the wetting of superhydrophobic surfaces depending on the liquid surface tension (Zu et al., 2010; Taylor, 2011). The Wenzel non-composite regime (Wenzel, 1936), often referred as pinning, is characterised by the adhesion of the liquid which is anchored in the surface cavities. The liquid expels the trapped air below the drop if the liquid surface tension is sufficiently low to allow the liquid to penetrate into the surface roughness. In the Cassie-Baxter composite regime (Cassie and Baxter, 1944), the liquid standing on the pillars of the surface traps air in the valleys of the structure. Therefore, the liquid can be easily removed from the surface. Both models relate apparent contact angle with the surface roughness. A relevant roughness parameter is the Wenzel roughness which is defined as the ratio of the real and the projected planar surface areas (Rioboo et al., 2008). However, this parameter is not necessarily sufficient to forecast the transition between wetting regimes because pinning is dependent on topography. The effect of height and distance between the pillars are currently being studied (Zu et al., 2010) to give better prediction of the wetting than the traditional models.

Dimensional analysis has been classically used to investigate the relationship between variables involved in the retention process (Lake and Marchant, 1983; Rein, 1993). The relevant dimensionless parameter governing the drop-surface interaction in absence of viscosity modification is the Weber number of the drop. It represents the ratio between the kinetic energy and the surface energy $We = \frac{\rho V^2 D}{\sigma}$, where ρ is liquid density, V is the drop velocity before impact, D is the drop diameter and σ is liquid static surface tension. Other relevant dimensionless parameters in the dynamics of drop impact are the Reynolds number where μ is the dynamic viscosity, and the Ohnesorge number which is relevant if viscosity varies.

Different impact outcomes have been identified on superhydrophobic materials as a function of drop size and velocity and surface roughness (Figure 2.1). For small roughness, a drop of low Weber number adheres in a Wenzel state. The static contact angle is small. As Weber number increases, a part of the drop can bounce, in what is referred to as partial rebound. At higher Weber number a drop can be shattered into several satellite drops, with a part of the drop adhered to the impact point, in what is referred to as pinning fragmentation. At intermediate roughness, low velocity drops adhere in a Cassie-Baxter regime. With increasing speed, the drop rebounds but this can only be observed on superhydrophobic surfaces under the Cassie-Baxter regime (Richard and Quere, 2000) if the receding contact angle is sufficiently high (Rioboo et al., 2008). For even greater speeds, when the impact pressure is sufficiently large, the liquid can penetrate into the cavities of the surface modifying the wettability regime from Cassie-Baxter to Wenzel regimes (Tsai et al., 2011). As a consequence, sticking, partial rebound or pinning fragmentation can occur. Finally, for higher roughness, a drop can, as a function of speed, either be deposited in a Cassie-Baxter regime, rebound or completely splash. In the latter case, the expending film is lifted and leads to a rim disintegration caused by hydrodynamic instabilities (Range and Feuillebois, 1998; Šikalo et al., 2002). The reasons for the fundamental instability of splashing, currently explained either by a Rayleigh-Taylor or Kelvin-Helmholtz instability, are still under discussion (Park et al., 2008).

Extensive work has be carried out on the physical understanding of impact on superhydrophobic surfaces (Bartolo et al., 2006; Reyssat et al., 2006) as well as impact modelling (Caviezel et al., 2008) and promising robust physical models have emerged from these theoretical advances (Taylor, 2011). As instance, Rioboo et al. (2008) proposed a constant Weber number as boundary between impact outcomes in their experiments on porous superhydrophobic surface using distilled water. Mercer et al. (2010) and Forster et al. (2010) proposed transition models based on a combination of dimensionless numbers to account the range of liquid used in pesticide application.

3.6 Materials and methods

3.6.1 Dynamic spray application bench

Drops were generated by a flat-fan nozzle XR11003VK (Spraying Systems Co, Wheaton, IL, USA) mounted on a height-adjustable boom sprayer. Spray mixture was pressurised and mixed in a 10 L stainless steel tank. A precision pressure gage was placed at the nozzle level to be independent of any pressure drop in supply pipes. Fluid intake was controlled by a solenoid valve. Nozzle height was set at 500 mm above the target.

A single passage of the nozzle was performed for each test. A linear displacement stage, actuated by a servomotor, moved the nozzle at a forward speed of 2 $m \cdot s^{-1}$ perpendicular to the camera-lighting axis. Different techniques for measurement of drop size and velocity distributions have used static nozzles (Tuck et al., 1997). It was however shown that spray deposits below a nozzle differs between static and moving nozzles because of the modified air entrainment process (Lebeau, 2004). Drop impacts were recorded using a high-speed

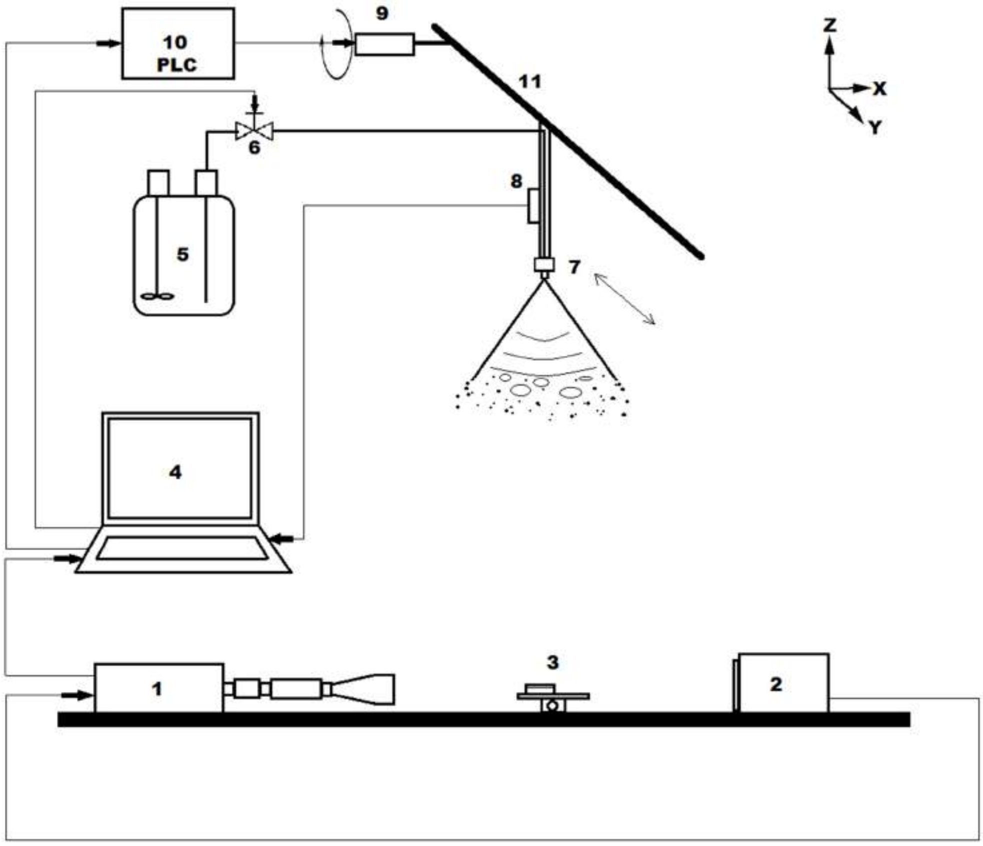


Figure 3.1: Dynamic spray application bench: (1) high-speed camera, (2) LED lighting, (3) target surface on linear stage, (4) computer, (5) pressurised tank, (6) solenoid valve, (7) nozzle, (8) pressure gage, (9) servomotor, (10) programmable controller, (11) linear stage.

camera (Y4 CMOS, Integrated Design Tools, Tallahassee, FL, USA) using backlighting to maximise the contrast. The acquisition frequency was set at 20000 images per second to ensure a good identification and characterisation of drop impacts. Shutter time was set to 9 μs with a +3dB sensor gain to get an average background grey level of roughly 200, with an 8 bit pixel depth. An optical system (12X zoom system, Navitar, Rochester, NY, USA) gave a 10.58 $\mu m \cdot pixel^{-1}$ spatial resolution (calibrated using the United States Air Force resolution test chart (MILSTD-150A, section 5.1.1.7), depth of field at about 2 mm and working distance at 341 mm (Navitar data sheets). A background correction was performed before tests with embedded camera software (Motion Studio, Integrated

Design Tools, Tallahassee, FL, USA) providing an homogeneous image. Sensing triggered the camera recording. A LED lighting (19-LED Constellation, Integrated Design Tools, Tallahassee, FL, USA) with a beam angle of 12.5° placed 500 *mm* behind the target surface provided both high illumination and uniform background to the images. The lighting was used in a pulsed mode and triggered by the image acquisition.

A horizontal slit plate (Figure 3.2) was placed 10 mm above the surface to select drops that are in the focal plane (target surface positioned directly under the centre of the flat fan nozzle). Slit width was smaller than the camera depth of field. The measurement zone was about 2 mm height by 10 mm long. The linear translation stage was used to adjust the target position in the camera focal plane. In this configuration, drop size and velocity can be measured just before impact. No secondary drops resulting from a splashing or a rebound that occurred out of the focal plane were taken into account in the analysis. A completely PTFE coated microscope blade (part number X2XES2013BMNZ, Thermo Fisher Scientific Inc., Waltham, MA, USA) was used in experiments. A static contact angle of 169° (sessile drop method, 5 replicates, CAM200, KSV Instruments, Helsinki, Finland) for a 5 μL distilled water drop characterises water repellent surface. The relevance of the use of this superhydrophobic surface as target surface has been studied in comparison with outdoor grown wheat leaves (Massinon and Lebeau, 2012a) using this method.

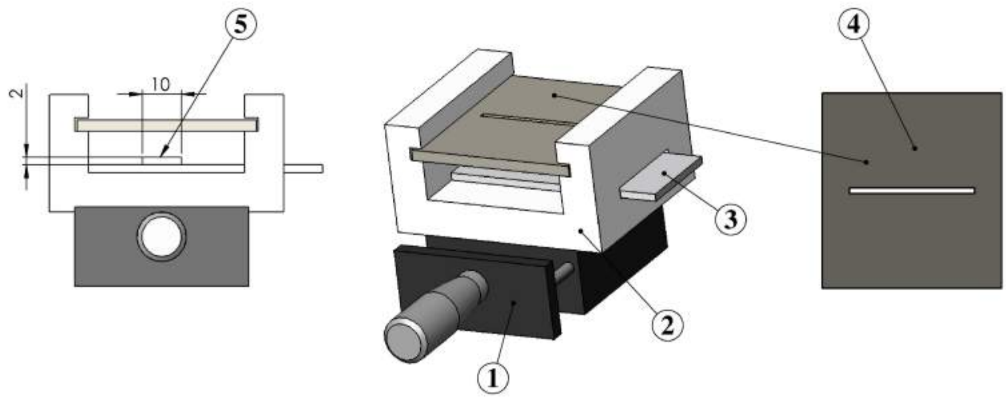


Figure 3.2: Target bracket: (1) linear stage, (2) blade holder, (3) superhydrophobic target surface, (4) slit plate (slit width corresponds to 1.5*mm* camera depth of field), (5) measurement area corresponding to the image size (10*mm* width × 2*mm* height).

3.6.2 Size and velocity measurements

The size and velocity of drops was determined in a two stage process. Firstly, in a manual screening phase, acquired images were viewed by an operator who encoded the frame number corresponding to the onset of a new drop in the upper part of the scene (Figure 3.3A) and a second frame was noted when the drop was located just above the surface, before impact (Figure 3.3B). As a result, the displacement of the drop between the two selected images is kept to around 1 mm for high accuracy speed measurements for slower drops. The operator also identified and recorded the impact type (as defined in section 3.5) based on subsequent frames (Figure 3.3C-F). These data were stored in a text file. In the second phase, selected images are screened by an image analysis procedure developed in Matlab (The MathWorks®Company, Natick, MA, USA). The first operation consisted of identifying and filling the objects in the image for a fixed threshold, followed by labelling. Once objects were identified, an equivalent diameter was computed using a corresponding circle with the same area as the drop. This was to take into account the non-spherical shape of the drops. The latter procedure was successively applied using two close segmentation thresholds to check on drop image sharpness. If the difference between diameters obtained for each threshold was greater than 10 μm, the drop was considered to be out of focus and was not taken into account for the further processing. Drop velocity was computed as the module of the vector defined by the difference in position between the drop centres between the two selected frames divided by the elapsed time. If multiple drops were found on the same image, the operator was prompted to select successive images or ones of interest. As a result a matrix of impact events was generated. It contained drop size and velocity, computed Weber number, impact type and frame number. Considering a ± 20 μm uncertainty in the distance between drop centres, the accuracy in the calculated velocity was a maximum of 2% at 8 $m \cdot s^{-1}$. Maximum uncertainty in drop diameter measurement was 10 μm.

Once drop size and velocity were determined, results were summarised in graphical form depending on drop size and velocity. Transitions were determined using a constant Weber number as boundary. The Weber number of transition was determined by the intersection between Weber number probability density distributions of the different impact outcomes. A drop of the Weber number of transition has an equal probability of belonging to different classes. In the log-log graphs of velocity versus diameter, a constant Weber number of transition corresponds to a straight line with a −0.5 slope. Finally, volumetric proportions of the spray in each class were computed and retention was assessed.

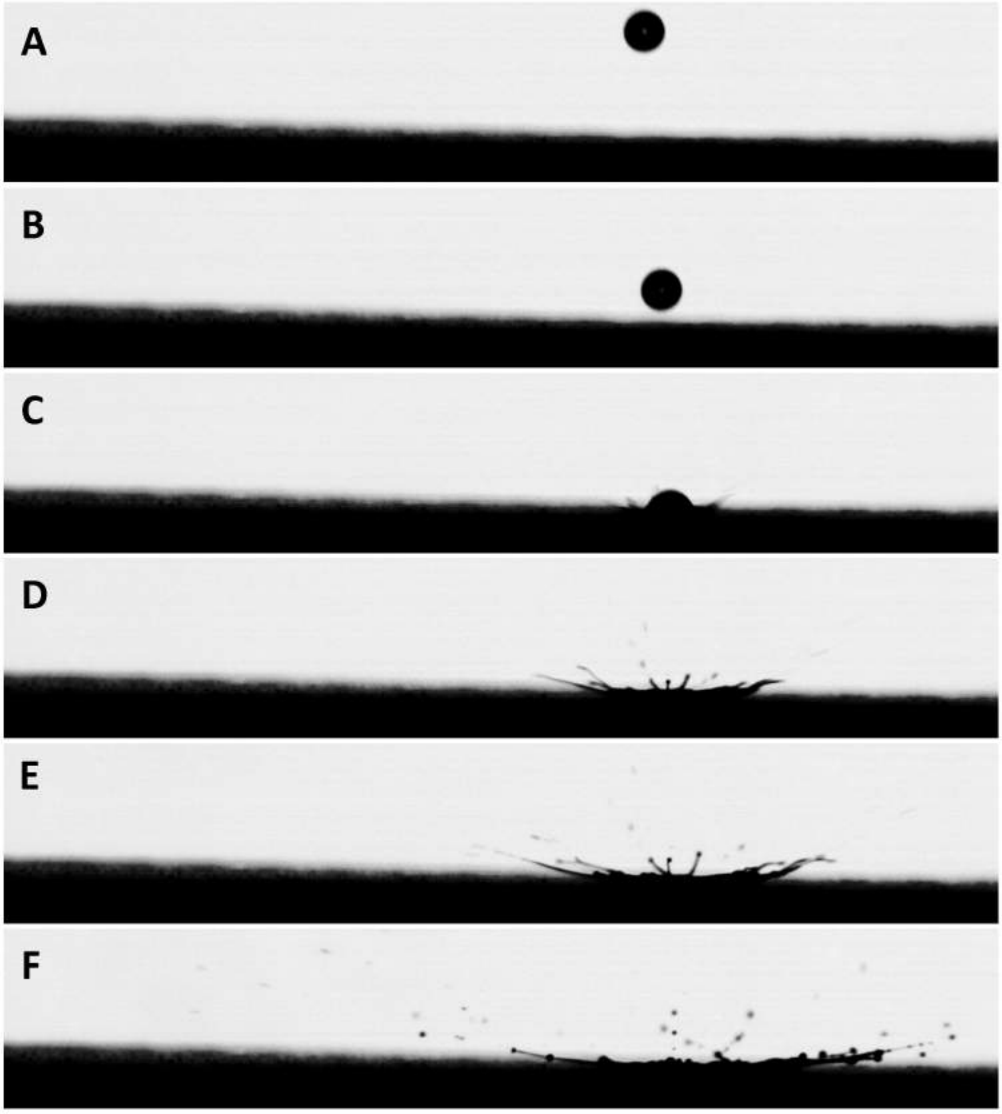


Figure 3.3: (**A**-**F**): Droplet splashing on the superhydrophobic blade. (**A**, **B**) Images used for the determination of speed and diameter by image analysis, (**C**-**F**) images used by the operator to determine impact type.

3.7 Results and discussion

3.7.1 Effect of pressure on retention (experiment 1)

Graphical outputs of the method for distilled water are presented in Figures 3.4, 3.5 and 3.6 for 0.2, 0.3 and 0.4 MPa spray pressure respectively. Overall, coarse drops with higher velocities were completely shattered into satellites drops (fragmentation, +). Intermediately sized drops, with diameters from roughly 100 μm to 300 μm bounced off the surface (rebound, •). Finally, fine drops with low velocity were directly adhered on the surface (adhesion, △). Adhesion refers to sticking both in Wenzel or Cassie-Baxter regime in this paper. Two clouds of points could be distinguished on these figures. The sigmoid-shaped cloud corresponds to primary impact. It represented the size and velocity distributions before impact resulting from sheet breakup, transport and evaporation of each drop. The second cloud of points, located below the latter, corresponds to secondary impacts. They originated from a rebound or a pinning rebound (○). The drops present a Cassie-Baxter wetting regime during impact, except for pinning rebound events for which the liquid undergoes a transition from Cassie-Baxter to Wenzel. A pressure increase leads to the production of more drops below 100 μm diameter. These small drops hit the target at a slightly higher velocity than their terminal velocity. They are found in the third cloud above the first impact cloud. The reason for this is the more energetic liquid sheet breakup (Sirignano and Mehring, 2000) due to increased pressure; this is confirmed by the decrease of the volumetric mean diameter (VMD) (Table 3.1). The VMD statistic indicates the diameter with half the spray volume is contained in droplets that were smaller than this value. Another hypothesis could be that a VMD decrease leads to an increase in induced airflow. More numerous and smaller drops exchange more momentum with surrounding air which induces a stronger downward airflow and a slightly higher impact velocity. The VMD decrease was also associated with a higher proportion of deposited drops. The proportion of splashing reached a maximum at 0.3 MPa spray pressure and then decreased at 0.4 MPa because there are simply less coarse drops. On Figures 3.4, 3.5 and 3.6, two limits are identified corresponding to adhesion/rebound boundary (A/R) and rebound/fragmentation boundary (R/F). The limits were determined using a constant Weber number (We) as described in section 3.6.2. All the WeA/R are pressure independent (Table 3.1). However differences between $We_{R/F}$ originate from the small number of observed drops characterised by a Weber numbers close to $We_{R/F}$. The limit should not be assessed using a single Weber number, but by defining a range of Weber numbers as a function of contact angle hysteresis (Rioboo et al., 2008).

Table 3.1: Details of experiments and data extracted from the imaging process.

	Distilled water Experiment 1			Break-Thru S240 Experiment 2		
Pressure [MPa]	0.2	0.3	0.4	0.3	0.3	0.3
Surfactant concentration [$\%V/V$]	/	/	/	25	0.05	0.1
Static surface tension [$mN \cdot m^{-1}$]	72.2	72.2	72.2	22.9	21.6	21.5
VMD [μm]	256	227	200	215	234	213
Number of droplets	199	269	355	186	183	169
Adhesion (A) [$vol.\%$]	4	9	13	29	39	53
Rebound (R) [$vol.\%$]	71	60	60	12	2	0
Fragmentation (F) [$vol.\%$]	2	31	27	59	59	47
$We_{A/R}$	0.3	0.3	0.4	21	24	/
$We_{R/F}$	70	60	50	125	110	/
$We_{A/F}$	/	/	/	/	/	95

Overall, the increase of initial energy has no detrimental effect on retention in these

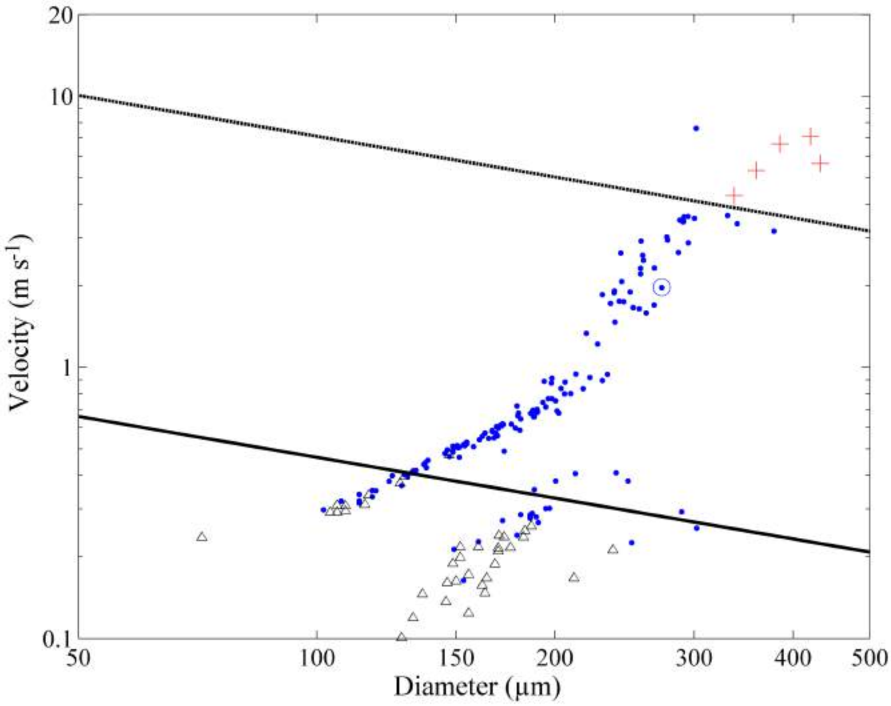


Figure 3.4: Impact outcomes on the superhydrophobic slide for distilled water at 0.2 MPa (Teejet 11003 nozzle at 0.5 m height): △ adhesion, ● rebound, ○ pinning rebound, + complete fragmentation, — Weber number of transition between adhesion and rebound (We = 0.3), - - Weber number of transition between rebound and fragmentation (We = 70).

conditions. Splashing is reduced and adhesion is increased because of big drop proportion depletion and small drop proportion increase. The increase of primary adhesion may however have a drastic effect on treatment efficacy, for instance on small or low LAI (Leaf Area Index) target such as those encountered in black-grass weeding.

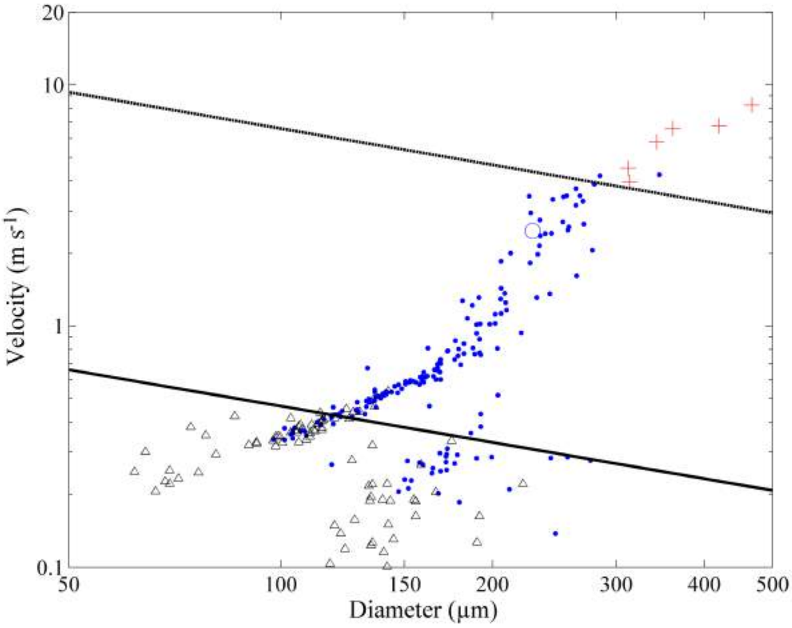


Figure 3.5: Impact outcomes on the superhydrophobic slide for distilled water at 0.3 MPa (Teejet 11003 nozzle at 0.5 m height): △ adhesion, • rebound, ○ pinning rebound, + complete fragmentation, – Weber number of transition between adhesion and rebound (We = 0.3), - - Weber number of transition between rebound and fragmentation (We = 60).

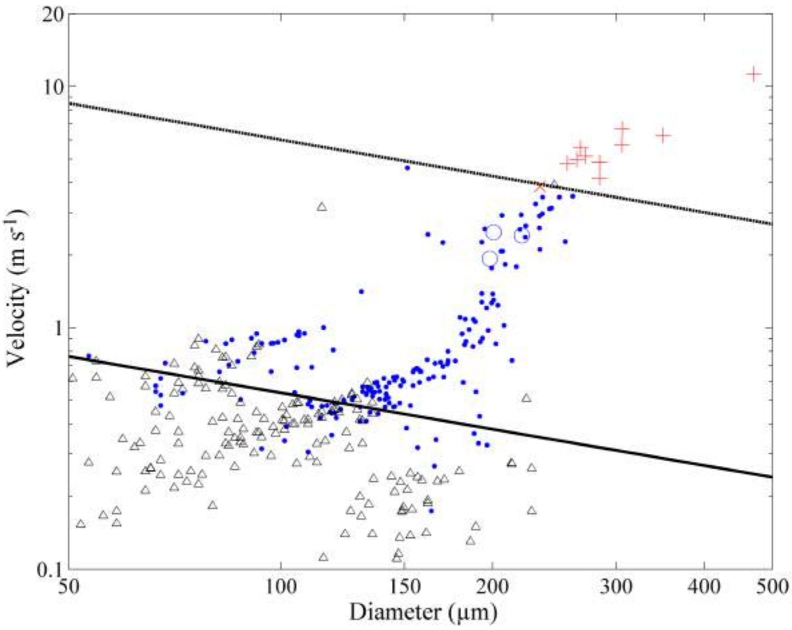


Figure 3.6: Impact outcomes on the superhydrophobic slide for distilled water at 0.4 MPa (Teejet 11003 nozzle at 0.5 m height): △ adhesion, • rebound, ○ pinning rebound, × pinning fragmentation, + complete fragmentation, – Weber number of transition between adhesion and rebound (We = 0.4), - - Weber number of transition between rebound and fragmentation (We = 50).

