

## Species-specific challenges for improving agrochemical spray performance on ryegrass

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**Summary** Ryegrass possesses unique surface and canopy characteristics that make it a difficult target for modelling spray retention. It has a complex canopy compared to other grass species. In addition, it possesses an extremely-difficult-to-wet waxy adaxial leaf surface character, which is usually represented in spray retention models. However, the dominant feature of a ryegrass canopy is the extremely-easy-to-wet abaxial leaf surface, which is readily targeted by sprays due to the specific plant growth form that provides substantial exposure of abaxial surface to the incident spray. An unusually high level of spray retention was observed on this species in comparison to other grass species that could not be explained using the available retention model. This was because of higher than expected retention by the easy-to-wet abaxial leaf surfaces and their dominance in the canopy for spray interception. However, this gain was negated by low uptake of glyphosate by the abaxial compared to the adaxial leaf surface. It was concluded that addition of a tank-mix surfactant could provide higher retention and uptake on the difficult-to-wet adaxial leaf surface of perennial ryegrass. The relative importance of surface and canopy characteristics of ryegrass needs to be considered in spray formulation and application strategies for enhanced spray performance.

**Keywords** Leaf surface wettability, contact angles, fractal dimension, retention models, glyphosate, organosilicone surfactants, L-77, uptake.

### INTRODUCTION

Currently available empirical spray retention models can predict spray retention with greater than 90% accuracy for a range of arable crop and weed species (Forster *et al.* 2006, Pathan *et al.* 2009). Key inputs in such models related to plant characteristics are numerical values representing adaxial leaf surface and individual plant canopy characteristics (complexity as well as size of the canopy). As with spray retention modelling, the adaxial leaf surface characteristics and agrochemical interactions are factored in uptake modelling, since this is the surface where the majority of uptake of retained spray is considered to occur in many plant species. However, in preliminary experiments, both annual ryegrass (*Lolium rigidum*) and perennial

ryegrass (*Lolium perenne*) were found to possess different wettability characteristics on adaxial (upper) and abaxial (lower) leaf surfaces. This feature is in contrast to that of many grass species where both leaf surfaces are difficult-to-wet (A.K. Pathan unpublished data).

Experiments were conducted to (a) demonstrate the effect of specific surface and canopy characteristics of perennial ryegrass on spray retention, and (b) determine relative uptake of glyphosate on adaxial and abaxial perennial ryegrass leaf surfaces. Selected data on other plant species from previous retention modelling work (Forster *et al.* 2006, Pathan *et al.* 2009) are presented for comparison with the ryegrass data and to highlight species-specific challenges for modelling spray retention posed by the unusual surface and canopy characteristics of perennial ryegrass.

### MATERIALS AND METHODS

**Plant materials** Plant species used were annual ryegrass, barley (*Hordeum vulgare* L.), barnyard grass (*Echinochloa crus-galli*), couch grass (*Agropyron repens* L.), crowfoot grass (*Dactyloctenium aegyptium*), pampas grass (*Cortaderia selloana*), perennial ryegrass, purple nutsedge (*Cyperus rotundus*), summer grass (*Digitaria sanguinalis*), wheat (*Triticum aestivum* L.) and Yorkshire fog (*Holcus lanatus*). These were raised in individual pots in controlled environment growth chambers for 4–6 weeks as described by Forster *et al.* (2006).

**Agrochemicals** The surfactant used was Silwet® L-77™. Glyphosate was used as formulated Roundup Transorb™ or as unformulated (pure) glyphosate isopropylamine (IPA) salt. Methods for measuring spray retention and droplet contact angles (CAs) (Forster *et al.* 2006) and uptake Gaskin (1995) have been described previously.

**Electron microscopy** Electron micrographs were obtained using equipment and techniques described by Pathan *et al.* (2008) for dehydrated samples.

**Statistical/fractal analysis** Fractal dimensions (FD) were derived as per Pathan *et al.* (2009). FD usually corresponds to the complexity of a geometrical object

(Borkowski 1999). It provides a unique mathematical expression to represent the geometry of complex, irregular and variable shapes, including plant canopies. Data were subjected to analysis of variance (Genstat 5) and a least significant difference (LSD) test was used to compare mean FD, retention and uptake values between treatments. Regression analysis was done using MS Excel™ software (Version 11).

