THE MECHANISM OF ORGANOSILICONE SURFACTANT-INDUCED ANTAGONISM OF GLYPHOSATE UPTAKE

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Summary. The addition of the organosilicone surfactant, Silwet L77, to glyphosate formulations antagonises the uptake of herbicide by adaxial leaf surfaces of *Paspalum dilatatum* Poiret. The adaxial leaf surface is stomatous but evidence for significant herbicide uptake by this pathway is lacking. Addition of glycerine to formulations containing Silwet L77 removes the antagonism to glyphosate uptake. Glycerine does not appear to have a pronounced humectant effect and it is concluded that antagonism and its alleviation by glycerine involves specific leaf surface-solution interactions that are clearly species specific.

INTRODUCTION

The organosilicone surfactant Silwet L77 enhances herbicide uptake principally by facilitating stomatal infiltration of solution (5, 6). The rapid flow of herbicide solutions into sub-stomatal cavities requires certain plant morphological characteristics and physical attributes of the solution to be satisfied. Open stomatal pores, appropriate ledge angles in the stomatal pore plus a low solution surface tension (< 30 mN/m) are requirements, (7, 10). In perennial ryegrass (*Lolium perenne* L.) and gorse (*Ulex europaeus* L.) these requirements are met and both field and laboratory studies have demonstrated the utility of using Silwet L77 with glyphosate and other herbicides (1, 2, 8, 9).

In some field studies the performance of herbicide formulations containing Silwet L77 has not been positive and laboratory studies have shown an antagonism to the uptake of glyphosate in several species (7). To date there has been no clear indication of the mechanism of Silwet L77-induced antagonism of herbicide uptake although it is unlikely to concern simple effects involving leaf surface or solution characteristics (7). This paper examines the extent of Silwet L77-induced antagonism of glyphosate uptake in paspalum (*Paspalum dilatatum* Poiret.), and approaches to formulation that may alleviate the problem.

METHODS

Plant material and experimental conditions. Plants of paspalum (cv. Grasslands Raki) were grown at 20/15°C with a photoperiod of 14 h, 70 RH and a PPFD of 300 μ mol/m^2/s in pots containing a medium of 1:1 soil and nutrient-supplemented potting mix. Plants were grown to the 3 to 5 leaf stage and the youngest fully expanded leaf used in all experiments. All experiments were fully randomised designs with a minimum of eight replicates. An analysis of variance was used to calculate standard errors of the means.

Herbicide formulations. A standard formulation equivalent to 0.72 kg /ha of glyphosate in 200 l water/ha was used in all experiments. Adjuvants were added on a volume basis with final concentrations of Silwet L77 in the range 0.1-0.5% (v/v) and glycerine at 6% (v/v). In uptake experiments 14C glyphosate, formulated as the isopropylamine salt was added to give a radioactive concentration of 30,000 d.p.m./μl.

Experimental methods. Uptake of ^{14}C glyphosate formulations involved application of 2x0.5 μl droplets to the adaxial leaf surface for 1 or 6 h before removal with 25 ml of a 2% (w/v) glyphosate solution followed by a chloroform wash. Aliquots were scintillation counted (6, 7). Contact angle measurements were made on intact leaf surfaces and calculated using Mack's equation (6, 7). Deposit drying rates were determined by application of 2x1 μl droplets to glass slides previously coated with wax extracted from leaves of paspalum. Wax extraction involved chloroform washes, a concentration step and application of a constant mass of wax to the glass slide, (11). All deposit drying rates were determined at 23°C and 60% RH and involved

determination of the time taken for deposit weight change to cease. The fluorescent dye, Uvitex 2B, was incorporated into herbicide formulations (1 mg/ml) and applied to leaf surfaces for 20 or 60 minutes before removal with a large volume of distilled water. Entry of solution into the leaf through stomatal pores was determined immediately by UV microscopy and a photographic record taken (6).

RESULTS AND DISCUSSION

Addition of 0.1-0.5% Silwet L77 to glyphosate significantly reduced herbicide uptake by paspalum after 6 h (Table 1). This compares with a 120% enhancement of uptake by addition of 0.1% Silwet L77 in *Lolium perenne* (6). While addition of the humectant, glycerine did not enhance uptake in the absence of Silwet L77, in combination there was positive promotion of glyphosate uptake over 6 h (Table 1). The most effective treatment contained 0.1% Silwet L77. The positive enhancement of uptake was also evident after a 1 h uptake period (Table 1). In this instance the advantage of adding glycerine was even more pronounced as any antagonistic effects of using Silwet L77 alone were not evident. Percentage uptake values of 7-8% were measured for all treatments in the absence of glycerine, (Table 1). Removal of epicuticular wax with chloroform revealed no significant treatment effects and the percentage of glyphosate incorporated into wax was always ≤1.0% of that applied.

