INFLUENCE OF SURFACTANT MIXTURES ON CUTICULAR UPTAKE OF GLYPHOSATE INTO GRASSES

Z.Q. LIU and J.A. ZABKIEWICZ

*New Zealand Forest Research Institute Ltd,
Private Bag 3020, Rotorua*

ABSTRACT

The uptake of glyphosate into wheat and two grass species in the presence of surfactants varied with surfactant structure, ethylene oxide (EO) content and concentration. A synergistic uptake enhancement into wheat and barnyard grass was observed when an aliphatic amine surfactant was mixed with either an alcohol or octylphenol nonionic surfactant with different EO content, at equivalent concentration. The effect of an amine+alcohol surfactant mixture on glyphosate uptake into wheat and ryegrass was compared with commercial glyphosate formulations.

Keywords: surfactant mixture, glyphosate, uptake, grass, ethylene oxide.

INTRODUCTION

The effects of numerous surfactants on foliar uptake of glyphosate have been investigated and many attempts have also been made to understand their mode of action (Gaskin and Holloway 1992; de Ruiter *et al.* 1994).

It has been found through empirical experiments that surfactants which don't cause extensive droplet spreading on plant foliage are good enhancers of glyphosate uptake (de Ruiter *et al.* 1992; Nalewaja and Matysiak 1995). As glyphosate is a systemic hydrophilic herbicide, any surfactant which increases the permeability of epicuticular wax, cuticle or the plasmalemma should promote its uptake.

Current knowledge of pesticide adjuvants indicates that one single surfactant is unlikely to have all the above properties. Higher ethylene oxide (EO) content surfactants which produce smaller spread areas on plant foliage usually have a limited effect on enhancing permeability of the cuticle or cell membrane, whereas those with lower EO content usually have the opposite effect. Combinations of different surfactants may meet foliar dosage and leaf penetration requirements. Foliar uptake may be optimised through the use of appropriate surfactant combinations, when applied to different species.

The objective of this work was to systematically test the effect of different surfactant combinations on the uptake of glyphosate into grasses, relative to representative commercial formulations.

MATERIALS AND METHODS

Plants

Wheat (*Triticum aestivum* L. cv. Advantage), ryegrass (*Lolium perenne* L. cv. Concorde) and barnyard grass (*Echinochloa crus-galli* L.) plants were grown from seed in a controlled environment as reported previously (Zabkiewicz *et al.* 1995). Experiments were performed when the plants of all three species reached the 4-5 leaf growth stage.

Surfactants

Surfactants used in this work and their properties are summarised in Table 1.

TABLE 1: Surfactants and their properties.

Product	Code	Hydrophobe	Mean molar EO content	Supplier
MON 0818 ¹	MON 0818	Aliphatic amine	15	Monsanto, NZ
Synperonic A6	A6	C13-C15 alkanols	6	ICI, UK
Synperonic A10	A10	C13-C15 alkanols	10	ICI, UK
Triton X-45	TX-45	Octylphenol	5	Rhom & Haas, USA
Triton X-100	TX-100	Octylphenol	10	Rhom & Haas, USA
Silwet L-77	L-77	Trisiloxane	8	OSi Specialities, USA

¹Surfactant type in Roundup.

Glyphosate formulation

The mono(isopropylammonium) salt of ¹⁴C-glyphosate (N-phosphonomethyl glycine) was used in all experiments. ¹⁴C-glyphosate (98.4% pure; Amersham) was added to an equimolar quantity of isopropylamine (99% pure; Aldrich) to form the commercially used monoisopropylamine salt. This was then diluted with a stock solution of either unlabelled glyphosate-isopropylammonium salt (GI), 'Roundup' (RDP, 360 g a.e./l; Monsanto), or 'Roundup GII' (RDP GII; 360 g a.e./l; Monsanto). Final ¹⁴C-glyphosate formulations containing 5 g a.e./l of GI and 5000-7000 dpm/μl radioactivity were prepared in distilled water with the addition of selected surfactants. To assist droplet retention, the control treatment (without surfactant) was made up in aqueous acetone (1:1,v:v).

Foliar application and uptake assessment

Applications of ¹⁴C-glyphosate were made to the central region of the adaxial surface of the youngest, fully expanded leaf on each wheat, ryegrass, or barnyard grass plant, 2-3 hours after the start of the photoperiod. Droplets (12 x 0.24 μl) were applied by a microsyringe. Every treatment contained 5 replicate plants (one leaf per plant) and all plants were kept under constant growing conditions (day/night temperatures: 20 C/15 C; 70% RH) for the uptake period.

The treated leaves were excised at 6 h after application for the screening of good surfactant mixtures and at 1, 2, 4, 6 and 24 h for the comparison of different glyphosate formulations. The treated leaves were washed with ethanol:water (1:1 by volume, 2 x 4 ml). Radioactivity in the washings was determined by liquid scintillation counting.

Foliar uptake was defined as ¹⁴C-glyphosate not recovered in the leaf wash and was calculated as a percentage of the applied dose. Glyphosate uptake data were subjected to analysis of variance and treatments were compared using least significant difference (LSD) tests.