3.7.2 Effect of surfactant concentration on retention (experiment 2)

Figures 3.7, 3.8 and 3.9 present phase diagrams of impact outcomes for three surfactant concentrations: 0.025, 0.05 and 0.1 (% V/V) respectively. At first glance, surfactant reduces the rebound. This effect is more pronounced as the surfactant concentration increases. These observations are corroborated with a gradual reduction of rebound proportion and decrease of the VMD (Table 3.1) as highlighted by Butler Ellis et al. (2001). For 0.1 (% V/V) concentration bouncing even disappears on this surface (Figure 3.9). At this concentration, the surfactant allows the liquid to expel the air located into surface cavities and to penetrate deeply inside the surface matrix (Taylor, 2011). The mixture is therefore able to undergo a Cassie-Baxter to Wenzel regime transition and no rebound is observed anymore. The splashing threshold decrease to a Weber number of 95 calculated with static surface tension. However, timescale for drop impact is very low and depends essentially on drop size (Richard et al., 2002), so a dynamic surface tension would be more suited in the Weber number calculation. For instance the contact time for a 100 μm drop is about 0.5 ms which may be too short to allow the adsorption of the surfactant onto the new interface. Accordingly a drop containing lower surfactant concentration can still bounce despite the low static surface tension. Surfactant concentration effect during splashing is observable at the solid-liquid interface, the central part of the drop sticking at the surface because of transition to Wenzel regime at this level. The splashing is therefore modified to a pinning fragmentation (×) as a substantial part of the drop adheres on the surface. As a consequence, a better characterisation of splashing is needed in further investigations to estimate the fraction of the drop that disintegrates in small drops from the part sticking to the surface.

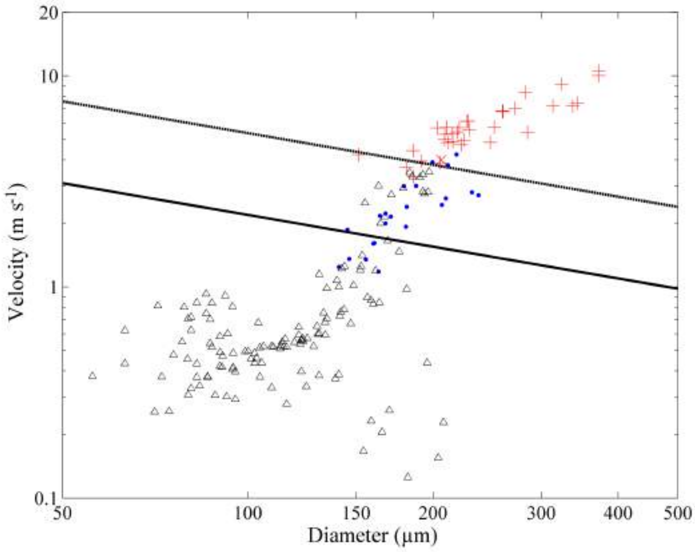


Figure 3.7: Impact outcomes on the superhydrophobic slide for 0.025 (% V/V) Break-Thru S240 surfactant in distilled water at 0.3 MPa (Teejet 11003 nozzle at 0.5 m height): △ adhesion, • rebound, × pinning fragmentation, + complete fragmentation, – Weber number of transition between adhesion and rebound (We = 21), - - Weber number of transition between rebound and fragmentation (We = 125).

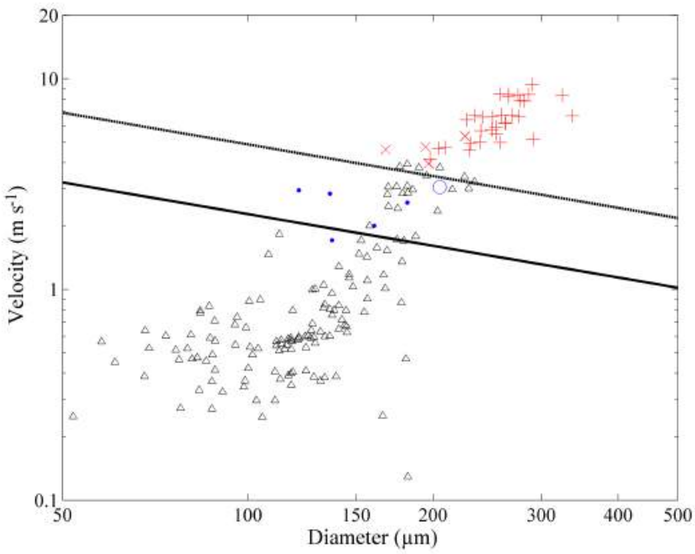


Figure 3.8: Impact outcomes on the superhydrophobic slide for 0.05 (% V/V) Break-Thru®surfactant in distilled water at 0.3 MPa (Teejet 11003 nozzle at 0.5 m height): △ adhesion, • rebound, ∘ pinning rebound, × pinning fragmentation, + complete fragmentation, – Weber number of transition between adhesion and rebound (We = 24), - - Weber number of transition between rebound and fragmentation (We = 110).

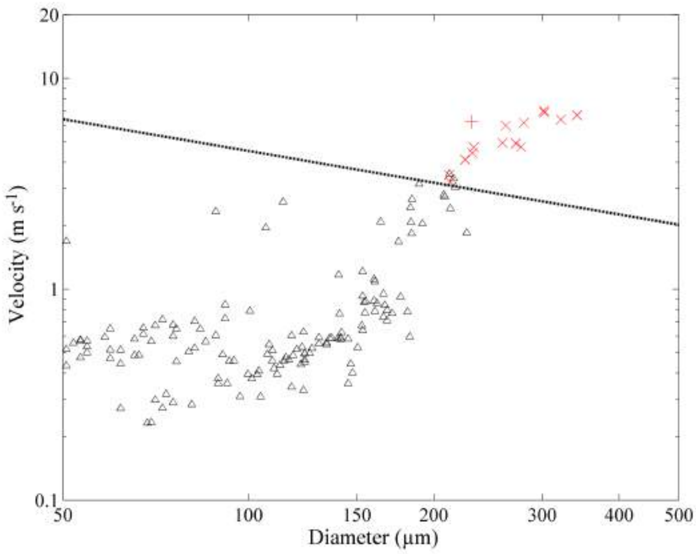


Figure 3.9: Impact outcomes on the superhydrophobic slide for 0.1 (% V/V) Break-Thru S240 surfactant in distilled water at 0.3 MPa (Teejet 11003 nozzle at 0.5 m height): △ adhesion, × pinning fragmentation, + complete fragmentation, - - Weber number of transition between adhesion and fragmentation (We = 95). Drop rebound totally vanishes and pinning fragmentation replaces complete fragmentation.

3.8 Conclusions

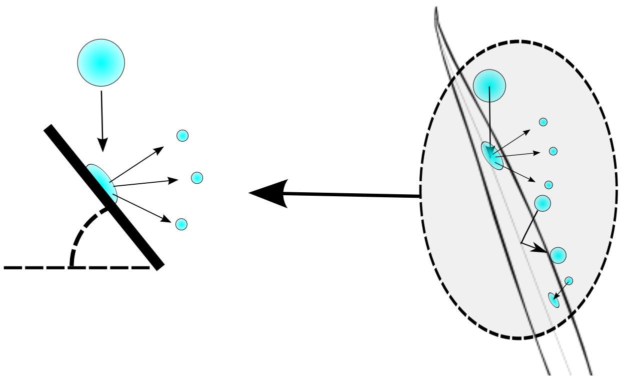
A measurement method of spray retention using both high-speed imaging and a superhydrophobic surface is proposed. The main interests are in the integration of all variables involved in a single trial, the production of realistic drop distributions leading to the onset of all impact types and the use of dimensionless number to forecast transitions between the impact outcomes.

On the basis of the conducted experiments, the method can highlight the effect of any modification of operational parameters on retention. Pressure modification affects retention by changing proportions in the different impact classes. The modification of the mixture surface tension affected the spray characteristics before impact as well as impact types and boundaries. The rebound progressively vanished with the increase of surfactant concentration. Splashing energy threshold is not highly modified but a pinning fragmentation appears because of Cassie-Baxter to Wenzel transition, what needs further investigations for precise quantification.

The method can be extended to investigate the effect of other parametrical changes such as the impact angle, spray height or nozzle kind. The use of a superhydrophobic reference guarantees the reproducibility of the trials and allows an overall ranking of the efficiency of application techniques and additives. The characterisation of natural leaf surface properties as well as liquid properties such as DST and polymeric additives (Bergeron, 2003) are promising research areas for the setup.

CHAPTER 4

Effect of surface orientation on spray retention and droplet impact behaviour probabilities



4.1 Chapter objectives and outline

This chapter focuses on the effect of various surface angles on the fate of spray droplets during impact since it is a preponderant factor on the fate of droplets impacting on slanted surfaces. Using the test bench described in chapter 3, the effect of surface orientation is studied in comparison between the artificial superhydrophobic surface and excised black-grass leaves. As transitions between droplet impact outcomes are not sharp (chapter 3), the impact phase diagram droplet velocity versus diameter (for instance figure 3.5) is divided into eleven energy classes. Class boundaries correspond to a constant Weber number and has been chosen because it represents the ratio between inertial to surface tension forces (Table 2.1). This descriptor is commonly accepted by physicists (Yarin, 2006) as indicator suited for describing the droplet splashing energy threshold. The volume of liquid of each impact outcome relative to the total volume within the energy class is computed for each of the eleven energy classes. Finally, an histogram that represents the spray droplet impact probabilities depending on the droplet impact energy is built in response to target (wettability and orientation) and droplet properties (diameter, velocity and dynamic surface tension) and will be used as foundation for the subsequent modelling approach described in chapter 6.

4.2 Appended publication

Autors: Massinon Mathieu, Boukhalfa Hassina and Lebeau Frédéric
Year: 2014
Title: The effect of surface orientation on spray retention
Status: Published
Journal: Precision Agriculture **15**:241-254
URL: http://hdl.handle.net/2268/161493

4.3 Abstract

Research in precision spraying investigates the means to reduce the amount of herbicide applied by directing droplets more accurately towards the weeds. The trend in the development of spot spraying equipment is an increase of the spatial resolution and new actuators that are able to target very small areas. However, there is a lack of methods for assigning rates of herbicides relating target to optimal droplet features. A wide range of droplet impact angles occurs during the spray application process because of droplet trajectories and the variability of leaf orientation. In this study, laboratory experiments were conducted to highlight the effect of surface orientation on droplet impact outcomes (adhesion, rebound or splashing) on two very difficult-to-wet surfaces: an artificial surface with a regular roughness pattern and an excised black-grass leaf with an anisotropic roughness pattern. Measurements were performed for different surface orientations with a high-speed camera coupled with backlighting LED. Droplets of two formulations (distilled water and distilled water plus a surfactant) were produced with a moving flat-fan hydraulic nozzle to obtain a wide range of droplet sizes and velocities, which were measured by image analysis. Increasing surface angle reduces surface area available for droplet capture. Droplet impact behaviors are then modified since surface tilt induces a tangential velocity component at impact and, consequently, a reduction of the normal component. Impact modifications have also been observed due to the anisotropic roughness pattern of a black-grass leaf. The integration of droplet-surface interaction information offers a significant way to further improve the precision spraying efficiency by considering the optimal droplet size, speed and ejection angle depending on the target surface and architecture.

4.4 Introduction

Chemical weed control continues to play a pivotal role to ensure a sufficient level of yield. Agrochemical use, however, is associated with ever increasing environmental, safety and cost concerns. Targeting pesticides more accurately is then of major concern for reducing the negative impact of weed chemical control. Conventional uniform application with hydraulic nozzles was optimized over many years to achieve better spray distribution over the crop and better biological efficiency while minimizing spray drift. Studies aimed at finding the best use of this spraying equipment depending on applied volumes, pesticide dose and crop growth stage and species, most often using field trials (Butler Ellis et al., 2004). Regarding spraying equipment, the development of the so-called controlled droplet application allowed reduction of the volume of pesticides per hectare applied with emphasis on the importance of applying the correct size of droplets for a given target with uniform droplet size distributions (Matthews, 2008). Besides, the notion of differential management of field areas derived from precision farming concepts has further resulted in a more precise application technique consisting of applying control measures only where weeds are located. The first advance was the introduction of variable rate technology that controls the applied amount of pesticide according to site-specific demand in the field based on spray maps generated before the treatment. This method requires large scale remote sensing techniques to build offline spray application prescription maps later used in the field to drive GPS spray controllers. Precision agriculture flow control has recently evolved to high resolution machine vision detection systems allowing real-time capabilities (Thorp and Tian, 2004). The detection and identification of individual weeds requires both high resolution machine vision technology systems (Tellaeche et al., 2008; Nieuwenhuizen et al., 2010) and an actuator for pesticide, delivering to the right target (Lee et al., 1999; Giles et al., 2002; Miller et al., 2012a). The main factor driving the development of spot spraying equipment is to maximize the number of droplets reaching their target. Droplet transport (Walklate, 1987; Ghosh and Hunt, 1998) and spray drift potential (Holterman et al., 1997; Mokeba et al., 1997; Baetens et al., 2007; Butler Ellis and Miller, 2010) were described intensively and many solutions were proposed to reduce their adverse effects. However, mechanisms governing spray retention, which is the amount of sprayed product actually retained by plant leaves, are still misunderstood despite the growing interest of researchers. On their part, the losses occurring during droplet impact on leaves amount to $5 - 92\%$ of the off-target component load of a herbicide application (Zabkiewicz, 2007). Miller et al. (2012b), in a quest for a suitable nozzle to perform plant scale control for use in spot spraying applications, highlighted that the use of larger and faster droplets in the spray gave an additional component of selectivity: retention on the onion crop was reduced from 6.35 μL for the nozzle delivering the slower and smaller droplets to 0.87 μL for the bigger and faster ones, a 7.5:1 ratio, while retention on filter paper was only modified in a 2:1 ratio. This means that, even if droplets impact their target, treatment efficiency differences may arise from retention variability depending on plant (species, wettability, growth stage and architecture) and droplet properties (size, velocity, dynamic surface tension). This has to be taken into account for development of spot spraying equipment and advantage can even be taken from differences of wettability between species for targeting specific weeds or reducing contamination of crops. The need for further investigation on the effect of coverage, dosage and placement on the leaves was also highlighted for further micro-spray systems development (Søgaard and Lund, 2007). The next gap to fill in the development of variable-rate technologies is the lack of methods for assigning rates of herbicide based on the results of a weed sensing procedure (Thorp and Tian, 2004). A better knowledge of droplet-leaf interactions by precision farming specialists is therefore requested to drive the development of the next generation of pesticide application technology.

Many parameters influence droplet behavior at impact, from droplet physico-chemical properties to target properties. Predominant factors affecting the spray retention are related to the target surface (Furmidge, 1962; Wirth et al., 1991; Journaux et al., 2011).

Plant leaves exhibit various degrees of wettability from very-easy to very-difficult-to-wet, depending on species and growth stages (Gaskin et al., 2005) owing to the coating of epicuticular wax at leaf surface (Barthlott et al., 1998). Surface wettability is often quantified using the static contact angle θ, which is the angle measured between the solid surface and the tangent to droplet at the point where liquid, solid and air meet. It reflects the relative strength of the liquid, solid and vapor molecular interactions. High static contact angle ($90° < \theta < 150°$) reflects hydrophobic surfaces. Static contact angle above 150° determines superhydrophobic surfaces. The superhydrophobic behavior of some leaves arises from the presence of a microstructure of the epicuticular wax. The superhydrophobicity is therefore a physical property of hydrophobic materials. In other words, the hydrophobicity provided to some leaves by waxes is enhanced by hairs that dramatically increase the small scale roughness of the leaf surface. In consequence, a droplet exhibits a very large static contact angle on such surfaces and is not able to stay on it at impact. It is well established that superhydrophobic species, such as blackgrass, are the most challenging target for efficient pesticide application. The present paper focuses therefore on such surfaces.

Two models describe the wetting of such surfaces based on Young's equation and liquid surface tension (Callies and Quéré, 2005; Taylor, 2011) at microscopic scale. In the Wenzel non-composite regime (Wenzel, 1936), often referred to as homogeneous wetting regime, the liquid wets and fills the surface cavities completely thanks to a sufficiently low liquid surface tension. The Cassie-Baxter composite regime (Cassie and Baxter, 1944) considers an interface composed of both solid and surrounding air trapped under the drop (Zu et al., 2010). The liquid is only in contact with the upper part of the relief because its surface tension is too high. Height and distance between pillars or pikes that make up the roughness of the surface are critical parameters to keep the drop in the Cassie-Baxter regime. A transition between the Cassie-Baxter to the Wenzel regime is possible and may be caused by droplet surface fluctuations when the droplet is resting on the surface at impact.

On superhydrophobic leaves, the outcome of droplet impact is a complex function of surface roughness, surface orientation, droplet size and velocity and liquid physico-chemical properties. Many studies focused on optimal droplet size required maximization of retention by plants under field conditions (Knoche, 1994; Butler Ellis et al., 2004). However, systematic laboratory tests are needed to gain more precise information at droplet scale. Impact outcomes of a single droplet on horizontal and dry superhydrophobic surfaces are known to be a function of droplet Weber number and surface roughness (Rein, 1993; Yarin, 2006). The Weber number represents the ratio of droplet kinetic energy to surface energy $We = \frac{\rho V^2 D}{\sigma}$, where ρ is liquid density, V is the drop velocity before impact, D is the drop diameter and σ is liquid static surface tension, where D is the droplet diameter $[m]$, V is the droplet velocity $[m \cdot s^{-1}]$, ρ is the liquid density $[kg \cdot m^3]$

and σ is the liquid surface tension $[N \cdot m^{-1}]$. The Wenzel's roughness factor, defined as the ratio of actual and projected planar or geometrical (measured in the plane of the interface) surface areas (Rioboo et al., 2008), indicates the surface roughness level. This ratio tends to one for a flat and smooth surface. For small Wenzel roughness and for low Weber number (Figure 2.1), a drop is deposited in the Wenzel regime. Higher Weber numbers lead to drop fragmentation, part of which sticks at the impact point. Depending on impact energy, a droplet can either bounce which is called partial rebound, or shatters into several satellite drops, which is called partial splashing. For intermediate Wenzel roughness, slow drops adhere in a Cassie-Baxter regime. For higher Weber number, the droplet bounces completely, which is only possible on superhydrophobic surfaces (Quéré, 2005). For even higher Weber number, impact pressure is so large that the liquid can penetrate surface cavities, which modifies the wetting regime from Cassie-Baxter to Wenzel. Transition from Cassie-Baxter to Wenzel wetting regime may also occur by reducing liquid surface tension. As a consequence, sticking, partial rebound or partial splashing may occur. Finally, for high Wenzel roughness, drops may either adhere in a Cassie-Baxter regime, rebound or splash completely depending on Weber number. The structure of surface micro-topography further modifies liquid macroscopic wetting. On unidirectional grooved surfaces, contact angles measured from the direction parallel to the grooves are larger than those measured from the perpendicular direction (Zhao et al., 2007). Surface micro-pattern also influences the macroscopic flows as directional splashing can occur (Tsai et al., 2011). Treating superhydrophobic leaves is a challenge accentuated by the angle of droplet impact due both to plant architecture and droplet trajectories. Jensen (2012) showed that angling a nozzle at 60° forward relative to the direction of travel increased herbicide efficacy on annual grasses, such as blackgrass, using flat-fan nozzles in field experiments. Obviously, surface angle reduces projected area intercepting droplet spray. Up to now, the effect of surface angle on droplet impact outcome has been weakly documented. Most studies (Stow and Hadfield, 1981; Mundo et al., 1995; Šikalo et al., 2005a; Bird et al., 2009) advocated the use of velocity normal component in computing dimensionless numbers to forecast impact outcome thresholds (Lake and Marchant, 1983). The optimal droplet features depending on those of the target are required to guide the further development of precision spraying technology. This paper shows how to consider the droplet angle at impact to find this optimum using a laboratory method devised to rank adjuvants according to their effect on retention in controlled conditions (Massinon and Lebeau, 2012b). More particularly, this study focuses on how leaf orientation may affect retention by plants. First, an artificial superhydrophobic surface was used to investigate adjuvant effect on retention as a function of surface angle. The artificial surface was used as a reference for systematic tests since variability owing to leaf position and age could hide differences between impact behaviors (Reichard et al., 1998). Afterwards blackgrass, a common weed in cereal crops, was investigated to see whether mechanisms highlighted on an artificial surface can be extended to natural surfaces.

4.5 Materials and methods

4.5.1 Dynamic spray application bench

Spraying system. The setup (Figure 3.1) was composed of a dynamic spray application test bench contained in a room where temperature and relative humidity were controlled. The dynamic bench consisted of a single extended range flat-fan nozzle (XR Teejet 11003VK, Spraying Systems Co, Wheaton, IL, USA) operating at 200 kPa. The nozzle was mounted 500 mm vertically above the target surface on a linear guide rail actuated by a servomotor at a forward speed of 2 $m.s^{-1}$. A single pass was performed for each spraying so that a volume of 160 L/ha was delivered during tests.

Backlit imaging system. Drop impacts were recorded with a high-speed camera (Y4, Integrated Design Tools, Tallahassee, FL, USA) at a frequency of 20000 frames per second with a 9 μs exposure time to provide experimental information on number, size and velocity of drops before impact, as well as drop impact behavior. An optical system (12X zoom system, Navitar, Rochester, NY, USA) provided 1016x185 pixels digital images with 11.3 $\mu m.pixel^{-1}$ spatial resolution, calibrated using the United States Air Force resolution test chart (MIL-STD-150A, section 5.1.1.7) and a camera depth of field at about 2 mm. Consequently, number density and spatial statistics were given from a probe volume of $11.48 \times 2.09 \times 2$ mm (image size $\times$ depth of field). The setup involved a pulsed LED lighting array (19-LED Constellation, Integrated Design Tools, Tallahassee, FL, USA), which was synchronized with the image acquisition in a backlit arrangement. Distance between LED array and camera was 500 mm. No heating problems arose in the probe volume. Light intensity on images was expressed in 8 bits grey levels with pixel value ranging from 0 for black to 255 for white. The whole optical system was tilted with respect to the target from 0 to 60°, so that image width was kept parallel to the surface independently of the angle of surface inclination.

4.5.2 Image analysis

The image processing technique used for measuring droplet size and velocity was non-intrusive. Owing to spray density, some droplets were located outside the probe volume. Such defocused drops were rejected since they represented a source of error. Similarly, droplets truncated by image edge or too small particles were not integrated in the procedure.

Image processing began with an automated identification of relevant images based on droplet movement to reduce the number of images to be treated. Since robust automated impact type identification was not available yet, pre-selected images were viewed by a human operator who recorded subsequent impact behavior on the basis of Figure 3.1. An image pair was selected for each droplet where the first image contained an incoming droplet at its top, with its center at approximately 1.3 *mm* from the target (depending on droplet size), and the second contained the droplet immediately before impact, the bottom of the droplet being at a distance depending on the droplet velocity and the camera acquisition rate. The algorithm loaded the first image and performed a background correction to enhance image quality and reduce background illumination inhomogeneities (based on 50 images without any droplet). Then the image was binarized and particles were detected and identified. Only in-focus droplets were selected based on gradient detection at the edges of droplets (Lecuona et al., 2000). The droplet diameter was computed using the following equation:

$$D = \sqrt{\frac{4A}{\pi}}$$

where A was the surface area calculated by summing all pixels belonging to the droplet. If several droplets appeared in the image due to a splashing event (10-20 droplets) or multiple incoming droplets (up to 5 droplets), the operator was prompted to select the droplet of interest on the two images by clicking on it with the computer mouse. The algorithm found the nearest droplet from the co-ordinates of the click. Droplet center co-ordinates (X,Y) are saved for subsequent determination of droplet velocity. An identical operation was performed with the second image. The droplet velocity was then computed using the following equation:

$$\vec{v}_{ij} = \frac{(X_j - X_i, Y_j - Y_i)}{\Delta t}$$

where subscripts i and j were respectively related to the drop on the first and second image, X and Y were the center co-ordinates andis the time interval between both selected images. The time between the two images of a pair was maximized to reduce the uncertainties on the droplet velocity determination, with the assumption that the computed velocity is the droplet velocity at impact on the target. The norm of the velocity vector was further used to build the results.

4.6 Results

4.6.1 Experimental conditions

Tap water constitutes the main carrier of agrochemicals. Since water hardness modifies surface tension, pure distilled water (static surface tension of 72 $mN.m^{-1}$) was firstly sprayed using the application bench. Agrochemicals mixture wettability is often improved by adding surfactants. In our experiments, mixture static surface tension was reduced to 21 $mN.m^{-1}$ (CAM200, KSV Instruments, Helsinki, Finland, sessile drop method, 5 replicates) thanks to a trisiloxane tank-mix surfactant (Break-Thru S240, Evonik Industries AG, Germany) added to distilled water at the recommended use concentration $(0.1\%V/V)$. These superspreaders (Venzmer, 2011) have a very low dynamic surface tension (DST), which inhibits droplet rebound (Massinon and Lebeau, 2012b) and may increase retention. A surfactant molecule contains a hydrophilic head and a hydrophobic tail. Surfactant molecules will diffuse in water and adsorb at interfaces between air and liquid and align themselves with the tails to air and heads to the water, which reduce the surface tension. During impact on the target, the droplet is deformed. The interface is stretched and gaps in the surfactant alignment appear at the interface. Surfactant molecules will spontaneously fill the gaps to restore the equilibrium. Surfactants are characterized by their adsorption rate, or ability to fill the interface gaps more or less rapidly. Super-spreader surfactants exhibit a very fast adsorption rate. This kinetic of adsorption can be described by the DST, which is the variation over time of the surface tension. If the adsorption time is smaller than the droplet impact time, which is about 2 ms, the droplet impact behavior can be greatly altered (Massinon and Lebeau, 2013) since surfactants are able to maintain a very low surface tension.

An artificial superhydrophobic surface (completely PTFE coated microscope blade, part number X2XES2013BMNZ, Thermo Fisher Scientific Inc., Waltham, MA, USA) was first sprayed at different orientations by a rotation of the camera-surface-lighting system of 0°, 30° and 60° around the axis X (Figure 3.1). The static contact angle of a distilled water droplet is 169° on the surface (CAM200, KSV Instruments, Helsinki, Finland), which is representative of very difficult-to-wet leaves (Massinon and Lebeau, 2012a). Ten sprayings were performed for each orientation and a new artificial surface was used for each spraying. Afterward, spray behavior was studied on excised leaf from indoor-grown blackgrass (*Alopecurus myosuroides* HUDS. (ALOMY), BBCH 13), which is a very-difficult-to-wet species (distilled water static contact angles around 155°) depending on position on leaf and surface groove direction. Five sprayings were performed on the adaxial leaf surface, which was positioned along the axis Y (Figure 3.1).