Table 1. The effect of Silwet L77 and glycerine on the uptake of glyphosate by paspalum.

		Gross uptake (%)	
Silwet L77 (% v/v)	Glycerine (% v/v)	Time (h) 1	6
0	0	8.8	18.8
0.1	0	7.3	6.8
0.5	0	8.0	7.6
0	6	5.6	17.6
0.1	6	27.9	29.7
0.5	6	16.9	24.5
s.e.		3.80	2.30

One effect of different glyphosate formulation on uptake may involve variations in the pathway of uptake. The surface tension of a glyphosate solution containing 0.1% Silwet L77 is 24.1 mN/m and this rises only slightly to 25.6 mN/m following the addition of 6% glycerine (7). The low surface tension values for formulations containing Silwet L77 are linked to low contact angles with the leaf surface and complete wetting after a time lag of 10-120 seconds, (Table 2). Previous work has shown that in *Lolium perenne* (6), *Ulex europaeus* (8) and *Vicia faba* L. (3), formulations with low surface tension and a complete surface wetting capability are likely to enter leaves through open stomatal pores. In the cases of *Lolium perenne* and *Vicia faba* this involved rapid stomatal entry of solution, with 1 h uptake values being enhanced by 220% and 300%, respectively for the two species, (3, 6).

Table 2. The effect of Silwet L77 and glycerine on the contact angle, time to complete surface wetting and deposit drying rate of glyphosate formulations. Values for s.e. in parentheses.

Silwet L77 (% v/v)	Glycerine (% v/v)	Contact angle (degrees)	Time to Complete wetting (seconds)	Deposit drying rate (% weight loss/min)
0	0	88.0 (1.58)	NW	8.7 (0.26)
0.1	0	0	19	9.6 (0.77)
0.5	0	0	IW	22.6 (0.60)
0	6	100.2 (1.16)	NW	8.0 (0.25)
0.1	6	45.0 (1.92)	120	9.7 (0.13)
0.5	6	0	<10	19.3 (0.22)

NW = non complete wetting
IW = instantaneous wetting

In the present study there was no rapid foliar uptake of formulations containing 0.1-0.5% Silwet L77 unless glycerine was included (Table 1). The evidence suggests that in paspalum rapid stomatal entry of solutions containing Silwet L77 alone is not occurring. There is partial corroboration from studies involving visualization of the behaviour of solutions containing a fluorescent indicator (3, 6, 7). Current experiments show that inclusion of the fluorescent dye Uvitex 2B in solutions containing Silwet L77 as the only adjuvant results in location of fluorescence around stomata but no evidence of significant solution movement into tissues adjacent to the stomatal pore. The results indicate that addition of Silwet L77 does not facilitate rapid stomatal entry of solution in paspalum.

The addition of glycerine to formulations containing Silwet L77 rapidly enhanced glyphosate uptake, with up to a threefold increase occurring within 1 h (Table 1). In experiments with Uvitex 2B there was greater enhancement of fluorescence around stomata with formulations containing glycerine. The addition of glycerine appeared to promote the stomatal route of entry although the uptake process was clearly saturated after approximately 1 h, with little further uptake of glyphosate occurring in the subsequent 5 h period, (Table 1).

The role of glycerine in promoting the uptake of glyphosate formulations containing Silwet L77 is difficult to interpret. Glycerine is recognised as possessing humectant properties which should have some delaying effect on droplet drying (4). Measurements made on artificial wax surfaces showed no major effect on droplet drying rates, particularly in the absence of Silwet L77 or when it was present at 0.1%, (Table 2). There was a minor reduction in the deposit drying rate when glycerine was added to solutions containing 0.5% Silwet L77.

The positive effect of adding glycerine to formulations containing Silwet L77 on the uptake of glyphosate by paspalum cannot be attributed to simple humectant properties and significant effects on delaying deposit drying. There are interesting surface phenomena because pre-treatment of paspalum leaf surfaces with Silwet L77 for 2 h stimulates the uptake of subsequently applied glyphosate, but not when the glyphosate is formulated with additional Silwet L77 (7). Major morphological features of the adaxial leaf surface of paspalum are not dramatically different from species such as *Lolium perenne* that show no antagonism (Dobson and Field, unpublished; 7). However there are differences in epicuticular wax composition with standard glyphosate formulations having a lower contact angle with the adaxial leaf surface of paspalum (88°) than *Lolium perenne* (118°). Interestingly another species showing antagonism, *Elytrigia repens* Beauv. has a contact angle of 82° (Field and Tisdall, unpublished). Current investigations are determining if relatively easy to wet surfaces provide a physico-chemical basis for antagonism. At present it is not clear how the addition of

glycerine may act to ameliorate antagonism and promote Silwet L77-induced uptake of glyphosate in species such as paspalum.

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