## RESULTS AND DISCUSSION

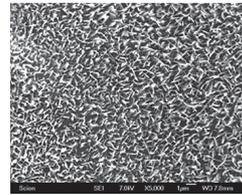
Leaf surface wettability is a critical factor governing agrochemical spray droplet adhesion and retention on plant targets. Traditionally, a plant species is characterised by contact angles of 20% aqueous acetone droplets on adaxial leaf surfaces (Gaskin *et al.* 2005). Grass species are generally difficult-to-wet targets because of the presence of highly crystalline epicuticular waxes on adaxial and abaxial leaf surfaces. For example, the 20% aqueous acetone CA on both surfaces of leaves of wheat, barley, crowfoot grass, summer grass, barnyard grass, Yorkshire fog and couch grass was 180°, classifying them as extremely difficult-to-wet targets. Out of the available grass species characterised for leaf surface wettability, only one (purple nutsedge) had a totally wettable adaxial leaf surface (selected data from preliminary experiments presented in Table 1).

**Table 1.** Contact angles (°) of 2 µL aqueous acetone (20% v/v) droplets on grass species with relatively easy-to-wet abaxial leaf surfaces.

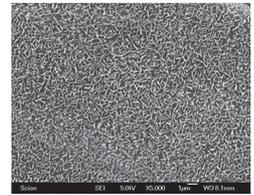
Species	Adaxial	Abaxial
Annual ryegrass	180	59
Perennial ryegrass	180	19
Pampas grass	180	94
Purple nutsedge	0	0

Traditionally, ryegrass (both annual and perennial) is classified as a difficult-to-wet target, based on its waxy adaxial leaf surface. This parameter is usually considered in making spray formulation and application decisions targeted at this species. However, the abaxial leaf surface of ryegrass is distinctively different in surface wettability, being easy-to-wet compared to the extremely difficult-to-wet adaxial leaf surface (Table 1). Significant differences between adaxial and abaxial leaf surfaces of ryegrass were also evident using an electron microscope (Plate 1), raising the possibility that other species within the *Lolium* genus may have differences between adaxial and abaxial surfaces similar to that observed for annual and perennial ryegrass. The adaxial surface of both ryegrass species

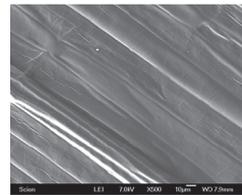
was covered with microcrystalline epicuticular waxes, which is a characteristic feature of difficult-to-wet grass species. However, the abaxial surface was devoid of crystalline waxes and was prone to destruction by the electron beam, indicating a relatively fragile composition. Preliminary experiments indicated that both ryegrass species are distinctively different to other grasses, but are similar to each other in leaf surface and plant canopy characteristics.



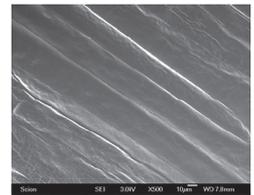
Perennial ryegrass (adaxial)



Annual ryegrass (adaxial)



Perennial ryegrass (abaxial)



Annual ryegrass (abaxial)

**Plate 1.** Leaf surface micromorphology of ryegrass species as revealed by scanning electron micrographs.

Among the many factors that determine the efficiency of spray performance, plant canopy architecture is intrinsic to plants. This factor generally cannot be manipulated for achieving better spray performance. The complexity of plant canopies can be represented by fractal dimension (FD) values (Pathan *et al.* 2009). In addition to species-specific differences in adaxial and abaxial leaf surface composition, perennial ryegrass displays a distinctively complex canopy, as characterised by a higher FD value in comparison to other grass species studied (selected data from Forster *et al.* (2006) and Pathan *et al.* (2009) are presented in Table 2). This is because of the presence of profuse, slender tillers and the twisting/flipping growth form of leaves in ryegrass species. This twisting behaviour in the canopy gives higher than normal exposure of the easy-to-wet abaxial leaf surfaces to the incident spray. This would lead to higher than expected spray retention if the abaxial surface was not accounted for in spray retention models. An unusually high level of spray retention per unit plant surface area (5.68 µL cm<sup>-2</sup>) relative to other grasses was observed.