4.6.2 Retention by reference artificial superhydrophobic surface

Spray impact characteristics, such as observed number of drops, volume median diameter (DV50) and total droplets volume as well as impact characteristics are given in Table 4.1. Features in Table 4.1 were merged from ten sprayings to reduce the inherent variability existing between spraying trials, which is related to the random droplet formation process. It is recognized that about 10000 droplets are required to obtain a stabilized particle size distribution. The values of DV_{50} and number of droplets are presented in Table 4.1 to get an idea of the spray characteristics during the trials with the specific nozzle and formulation, but do not present values built on a sufficiently large droplets sample. As

Table 4.1: Spray features immediately before impact on an artificial superhydrophobic surface with a regular roughness pattern (merged from ten sprayings). C-B: Cassie-Baxter, W: Wenzel

	Distilled water			0.1 % V/V Break-Thru ®S240		
Surface angle α, [$\circ$]	0	30	60	0	30	60
Number of droplets at impact (N)	236	197	62	270	141	63
$N \cdot \cos\alpha$	236	204	118	270	233	135
Total droplet volume (V), 10^{-10} m^3	7.0	5.9	1.9	5.8	4.6	2.1
$V \cdot \cos\alpha$	7.0	6.1	3.5	5.8	5.0	2.9
DV_{50}, [μm]	231	219	219	207	236	224
Adhesion, [$\%vol.$]	7.4	2.3	4.8	69.3	52.7	50.3
Rebound C-B, [$\%vol.$]	42.8	57.0	75.7	1.6	3.8	10.1
Rebound W, [$\%vol.$]	1.1	0.0	0.0	0.0	0.0	0.0
Splashing C-B, [$\%vol.$]	10.6	26.4	19.5	1.2	0.0	4.4
Splashing W, [$\%vol.$]	38.1	14.3	0.0	27.9	43.5	35.2

expected for both liquids, the number of droplets landing on the surface diminishes by increasing surface angle. The observed volume reaching the surface decreases accordingly. A reducing of droplet interception by the target proportional to the cosine of the surface angle was expected. This is not observed and discrepancies between observed and projected values grow with the surface angle. For both formulations, increasing surface angle reduces adhesion and increases rebound occurrence. On an already tilted target surface, further increase of surface angle does not seem to have any effect on adhesion proportion. Partial rebound (Wenzel wetting regime) is only and scarcely observed for distilled water on a horizontal surface. By increasing surface angle, the normal velocity component is reduced. There is, therefore, not enough impact pressure to overcome the energy transition threshold between Cassie-Baxter and Wenzel wetting regimes. The super-spreader solution is able to expel the air trapped in surface roughness and spreads on the surface in Wenzel wetting state thanks to its lower DST. Rebound is therefore widely reduced using the super-spreader. Some drops containing surfactant molecules can however still bounce off a tilted surface. This effect increases with surface angle. Both fragmentation outcomes represent together nearly half of the volume sprayed on a horizontal surface for distilled water. Fragmentation decreases as surface angle increases for water while it increases for surfactant solution because of its lower surface tension. Partial splashing is beneficial for retention since a significant proportion of the drop may stick on the surface. For water, this proportion decreases with increasing surface angle, as partial rebound. With a surfactant solution, a few drops splash totally again because of their weak DST. An impact phase diagram of the response to an application method of a target surface is presented in Figure 4.1, depending on droplet size and velocity immediately before impact on the

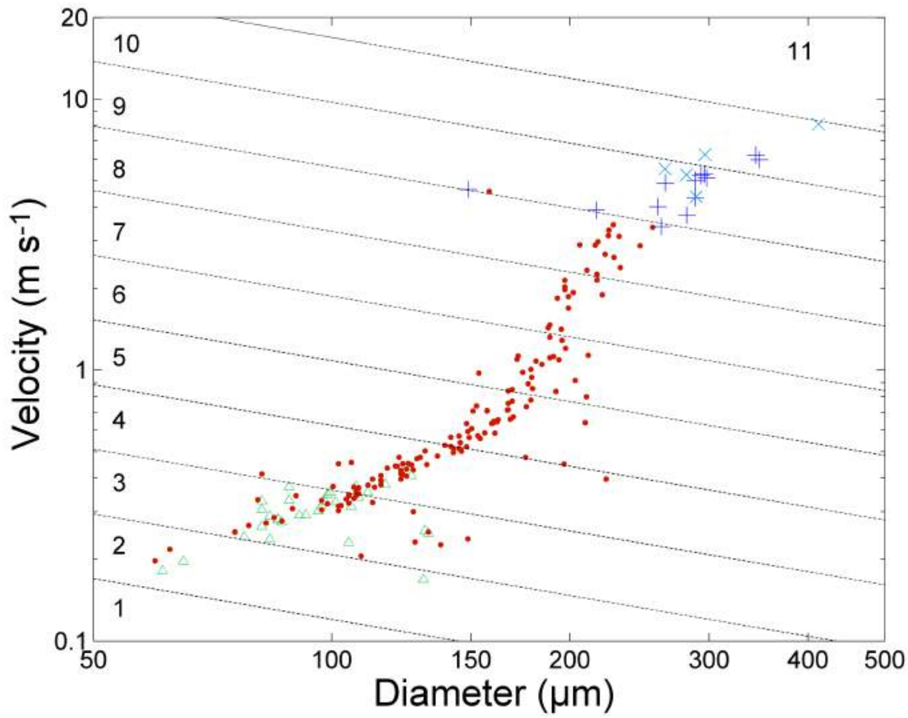


Figure 4.1: Relation between drop velocity and diameter (Teejet XR11003VK flat fan nozzle, 200 kPa, distilled water) and impact outcomes (△ adhesion, ● total rebound, × partial splashing and + total splashing) ranked in eleven energy classes for the artificial super-hydrophobic surface tilted of 30° from horizontal.

target, taking into account real evaporation and drag force during transport. Depending on the drop impact energy, impact outcomes succeed as described in Figure 2.1. The impact phase diagram (Figure 4.1) is divided into eleven energy classes. Class boundaries correspond to a constant Weber number. The first limit was set to a Weber number of 0.02. The first energy class contains drops with a Weber number below 0.02. Successive boundaries correspond to a three times increase of drop Weber number (Table 4.2). Boundary progression was chosen to collect enough drops to compute a representative probability of occurrence for each impact outcome within classes. Weber numbers are computed with static surface tension of distilled water and velocity modulus. Since surface tension is the main drop factor involved in impact outcome, the energy scale can be used for formulation comparison. Figure 4.2 presents volume distribution maps for six trials performed for two liquids at various surface orientations. Proportions of impact outcomes relative to the total volume are computed within eleven impact energy classes. For distilled water (Figures 4.2a,b,c), adhesion proportion decreases monotonically to reach zero for the sixth energy class ($We < 4.86$) on the horizontal surface (Figure 4.2a) and energy class 5 ($We < 1.62$) at 30° and 60° (Figure 4.2b and 4.2c respectively). Adhesion is gradually substituted by rebound below these thresholds. For instance, adhesion has 55% probability of occurrence in the third energy class on the horizontal surface (Figure 4.2a). Finally, for higher

Table 4.2: Correspondence between energy class labels and upper class boundaries We_W

Energy class label	Upper class boundary (We_W)
1	2.00E-02
2	6.00E-02
3	1.80E-01
4	5.40E-01
5	1.62E+00
6	4.86E+00
7	1.46E+01
8	4.37E+01
9	1.31E+02
10	3.94E+02
11	inf

Weber numbers, rebound is substituted by splashing. The rebound/splashing boundary is sharper than the adhesion/rebound transition. A splashing threshold is located between the eighth and ninth energy class for 0° (Figure 4.2a) and 30° (Figure 4.2b) but between ninth and tenth class at 60° (Figure 4.2c). For surfactant solution (Figures 4.2d,e,f), the situation is quite different. As already seen in Figure 4.1, total rebound is dramatically reduced in favor of adhesion. However, increasing surface angle induces a slight rise in rebound occurrence. As for distilled water, the fragmentation threshold is reduced with angle increase (eighth class at 60°, Figure 4.2f). Due to reduction of observed droplets with increasing surface angle (Figures 4.1), some classes are empty in the measurements (Figure 4.2f).

4.6.3 Retention by blackgrass leaf

The number of droplet impacts was quite low during these experiments for practical reasons. Interpretations are then difficult but the trends can however be outlined. The probability of adhesion at first impact is in the low tens whatever leaf angle for distilled water (Table 4.3). A slight growth of rebound proportion is observed with increasing leaf angle. Fragmentation proportion decreases accordingly, essentially in the Cassie-Baxter wetting regime. For surfactant, adhesion proportion is in the low twenties, with a slight decrease with increasing leaf angle. Rebound is non-existent on horizontal blackgrass leaf, measurements that may be related to low number of droplets in the relevant energy class for this trial. About 60% of spray volume splashes. On a horizontal surface, a high proportion of partial splashing is corroborated by the absence of rebound. By increasing leaf inclination, total splashing (Cassie-Baxter wetting regime) takes over partial splashing (Wenzel wetting regime) because of the lower normal velocity component, which increases splashing threshold energy.

The epidermis outermost layer of a blackgrass leaf is comprised of hairs and a structure

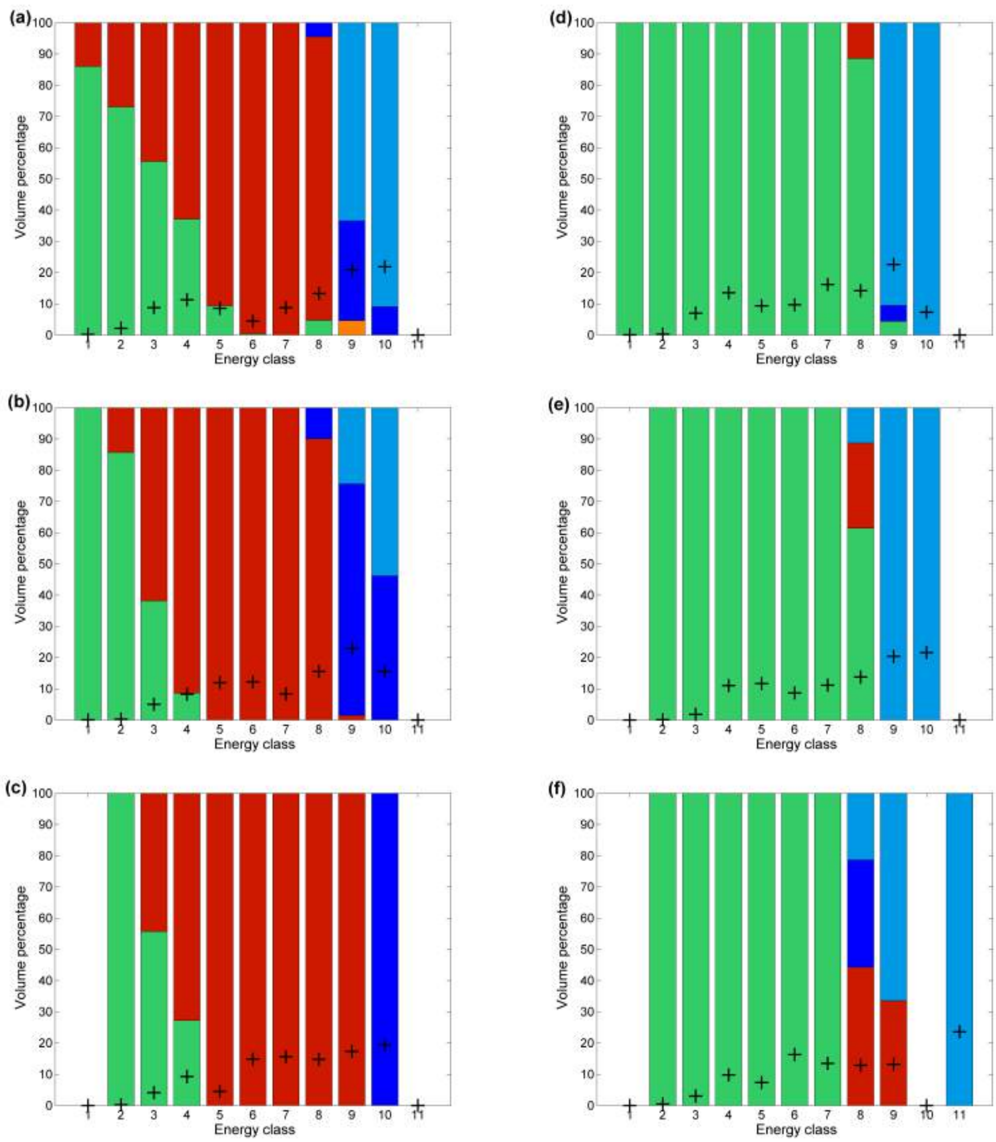


Figure 4.2: Impact outcome probability as a function of energy classes on artificial superhydrophobic surface (green: adhesion, red: total rebound, orange: partial rebound, dark blue: total splashing and sky blue: partial splashing), + volume proportion of each energy class relative to total volume observed before impact: (**a**-**b**-**c**) distilled water, (**d**-**e**-**f**) Break-Thru ®S240 at 0.1% V/V in distilled water, (**a**-**d**) horizontal surface, (**b**-**e**) 30° surface angle and (**c**-**f**) 60° surface angle.

of unidirectional grooves. This specific leaf roughness pattern clearly affects drop impact behavior compared with an artificial surface with a regular pyramidal roughness pattern. First, a slight occurrence of partial rebound is only observed on a leaf inclined at 30° for both liquids, which seems to correspond to the mean hair inclination on a blackgrass leaf. Secondly, fragmentation outcomes are directional and symmetrical since secondary droplets are ejected preferentially in both ways along surface grooves. All this highlights the variability at the leaf scale.

Table 4.3: Spray features immediately before impact on black-grass leaf with an anisotropic roughness pattern (merged from five sprayings).

	Distilled water			0.1 % V/V Break-Thru ®S240		
Surface angle α, [$\circ$]	0	30	60	0	30	60
Number of droplets at impact (N)	42	29	25	22	33	12
$N \cdot \cos\alpha$	42	36	21	22	19	11
Total droplet volume (V), $10^{-10}\ m^3$	1.4	1.4	0.9	0.6	1.7	0.3
$V \cdot \cos\alpha$	1.4	1.2	0.7	0.6	0.5	0.3
DV50, [μm]	230	213	265	230	269	218
Adhesion, [$\%vol.$]	2.7	13.7	5.8	17.5	19.6	12.3
Rebound C-B, [$\%vol.$]	25.1	34.1	46.8	0.0	9.0	3.1
Rebound W, [$\%vol.$]	0.0	2.8	0.0	0.0	6.5	0.0
Splashing C-B, [$\%vol.$]	70.1	49.4	38.3	39.1	61.4	63.1
Splashing W, [$\%vol.$]	2.1	0.0	9.1	43.4	3.5	21.5

4.6.4 Surface comparison

From the comparison of results for both surfaces (Table 4.1 and 4.3), increasing surface angle leads to increased rebound proportion for distilled water. The splashing energy threshold is lower on a blackgrass leaf, which increases splashing and decreases rebound volume proportions accordingly. As expected, surfactant increases adhesion at first impact compared to distilled water. The effect is more pronounced on an artificial surface than on the blackgrass leaf surface. Rebound is almost annihilated on both surfaces by decreasing DST. Rebound is replaced by adhesion on a synthetic surface and by fragmentation on the leaf surface, which was not expected. Nevertheless rebound proportion increases with increasing surface angle on both surfaces. Splashing energy threshold is also reduced owing to the directional roughness patterns of the leaf surface. The amount of liquid left on the surface after a splashing in the Wenzel regime is not negligible in the overall retention by the plant as this impact outcome occurs always for larger droplets, which represents a huge part of the total volume despite their lower occurrence. It could be interesting to relate the impact outcomes with the overall retention in further studies.

4.7 Conclusions

An experimental technique for investigating droplet behavior at impact was proposed to guide the improvements of spray application technologies needed in the context of precision farming. Concerning spot spraying, the discontinuous nature of application drives the development of small nozzles able to target a single plant. For such a small area, there is a temptation to use bigger droplets directed straight downwards to be less prone to drift and offer a better control of their trajectory toward the target, what may be highly detrimental to retention. A complete understanding of the behavior at impact of these droplets as a function of the plant surface and architecture is therefore highly necessary to choose the optimal compromise between droplet size, speed and ejection angle.

In this paper, the technique has been used to investigate how the spray application features may influence spray retention efficiency depending on target properties. The broad droplet size and velocity distribution of a hydraulic nozzle was used to explore a wide range of impact energy classes. The emphasis was set on the effect of droplet impact angles since a wide range of orientation can be encountered during spray application because of droplet trajectory and leaf angle variabilities. At first glance, increasing leaf angle reduces the surface area available to droplet capture by plants, which reduces retention. Droplet impact behavior is modified since surface tilt induces a tangential velocity component and, consequently, a reduction of the normal component. Reduction of the normal velocity component mitigates transition from the Cassie-Baxter to the Wenzel wetting regime during impact on a regular roughness pattern surface. A blackgrass leaf that presents an anisotropic roughness pattern favors fragmentation compared to the artificial surface where the rebound proportion is higher. Direct adhesion represents a low spray volume proportion whatever the surface tested except when using the super-spreader on an artificial surface. In general, direct adhesion is almost constant with increasing surface angle. For distilled water, fragmentation proportion decreases with increasing surface angle on both surfaces. Fragmentation is essentially comprised of total splashing.

Treating grass weeds with a predominant vertical leaf orientation such as blackgrass appears to be very difficult using sprays directed more or less vertically downwards. If bigger droplets are preferred to gain trajectory controllability, a super-spreader is highly recommended to reduce losses on these superhydrophobic targets. An angled spray for maximizing the impact occurrence on the leaf should be used to further improve retention.

CHAPTER 5

Comparison between artificial and wheat surfaces and assesment of herbicide formulations retention efficiency on black-grass leaf surfaces

5.1 Chapter objectives and outline

This chapter aims at highlighting the potential of the experimental method proposed in the chapter 3 and 4. It gathers results from 2 conference proceedings. Firstly, a comparison of the spray impact behaviour on the artificial surface with its behaviour on outdoor grown wheat leaves is performed (section 5.3). Since the wettability of both surfaces is similar, the question is to asses the variability of droplet impact behaviours and to highlight the relevance of using this artificial surface as standard for ranking application techniques. In the second section (section 5.4), it is investigated whether increased black-grass weeding efficiency by reduced volume per hectare observed during 2010 Arvalis field trials may be related to increased pesticide application method efficiency. Weed control trials at early stage during 2010 (Perriot and Denis, 2011) in wheat resulted in an increased efficiency on blackgrass at half pesticide dose when spraying at 65 L/ha comparatively to 150 L/ha volume. At 65 L/ha, black-grass control was also improved by adjuvant use but only a faint effect was observed because of too high control efficiency at 65 L/ha. An explanation may lie in the theories of droplet impacts on difficult-to-wet targets. In this chapter, these 2 conference papers are summarised in order to highlight the main original contributions.

5.2 Appended publications

Autors: Massinon Mathieu and Lebeau Frédéric
Year: 2012
Title: Comparison of spray retention on synthetic superhydrophobic surface with retention on outdoor grown wheat leaves
Status: Conference Proceedings
Conference Name: Aspects of Applied Biology **114**, International Advances in Pesticide Application, pp. 261-268
Place: Hof Wageningen, The Netherlands
URL: http://hdl.handle.net/2268/108367

Autors: Massinon Mathieu, Denis Thierry, Perriot Benjamin and Lebeau Frédéric
Year: 2012
Title: Assessment of pesticide application method efficiency by high-speed image analysis
Status: Conference Proceedings
Conference Name: International Conference of Agricultural Engineering CIGR-AgEng2012
Place: Valencia, Spain
URL: http://hdl.handle.net/2268/124786

5.3 Comparison of impact behaviours between artificial and wheat leaf surfaces

5.3.1 Introduction

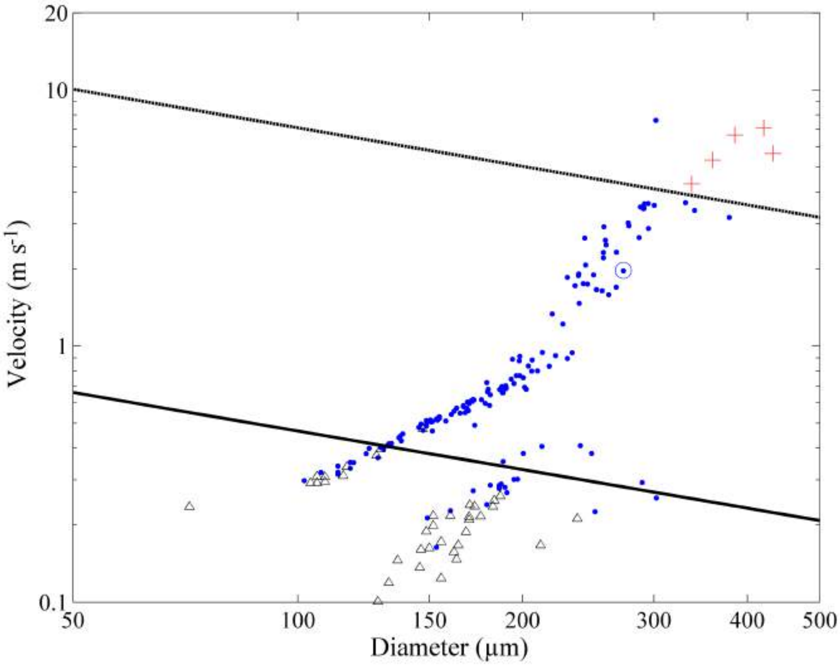
A method has been designed to test the retention of drops generated by a moving agricultural nozzle using high speed imaging both on synthetic and leaf surfaces (Chapter 3). The method allows a precise investigation of spray retention by a characterisation of impact speed, drop diameter and impact behaviour. This paper presents a comparison of the spray impact behaviour on the synthetic surface with its behaviour on outdoor grown wheat leaves fixed on a microscope slide for various concentrations of a non-ionic surfactant (0, 0.025, 0.05 and 1% V/V). Leaf surfaces are excised from outdoor grown wheat (*Triticum aestivum* L. cv Julius) and fixed on a microscope slide with a double-sided tape. Manipulations of leaf surfaces are made with care using latex gloves to avoid modifications of surface properties. The tip and base of the leaves were tested. Results have been merged to be representative of the whole leaf.

5.3.2 Results and discussions

Distilled water

Figure 5.1 presents spray experiment results as a function of drop diameter and the impact velocity on a log-log scale graph for distilled water. Each symbol represents the drop impact outcome. Most of the drops of the spray are scattered along a sigmoid curve because of the deceleration from initial speed. For diameters below $200\mu m$, drops impact the surface near their terminal velocity after covering the 50 cm height distance. For diameters above $200\mu m$, drops are impacting at a higher velocity because of their higher Stokes relaxation time. On the Teflon superhydrophobic slide (Figure 5.1 A), the different outcomes are sharply separated by Weber boundaries. Outcome distributions are characteristic of the theoretical high Wenzel roughness behaviour. Only a few drops were deposited in the Cassie-Baxter regime and most drops bounced. Some drops came back in the field of view and undergo a secondary impact. The most energetic drops splash at impact. At first glance, the behaviour on the wheat leaves presents a much wider variability (Figure 5.1 B). However, clear similarities appear when examined more closely. Rebound still occurs for a wide range of Weber numbers but deposits appear probably because of the natural surface heterogeneity. This may also be related to dirt as it is well established that superhydrophobicity is very sensitive to any soiling of the surface. Indeed retention tests showed a clear difference between outdoor and greenhouse grown plants. The splashing boundary is quite similar, what is consistent is the fact that this boundary is known to be less related to the surface properties than to the fluid rheology.

(A)



(B)

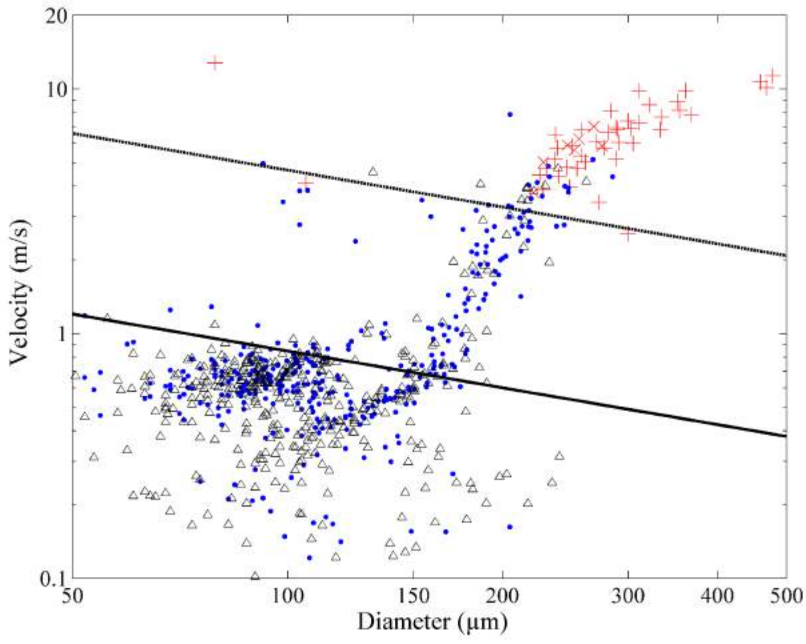


Figure 5.1: Outcomes after drop impact for distilled water on Teflon slide (**A**) and winter wheat leaf (**B**). △ adhesion, • rebound, ○ pinning rebound, × pinning fragmentation and + complete fragmentation. – Weber number of transition between adhesion and rebound (A: We=0.2; B: We=1),- - Weber number of transition between rebound and fragmentation (**A**: We=70; **B**: We=30).

Surfactant formulations

A trisiloxane tank-mix adjuvant (Break-Thru S240, Evonik Industries AG) was sprayed on target surfaces at 3 concentrations in distilled water: 0.025, 0.05 and 0.1% v/V. Distilled water was tested as a reference. At least five replicates were conducted for each formulation/surface combination. Static surface tension was measured with the sessile drop method in five replicates (Table 5.1). The latter was used to calculate Weber numbers for transitions between impact types. Figure 5.2 presents the effect of different surfactant concentrations on both surfaces. On the Teflon slide (Figure 5.2A,C,E), increasing the surfactant concentration leads progressively to the vanishing of the rebound events. Complete extinction is observed for the highest concentration tested, 0.1% surfactant solution, that corresponds to the manufacturer recommendation. The Weber number characterising the adhesion/rebound transition increases accordingly. It can also be observed that at 0,025% the remaining rebound events were surrounded by adhesions. The high Weber number adhesion probably corresponds to the pinning caused by a Cassie-Baxter to Wenzel transition resulting from the impact energy and surfactant effect. Splashing occurred

Table 5.1: Static surface tension (five replicates, CAM200, KSV) and volumetric percentages in impact classes for each formulation

Formulation		Distilled water	BT 0.025%	BT 0.05%	BT 0.1%
Static surface tension (N/m)		0.072	0.023	0.022	0.022
	%vol adh.	4.26	28.83	38.68	52.63
Teflon slide	%vol reb.	70.12	12.27	2.58	/
	%vol frag.	25.62	58.90	58.74	47.37
	%vol adh.	25.06	19.45	26.85	38.60
Wheat leaf	%vol reb.	27.32	19.91	13.77	12.60
	%vol frag.	47.62	60.64	59.38	48.8

at a slightly lower Weber number with increasing surfactant concentration. On the wheat leaf (Figure 5.2B, D, F), a higher variability of the outcome of impacts was observed but rebound disappeared for lower Weber numbers. The observed variability was not found related on the location of the impact on the leaf but seems related to variability between leaves. It is suspected that it originates from fouling differences between outdoor grown leaves. On both surfaces, splashing is replaced by a pinning fragmentation at the higher surfactant concentration.