Determination of spread area of glyphosate formulations

An image analyser (V for Windows) was used to measure the spread areas of the 0.24 ml droplets on the adaxial leaf surface of plants. A minimum of 10 replicates on separate leaves were used for each treatment.

RESULTS

Effect of different surfactants on glyphosate uptake into wheat foliage

Water soluble (ie higher EO content) surfactants, TX-100, A10 and MON 0818, gave smaller droplet spread areas on wheat leaves and enhanced penetration of glyphosate significantly (P=0.05), relative to the glyphosate control, despite the latter providing the highest dose of all treatments (Table 2). Uptake ranged from 53% to 58% (at 6 h after application). Lower EO content surfactants, TX-45 and L-77, caused greater droplet spreading, hence lower leaf dosage and lower uptake into wheat foliage (17-28%). The A6 surfactant which produced an intermediate spread area and leaf dosage, had a 50% glyphosate uptake after 6 h.

TABLE 2: Glyphosate uptake into wheat in the presence of different surfactants (6 HAT).

Surfactant and concentration	Uptake (%)	Spread area (mm ²)	Glyphosate dose (µg/mm ²) ¹
GI (control)	22.9 bc	0.8 d	1.50
+ 0.2% MON 0818	57.8 a	0.9 d	1.33
+ 0.2% A6	50.0 a	6.7 c	0.18
+ 0.2% A10	53.1 a	1.2 d	1.00
+ 0.2% TX-45	27.8 b	14.7 b	0.08
+ 0.2% TX-100	57.4 a	1.1 d	1.09
+ 0.2% L-77	17.4 c	25.0 a	0.05

Means within columns sharing common postscripts are not significantly different (P=0.05).

¹Dose = amount of glyphosate applied / spread area.

Effect of different surfactants together with MON 0818 on glyphosate uptake into wheat foliage

Three surfactant combinations (MON 0818 +A6, +A10 and +TX-100) that produced smaller droplet spread areas and intermediate dosages, showed a synergistic effect on glyphosate uptake, increasing it to 90%-94% (Table 3). Although the mixture MON 0818+TX-45 had a higher spread area and lower dosage than MON 0818 on its own, it showed very similar uptake (64% vs 55%).

TABLE 3: Glyphosate uptake into wheat in the presence of surfactant combinations (6 HAT).

Surfactants and concentrations	Uptake (%)	Spread area (mm ²)	Glyphosate dose (µg/mm ²)
0.2% MON 0818	55.4 b	0.9 d	1.33
0.1% MON 0818 + 0.1% A6	90.3 a	2.3 b	0.52
0.1% MON 0818 + 0.1% A10	93.4 a	1.4 c	0.86
0.1% MON 0818 + 0.1% TX-100	94.4 a	1.2 cd	1.00
0.1% MON 0818 + 0.1% TX-45	64.3 b	6.1 a	0.20

Means within columns sharing common postscripts are not significantly different (P=0.05).

Effect of TX-45 with MON 0818 at different ratios on glyphosate uptake into wheat foliage

It was found that the proportion of TX-45 in a mixture with MON 0818 was important for uptake, at constant total surfactant concentration. A higher percentage of TX-45 tended to give increased droplet spread area and reduced the percentage uptake (Table 4). Glyphosate uptake reached 93% (6 HAT) for the ratio of MON 0818:TX-45 at 3:1 (w:w).

Effect of different surfactant combinations on glyphosate uptake into barnyard grass

Three surfactant combinations found to enhance glyphosate uptake into wheat (MON 0818+A10, +TX-100 and +TX-45), were also tested on barnyard grass foliage.

Glyphosate uptake in the presence of MON 0818 alone was much lower into barnyard grass than into wheat foliage, with only about 17% uptake after 6 h. The addition of another surfactant again enhanced the uptake into this species, though MON 0818+TX-45 didn't promote uptake as much as the other two combinations (Table 5). In all cases spreading and dosages were similar to that observed with wheat.

TABLE 4: Glyphosate uptake into wheat in the presence of MON 0818+TX-45 (6 HAT).

Surfactants and concentrations	Uptake (%)	Spread area (mm ²)	Glyphosate dose (µg/mm ²)
0.2% MON 0818	57.8 c	0.9 c	1.33
0.16% MON 0818 + 0.04%TX-45	80.4 b	1.1 c	1.09
0.15% MON 0818 + 0.05%TX-45	93.1 a	1.1 c	1.09
0.1% MON 0818 + 0.1% TX-45	64.3 c	6.1 b	0.20
0.05% MON 0818 + 0.15% TX-45	44.8 d	14.1 a	0.08
0.2% TX-45	27.8 e	14.7 a	0.08

Means within columns sharing common postscripts are not significantly different (P=0.05).

TABLE 5: Glyphosate uptake into barnyard grass in the presence of surfactant combinations (6 HAT).