Regression analysis, using this high spray retention and adaxial leaf surface 20% CA data, indicated ryegrass is an outlier species (Figure 1a). However, when the contact angle value for the abaxial leaf surface (19°) was substituted for that of the adaxial leaf surface (180°), the regression model improved significantly, explaining 88% of the underlying variation (Figure 1b). The results indicate that the easily-wetted abaxial leaf surface of ryegrass and its significant exposure to the incident spray was responsible for higher than expected spray retention on perennial ryegrass. In fact, there was high retention with water alone (Table 3). Organosilicone surfactants such as L-77 are often used to reduce surface tension of spray solutions and enhance spray retention on waxy leaf surfaces (Stevens *et al.* 1993). However, using L-77 at varying concentrations did not improve spray retention at all on perennial ryegrass compared to not using it (Table 3).

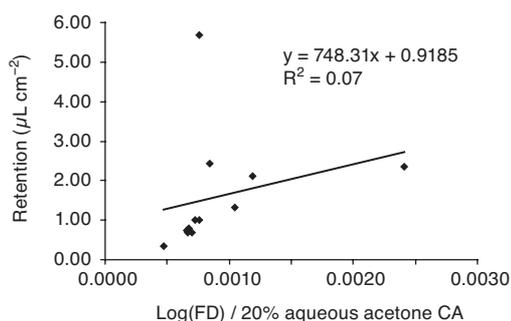
The results strongly suggest that the adaxial difficult-to-wet surface of perennial ryegrass was not

a dominant feature of its canopy. Instead, the easy-to-wet abaxial leaf surface intercepted the majority of the spray solution. This hypothesis is also supported by the fact that water alone provided better retention than using L-77. The lower retention of L-77 could be due to run-off from easy-to-wet perennial ryegrass

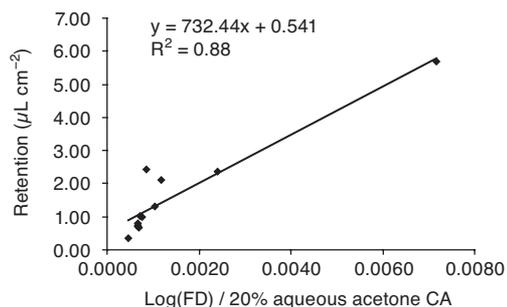
**Table 2.** Retention of sprays (0.01% L-77) by plant species with varying complexities (FD values), sprayed at application rate of 250 L ha<sup>-1</sup>.

Species	Canopy FD	Spray retention (μL cm <sup>-2</sup> )
Barley	1.32	0.80
Bean	1.10	0.99
Cabbage	1.20	0.68
Onion	1.32	0.69
Perennial ryegrass	1.37	5.68
Purple nutsedge	1.30	1.60
Wheat	1.31	0.75
LSD (P = 0.05)	0.03	0.62

(a) Perennial ryegrass adaxial CA 180°



(b) Perennial ryegrass abaxial CA 19°



**Figure 1.** Spray retention (0.01% L-77) versus ratio of fractal dimension of canopy (FD) and 20% aqueous acetone contact angles (CA) for 12 different plant species, including perennial ryegrass.

**Table 3.** Spray retention of L-77 by perennial ryegrass sprayed at nominal application rate of 100 L ha<sup>-1</sup>.

Treatment	Surface tension (mN m <sup>-1</sup> )	Spray retention (μL cm <sup>-2</sup> )
Water	72	1.77
L-77 (0.01%)	41	1.32
L-77 (0.025%)	26	1.34
L-77 (0.1%)	19	1.32
LSD (P = 0.05)		0.18

**Table 4.** Differential uptake of glyphosate (%) on perennial ryegrass leaf surfaces.

Formulation	Surfactant	Adaxial surface	Abaxial surface
Roundup Transorb (2.7%)	None	47	3
Roundup Transorb (2.7%)	L-77 (0.1%)	–	12
Roundup Transorb (1.8%)	L-77 (0.1%)	78	–
Glyphosate IPA (1%) <sup>A</sup>	None	– <sup>B</sup>	5
Glyphosate IPA (1%)	L-77 (0.1%)	–	42
LSD (P = 0.05)			23

<sup>A</sup> Unformulated (pure) glyphosate;

<sup>B</sup> Droplet did not stick;

– No data available.

abaxial leaf surfaces promoted by low surface tension of spray solutions containing L-77. Retention data would suggest that L-77 addition does not enhance spray efficiency in perennial ryegrass. However, efficacy of a systemic herbicide is not determined by retention alone. Enhanced uptake of the herbicide retained on plant surfaces is essential for achieving the desirable efficacy. Hence, the abaxial leaf surface should have high uptake potential as well for overall spray performance.