5.3.3 Conclusions

Results clearly show high similarities between drop behaviour during impact on the synthetic superhydrophobic surface and wheat leaves. The possible different outcomes were observed on both surfaces and were consistent with recent theoretical developments on superhydrophobic materials. The use of synthetic surface is more suited to identify

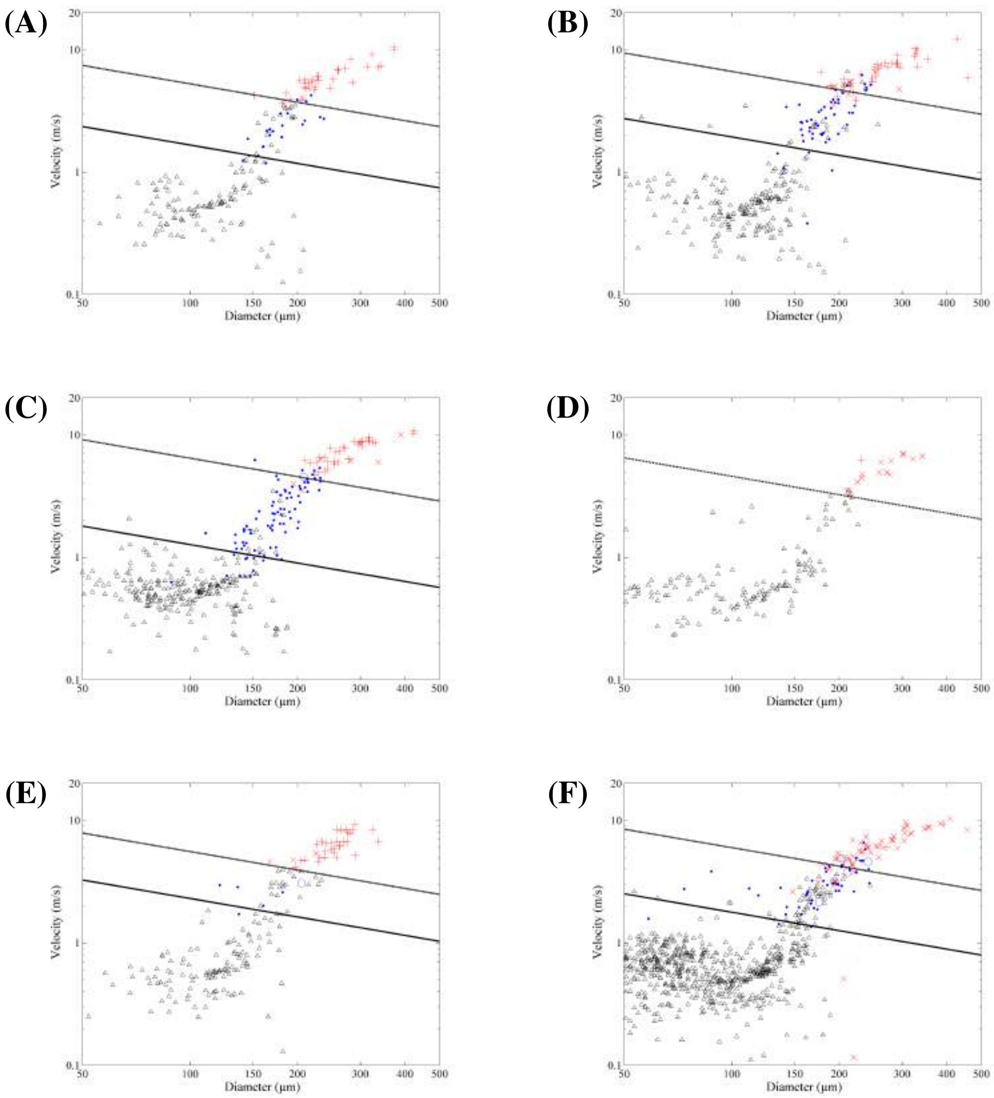


Figure 5.2: Outcomes after drop impact. (**A**, **C**, **E**) Teflon slide, (**B**, **D**, **F**) Wheat leaf, (**A**-**B**) 0.025% surfactant, (**C**-**D**) 0.05% surfactant and (**C**-**F**) 0.1% surfactant. △ adhesion, • rebound, ○ pinning rebound, × pinning fragmentation and + complete fragmentation. – Weber number of transition between adhesion and rebound (**A**-**F**: We=12; We=6; We=24; We=17; /, We=15), - - Weber number of transition between rebound and fragmentation (**A**-**F**: We=120; We=180; We=140; We=200; / ; We=170), - - Weber number of transition between adhesion and fragmentation (**D**: We=100).

and quantify precisely the effect of the surfactant because of lower variability. Results show the relevance of a synthetic surface for use as reference for the assessment of spray application efficiency. The reference surface avoids the natural variability of leaves and is therefore more suited to conduct comparative assessment of formulation retention performance. Future work will focus on different surfactants presenting various dynamic surface tensions (DST) as the time scale of drop deformation during impact is very low (< 5 ms). As a result, attention must be paid to the value of DST to be used to accurately predict impact outcome. Other rheological properties will also be investigated as the use of non-Newtonian fluids is a promising way to reduce fragmentation. It was observed that wheat leaves present an anisotropic surface that influences the impact outcome, satellite drops being directed preferentially along the main axis. Consequences on retention should be studied further. Moreover leaf angle effects should also be studied further (this was done ine chapter 4). Last but not least, fouling is suspected to reduce drastically rebound in practical application on outdoor grown leaves, what was observed in previous retention studies.

5.4 Assessment of herbicide formulations retention efficiency on black-grass leaf surfaces

5.4.1 Introduction

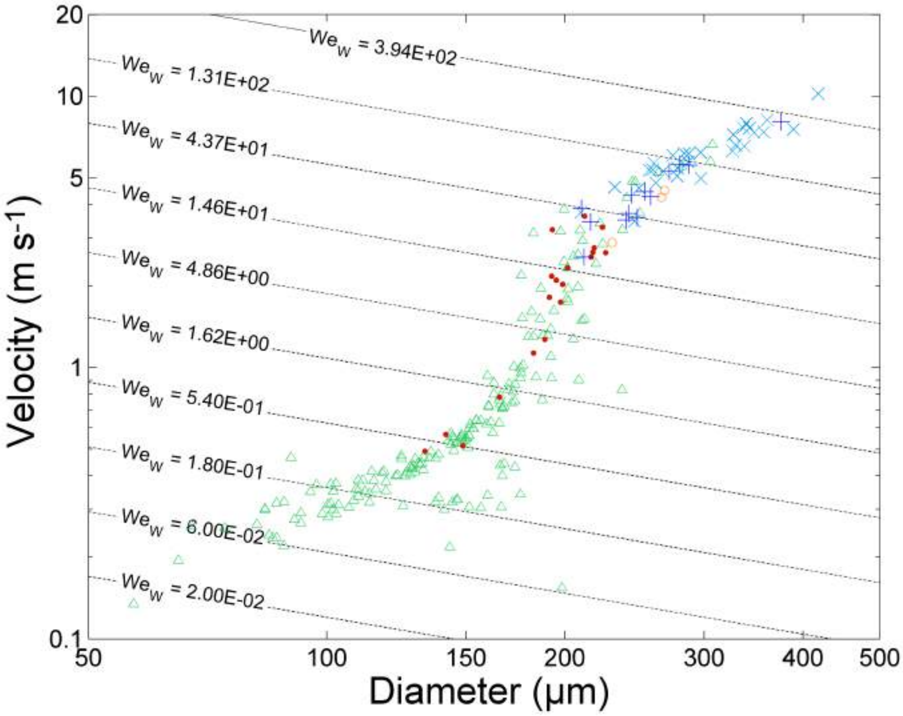
An herbicide (Archipel®[125 g/ha] + Actirob®[1 L/ha]) has been applied at two volumes per hectare in laboratory spray trials to explain the results obtained with those in fields trials. Firstly, an usual volume of 150 L/ha was applied with a XR11002 nozzle (Teejet®) at 0.2 MPa pressure. Nozzle forward speed was set to 5.2 km/h. Secondly, a reduced volume of 65 L/ha was applied with a XR110015 nozzle (Teejet®) at 0.15 MPa. Nozzle forward speed was set to 7.7 km/h. In addition, the effects of adjuvants (Epsotop®[1%] + Heliosol®[0.5%]) have been studied at a reduced volume of 65 L/ha. Target surfaces were excised leaves excised from indoor-grown blackgrass and fixed on a U-shaped bracket. Spraying was performed on the adaxial face. Leaves were handled taking care not to alter their surface. Ten spraying were performed with a new leaf for each trial for a total of thirty sprayings.

5.4.2 Results and discussions

The impact outcomes observed on blackgrass leaf for both spray volumes as a function of droplet diameter and velocity are presented in figures 5.3(A) and 5.4(A) where each point represents a drop impact. The impact phase diagram is discretized into 11 energy classes. The class boundaries correspond to a constant dimensionless Weber number of the drop before impact. The first limit was set to a 0.02 Weber number and higher limits follow a times 3 progression for a constant spacing in log/log scale. The water Weber number (We_W) was computed with the water surface tension value 72.2 mN/m. This way, we create an energy scale that depends only on the physical parameters of the drops. Energy class number 11 was the higher impact energy class observed. For each energy class, the volume of droplets for each impact outcome is computed and normalized regarding to the total volume in this energy class. These proportions are finally presented in stacked histograms (Figure 5.3(B) and 5.4(B)).

Volumetric percentage in each impact class is computed on the basis of observed droplet diameters before impact. This method that allows a quantification of the proportion of the different outcomes during impact must be interpreted only as indicative because the number of drops used to compute them is quite low. However, an increase of the adhesion proportion was observed at a reduced volume of 65 L/ha (Table 5.2), which is corroborated by comparing Figure 5.3 and 5.4. The rebound proportion remained almost unchanged at respectively 6 and 7% but the fragmentation decreased in return. This resulted mainly from the volume median diameter (VMD) that was slightly decreased by the reduction

(A)



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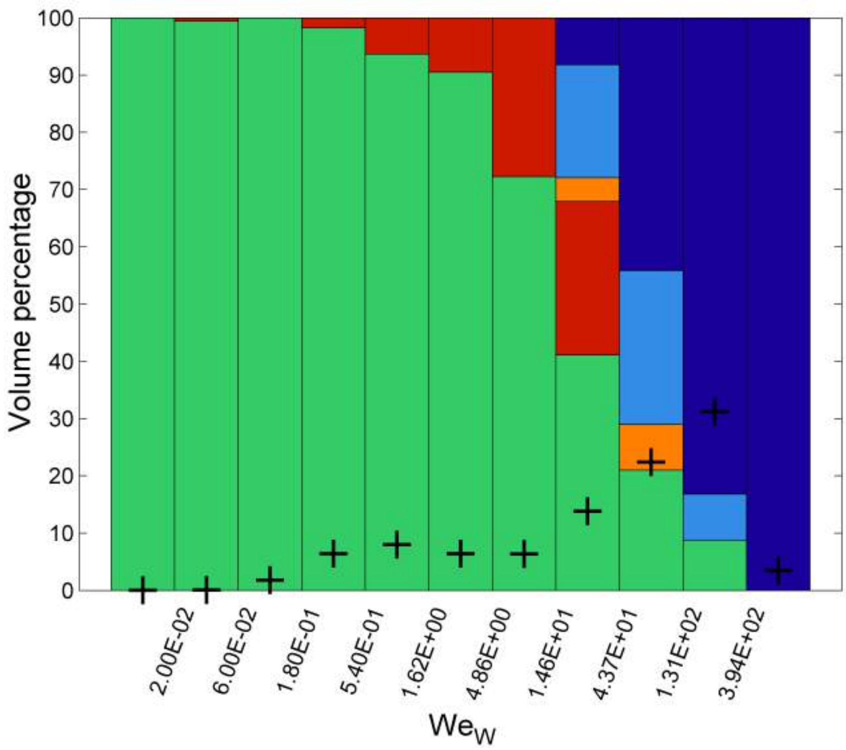


Figure 5.3: Outcomes after droplet impact on black-grass leaf for 150 L/ha application without surfactants. Droplet impact phase diagram (**A**) and corresponding impact probabilities in each energy class for each impact outcomes (**B**). △ adhesion, • rebound, ○ pinning rebound, × pinning fragmentation and + complete fragmentation. + is the relative volume of each energy class.

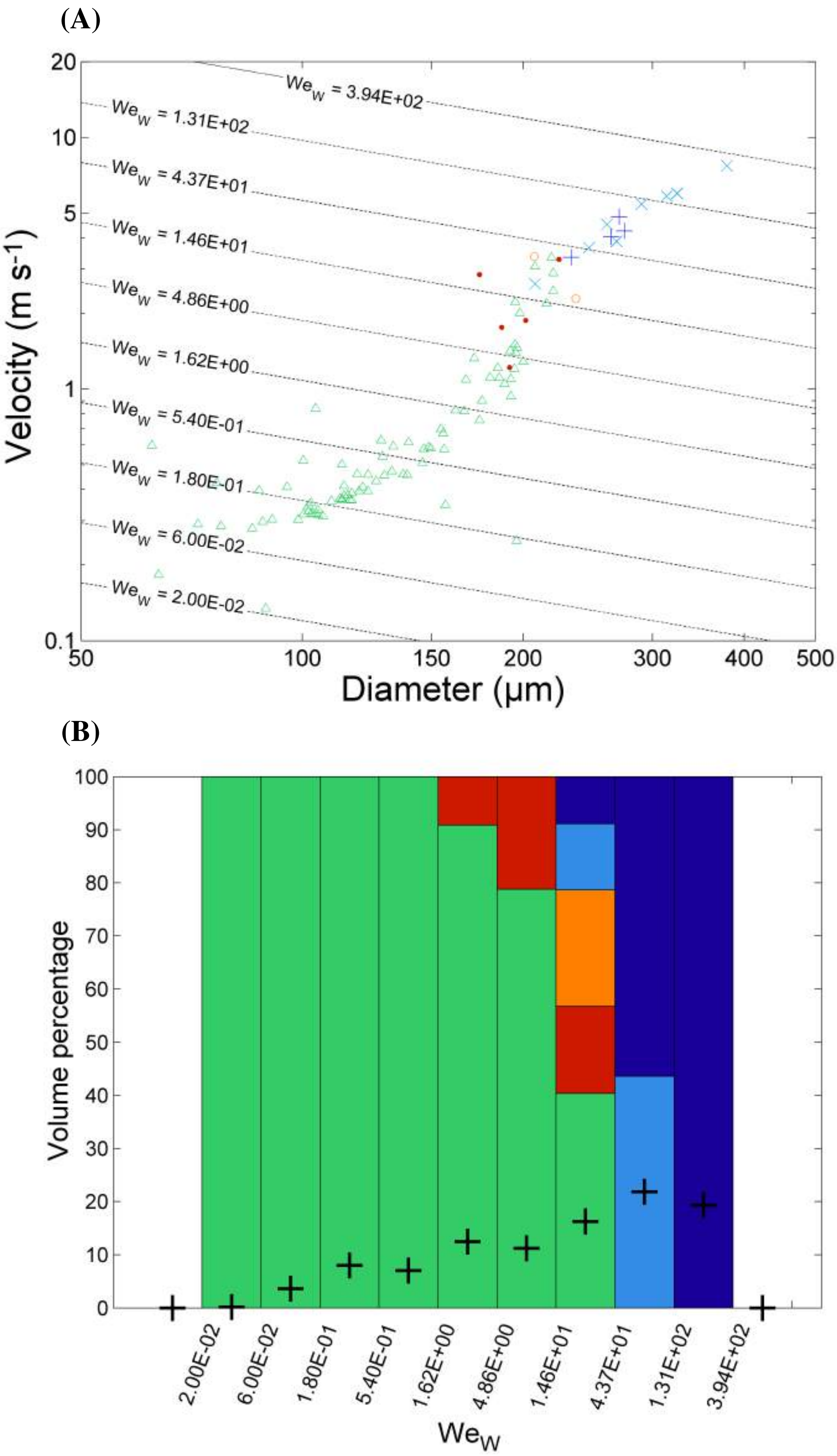
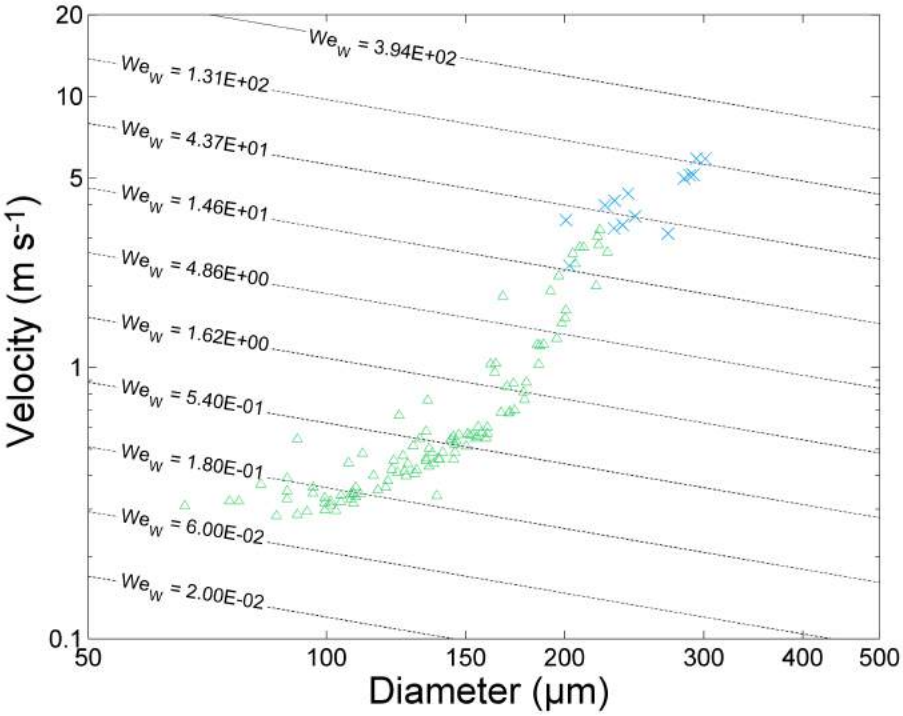


Figure 5.4: Outcomes after droplet impact on black-grass leaf for 65 L/ha application without surfactants. Droplet impact phase diagram (**A**) and corresponding impact probabilities in each energy class for each impact outcomes (**B**). △ adhesion, • rebound, ○ pinning rebound, × pinning fragmentation and + complete fragmentation. + is the relative volume of each energy class.

(A)



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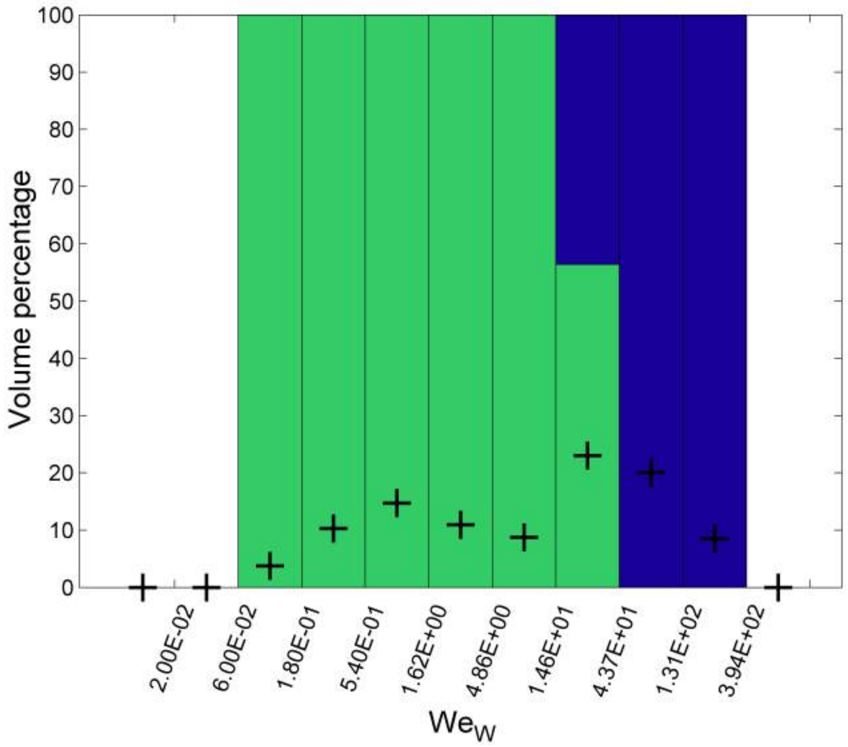


Figure 5.5: Outcomes after droplet impact on black-grass leaf for 65 L/ha application with surfactants. Droplet impact phase diagram (**A**) and corresponding impact probabilities in each energy class for each impact outcomes (**B**). △ adhesion and × pinning fragmentation. + is the relative volume of each energy class.

to 65 L/ha because of nozzle and pressure changes. The use of the adjuvants resulted in a complete disappearance of the rebound and Cassie-Baxter regime from trials (Figure 5.5). With adjuvants, the splashing occurred for a lower energy class but the proportion of fragmentation decreases because of reduced VMD caused by dynamic surface tension decrease.

Considering only the proportion of adhesion, the relative increase between 150 and 65 L/ha was about 18% in laboratory tests, which is consistent with the efficacy increase highlighted with 2010 field trials. The proportion of drops undergoing a fragmentation in the Wenzel regime during impact (×) was reduced at 65 L/ha. As part of the drop then sticks on the surface and increases, this class may also affect retention but the proportion remaining on the leaf has still to be investigated.

Table 5.2: Summary of data extracted from imaging process averaged on ten sprayings.

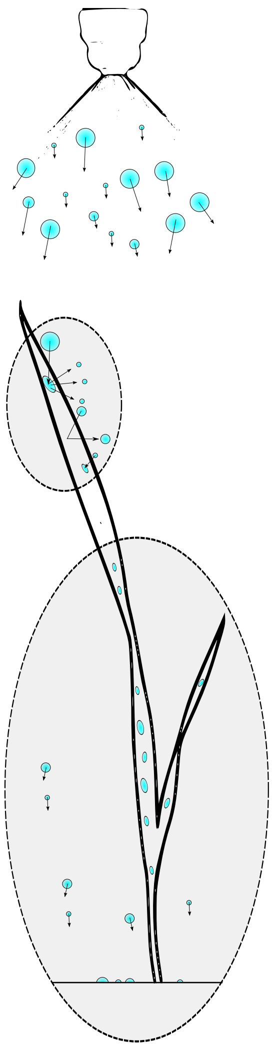
Formulation	Without adjuvants		With adjuvants
Applied volume [L/ha]	150	65	65
Adhesion, % vol.	38	45	61
Rebound(Cassie-Baxter), % vol.	7	6	0
Rebound(Wenzel), % vol.	2	3	0
Fragmentation (Cassie-Baxter), % vol.	12	12	0
Fragmentation (Wenzel), % vol.	41	34	39
Number of droplets	248	100	122
VMD (μm)	240	206	192
Volume observed (μL)	0.893	0.259	0.265

5.4.3 Conclusions

On one hand, the increased efficiency observed in the Arvalis 2010 field trials at 65 L/ha is consistent with the small VMD change resulting from smaller nozzle caliber that allows 18% more volume of small drops to adhere at primary impact on the difficult-to-wet blackgrass leaf. However, the effect is quite faint. The efficiency improvement at reduced volume was not observed anymore in 2011 field trials, as both volumes showed bad efficiencies. On the other hand, the adjuvant interest was emphasized in the laboratory as the results clearly highlighted that the effect of the adjuvant use on retention is far higher that the effect of volume per hectare reduction but field trials where too efficient to mark any significant difference. It is clear that the response to the volume depends on numerous parameters such as the plant sensibility to sulfonylureas. As spray application efficiency in the fields relies on multiple, often non-linear factors, it remains difficult to explain field observations on the basis of a single variable as spray retention. However, the developed method increases the understanding of the interaction between physicochemical properties, drop and target characteristics. It can be used to guide future field trial setup. Effect of spray angle, relation between impact and retention for the different impact outcomes are subject of further research to improve the understanding of parameters that may affect the efficiency at the field level.

CHAPTER 6

Study of retention variability on an early growth stage herbaceous plant using a 3D virtual spraying model



"The purpose of models is not to fit the data but to sharpen the questions."
Samuel Karlin (1983)

6.1 Chapter objectives and outline

Existing models of spray retention are either based on statistical fittings of huge data from single droplet impaction studies (Forster et al., 2005) or on the use of semi-empirical laws originating from systematic physical studies of droplet impact on artificial surfaces (Dorr et al., 2014). Some models include the plant architecture but have a poor droplet impact description (Cox et al., 2000). In any cases, retention models try to extend results obtained in specific conditions to more complex situations and fails to provide reliable results since there is no evaluation of the inherent variability of the retention process. This chapter deals with the integration of previous experimental data into a virtual spray model, especially the droplet impact probability histograms proposed in chapter 4. The model computes the interception of droplet trajectories with the realistic 3D plant architecture and assigns an impact behaviour to each intercepted droplet based on outcome probabilities according to the droplet impact energy and its incidence angle.

Some assumptions are made during this modelling step. The model considers only primary droplet impacts since droplet recapture is unlikely and would represent a very small proportion of the total retention by the plant when treating small plants with slanted leaves with relatively low application volumes. Droplet diameters are derived from droplet size measurements. Droplet trajectories are assimilated as straight lines immediately above the 3D plant model, which means that air advection/turbulence is not included in the model. Their directions are derived from the observation of droplets produced by a moving agricultural nozzle (chapter 3). Another assumption concerns the edge effects within the intersection algorithm, *i.e.* droplet diameter is not considered in the ray/triangle intersection computation. The modification of the droplet behaviour subsequent to an impact at the edge of a leaf is neither taken into account.

The proposed approach enables systematic parametric studies to understand and assess the importance of each factor on the final retention. It also provides an estimate of the variability of retention at the plant scale. The variability of retention levels by the weed plants results in the application of sublethal doses. If this recursively happens, a weed population is able to quickly develop high levels of resistance as multiple weaker mechanisms (minor alleles) are selected and enriched (Neve and Powles, 2005).

6.2 Appended publication

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6.3 Abstract

A model predicting the spray droplet interception and retention by a single virtual plant has been developed. The model was based on three main experimental inputs: the 3D architecture of a barley plant, the spray quality and the droplet impact behavior. Two contrasted formulation scenarios, limits of the common range covered by pesticide application in terms of surface tension, were tested by changing the droplet behavior at impact in the model. Simulations were undertaken for studying the variability of spray retention resulting from spray quality, applied volume and plant size for a difficult-to-treat target. Results showed that the spray retention efficiency ranged from 6.8% to 96.6% of a theoretical full adhesion scenario, where all intercepted droplets were captured, according to spray quality for the two formulation scenarios tested. Average retention increased with increasing spray fineness, applied volume per hectare and plant size. Variability of deposits, evaluated using the coefficient of variation of simulated retentions, was found to be a function of the mean droplet density according to $CV \propto N^{-0.68}$, where CV is the coefficient of variation and N the number of droplet per square centimetre. Variability was also found to be a function of the plant size according to a relation $CV \propto S^{-0.5}$, where S is the total leaf area of the plant model. The variability of deposits increased with decreasing spray fineness, applied volume per hectare and plant size because of the reduced number of droplets contributing to retention. Wetting properties greatly influenced retention but surprisingly poorly influenced the variability of deposits. Such a modeling approach that is capable of an independent investigation of the influence of various parameters on spray retention can be used to improve understanding of application methods and adjuvants that could help minimizing development of resistance in problematic weed species.

6.4 Introduction

The economically and environmentally driven reduction of applied doses of agrochemicals must be performed carefully to keep high efficacy. This must be done according the plant species and growth stage as some operating choices on a given target can be inefficient and present high efficacy variability (Knoche, 1994). For instance, the variability of pesticide deposits on target plants, which could be used as indicator of application efficacy, may increase when using large droplets on small targets for comparable application volumes (Miller et al., 2010), and this variability tends to increase with reducing application volumes (Butler Ellis et al., 2007). The variability of spray deposits arise from the application technique, e.g. the volume per hectare applied, the droplet size distribution, droplet impact velocity and droplet directions in relation with the plant and canopy architecture because some misdirected droplets may miss their target. Another source of variability originates from the different droplet impact behaviors that may occur on a leaf surface; mainly adhesion, rebound and splashing, depending on the surface hydrophobicity and roughness, its orientation and the droplet impact energy and surface tension. When using agrochemicals for weed control, the variability of applied doses can lead to the selection of naturally resistant individuals in the weed population because of the insufficient dose received for killing the plant (Henriet and Maréchal, 2009). Faced to the great complexity of a spray application due to the number of factors involved that are inextricably linked, comprehensive spray retention trials become a resource consuming task that could be overcame by using a simulation approach (Nairn et al., 2013).

Mathematically and physically based models are developing increasingly to understand, predict and optimize the spray application of plant protection products. The first models that focused on the droplet transport were based on the resolution of the ballistic droplet motion equations (Marchant, 1977). Then trajectory models were improved by including the atmosphere turbulence statistics in random-walk models (Holterman et al., 1997; Walklate, 1987) or using a computational fluid dynamics modeling taking into account drift (Reichard et al., 1998). However, such models have a simple assumption of the droplet impact behavior on leaf surfaces, that is to say if the plant intercepts the droplet it is always retained, or the droplet impaction is seen as a binary event; adhesion or splashing with transition boundary between them depending on Ohnesorge and Reynolds numbers (Vander Wal et al., 2006). The description of the plant architecture is often made using geometric fittings (Cox et al., 2000) or using existing functional-structural models (Dorr et al., 2008). The development of fast and low cost 3D scanning systems could be an interesting alternative for modeling purpose (Paulus et al., 2014). More particularly, such devices could provide the real architecture at the plant scale, even for early growth stage weeds that present small, stiff and superhydrophobic leaves, on which a treatment could be very variable.

Spray-canopy interaction models are being developed taking advantage of 3D scanning systems including the droplet behavior at impact. Spray retention models are based on the possible behaviors of droplets during impaction on leaf surfaces including physical parameter known to determine the droplet-leaf interactions (Massinon and Lebeau, 2013; Taylor, 2011). A possible approach consists on using process-driven models that include experimental correlations between physicochemical parameters and the droplet impact behavior on leaf surface (Dorr et al., 2014) or using an universal spray adhesion model based on a huge experimental studies of droplet impaction using microdrop generator (Forster et al., 2005) on various leaf surfaces. While these approaches can be easily generalized for any new spray scenario, discrepancies between predicted and measured retentions may arise when using the model in out of the range from which they have been designed for, for instance on hairy leaves. Such models focus on the mean spray retention levels without consideration of the variability linked to a spray application of pesticide, in which some agronomic consequences are not perceived i.e. herbicide resistance. Finally, the behavior of the whole range of spray droplets could be studied on an artificial or natural superhydrophobic surface using high speed imaging (Massinon et al., 2014; Massinon and Lebeau, 2012b). Using this approach, the probability of droplet impact for each possible outcome is assessed depending on the droplet impact energy, the leaf surface wettability and the leaf orientation. This approach highlights the coexistence of different droplet impact outcomes for similar impact energy that may arise from the spatial variability of leaf surfaces. This approach makes use of the real spray impaction behavior on a given target surface but requires experimental data for every new leaf type, impaction angle and spray formulation.

Using the latter approach, a spray retention model based on spray droplets behavior at impact on 3D plant architecture is developed in this paper. The in silico model is used to independently investigate the role of some key factors expected to affect spray retention variability on a difficult-to-treat plant, i.e. superhydrophobic leaf surface coupled with small and slanted leaves. It has been chosen as a combination of a typical droplet behavior on superhydrophobic surface and herbaceous plant architecture with thin slanted leaves. Particularly, the effect of plant size as a function on the spray quality and the applied volume on spray retention will be discussed for two extreme wetting scenarios, called low and high wetting scenarios in this paper. The target surface is artificial in order to focus on the contribution of the application technique and the plant architecture to the overall variability of spray retention. The final goal being to assess the mean retention levels and the related variability resulting from the spray application technique and the formulation tested.

6.5 Materials and methods

6.5.1 Model overview

Models of droplet interception, impaction and retention have been developed to study the effect of involved factors and their interactions on the variability of spray retention by plant leaves. These models were integrated into an algorithm that requires three mains experimental inputs from laboratory measurements for computing spray retention (amount of product actually retained by the plant per leaf surface projected unit area): the plant architecture, the droplet size and velocity distributions and the spray droplet impact behaviors. The algorithm has been developed on a generic mathematical software package, Matlab®, and run on a standard personal computer.

6.5.2 Plant architecture

A DAVID Structured Light Scanner SLS-2 (DAVID Vision Systems GmbH, Koblenz, Germany) was used to reconstruct a 3D plant model. It is composed of an industrial USB CMOS monochrome camera (1280 x 960 pixels, 25 FPS) with a focusable lens (12mm) and a HD video projector providing structured light patterns. This 3D system allows a scan size of 60-500 mm with accuracy up to 0.1% of the object size. The calibration was performed using the DAVID calibration panels set. An indoor grown barley plant at two leaf growth stage has been chosen to provide the 3D plant architecture model, a plant often used in laboratory retention trials. The scanning was performed using the DAVID Laserscanner Pro Edition 3 software. The plant was placed on an accurate custom made rotating table and scanned at 30° steps over 360°. The scanner used 58 time-coded white light patterns with phase shift which were oriented both horizontally and vertically. The result of a scan was filtered with a quality check implemented in the software. For every point of the cloud, a confidence value is computed based on the measured surface reflections. Points with low confidence level were removed. This parameter was set at 0.5 in the DAVID Laserscanner Pro Edition 3 software. Some data points belonging to the background were removed using the cleaning tool of the software for each scan. The alignment of the scans was also performed using the DAVID Laserscanner Pro Edition 3 software, using the imposed angle of rotation of the rotating table as constraint. The fusion algorithm is based on a fast pairwise surface registration (Winkelbach et al., 2006). One hundred point pairs between scans were created and 20 iterations were performed in the surface registration. During the fusion, the resolution was set at 4000 in the software, providing an expected vertex spacing of about 60 μm. The 3D plant surface was exported in STL format (STereo Lithographic) and was composed of a dense mesh of triangles comprised of 2 449 710 vertices and 816 570 faces (Figure 6.1). The reconstructed virtual plant was not watertight, which means that holes were not closed during the fusion of the different views. The scanning procedure provided high levels of microsurface details that were not essential in this study since they resulted in undesired surface orientation gradients (Kempthorne et al., 2015) that may skew the droplet incidence angle computation. In addition of this, a high density mesh required a higher computational time for the spray droplet interception algorithm (described below). The main objective was to obtain a realistic virtual representation of a whole herbaceous plant that can be used in an agricultural spray retention model as a reference for comparative simulations. The number of triangles of the 3D plant mesh was therefore reduced of a factor 1000 using the quadratic edge collapse decimation filter (Garland and Heckbert, 1997) implemented in MeshLab (free and open-source 3D mesh processing software) and resulted in a new mesh comprising 816 faces and 2448 vertices. Geometric features of the plant model before and after the mesh simplification are provided in Table 6.1. The projected leaf area relative to the vertical spray direction has been computed using image segmentation on the projected view of the plant model in the normal plane (ground). The simulation time was therefore reduced according to the same ratio. The mesh simplification reduced the total leaf surface area but preserved the overall shape of the plant. In consequence, the computed retention rates will also be smaller, which was not problematic from a comparative point of view of the simulations. Nevertheless, improvements of the surface reconstruction could be reached using the recent approach proposed by Kempthorne et al. (2015), which guarantees surface reconstruction with continuous gradient. Another interesting approach could be based on the Lindenmayer system (Prusinkiewicz and Lindenmayer, 1990) to provide a well characterized plant model that could be used as a standard for comparing existing spray retention models.

Table 6.1: Dimensional features of the 3D barley plant used in simulations.

Mesh simplification	No	Yes
Dimensions [x y z], cm	2.70 x 2.56 x 20.46	2.62 x 2.47 x 20.35
Total leaf area, cm^2	25.26	20.32
Projected leaf area, normal plane [0 0 1], cm^2	1.62	1.43
Number of triangular faces	816 570	816
Number of vertices	2 4497 710	2 448

6.5.3 Droplet features and virtual nozzle

Droplet size distributions of six flat-fan hydraulic nozzles were used to explore various common spray qualities (see Figure 1.1). The droplet size distributions were measured by high-speed shadow imagery 500 mm downwards the outlet of the nozzle (De Cock et al., 2015) with water. Table 6.2 shows reduced descriptors of the droplet size distributions. The

Figure 6.1: Reconstructed 3D model of a two leaf barley plant: (left) mesh of triangles comprised of 2 449 710 vertices and 816 570 faces, (right) mesh of triangles comprised of 2448 vertices and 816 faces.

choice of these nozzles/pressure combinations has been made according to the ISO draft standard (ISO 25358) for classification of droplet size spectra. These nozzles/pressures are expected to be used as boundaries between very fine (VF), fine (F), medium (M), coarse (C), very coarse (VC), extra coarse (XC) and ultra coarse (UC) classes. From these measurements, a virtual nozzle was built by drawing droplet diameters randomly until a given volume per hectare was reached using the Pearson system for random numbers (beta

Table 6.2: Reduced descriptors of the droplet size distributions for the six nozzles used in the simulations.

Nozzles and pressures	11001 at 4.5 bars	11003 at 3.0 bars	11006 at 2.5 bars	8008 at 2.0 bars	6510 at 1.5 bars	6515 at 1.5 bars
Class boundary	VF/F	F/M	M/C	C/VC	VC/XC	XC/UC
Dv10 [μm]	88	119	138	165	201	221
Dv50 [μm]	154	239	304	375	479	532
Dv90 [μm]	232	414	532	612	786	927

distribution). Random droplet diameters were generated to provide a good match with the initial size distribution parameters: the mean, standard deviation, skewness and kurtosis. Fitting a continuous distribution on the discontinuous measured droplet size distributions allowed generating the whole possible droplet diameters from spray application. Then, a virtual sprayed area was chosen at one square meter. Droplet coordinates were drawn within this area using uniformly distributed random numbers U(0,1000) in millimeters. The sprayed area was afterwards divided into a grid of squares of identical size. The size of the cells has been adapted to fit to the 3D plant model. Each grid cell contains a different droplet size distribution resulting in various applied volumes representative of the field spatial variability. Figure 6.2 shows, for instance, the variability between 144 droplet size distributions (12x12 grid) depending on the nominal applied volume per hectare. The coefficient of variation decreases as the nominal volume per hectare increases because the number of droplets increases. The spatial variability in applied volume is the first reason of variability in spray retention. Droplet velocity for each diameter was randomly drawn from a normal distribution N(μ, σ), where the mean μ was computed from droplet transport and evaporation equations (Guella et al., 2008) with still air hypothesis at 21°C and 55% RH, water droplets at 20°C with 16 m/s of initial velocity and the standard deviation σ was chosen at 0.1 m/s based on droplet impaction observation (Massinon and Lebeau, 2012b). Droplet trajectories immediately above the plant were assimilated as straight lines. Directions were drawn from the normal distribution N(μ, σ), where μ is the main spray direction and σ were chosen at 10° and 20° for the short and long axis of flat-fan spray ground pattern, respectively.

6.5.4 Spray impact on the 3D plant architecture and retention

The droplet interception by the plant model consists of testing whether each droplet direction intersects one triangle of the 3D plant mesh. A fast ray/triangle intersection algorithm has been implemented in the model according to Möller and Trumbore (1997). It translates each triangle to the origin of the coordinate system and transforms it into a unit triangle lying in a given plane, with the ray direction aligned with the normal axis to the

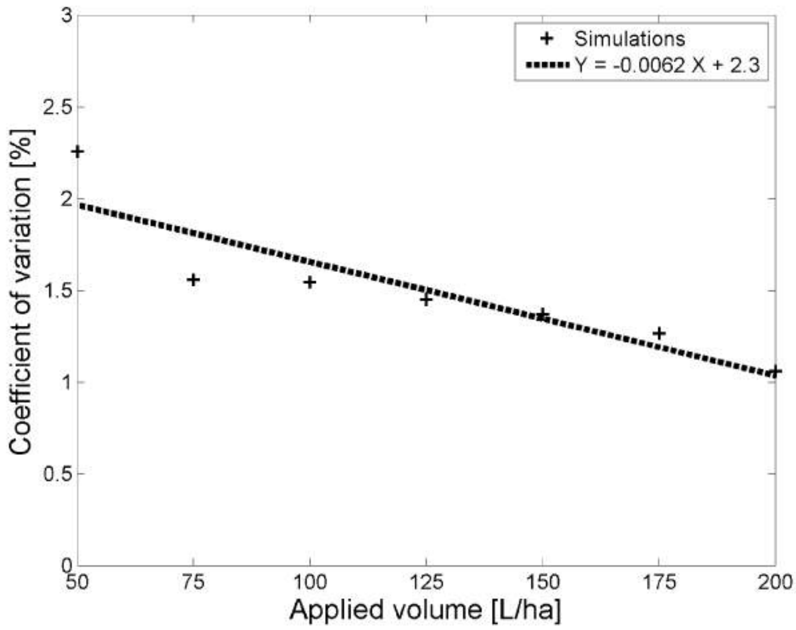


Figure 6.2: Variability of the effective applied volumes depending on the nominal applied volume (11003 flat-fan nozzle at 3 bars, 144 droplet size distributions).

plane. The outputs of the algorithm are the intersection coordinates and the intersection distance from the ray origin. The algorithm keeps the first intersection between each droplet direction (ray) and the triangle. Triangles were considered as one sided, which means that intersections in single direction are counted and intersections with back facing triangles are ignored. Border points of the triangle were included. If a droplet was intercepted by a triangle of the 3D mesh, the impact behavior was used to determine the contribution of this droplet to the final retention. A droplet may either adhere, rebound or splash depending on its impact energy represented by the dimensionless Weber number $We = \frac{\rho V^2 d}{\sigma}$, where ρ is the liquid density, V is the droplet velocity at impact, d is the droplet diameter and σ the liquid surface tension, and the leaf surface wetting regime.

The spray impact behaviors were measured on an artificial superhydrophobic surface used as a model of superhydrophobic leaf surface. The artificial surface was a completely polytetrafluoroethylene (PTFE) coated microscope blade (part number X2XES2013BMNZ, Thermo Fisher Scientific Inc., Waltham, MA, USA) with a roughness structure that enables a static contact angle of 169 ± 2° (sessile drop method, 5 replicates, CAM200, KSV Instruments, Helsinki, Finland) for a $5\mu l$ distilled water droplet. The relevance of the use of this superhydrophobic surface as reference target surface has been studied in comparison with outdoor grown wheat leaves (Massinon and Lebeau, 2012a) using the method described in Massinon and Lebeau (2012b). This target surface has been chosen to control the variability linked to the surface in this study and therefore focus on the variability that the application technique and the plant size may introduce in the final spray retention. From image analysis, a phase diagram of the droplet impact velocity and diameter is plotted in Figure 6.3 for a surface angle of 30° from the horizontal. Each point represents a droplet. In this study, only the first impacts of droplets on the plant model was computed because secondary impacts of droplets are very unlikely due to the low plant size and its vertical leaves. The impact phase diagram is divided into eleven energy classes whose boundaries correspond to a constant Weber number (We_W) computed with the water surface tension. The first limit was set at $We_W = 0.02$. The first energy class contains droplets with a We_W below 0.02. Successive boundaries correspond to a three times increase of the We_W. Such a phase diagram was constructed from ten sprayings using a flat-fan nozzle mounted on a moving rail (Massinon and Lebeau, 2012b). In each energy class, the relative volumes of the various impact types were computed and assimilated as impact probabilities (Figure 6.4) (Massinon et al., 2014). The energy class boundaries were chosen for gathering enough droplets for the assessment of the impact probabilities and for highlighting smooth transition between impact outcomes since different impact types may coexist at similar droplet impact energy levels (smaller droplets in Figure 6.3). This effect has to be linked with the relative size of the droplet and the surface roughness; when the droplet and the roughness size are close to each other, this may result either in an adhesion or a rebound for the same impact energy level depending on where the droplet impaction occurs (either on the top or in the bottom of the roughness structure). For leaf surfaces, fouling, abrasion of epicuticular waxes or surface defects may increase this effect and lead to the onset of large contact angle hysteresis which promotes the liquid pinning on the surface (Chang et al., 2009; Ensikat et al., 2011). In the interception algorithm, the impact outcome is given to each droplet based on the probability maps such as Figure 6.4 using the droplet incidence angle on the 3D plant model and its Weber number. The impact probability is computed by linear interpolation between the probability map measured for 0, 30 and 60° of surface orientations (Massinon et al., 2014). At 90° (vertical target surface), the impact probability is zero and the impact map was set at 100% of rebound. Tables 6.3 and 6.4 show the droplet impact probabilities on the artificial superhydrophobic surface depending on the droplet incidence angle and We_W for the low and high wetting scenario respectively. When a droplet is splashing on an hairy leaf surface or a leaf with other micro-roughness structures (waxes), a part of the droplet may be trapped into the surface roughness depending on the liquid surface tension and the droplet impact pressure (Boukhalfa et al., 2014), such pinning impacts occur when the droplet lies in the Wenzel wetting regime (Wenzel, 1936), and are referred to as partial splashing in this paper. This behavior was included in the algorithm by multiplying the volume of the droplet by the proportion of droplet in volume remaining on the surface after a splashing in Wenzel wetting regime. This proportion, K, varies from 0 and 1. The choice of value for this parameter is described here after depending on the formulation scenario tested. Two contrasted scenarios of spray droplet impact behaviors have been tested as

Table 6.3: Impact probabilities (%) depending on the droplet incidence angle and water Weber number for the 'low wetting' scenario on the artificial superhydrophobic surface. A: adhesion, R: rebound, S: splashing.

Surface angle	0°			30°			60°			90°		
Energy class upper limit (We_W)	A	R	S	A	R	S	A	R	S	A	R	S
0.02	86	14	0	100	0	0	100	0	0	0	100	0
0.06	73	27	0	86	14	0	100	0	0	0	100	0
0.18	56	44	0	38	62	0	56	44	0	0	100	0
0.54	37	63	0	9	91	0	27	73	0	0	100	0
1.62	9	91	0	0	100	0	0	100	0	0	100	0
4.86	0	100	0	0	100	0	0	100	0	0	100	0
14.58	0	100	0	0	100	0	0	100	0	0	100	0
43.74	5	91	4	0	90	10	0	100	0	0	100	0
131.2	0	0	100	0	1	99	0	100	0	0	100	0
393.7	0	0	100	0	0	100	0	0	100	0	100	0
inf	0	0	100	0	0	100	0	0	100	0	100	0

Table 6.4: Impact probabilities (%) depending on the droplet incidence angle and water Weber number for the 'high wetting' scenario on the artificial superhydrophobic surface. A: adhesion, R: rebound, S: splashing.

Surface angle	0°			30°			60°			90°		
Energy class upper limit (We_W)	A	R	S	A	R	S	A	R	S	A	R	S
0.02	100	0	0	100	0	0	100	0	0	0	100	0
0.06	100	0	0	100	0	0	100	0	0	0	100	0
0.18	100	0	0	100	0	0	100	0	0	0	100	0
0.54	100	0	0	100	0	0	100	0	0	0	100	0
1.62	100	0	0	100	0	0	100	0	0	0	100	0
4.86	100	0	0	100	0	0	100	0	0	0	100	0
14.58	100	0	0	100	0	0	100	0	0	0	100	0
43.74	90	10	0	60	30	10	0	40	60	0	100	0
131.2	5	0	95	0	0	100	0	30	70	0	100	0
393.7	0	0	100	0	0	100	0	0	100	0	100	0
inf	0	0	100	0	0	100	0	0	100	0	100	0

range boundaries of the possible spray liquids wettability. The first scenario involved to simulate spraying pure water. With water, the volume proportion of bouncing droplets into the impacting spray is high (Table 6.3). This first scenario is therefore qualified of 'low adhesion scenario' in this paper. The parameter K (used for splashing outcomes) depends on leaf angle and its value was determined by linear interpolation from 0.45 for horizontal surface to 0 for vertical surface. The second scenario reflected the use of a super spreader surfactant. The static surface tension of such a non-ionic surfactant used in the impaction experiments was $21.5 \pm 0.1 mN/m$ (5 replicates, CAM200, KSV Instruments, Helsinki, Finland). Because of the drastic reduction of the dynamic surface tension of the spray mixture, the proportion of bouncing droplets is reduced in favor of adhesion (Table 6.4). This scenario will therefore be referred to as 'high adhesion scenario'. The proportion K was chosen at 0.6 whatever the leaf angle for the non-ionic surfactant because of its very low dynamic surface tension (DST). It should be noted that the Weber number has been computed using the water surface tension for comparison purpose between formulations. However when dealing with surfactants, it is well established that the DST better correlated with retention (Anderson and Hall, 1989; Dorr et al., 2015), for which the appropriate time scale for its measurement scales with droplet contact time on the target surface (Richard et al., 2002). The contact time can be very small and the DST remains therefore difficult to measure. A fluid density of $1000 kg.m^{-3}$ and surface tension of $72 mN.m^{-1}$ were used for the two wetting scenarios.

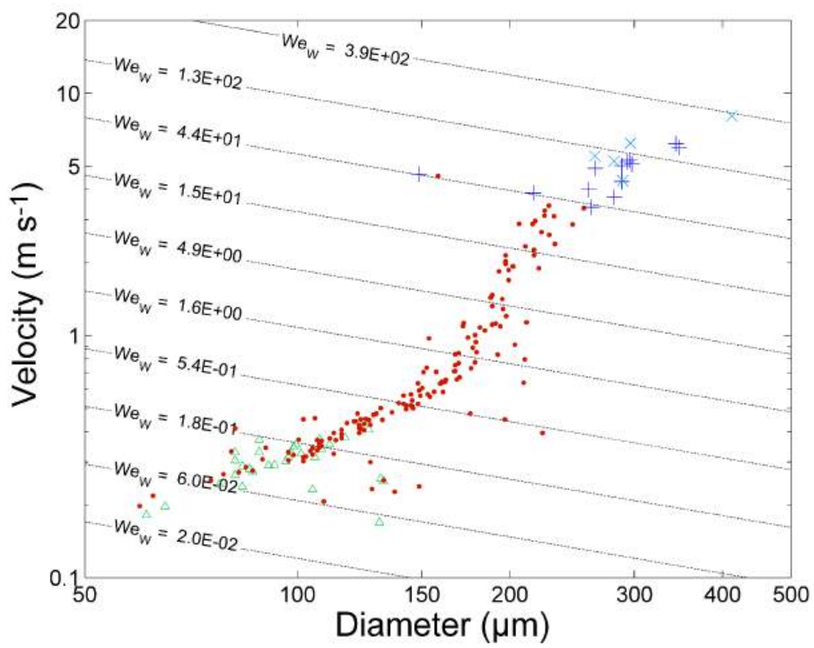


Figure 6.3: Impact outcome observations on the superhydrophobic artificial surface tilted at 30° from horizontal for the low adhesion scenario (Teejet 11003 nozzle at 0.3 MPa, 0.5m height) as a function of the droplet impact velocity and droplet diameter. impact outcomes (△ adhesion, • total rebound, × partial splashing and + total splashing). Dotted lines are constant Weber number computed with the water surface tension and represent energy impact class boundaries.

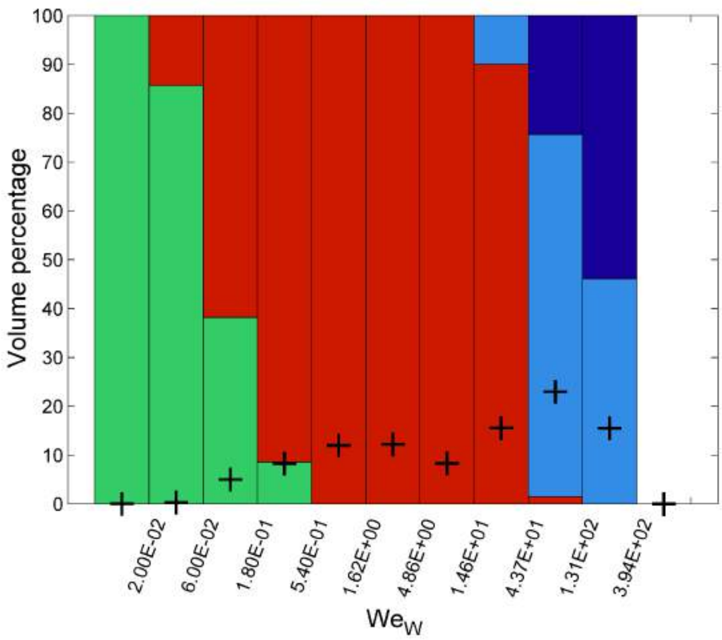


Figure 6.4: Impact outcome probability as a function of the water Weber number on the artificial superhydrophobic surface tilted at 30° from horizontal for the low adhesion scenario: green: adhesion, red: rebound, deep blue: Cassie-Baxter splashing and sky blue: Wenzel splashing, + volume proportion of each energy class relative to total volume observed before impact.

6.6 Results and discussions

One hundred different droplet size distribution samples have been used for each nozzle. This number was chosen to stabilize the mean retention. To avoid the variability due to droplet size distribution, the same set of 100 spray samples were taken for each simulation. Simulations were performed by applying a rotation around the vertical axis of the 3D plant model by steps of 15°, resulting in 25 different orientations of the plant sprayed each time with the same 100 droplet size distributions. The 3D plant model was always re-centred into the cell. The outputs of the simulations were the 100 computed spray retention for each of the 100 droplet size distribution samples. The spray retention was computed as the volume of retained liquid divided by the projected total leaf area along the main (vertical) spray direction. From the set of the 100 spray retentions, the coefficient of variation was computed as an indicator of the variability of deposits and therefore, an indicator of the efficacy of a treatment. A high coefficient of variation indicates a poor treatment efficacy since some plants may receive insufficient amount of active substance to achieve its effect.