Uptake experiments examined relative uptake of glyphosate (formulated and unformulated) with and without an organosilicone surfactant. An inherent tendency of lower uptake of glyphosate (formulated or in pure form) was observed on the abaxial leaf surface compared to that on adaxial leaf surface (Table 4), confirming earlier work by Bishop (1987). The surfactant could not increase uptake of formulated glyphosate (Roundup Transorb) on the abaxial leaf surface to similar levels on the adaxial leaf surface. When unformulated glyphosate (IPA) was used, L-77 did bring a significant increase in uptake on the abaxial surface, to a similar level as formulated glyphosate (without any tank-mix surfactants) on the adaxial surface. Thus, L-77 significantly improved uptake of unformulated (pure) glyphosate IPA on the abaxial leaf surface, but failed to do so for formulated Roundup Transorb. This may be due to unexplained chemical interactions between abaxial leaf surface waxes, co-formulants in Roundup Transorb and L-77 itself. Further studies are required to confirm this hypothesis.

Uptake data suggest that despite the high levels of retention by easy-to-wet abaxial ryegrass leaf surfaces, surfactant enhanced spray retention and uptake on difficult-to-wet adaxial leaf surfaces would be required for better overall spray performance, since this is the surface from where the highest level of glyphosate uptake occurs in ryegrass. If similar trends are observed with other systemic agrichemicals, then differential retention/uptake from ryegrass surfaces would need to be accounted for in making spray application decisions.

It is concluded that the easy-to-wet abaxial leaf surface is a dominant feature of the ryegrass canopy that is responsible for higher than expected spray retention. These features of ryegrass surfaces and canopy need to be accounted for in making spray application decisions. The abaxial leaf surface enables high retention of the applied herbicide, but the retention gain is negated by lower uptake from the abaxial leaf surface. Addition of tank-mix surfactants could provide a relatively better choice for enhanced retention as well as uptake from adaxial surfaces of

perennial ryegrass. The relative importance of surface and canopy characteristics needs to be considered when determining spray formulation and application strategies for enhanced spray performance on ryegrass.

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#### REFERENCES

- Bishop, N. (1987). The influence of environment, season, plant growth stage and herbicide formulation on the activity of glyphosate applied to *Lolium perenne*. PhD thesis, University of Canterbury, 217 pp.
- Borkowski, W. (1999). Fractal dimension based features are useful descriptors of leaf complexity and shape. *Canadian Journal of Forest Research* 29, 1301-10.
- Forster, W.A., Kimberley, M.O., Steele, K.D., Haslett, M.R. and Zabkiewicz, J.A. (2006). Spray retention models for arable crops. *Journal of ASTM International* 3, Paper ID JAI13528 (available at <http://www.astm.org>).
- Gaskin, R.E. (1995). Effect of organosilicone surfactants on the foliar uptake of herbicides: stomatal infiltration versus cuticular penetration. Proceedings of 4th International Symposium on Adjuvants for Agrochemicals, ed. R.E. Gaskin, pp. 243-8. (International Society for Agrochemical Adjuvants, Wageningen, The Netherlands).
- Gaskin, R.E., Steele, K.D. and Forster, W.A. (2005). Characterising plant surfaces for spray adhesion and retention. *New Zealand Plant Protection* 58, 179-83.
- Pathan, A.K., Bond, J. and Gaskin, R.E. (2008). Sample preparation for scanning electron microscopy of plant surfaces – horses for courses. *Micron* 39, 1049-61.
- Pathan, A.K., Kimberley, M.O., Forster, W.A., Haslett, M.R. and Steele, K.D. (2009). Fractal characterisation of plant canopies and application in spray retention modelling for arable crops and weeds. *Weed Research* 49, 346-53.
- Stevens, P.J.G., Kimberley, M.O., Murphy, D.S. and Policello, G.A. (1993). Adhesion of spray droplets to foliage: the role of dynamic surface tension and advantages of organosilicone surfactants. *Pesticide Science* 38, 237-45.