6.6.1 Effect of spray quality and spray droplet impact behaviors

A full droplet adhesion scenario has been performed for the different spray qualities at an application volume of 100 L/ha as benchmark (Figure 6.5). The full adhesion means that all droplets are retained at impact. Retention was slightly greater than the nominal applied volume (100 L/ha) because droplets may impact the bottom of the plant thanks to their non-vertical trajectories. The increase of median retention ranged from 9% for the coarser spray nozzle to 14% for the finer spray nozzle because the number of droplets was higher. The variability of deposits was consequently greater for the coarser nozzles on this vertical target. The retention would have gradually tended towards the nominal applied volume as the plant leaves would have been more and more horizontal. For the

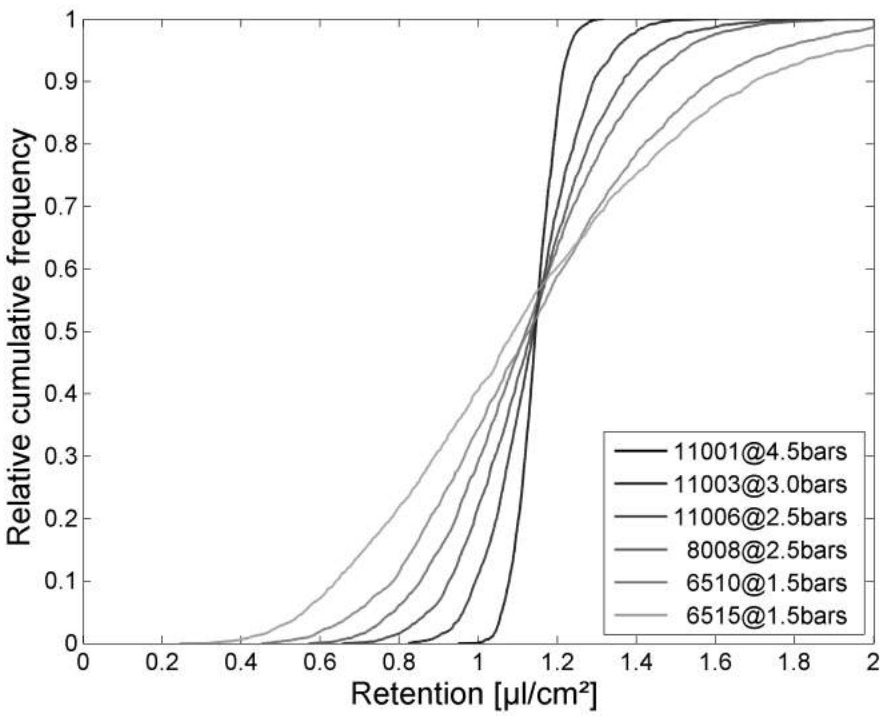


Figure 6.5: Relative cumulative distributions of spray retention observed for various spray qualities at 100 L/ha application for the full adhesion scenario: 100 different sprays at 25 different orientations for each spray quality on the same original size plant.

'low adhesion' scenario (Table 6.5), the finer spray provided a much greater retention than other sprays because of the small proportion of the droplets lying in the rebound and splashing impact outcomes. For the high adhesion scenario, the reduction of the dynamic surface tension resulted mainly in an increase of the retention as expected because rebound almost disappeared (Table 6.3 and 6.4). The benefit when using a super spreader surfactant increased as the spray quality increased, ranged from 3.38 times for the finer up to 9 times for the coarser spray quality (Table 6.5), because of the increased contribution of splashing droplets (larger droplets) in retention due to the pinning. Retention in the high adhesion scenario amounts almost to 96% to the full adhesion scenario for the finer spray quality, highlighting the high performance of surfactants with very small dynamic surface tension with very small droplets. Whatever the scenario, retention decreased as the mean droplet size increased and the droplet density decreased (number of droplets per square centimeter, Table 6.8) as highlighted by Miller et al. (2010). The modelled retention process efficiency (Table 6.5) ranged from 6.8% to 96.6% of a theoretical full adhesion scenario, which is close to the 10 to 100% range stated by Zabkiewicz (2007) for an herbicide application. The variability of deposits increased as the spray coarseness increased because the number

Table 6.5: Median retentions [$\mu l/cm^2$] for different formulation scenarios and spray quality boundaries at 100 L/ha application and ratios with respect to full and low adhesion scenarios [-].

Scenarios	VF/F	F/M	M/C	C/VC	VC/XC	XC/UC
Low adhesion	0.327	0.144	0.111	0.091	0.079	0.075
High adhesion	1.104	0.890	0.799	0.744	0.717	0.674
Full adhesion	1.144	1.136	1.131	1.120	1.117	1.094
Low/Full adhesion	0.286	0.127	0.098	0.081	0.071	0.068
High/Full adhesion	0.966	0.784	0.706	0.665	0.642	0.646
High/Low adhesion	3.380	6.188	7.213	8.167	9.094	8.999

of impacts also decreased (Table 6.6). These coefficients of variation were not stabilized for the coarser spray quality because the number of droplets was insufficient. For instance, these coefficients of variation were different when moving the plant model into the cell grid and repeating the simulations. The value of the coefficient of variation was therefore not indicated in Table 6.6 for the coarser nozzle in the low adhesion scenario. Consequently, such coarse nozzles should not be used when treating small and hydrophobic species as highlighted by Miller et al. (2010), despite their high drift mitigation potentiality. Finally, no significant differences in variability were observed between the low and high adhesion scenarios, showing the leading influence of spray quality in retention variability. The

Table 6.6: Coefficients of variation [%] for different formulation scenarios and spray quality boundaries at 100 L/ha application.

Scenarios	VF/F	F/M	M/C	C/VC	VC/XC	XC/UC
Low adhesion	4.722	8.761	12.579	17.214	26.706	N/A
High adhesion	4.185	8.534	13.440	18.002	26.774	37.386
Full adhesion	4.494	10.220	15.476	19.781	28.279	38.088

minimal retained volume of herbicide is an important parameter in weed control efficacy because an insufficient dose may reveal resistance in weed populations. For a given spray quality, Table 7 shows an increase of the minimal dose from 3 to 9 times with the high adhesion scenario relative to the low adhesion scenario. Whatever the spray quality studied, the minimal retained volume decreased as the spray coarseness increased, which

Table 6.7: Minimal retentions [$\mu l/cm^2$] for 100 L/ha application with the different spray quality boundaries and high to low adhesion scenario ratio.

Scenarios	VF/F	F/M	M/C	C/VC	VC/XC	XC/UC
Low adhesion	0.2728	0.1039	0.0708	0.0520	0.0333	0.0221
High adhesion	0.9395	0.6797	0.4985	0.4047	0.3101	0.1779
Full adhesion	0.9480	0.8216	0.6549	0.5701	0.4514	0.2434
High/Low adhesion	3.44	5.54	7.04	7.78	9.31	8.05

was related to the decrease of the number of droplets per unit surface area. The treatment efficacy could be derived from these cumulative distributions of Figure 6.6: for instance, in 10% of the simulations for the 11001 nozzle, the plant retained 0.30 $\mu L.cm^{-2}$ for the low adhesion scenario and 1.04 $\mu L.cm^{-2}$ for the high adhesion scenario. If the required dose to control a given pest would have been at 0.4 $\mu L.cm^{-2}$, the use of a surfactant would have been mandatory. Almost 100% of the pest population would have been controlled with the 11001 nozzle, while only 90% of the plants would have received enough active ingredients with the 6515 nozzle.

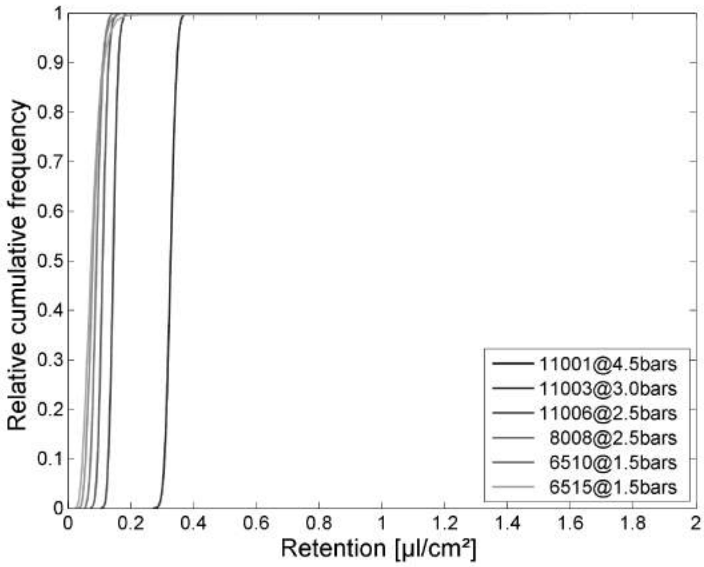
6.6.2 Effect of volume per hectare applied and spray quality

As expected, the coefficients of variation of spray retention increased both as the spray coarseness increased and applied volume decreased (Figure 6.7), because the number of droplet interceptions by the plant model at original scale decreased (Table 6.8). In the context of a global trend to reduce application rates and promote drift mitigation techniques, often relying on coarser spray qualities, the variability of retention at the plant scale is therefore expected to increase dramatically on small difficult-to-treat targets. Figure 6.8, that present the CV versus the number of intercepted droplets per unit of projected leaf area for the high adhesion scenario, highlights the preponderance of spray quality on retention variability even if the effect of the applied volume is not negligible.

Table 6.8: Average number of droplets per square centimeter intercepted by the plant model depending on the applied volume for each spray quality boundary.

Spray quality boundaries	50 L/ha	75 L/ha	100 L/ha	125 L/ha	150 L/ha	175 L/ha	200 L/ha
VF/F	608.7	915.5	1217.3	1715.4	1825.6	2402.2	2435.9
F/M	228.7	342.2	455.6	641.4	682.1	895.2	908.6
M/C	142.1	212.3	282.6	397.8	423.5	559.8	564.1
C/VC	84.9	127.1	169.3	239.3	252.8	333.5	337.4
VC/XC	45.5	69.2	91.5	130.3	138.2	180.6	182.7
XC/UC	36.5	52.6	71.1	101.4	106.1	140.4	141.8

(A)



(B)

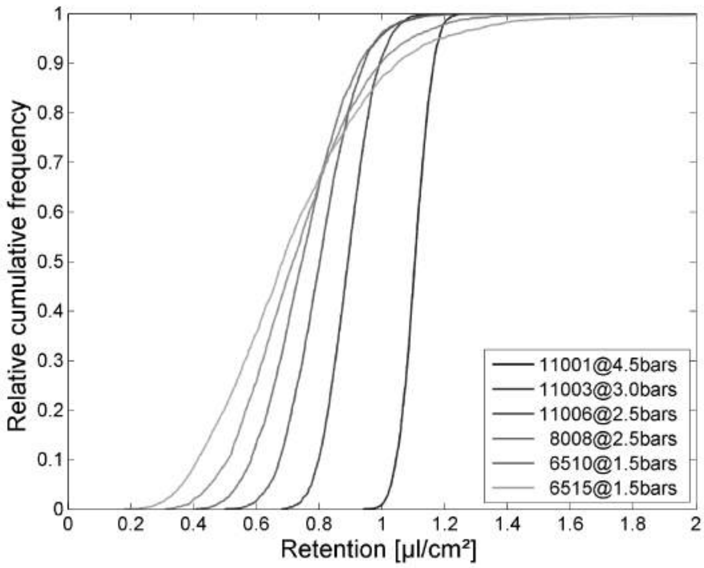


Figure 6.6: Relative cumulative distributions of spray retention for various spray quality boundaries at 100 L/ha application on the same plant: low adhesion (A) and high adhesion scenario (B).

6.6.3 Effect of plant orientation and size

Plant orientation

Figure 6.9 shows the coefficients of variation for the different spray quality boundaries at 100 L/ha at different plant rotation angles (step of 15°) relative to the vertical plant model axis for the high adhesion scenario. Each coefficient of variation was computed

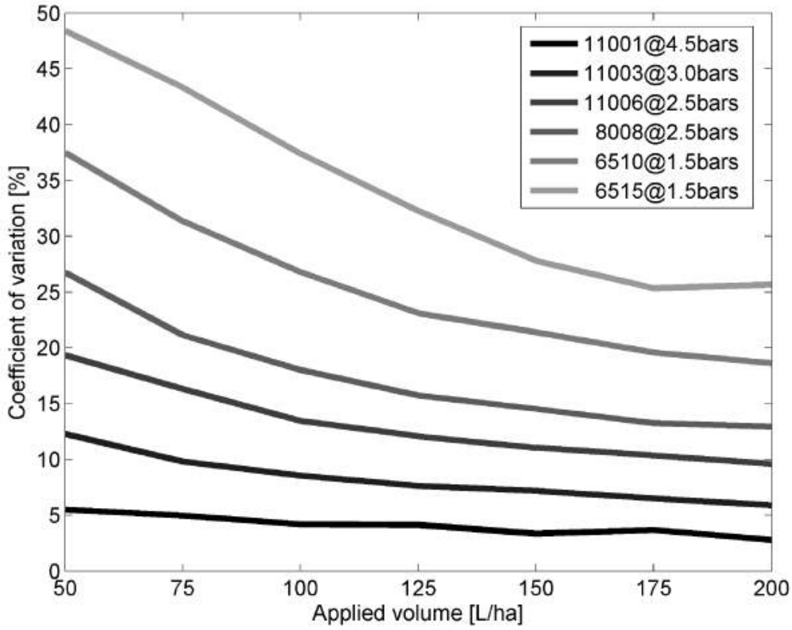


Figure 6.7: Effect of applied volume on the retention variability for the high adhesion scenario anddifferent spray qualities.

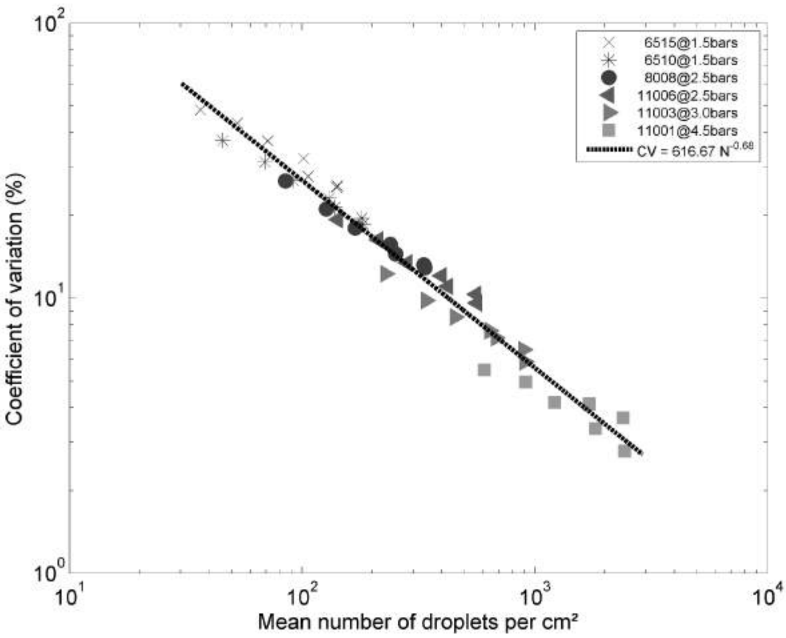


Figure 6.8: Retention variability depending on the mean number of droplets per unit of projected leaf area for all spray qualities and the high adhesion scenario.

from 100 simulations. This test aimed at highlighting whether the plant model orientation may lead to differences in spray retention. As already showed, the coefficient of variation increased as the nozzle size increased. All the profiles looked almost circular reflecting no influence from the plant rotation because the spray direction was mainly vertical, tending towards a very circular profile with increasing the number of droplets and reducing the nozzle size. There were no differences between the two scenarios tested.

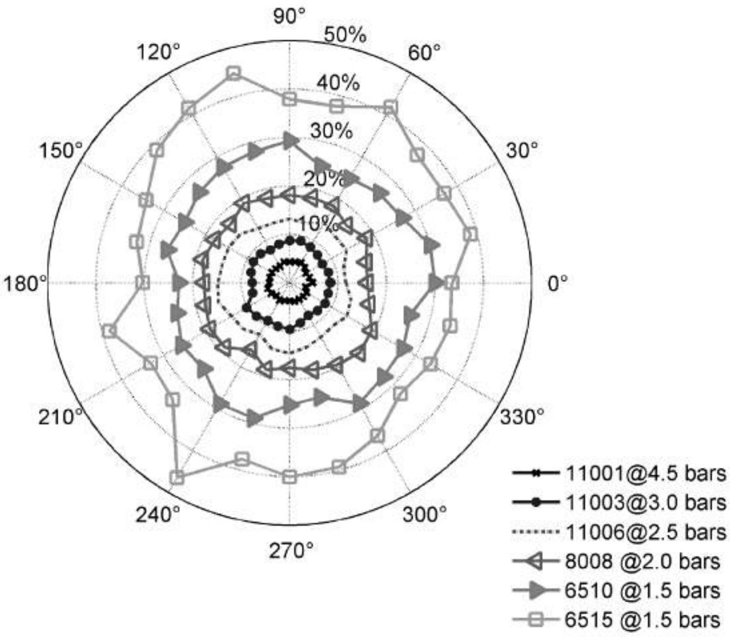


Figure 6.9: Coefficient of variation [%] depending on a rotation of the plant model around the vertical axis by step of 15° for the high adhesion scenario and different spray quality boundaries at 100 L/ha.

Plant size

The effect of plant size has been studied by changing the plant size with various scale factors, from 0.05 to 2 corresponding to a $0.051 - 81.222cm^2$ range of plant leaf surface area. The X, Y and Z vertex coordinates were multiplied by the same scale factor (SF). Simulations were performed using the fine/medium spray quality boundary at 100 L/ha for the high adhesion scenario (Figure 6.10). The coefficient of variation decreased as the scale factor increased according to the fitted relation $CV = 8.33 \cdot SF^{-1}$. The new total plant leaf area is computed as $S = S_0 \cdot SF^2$ where S_0 is the initial total plant leaf area. Re-writing the first expression of CV using the definition of S gives $CV = 8.33 \cdot (\frac{S}{S_0})^{-0.5} = 8.33 \cdot S^{-0.5} \cdot S_0^{0.5} = 37.55\ cm \cdot S^{-0.5}$ with $S_0 = 20.32\ cm^2$ (Table 6.1).

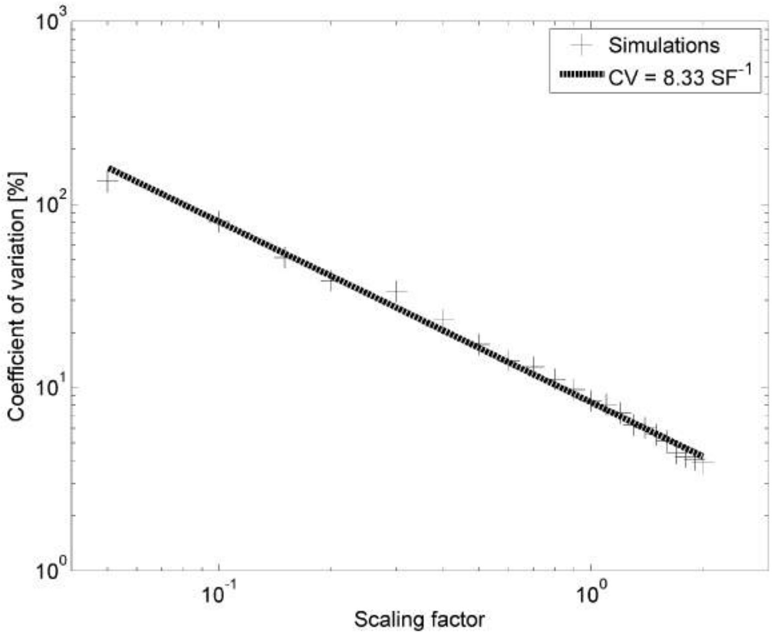


Figure 6.10: Coefficient of variation [%] as a function of the scaling of the plant model for the fine/medium spray quality boundary and high adhesion scenario.

6.7 Conclusions

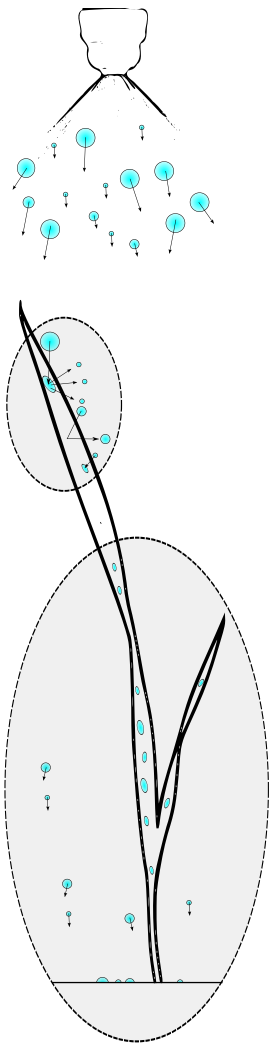
A 3D virtual spraying model to predict spray droplet interception and retention by single plant architecture has been developed and used for focusing on the variability of deposits in still air hypothesis. The model was based on the measured 3D plant architecture, on the use of a virtual nozzle for providing representative droplet size distributions and on spray droplet impact outcomes characterized with high-speed imaging and image analysis.

The variability of spray retention by a single 3D plant model was investigated as a function of the spray quality, the volume per hectare applied and the plant size for two contrasted formulation scenarios representative of low and high spray liquid wetting properties. Results showed that retention ranged from 6.8% to 96.6% of a full adhesion depending on spray quality and formulation scenario. Average retention increased with increasing spray fineness, applied volume per hectare and plant size. The variability of deposits increases with decreasing spray fineness, applied volume per hectare and plant size because of the reduced number of droplet contributing to retention. The variability of deposits is mainly related to the spray quality. Such a modeling approach can be used to improve understanding of application methods and adjuvants that could help minimizing development of resistance in problematic weed species. It could also be used to determine the optimum time of spraying by predicting the optimal retention potential depending on the target (Combellack, 1981).

Further studies may seek to find optimum spray droplet trajectories for such difficult targets that maximize retention acting on pesticide application method, e.g. spray angle modification. A plant architecture database at weeding growth stage will be further used to estimate the variability of retention that is encountered in field in order to relate deposits variability and the risk of herbicide resistance emergence.

CHAPTER 7

Parameter sensitivity analysis on the spray retention and its variability



7.1 Chapter objectives and outline

This chapter offers an insight of the potentialities of the proposed model (chapter 6). Results showed in this chapter originate from 3 conference proceedings. The first part (section 7.3) is an attempt to assess the spray retention model accuracy by comparing the actual retention on plants evaluated in laboratory with the predicted retention by the model. The plant architecture was measured before retention tests using a structured light scanner (section 6.5.2). The number of plants used in this paper was insufficient to fully validate the model but allowed to discriminate retentions for two contrasted formulation surface tension ranges and provided an estimate of spray retention at the plant scale within the right order of magnitude. The second paper (section 7.4) investigate theoretically the effect of a gradual modification of the formulation surface tension within the retention model. To achieve this, logistic fittings were applied on droplet impact behaviour probability histograms (chapter 4). The logistic fit best reflects the shape of the droplet impact probability histogram based on observation. As a result, various droplet impact outcomes probabilities were generated (figure 7.3). The third conference proceeding (section 7.5) focuses on the effect of the modification of the application technique by using reduced span sprays on retention and its variability between plants. Like chapter 5, only the original contributions are presented in this chapter. Results of this chapter highlight that some enhancements in spray retention on difficult to treat plants are potentially achievable by acting on the droplet size distribution and the formulation surface tension and the optimal application technique depends on the target properties.

7.2 Appended publications

Autors: Massinon Mathieu, Ouled Taleb Salah Sofiene, De Cock Nicolas, Dumont Benjamin and Lebeau Frédéric
Year: 2014
Title: Evaluation of process-driven spray retention model on early growth stage barley
Status: Conference Proceedings
Conference Name: International Conference of Agricultural Engineering
Place: Zurich, Swiss
URL: http://hdl.handle.net/2268/168460

Autors: Massinon Mathieu, De Cock Nicolas, Ouled Taleb Salah Sofiene and Lebeau Frédéric
Year: 2015
Title: Computer simulation of spray retention by a 3D barley plant: effect of formulation surface tension
Status: Conference Proceedings
Conference Name: Communications in Agricultural and Applied Biological Sciences **80**
Place: Ghent, Belgium
URL: in press

Autors: Massinon Mathieu, De Cock Nicolas, Ouled Taleb Salah Sofiene and Lebeau Frédéric
Year: 2016
Title: Reduced span spray - Part 1: Retention
Status: Conference Proceedings
Conference Name: Aspect of applied Biology ,**132**, International Advances in Pesticide Application
Place: Barcelona, Spain
URL: in press

7.3 Evaluation of the retention model performances

7.3.1 Introduction

The aim of this paper is to evaluate the potential of a droplet interception model linking actual spray retention with the proposed retention model and including the actual plant architecture. For this purpose, the model evaluation was performed on barley plants by comparing the actual to the predicted retention as a function of the spray mixture for the same single nozzle and the model was parametrized to fit at best the situation.

7.3.2 Retention trials

The model evaluation was performed by applying two contrasted formulations to barley plants using with a single flat-fan nozzle XR11003 operating at 0.2 MPa: tap water and tap water plus 0.1% V/V of Break-Thru S240 (organosilicone surfactant, Evonik Industries AG, Essen, Germany). Natrium fluorescein was incorporated into the two tank-mixes for quantifying the spray mixture actually retained by plants. Spring malting barley plants were grown in an indoor cultivation chamber in individual pots. Barley plants at growth stage BBCH 11 were sprayed 500 mm underneath the nozzle outlet for each mixture to assess the retention variability between plants. The actual volume per hectare applied, input of the model, was evaluated during the trials using 6 pieces of glass veil of 20 cm^2. Barley plants and pieces of glass veil were transferred afterwards in 20 ml of buffer solution (K_2HPO_4 at 8.71 g/L). Each solution was analyzed using a spectrophotometer (RF-1501, Shimadzu Corporation) at 460 nm excitation wavelength and 540 nm emission wavelength.

7.3.3 Simulations

Simulations were performed on the 3D plant architectures identically positioned to the barley plants during the retention tests. For each plant, 144 different droplet size distributions were applied by the algorithm, while only one measure is possible for the actual retention. So, a possible way to evaluate the model is therefore to see whether the measured retention belongs to the range of the simulations within 99.9% confidence interval and to compare the regression line to the 1:1 perfect match line (Figure 7.1). At first glance, predicted and measured retentions are in good agreement. As expected, the retention is greater for the surfactant. Furthermore, the variability between simulations seems greater than for water, which has a greater surface tension. The model evaluation can also been performed by comparing observed and simulated values according different criteria (Willmott, 1981):

- the root mean square error: $RMSE = \sqrt{\frac{1}{N}\sum(Z_i - \hat{Z}_i)^2}$, where N is the number of observations, Z_i and $\hat{Z}_i$ represent the observed and simulated variables respectively. RMSE should be as minimal as possible.

- the decomposition of the RMSE between the systematic mean square error $RMSEs = \sqrt{\frac{1}{N}\sum(b + aZ_i - Z_i)^2}$ and the unsystematic mean square error $RMSEu = \sqrt{\frac{1}{N}\sum(b + aZ_i - \hat{Z}_i)^2}$, with the parameters of the linear regression: slope a and intercept b.

- the relative RMSE: $RRMSE = RMSE/\bar{Z}$

- the normalized deviation: $ND = \frac{\sum_i Z_i - \sum_i \hat{Z}_i}{Z_i}$, should be < 0.1

– and the model efficiency, should be $EF = 1 - \frac{\sum_i(\hat{Z}_i - Z_i)^2}{\sum(Z_i - \bar{Z}_i)^2} > 0.5$

In a general way, the model provided an average under-estimation of about 7% (ND) with model efficiency (EF) of about 0.9. A systematic error (RMSEs, systematic) attributed to a bias in the model appears to be greater than the random error (RMSEu, unsystematic).

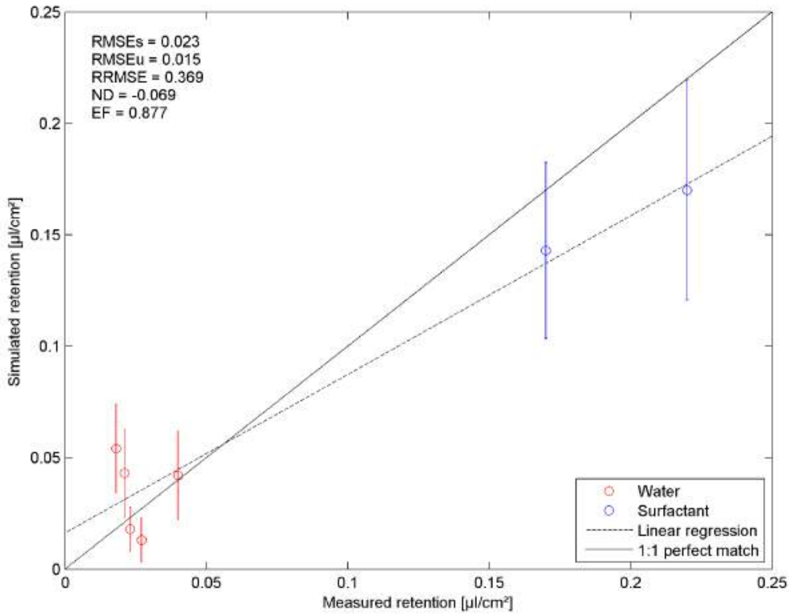


Figure 7.1: Predicted versus actual retention on barley plants (BBCH 11) for water (5 plants) and the organosilicone surfactant (2 plants) with 99.9% confidence intervals. Each data point represent the spray retention by a single plant in this simulated/observed retention diagram.

7.3.4 Conclusions

The model was able to discriminate between mixture wettabilities, which were affected by surface tension modifications. The spray retention increased as the mixture surface tension decreased. The variability of deposits also decreased as the surface tension decreased.

A case study was chosen and the model was parametrized to fit at best the situation. The predicted retention was compared with the measured retention by the dosage of a fluorescent tracer added to the spray mixture. The model was able to discriminate between mixture surface tensions and provided a good prediction of retention. However, the number of trials was clearly not sufficient to validate the model. To reach this objective, a great number of plants have to be sprayed in order to consider the variability of the spraying process. The plant orientation relative to the main spray direction should be investigated in the future. The greater RMSEs indicates that some work is required, especially in droplet impact behavior modification as a function of the impact angle. The under-estimation of the model for the surfactant retention has to be studied further.

7.4 Effect of formulation surface tension on spray retention

7.4.1 Introduction

The aim of this study is to explore theoretically the effect of a range of mixture surface tensions, between pure water and a solution with non-ionic surfactant exhibiting super spreading properties, on the spray retention and its variability for foliar application of pesticides on barley leaf surface. From the impact probabilities of Figure 7.2, logistic fittings were applied for the three impact outcomes to obtain parametrised curves for the two extreme wetting scenarios according the following model (sigmoid function), as the logistic model was highlighted as the best model of adhesion from the extensive work of Stevens et al. (1993) and Forster et al. (2005). :

$$y(x) = \frac{A}{1+exp(\frac{a-x}{b})}$$

where A is the curve's maximum value, a is the x-value of the sigmoid midpoint and b is the steepness of the curve. The eleven energy classes were numbered from 1 to 11 (see correspondences with Weber numbers in table 4.2). Logistic regressions were performed using these discontinued values for the x-axis. The logistic regression was applied for the adhesion and the splashing impact behaviours. For rebound, the probability distribution was calculated for the range of energy classes by subtracting their probability for adhesion and splashing from 1. The values of the parameters for the different logistic regressions were set as follow: for adhesion, A=1, b=0.5 and a varied from 1 to 7 in order to explore theoretically the range of spray mixture impact behaviour in terms of surface tension (Figure 7.3). For splashing, A=1, b=0.2 and a=9 anytime. This range of spray impact probabilities was used in the interception algorithm to provide the impact outcome of each droplet of the virtual nozzle. Then the contribution of each droplet to the final retention [$\mu L.cm^{-2}$] was computed using the interception and retention models.

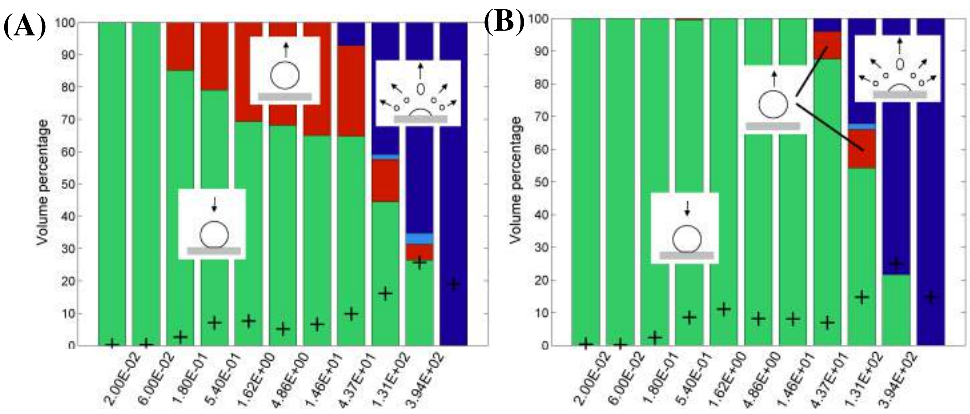


Figure 7.2: Spray droplet impact probabilities depending on the droplet impact energy (upper energy class boundary expressed using the water Weber number) on a horizontal excised barley leaf at two leaf growth stage. Pure water (A), non-ionic surfactant at 0.1%V/V in pure water (B). The droplet impact types (adhesion, rebound and splashing) are depicted on histograms. **+** is the relative volume proportion of droplets in each energy class for this nozzle.

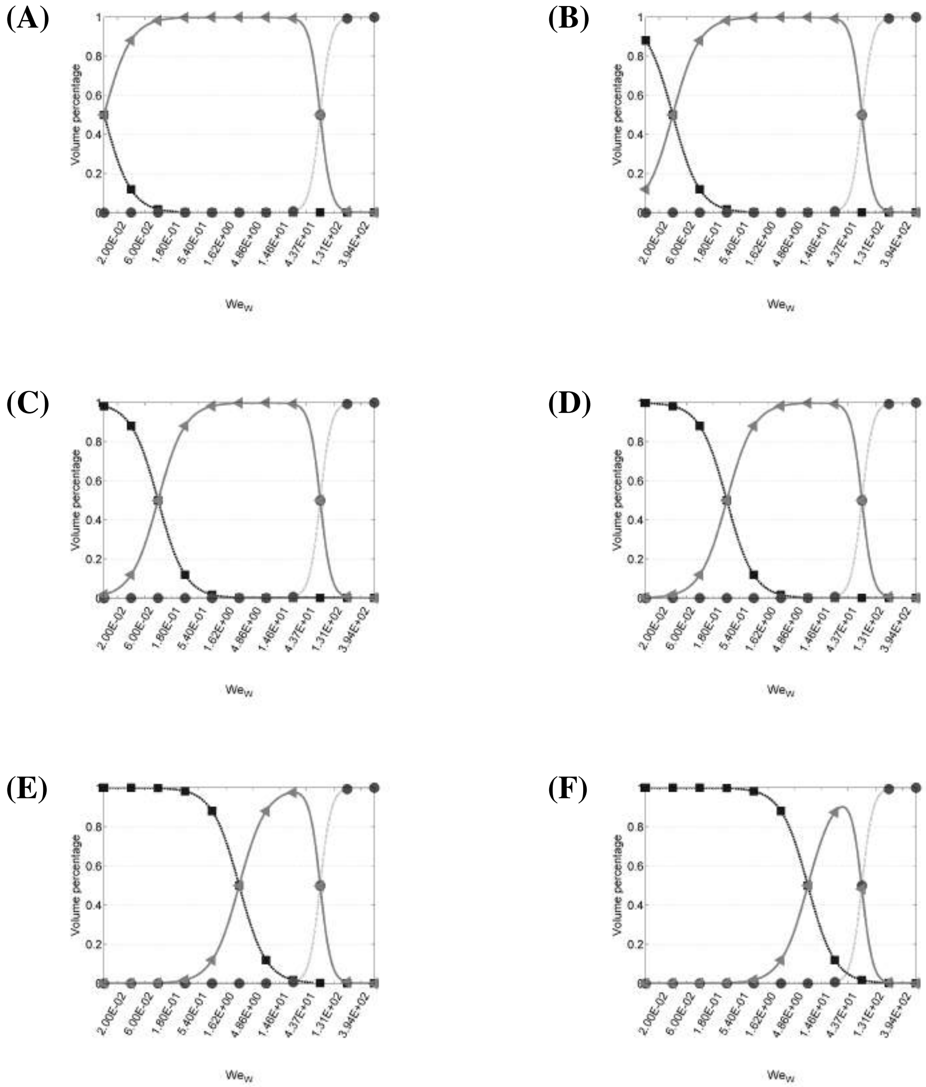


Figure 7.3: Various droplet impact outcome probabilities depending on the water Weber number: Adhesion (square), rebound (triangle) and splashing (circle). Parameter 'a' is the adhesion sigmoid midpoint in energy class number (see Table 4.2: (**A**) a=1, (**B**) a=2 , (**C**) a=3 , (**D**) a=4, (**E**) a=6, (**F**) a=7.

7.4.2 Variation of the adhesion proportion within the logisitic fitting

Figure 7.4 shows the simulated mean spray retention, expressed in microliters of retained liquid per unit of projected surface area of the 3D plant over the ground, for the six nozzles, for 100 and 200 L/ha depending on the proportion of adhesion (gradual increase of the sigmoid midpoint, parameter ‘a’ see Figure 7.3). The pinning proportion K was set to 0 here, meaning that no liquid remains on the plant after a splashing (Cassie-Baxter wetting regime). The retention was always smaller than the applied volume (100 L/ha = 1 $\mu L.cm^{-2}$) whatever the spray quality tested because of losses at impact and the droplet that were not intercepted. Retention increased as the adhesion proportion increased whatever the spray quality. For the finer spray quality (11001 nozzle) retention tended towards the applied volume when the proportion of adhesion increased. The coarser nozzles are less influenced by the adhesion proportion because the majority of the droplets lies in greater energy classes where splashing is dominant. The same trends were observed at 200 L/ha.

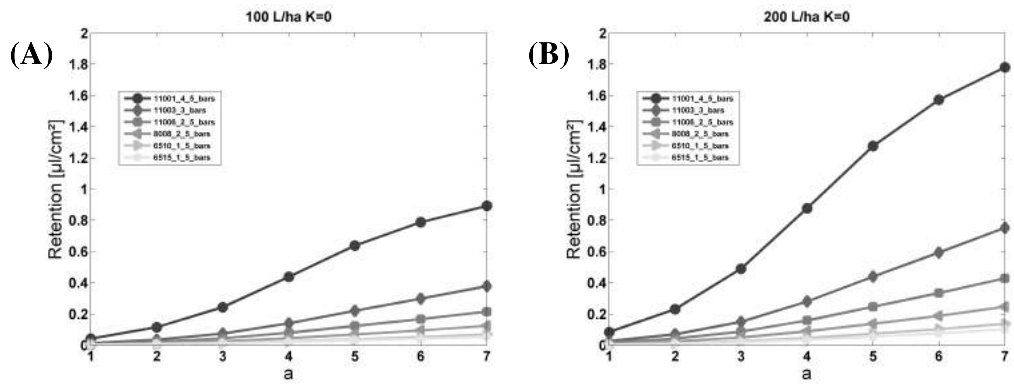


Figure 7.4: Simulated mean spray retention [$\mu L.cm^{-2}$] depending on the proportion of adhesion determined by the parameter ‘a’ of the logistic fitting. **(A)** 100 L/ha and **(B)** 200 L/ha.

7.4.3 Variation of the pinning proportion

Figure 7.5 shows the effect of the pinning proportion (K) (Boukhalfa et al., 2014) on the mean spray retention for the six spray qualities at 100 L/ha (Figure 1.1). Finer spray (11001 nozzle) was not influenced by the pinning proportion because they contain no splashing droplets. The influence of the pinning proportion increased as the mean droplet size (DV50, Table 6.2) increased, tending towards the value of this pinning proportion when droplets were mainly found in higher energy classes. The increase of retention thanks to the increase of adhesion proportion was gradually reduced for coarser sprays.

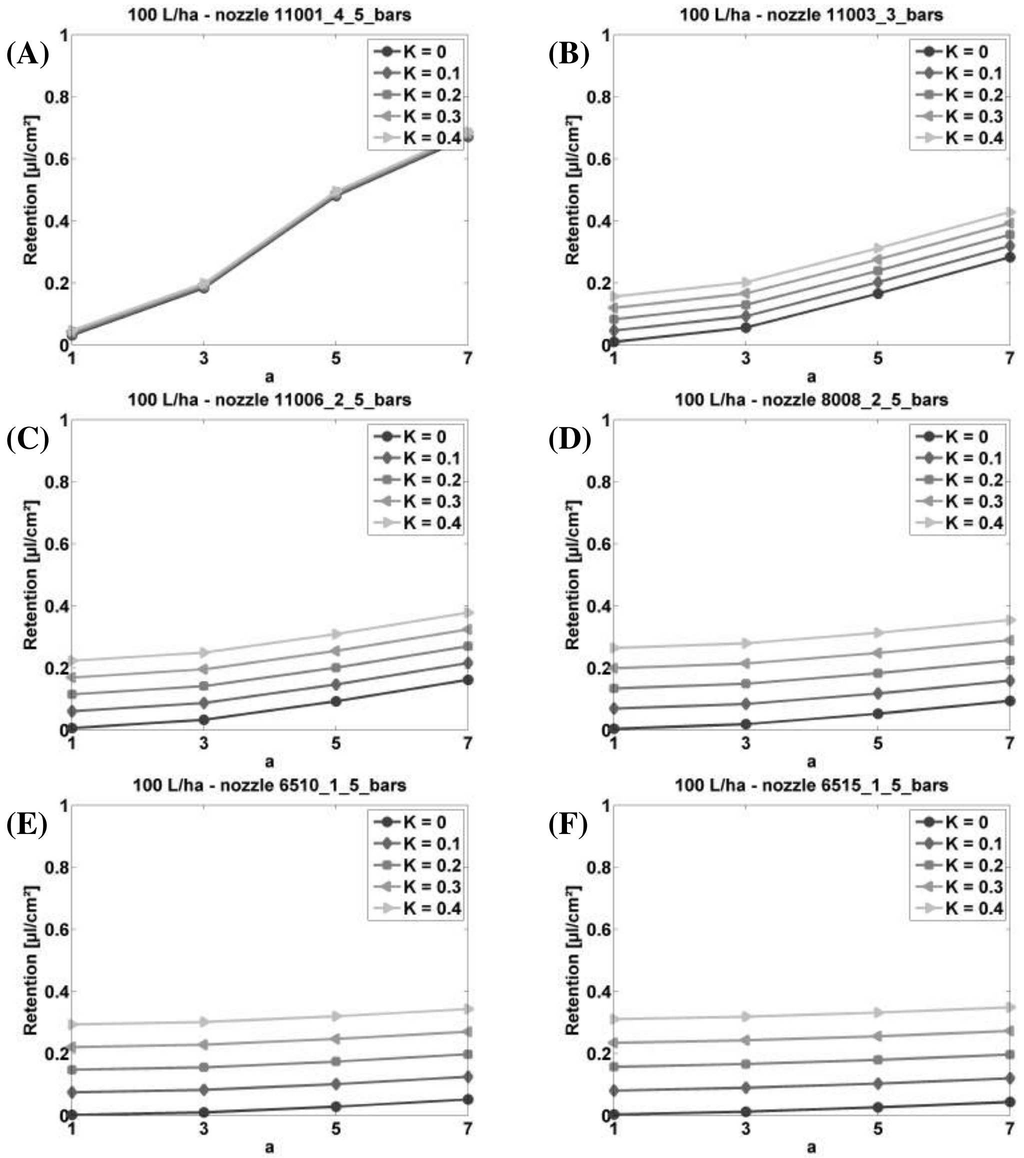


Figure 7.5: Effect of pinning proportion (K) on the mean spray retention by the 3D plant model depending on the adhesion proportion and the spray quality at 100 L/ha: **(A)** VF/F, **(B)** F/M, **(C)** M/C, **(D)** C/VC, **(E)** VC/XC, **(F)** XC/UC. K ranged from 0 to 0.4.

7.4.4 Variation of the plant size

Figure 7.6 shows the effect of the modification of the plant size on the spray retention (Figure 7.6, A) and the associated variability (Figure 7.6, right) depending on the adhesion proportion for a 11001 nozzle at 100 L/ha with a pinning proportion set to zero. The plant size was modified with various scale factors ranging from 0.05 to 2 and corresponding to a 0.051-81.222 cm^2 range of plant leaf surface area. The X, Y and Z vertex coordinates of the 3D plant model were multiplied by the same scale factor (SF). As expected, mean retention was found not depending on the plant size because retention is expressed in microlitre of retained liquid per unit or projected leaf surface area. Retention increased with the increase of the proportion of adhesion. The spray variability was evaluated using the coefficient of variation (CV) computed from the 100 replicated simulations. A high coefficient of variation may result in a poor treatment efficacy since some plants may receive insufficient amount of active substance to achieve its effect. CV decreased as the plant size increased because retention resulted from a greater number of intercepted droplets. CV also decreased as the adhesion proportion (parameter a, Figure 7.3) increased because of the reduced proportion of rebound.

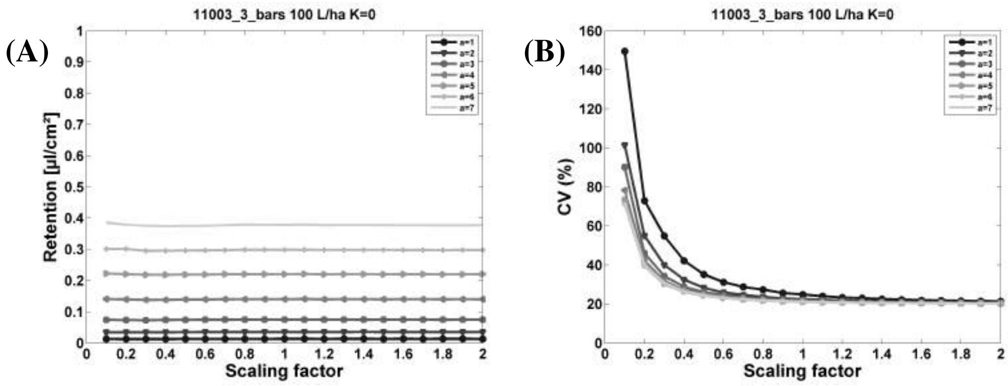


Figure 7.6: Effect of plant size on the predicted retention **(A)** and the coefficient of variation **(B)** for 7 adhesion proportions (parameter ‘a’), from 1 to 7.

7.5 Effect of application technique on retention: reduced span sprays

7.5.1 Introduction

Plant protection products are accredited with buffer zones. To reduce the size of these buffer zones in ground applications, farmers may use drift reduction technologies (DRT) such as shielded sprayers, air assistance sprayers, but also by acting on the droplet size distribution by changing the nozzle type and the operating pressure. Increasing the mean droplet size will reduce the risk of drift because smaller droplets are prone to drift. Reducing the percentage of spray volume in smaller droplet sizes is also possible by reducing the span factor of the droplet distribution. However, smaller droplets are better for adhesion on leaf surfaces because their impact energy is reduced. Finding an optimal droplet size distribution reducing drift while maximising the spray retention remains a difficult task because of the numerous factors that are involved (Knoche, 1994). For instance, when using air-induction nozzles for early grow stage weed control, poor treatment efficacies may result from high variabilities of deposits (Butler Ellis et al., 2007), this variability being influenced by the application volume and the method of application. The variability of deposits on the target will increase both by reducing applied volumes and by applying larger droplets. The plant properties also influence the retention efficiency:

early grow stage weeds with superhydrophobic, small and slanted leaves increase the variability of a retention (chapter 6). This study aims at highlighting the effect of the use of a reduced span on the spraying efficacy in ground applications with hydraulic nozzles. It focuses on the spray retention by a virtual plant with a numerical approach comprising a versatile virtual spraying model that can be used to theoretically predict the mean levels as well as the variability of spray deposits at the plant scale. Eighteen droplet size distributions with volumetric mean diameters (VMD) of 200, 250 and 300 μm and span factors of 0.05, 0.2, 0.4, 0.6, 0.8 and 1 were drawn from normal distributions $N(\mu, \sigma)$, where the mean μ corresponded to the VMD and σ was adapted in order to obtain the desired span factor. Droplets were drawn until reaching the volume of 50 L/ha on a ground surface area of one square meter. Figure 7.7 shows, for example, six droplet size distributions of VMD=200μm for different span factors. The range of VMDs tested in this study has been chosen to prevent drift (smaller droplets) while preserving an expected good retention. The expected span factor of hydraulic nozzles is around 1.3 (De Cock et al., 2015; Womac, 2000) and around 0.6 for rotary atomizers (Matthews, 2008; Gebhardt, 1988). Three possible wetting scenarios were tested by the model for various

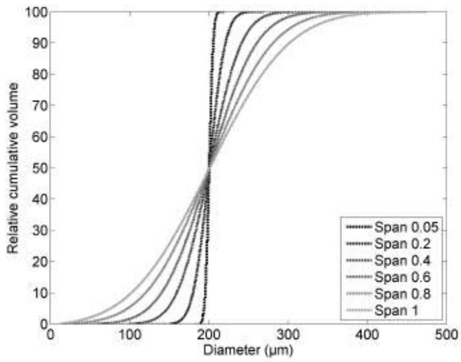


Figure 7.7: Cumulative droplet size distributions of $\mu = 200\mu m$ for different span factors.

spray characteristics detailed previously on a difficult-to-wet surface (Figure 7.8): low (Figure 7.8 A,B), intermediate (Fig 7.8 C,D) and high wettability (Figure 7.8 E,F). Figure 7.8 is given as an example of impact probability maps used in the algorithm (surface tilted at 45°) for three impact outcomes that may occur in foliar spray applications: adhesion, rebound and splashing. The impact probabilities remained constant for the intermediate wetting scenario depending on the incidence angle. Figure 7.8 also shows the relative spray volume within each energy class for two extreme spans: span of 0.05 (Figure 7.8 A,C,E) and span of 1 (Figure 7.8 B,D,F). Figure 7.8 summarises spray droplet behaviour at impact, therefore an estimated final retention by the target surface can be quickly obtained in relation with the spray characteristics.

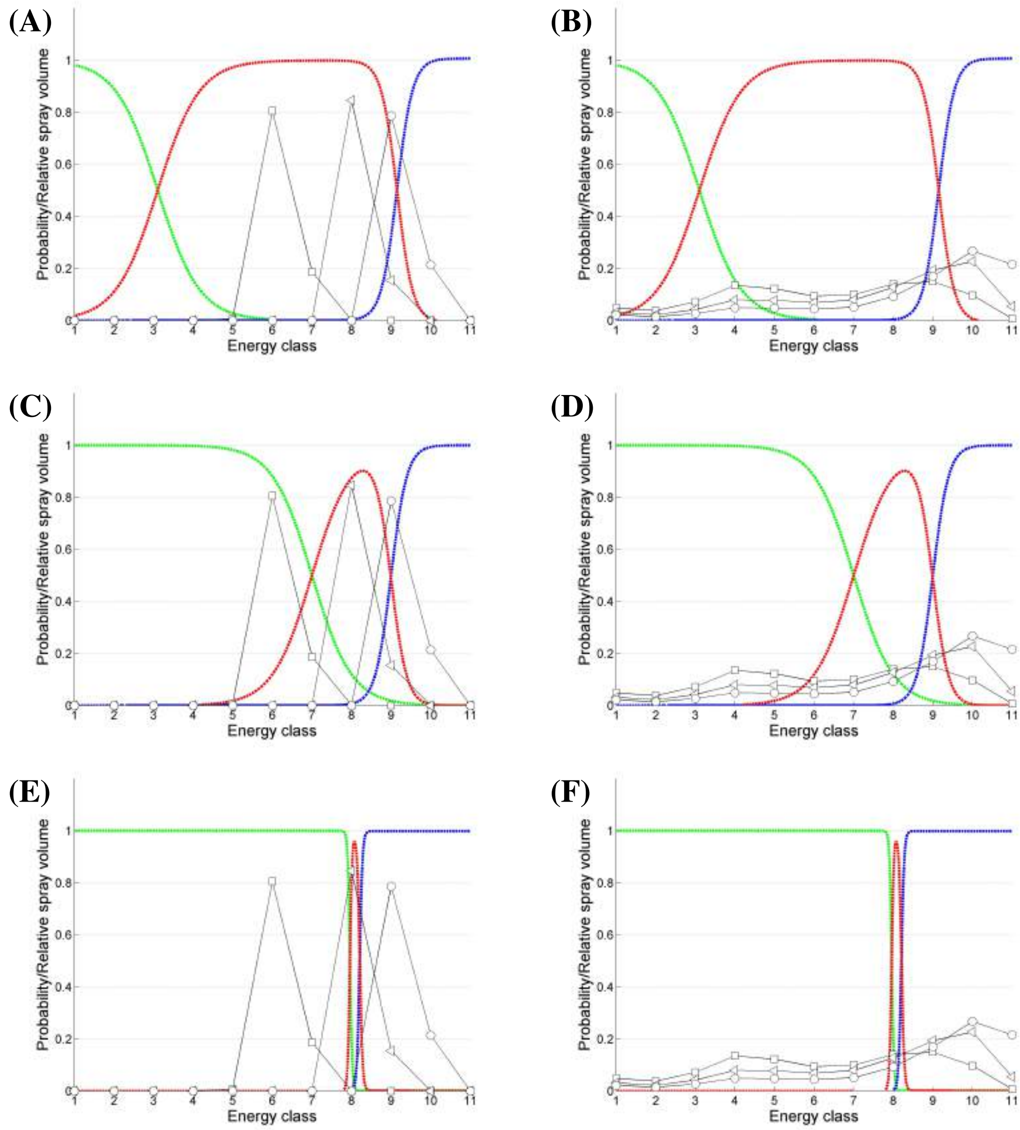


Figure 7.8: Spray droplet impact probabilities depending on the impact energy (water Weber number) for an artificial superhydrophobic surface: ··· *adhesion*, ··· *rebound*, ··· *splashing*, relative volume of the spray within energy classes: —□— VMD = 200μm, —◁— VMD = 250μm, —○— VMD = 300μm, (**A**-**C**-**E**): span factor = 0.05, (**B**,**D**,**F**): span factor = 1. (**A**,**B**): low wettability scenario, (**C**,**D**): intermediate wettability scenario and (**E**,**F**): high wettability scenario. Parameter 'K' was set at 0.5 for all the simulations.

7.5.2 Results and discussions

The relevance of using a reduced span factor spray in relation with the mean droplet size is given in Figure 7.9 and 7.10 for various wetting scenarios. Figure 7.9 presents the relative retention, defined as the actual retention by the target ($\mu L/cm^2$ of projected plant surface area on the ground) divided by the nominal applied volume for 18 VMD/span combinations and 3 formulation scenarios (Figure 7.8). Figure 7.10 shows the coefficient of variation of spray retention resulting from the simulations which can be used as an indicator of the variability of deposits (Butler Ellis et al., 2007). Table 7.1 presents the mean number of intercepted droplets per unit of projected leaf surface area (1.43 cm^2).

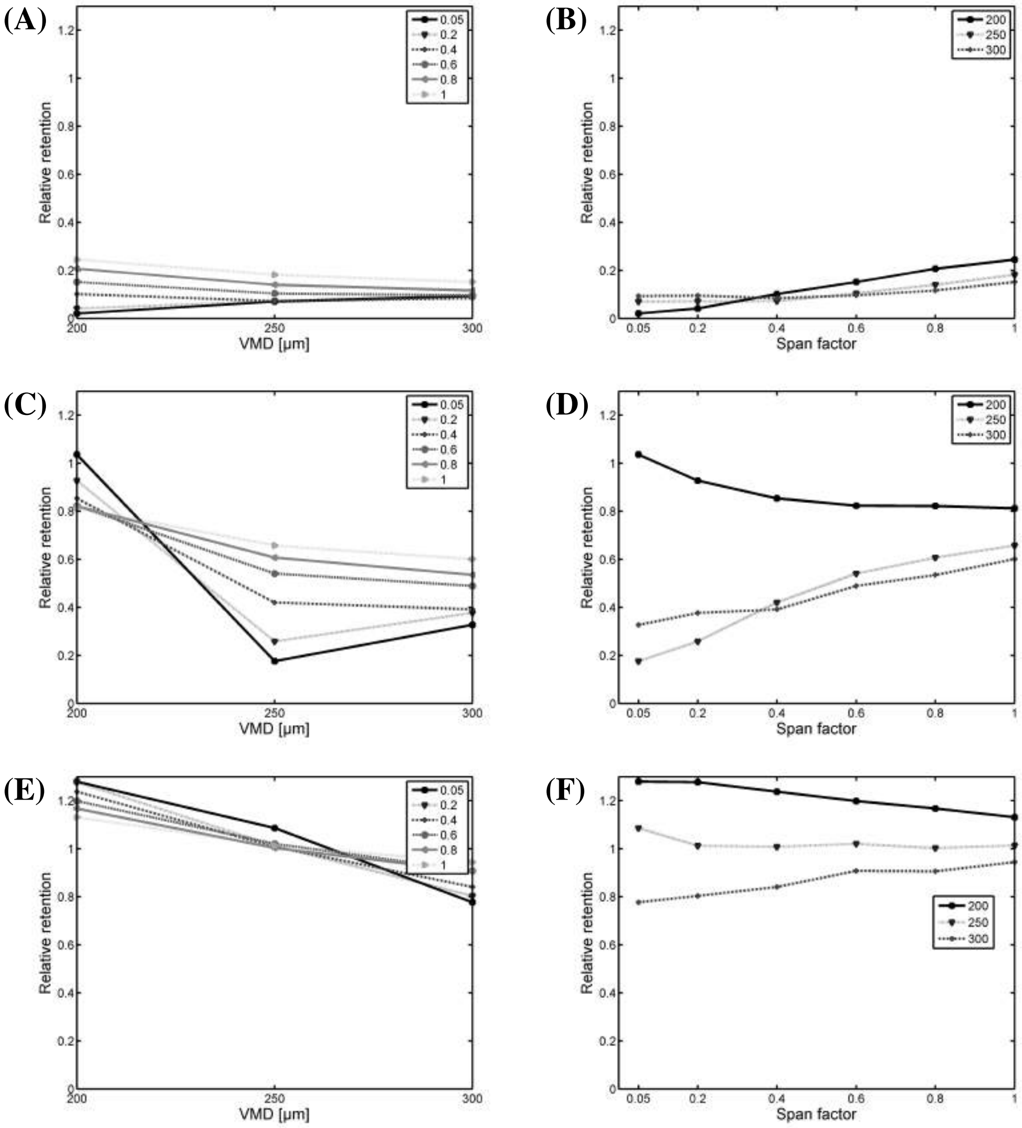


Figure 7.9: Relative mean retention for various VMD (**A**,**C**,**E**), span factors (**B**,**D**,**F**) and formulation scenarios: (**A**,**B**) low wettability, (**C**,**D**) intermediate wettability and (**E**,**F**) high wettability. Each point represents 100 virtual sprayings on the same plant architecture.

Table 7.1: Average number of intercepted droplets per projected leaf surface area $[N.cm^{-2}]$ for an application of 50 $[L.ha^{-1}]$

VMD $[\mu m]$	Span factor					
	0.05	0.2	0.4	0.6	0.8	1.0
200	152	159	181	268	901	2440
250	78	81	92	150	621	1817
300	45	47	53	88	419	1387

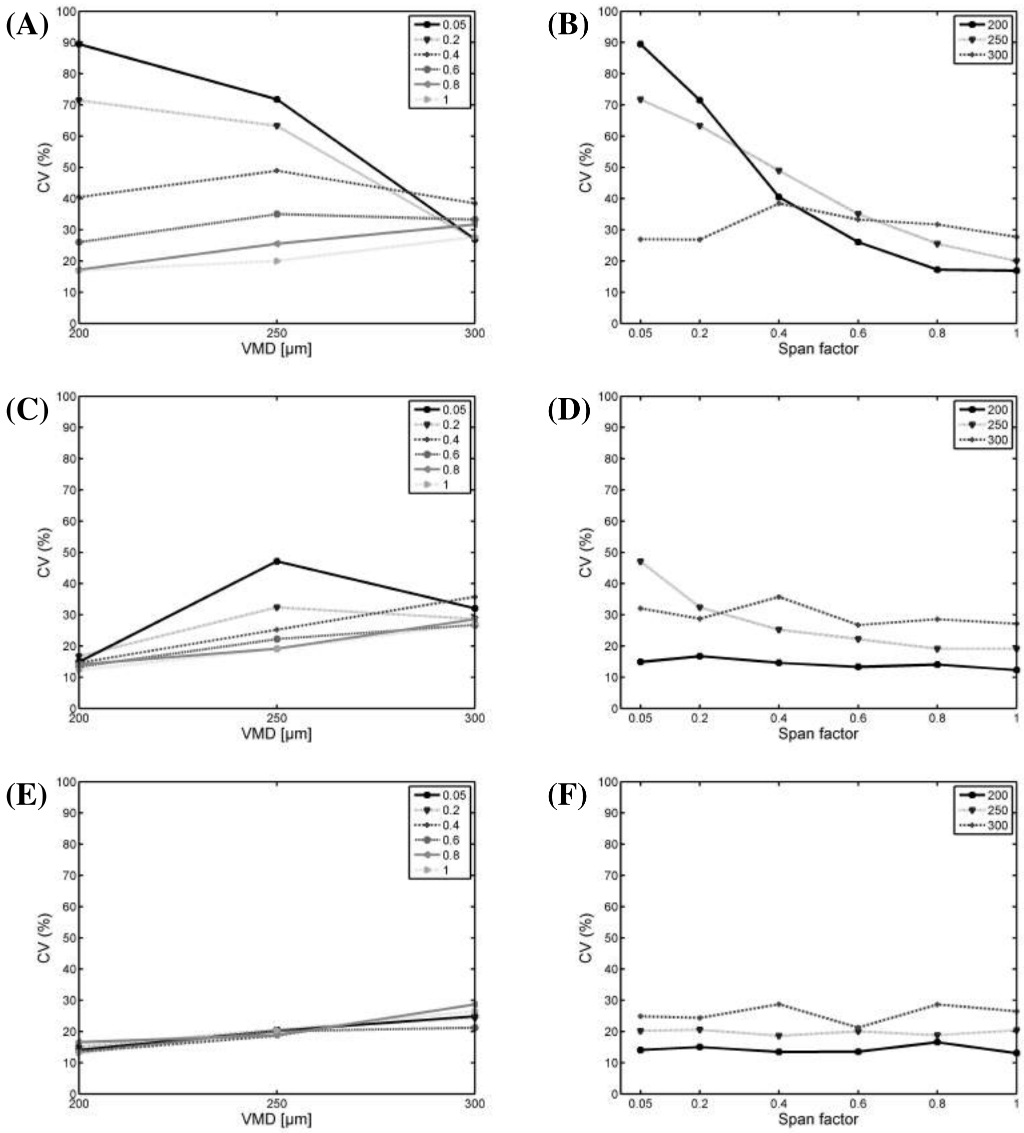


Figure 7.10: Coefficients of variation [%] for various VMD (**A**,**C**,**E**), span factors (**B**,**D**,**F**) and formulation scenarios: (**A**,**B**) low wettability, (**C**,**D**) intermediate wettability and (**E**,**F**) high wettability. Each point represents 100 virtual sprayings on the same plant architecture.

Mean deposit levels increased with increasing spray mixture wettability scenario (Figure 7.9) as expected. For the 'low wetting scenario' (Figure 7.9A,B), a slight influence of the VMD is highlighted on the relative retention. Retention increased with increasing span factor because droplets covered more energy classes contributing the spray mixture adhesion (Figure 7.8 A,B). Moreover, it can be noted than the coefficient of variation decreased with increasing span factor (Figure 7.10 B), especially for VMDs of 200 and 250 μm. A low retention with high variability denotes very poor expected treatment efficacies. For the 'high wetting scenario' (Figure 7.9 E,F), the mean level of deposits decreased as the VMD increased because the number of droplets lying in the rebound outcome increased. It should be noted that the relative retention can be greater than unity: this is due to the plant architecture since droplets can be intercepted by the lower part of the 3D plant. The retention also decreased as the span factor increased; except for a VMD of 300 μm because these spray distribution is centred within the rebound's range of existence. Variability of deposits seems rather constant for this scenario. For an 'intermediate wetting scenario' (Figure 7.9 C,D), the VMD of 200 μm clearly stands out: an increase of VMD will shift droplets towards higher energy classes where the probability of rebound and splashing is greater (Figure 7.8 C). Higher spans will lead to an increase of the probability of other impact outcomes. In terms of variability of deposits, CV increased with increasing VMD and seems rather constant as a function of the span factor, excepted for the VMD of 250 μm (Figure 7.10 D) which seems to decrease with increasing span factor because more droplets contribute gradually to adhesion. Using reduced span spray with a poorly chosen VMD may result in very low retention efficiencies, such as figure 7.9 C with VMD of 250 μm.

7.5.3 Conclusions

The following conclusions arise from the previous results:

- Droplet impact behaviours strongly affect spray retention. This has been highlighted in chapters 4 and 6 through the droplet impact behaviours histograms.
- There is a greater sensitivity to the droplet impact behaviours when using reduced span sprays.
- If the objective is to reduce the span for mitigating the risk of drift, care has to be taken in the selection of the mean droplet diameter in relation with the target surface wetting properties.

CHAPTER 8

Conclusions and perspectives

In pesticide spray applications, it is common practice to use additives to enhance mixture retention by plant leaf surfaces. The effects of additives on spray retention are classically assessed by conducting retention tests in laboratory or in the field. These tests often involve spraying plants at a given growth stage and measuring the amount of pesticide retained by leaves. They are however not fully satisfactory as they suffer from high variability that weakens their discriminating power due to various architecture and wettability of target plants. Moreover, this integrated approach offers no insights of the physics behind spray retention. Indeed retention is mainly determined by the droplet impact behaviours on leaf surfaces resulting from their wettability as well as the droplet physico-chemical and dynamic properties.

Retention is thus alternatively assessed using models based on droplet and surface properties that can be easily measured in laboratory (Taylor, 2011; Gaskin et al., 2005). These process-driven models are based on droplet impact physics to predict retention on the plant architecture for any new spray scenario (Cox et al., 2000; Dorr et al., 2014). Preponderant parameters involved in droplet behaviour at impact have been identified so far, such as droplet size and velocity, formulation surface tension and surface wettability. However, these latter parameters can vary widely both in different time scale *i.e.* dynamic surface tension or droplet velocity, and in spatial scale *i.e.* surface roughness, dynamic contact angles or droplet spreading area, resulting in a wide variability of droplet impact behaviours on some plant leaves. This may explain discrepancies observed so far between retention modelled on physico-chemical basis and measurements. A great number of droplet impact observations in realistic spray conditions is therefore needed to further improve retention assessment. This thesis aimed at gaining a deeper understanding of the interactions between droplets and leaf surfaces and propose recommendations to better control difficult-to-wet weeds. Faced to the broad scale range involved in spray application, a multiscale approach has been chosen to better address the variability in spray retention.

As a starting point of this thesis, a review of the parameters involved in spray retention at the macroscopic and microscopic scales was proposed in chapter 2 to get an overview of the current knowledge about leaf wetting and spray retention. It was shown that involved parameters are inextricably linked and the droplet physiochemical properties have to be properly optimised according to the target properties to maximize the retention. Some weeds, such as black-grass (*Alopecurus myosuroides* Huds.), are very problematic targets for spray applications because the amount of active ingredient retained by leaves can be very low and variable due simultaneously to their small, slanted and superhydrophobic leaf surfaces.

The first objective of the thesis has been achieved in chapter 3 by proposing an experimental method for studying spray droplet impact on superhydrophobic surfaces (microscopic scale). Based on the use of high-speed imaging, a reference superhydrophobic surface and a moving hydraulic nozzle, the experimental facility allowed controlling all variables involved in spray retention. Thanks to the generation of realistic droplet size distributions, all impact outcomes encountered in practice were revealed, which render achievable to explore the whole possible range of droplet size and velocity in a single trial, unlike what may provide droplet-on-demand generators (Reichard et al., 1998; Forster et al., 2005). The method provided quantitative measurements of the droplet diameter, velocity and incidence angle immediately before impact on the target surface, which is needed for computing the droplet impact energy. Qualitative information, such as droplet impact outcomes, were also derived using the technique. From this study, it was shown that transitions between impact outcomes are not sharp, various impact outcomes coexisting for similar impact energy especially adhesion and rebound outcomes (figure 5.1). Impact energy classes were discriminated using an observed impact energy threshold (Weber number). Weber numbers of transition were determined by the intersection of the probability density functions of Weber numbers of the different impact outcomes, which enabled computation of relative volume of each impact outcome. The choice of the Weber number as indicator for droplet impact outcome transition is quite straightforward since the Weber number represents the ratio between droplet kinetic energy and surface energy (Rioboo et al., 2008; Lake and Marchant, 1983). This test bench was found particularly suited to rank spray mixture additives since all other parameters can be fixed. The high degree of hydrophobicity of the artificial surface is very discriminant when ranking surfactants with low dynamic surface tension.

Using the spray application test bench (chapter 3), it was highlighted that the reduction of the dynamic surface tension using surfactants mainly acts on the transition between adhesion and rebound as described by Richard et al. (2002). Transition between rebound and fragmentation are rather sensitive to the modification of the viscosity on a given target surface. Such information is valuable for industrials who want to clarify the relationships between formulation and resulting spray impact behaviour for guiding their developments. It also fills the gap between systematic studies of droplet impact from fundamental physical research and retention studies of agronomists thanks to an overall multiscale approach, from the droplet to the field.

Since the droplet incidence angle, that results from the various droplet trajectories and the various leaf angles, was identified in chapter 2 as an influencing factor, chapter 4 focused on the modification of the droplet impact behaviour depending on the mean droplet incidence angle in order to reach the second objective of the thesis. The tilt of the target surface resulted in a reduction of the projected area available for droplet interception. An angled droplet impact leads to the reduction of the normal component and induces a tangential component of the impact velocity. This results in shift from Wenzel to Cassie-Baxter wetting regime since there is not enough impact energy to break the energy barrier for droplet pinning. As a result, the droplet rebound may exist at higher impact energies. In this chapter, transitions between impact outcomes were improved by a discretisation of the droplet impact energy space into eleven energy classes during experiments. The choice of the size of these energy classes was driven by a compromise between a minimal number of droplets within each class and the resolution needed for modelling purpose, *i.e.* having continuous impact behaviour probability histograms. It appears from this study that treating grass weeds with predominant vertical leaf orientation remains very difficult using sprays directed vertically downwards, highlighting the need of a spray-plant interaction model (chapter 6) for assessing the potential of using alternative spray application technique, such as angled sprays (Jensen, 2007).

Chapter 6 provided a spray-plant interaction model based on the droplet impact histograms in order to accomplish the final objective of this thesis. It computes the interception of droplet from a virtual nozzle by a 3D plant model of a real plant architecture. The retention was computed as the contribution to adhesion of each droplet at primary impact, based on droplet impact behaviour histograms (chapter 4). Considering only primary impacts of droplets remains an acceptable assumption when treating small plants with slanted leaves with relatively low applied volumes. Indeed droplet recapture is unlikely and would represent a very small proportion of the total retention by the plant. Thanks to the various droplet size distributions drawn by the model and the different droplet impact outcomes, the variability between simulations on the same plant was quantified under the specific assumptions of the model. This practical tool proved to be a valuable technique for screening the operational choices according to the target and the formulation both in terms of average levels and variability of deposits retained by the target leaf surface. In the droplet intersection algorithm used in this thesis (section 6.5.4), some assumptions have been made. Firstly, droplet trajectories are assimilated as straight lines immediately before collision with the plant model without consideration of airflows surrounding the plant surface. These air currents can deflect smaller droplets when they arrive close the plant surface because of their low relaxation time (Spillman, 1984). Hereby, droplets follow airstreams at the surface and impaction is hindered (Matthews, 2008). Therefore, how important is the contribution of variable airflows due to micrometeorology and turbulence resulting from the spray application to retention variability? Another limitation of the proposed approach concerns droplet intersections close to the edge of leaves since droplet size is not taken into account in the algorithm. Finally, another hypothesis taken in this work concerned the unlikelihood of droplet impact on an already wetted leaf surface. This hypothesis remains acceptable at low application volumes but could clearly affect droplet impact outcomes at higher rates (Yarin, 2006). All these limitations could be addressed by further developments of the model.

Droplet impact probability histograms were afterwards fitted using using a logistic model in order to reduce the number of parameters involved (chapter 7.4) and to better describe the transition between droplet impact behaviours. This logistic model was highlighted as the best model of adhesion from the extensive work of Stevens et al. (1993) and Forster et al. (2005). This approach enables to quickly constitute a database in relation with application conditions that could be used prior to field trials would allow discriminating poorer efficacies expected to result from inappropriate operating choices and reduce their costs, but also to allow more fundamental research about leaf wetting, spray retention and its variability.

In the context of risk of herbicide resistance emergence (Moss, 2013), the variability of retention between weed plants is a predominant factor that can be increased when treating at reduced volumes per hectare because the number of droplet per surface unit area is decreasing (Butler Ellis et al., 2007; Miller et al., 2010). This trends is also observed when treating small plant architecture if the available leaf surface for droplet interception is reduced. The virtual spray-plant interception model proposed can help at assessing the potential risk of resistance emergence due to unapporperiate formulation and spray quality used resulting in highly variable retention at the plant scale.

Faced to the results presented in this thesis, many perspectives are opened for further work and some practical recommendations are proposed in order to meet the last objective of the thesis. Concerning the droplet size, it is well established that smaller droplets are prone to drift and should therefore be avoided despite their good adhesion properties. For mitigating the risk of drift, beyond the respect of good spray application practices, it is common to use larger droplet sizes. However, for a given volume per hectare, the number of droplet per surface unit area will decline with increasing mean droplet size. Since the potential number of intercepted droplet will be smaller, the variability of the treatment will raise (Butler Ellis et al., 2007; Miller et al., 2010). The mean level of retention could drop due to the numerous secondary droplets resulting from the shift towards detrimental fragmentation impact outcomes. However, it has been showed in chapter 3 that the droplet fragmentation threshold is found to be mainly dependent to droplet impact energy, less to target surface properties and formulation surface tension. Larger droplets could however be profitable in herbicide applications in combination with low dynamic surface tension surfactants thanks to the shift from Cassie-Baxter to Wenzel wetting regime allowing droplet pinning that can contribute significantly to retention (Boukhalfa et al., 2014). The ejected droplets could also be profitable for rentention in high leaf area index crops, since secondary droplets could be recaptured by other leaves in the canopy (Butler Ellis et al., 2004). On plants with small, slanted and superhydrophobic leaves, such as weeds at early growth stages, the use of low DST surfactants improving spray mixture wettability is highly advised to reduce droplet rebound occurrence. To achieve this goal, surfactants should have a very low dynamic surface tension at time scales under 3-5 ms to be effective.

Spray retention could be improved by changing the spray application technologies commonly used, *i.e.* uniform spraying with hydraulic nozzles directing droplets downwards. Firstly, by acting on the droplet size distribution for instance by using narrow span sprays with controlled droplet application (CDA) (Gebhardt, 1988). This approach involved the modification droplet formation mechanism. The main advantage of such device is to provide narrow droplet size distribution by eliminating small and large droplets of the spray. However, it has been showed that the spray performance of CDA and hydraulic nozzles did not differ consistently (Matthews, 2008) despite differences in droplet size distributions and this approach resulted in some commercial solutions (Micromax from Micron Group, UK or Girojet from Tecnoma, France). Efficient use of narrow span sprays still requires information on the biological needs to optimize droplet size (Knoche, 1994). The proposed spray-plant interaction model is therefore very usefull for answering to such question. It has been showed from results of the chapter 7.5, that very low retention could be obtained when the mean droplet size is poorly chosen (figure 7.9 C) and could lead to treatment failures. The spray-plant interaction model can thus be used for guiding the further developments of new nozzles (De Cock et al., 2014). Another solution for improving herbicide applications lies in the use of angled sprays, in order to increase the projected plant capture surface area (Jensen, 2007). The determination of the optimal nozzle tilt could be studied numerically using a spray-plant interaction model. Thirdly, the current change in paradigm passing through the use of precision farming concepts, such as spot or patch spraying, micro-spray systems or variable-rate technologies, still requires advisory systems for guiding their developments (Søgaard and Lund, 2007; Thorp and Tian, 2004).

In chapter 5, the relevance of a synthetic surface for use as reference for the assessment of spray application efficiency was highlighted. Similar impact outcomes were observed on natural and artificial superhydrophobic surfaces and were consistent with recent theoretical developments on superhydrophobic materials. The reference surface avoided the natural variability of leaves and its high level of wettability provided a spray retention test bench more suited to conduct comparative assessment of formulation retention performance. It was observed that wheat leaves present an anisotropic surface that influences the impact outcome, satellite droplets being directed preferentially along the main axis (Zhao et al., 2007). Consequences on retention should be studied further. Leaf surface fouling was suspected to reduce drastically the droplet rebound in practical application on outdoor grown leaves, which render field trial tests even more variable. More fundamental studies could be performed for understanding factors behind the variability of droplet impact outcomes on leaf surfaces and derive models to predict droplet impact outcome probabilities. On the basis of a larger leaf surface properties database, it could be possible to link droplet behaviours with the underlying physical mechanisms. This would render the model able to predict any new leaf/droplet/formulation combination. This should pass through a deeper analysis of the wettability of leaf surfaces depending on the growth stage. For instance, a study of the leaf microstructure that can contain, for example, hairs, trichomes, stomata, veins, and wax structures (Barthlott et al., 1998; Taylor, 2011) as well as orientation of leaf surface could be performed in order to gain better insight of the wetting mechanisms. Especially, the transition between droplet adhesion and bouncing impact outcomes, which is not sharp due to the coexistence of the two behaviours for similar impact energy levels (figure 5.1 B), should be improved to include factors relative to the surface roughness and including contact angle hysteresis (He et al., 2003) or the solid fraction (surface fraction corresponding to the top of the relief) (Bico et al., 2001) for instance. Further model improvements should take into account the relative size between droplet and roughness structure size (figure 8.1), as smaller droplet could experience more variable impact conditions (zone with or without hairs) than larger ones that take up more space during spreading phase. The approach should rely on experimental droplet impact studies and the use of methods for leaf surface roughness characterisations (Journaux et al., 2011; Nairn et al., 2011). The weathering of leaf surface could also be studied since rain, wind and dust could alter the wetting state of leaves by abrading leaf epidermis. Since wettability may change spatially with the age of the leaf or because environmental abrasion, a leaf surface properties database would be helpful for modelling purposes.

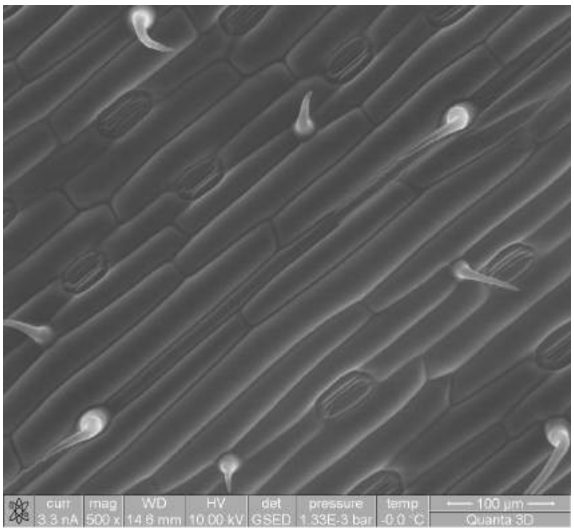


Figure 8.1: SEM micrograph of the surface of a wheat plant at early growth stage (Journaux, unpublished).

The proposed tool could also be used to determine the optimum time of sprayings by predicting the optimal retention potential depending on the target (Combellack, 1981). A better knowledge of the droplet/target interactions should therefore rely on improving plant phenotyping for characterising the plant architecture, such as the recent advances of Kempthorne et al. (2015). A given plant morphology could be characterised using a formal grammar system, such as the Lindenmayer system (Prusinkiewicz and Lindenmayer, 1990), in order to enable comparison of different models of spray retention with the same plant model. In the field, the weed population is composed of plants of various size. A database of weed architectures for different species at different growth stages could be built in order to determine the optimal growth stage for weed control.

The final outstanding question is to link spray application choices with the biological efficacy of herbicides. It will need to merge deposition, retention, uptake and translocation models taking into account some open questions, such as how does the coverage and droplet size for a given deposition affect the overall biological efficacy?

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