Surfactants and concentrations	Uptake (%)	Spread area (mm ²)	Glyphosate dose (µg/mm ²)
0.2% MON 0818	16.7 c	0.9 c	1.33
0.1% MON 0818 + 0.1% A10	61.3 a	1.3 a	0.92
0.1% MON 0818 + 0.1% TX-100	64.1 a	1.2 ab	1.00
0.15% MON 0818 + 0.05% TX-45	39.7 b	1.1 b	1.09

Means within columns sharing common postscripts are not significantly different (P=0.05).

Comparison of glyphosate uptake and rate for different formulations

The effect of a representative surfactant combination (MON 0818+A10) on glyphosate uptake and rate was compared with RDP and RDP GII on wheat and ryegrass foliage. The RDP and RDP GII formulations had 0.25% surfactant concentrations and hence the MON0818 + A10 surfactant concentration was also used at 0.25% total (at a 1:1 ratio).

Although glyphosate uptake after 24 h was similar for all three formulations on wheat, distinct differences in uptake rate were observed, especially during the first 6 h (Fig. 1A). The surfactant combination (MON 0818+A10) showed the fastest uptake (60% after 1 h), followed by RDP GII (31%) and RDP (11%).

FIGURE 1: Glyphosate uptake rate with surfactant combination, RDP or RDP GII on wheat (A, LSD_{0.05} =7.0) and ryegrass (B, LSD_{0.05} =10.9) foliage.

On ryegrass, both commercial glyphosate formulations provided much slower uptake, compared to that observed on wheat foliage (Fig. 1B), but RDP GII had again faster and greater uptake compared with RDP (11% vs 5% after 1 h; 82% vs 42% after 24 h). The surfactant combination had the most rapid and highest overall uptake (42% after 1 h; 92% after 24 h).

DISCUSSION AND CONCLUSIONS

The addition of other surfactants to the original 'Roundup' formulation has often enhanced uptake and efficacy (Gaskin and Zabkiewicz 1989; Sandbrink *et al.* 1993; Wales and Griffiths 1995). As the total surfactant concentration in the spray solution was increased in all these studies, it is impossible to distinguish whether this was due to a simple additive, or a synergistic effect between an existing formulation surfactant and added surfactants.

Current work using different surfactant combinations, at controlled rates, has revealed that the application of two surfactants together, of different EO content, or different structure, could produce a highly synergistic effect on glyphosate uptake. This improved uptake was obtained while the total surfactant concentrations in the treatment solution remained unchanged. This implies that by using suitable surfactant combinations, glyphosate uptake can be further improved. Extremely rapid and high levels of uptake achieved by such combinations would further improve rainfastness and field efficacy of glyphosate.

The current studies confirmed the importance of droplet spread area (hence actual glyphosate doses) on leaf surfaces for uptake (Liu and Zabkiewicz 1997). A higher dosage does seem to enhance uptake, as would be expected in a cuticular diffusion process. Previous work has shown this to be important when all other factors are the same. However, this study demonstrates that surfactant structure, and/or composition of a mixture, is even more important in enhancing uptake. Droplet spread and the resulting change in a.i. dosage may not be the only driving factor for uptake. Droplet drying and formulation concentration changes may also affect the behaviour of the water component, either through evaporation, surface retention or cuticular hydration. A better understanding of the fundamental mechanism responsible for the synergistic effects of surfactant combinations on glyphosate uptake is still required.

REFERENCES

- de Ruiter, H., Meinen, E. and Verbeek, M.A.M., 1992. Influence of the type and concentration of surfactant on glyphosate absorption; relevance of drop spreading and drying time. Pp. 109-116. *In*: Adjuvants for Agrichemicals, C.L. Foy, (Ed), CRC Press, Boca Raton.
- de Ruiter, H., Verbeek, M. A. M. and Uffing, A.J.M., 1994. Influence of ammonium sulfate and two surfactants on the phytotoxicity and uptake of glyphosate. *Med. Fac. Landbouwwet. Rijksuniv. Gent* 59-3b: 1403-1408.
- Gaskin, R.E. and Zabkiewicz J.A., 1989. The effect of surfactants on the uptake and translocation of glyphosate in Yorkshire fog. *Proc. 42nd NZ Weed and Pest Control Conf.*: 128-131.
- Gaskin, R.E. and Holloway P.J., 1992. Some physicochemical factors influencing foliar uptake enhancement of glyphosate-mono(isopropylammonium) by polyoxyethylene surfactants. *Pestic. Sci.* 34: 195-206.
- Liu, Z.Q. and Zabkiewicz J.A., 1997. Cuticular uptake of glyphosate into wheat with organosilicone surfactant. *Proc. 50th NZ Plant Prot. Conf.*: 129-133.
- Nalewaja, J.D. and Matysiak R., 1995. Ethoxylated linear alcohol surfactants affect glyphosate and fluzifop absorption and efficacy. Pp. 291-296. *In*: Proc. of Fourth Int. Symp. on Adjuvants for Agrochemicals, R.E. Gaskin, (Ed), Melbourne, NZFRI Bulletin No.193.
- Sandbrink, J.J., Dayawon, M.M. and Kassebaum J.W., 1993. Non-silicone-based surfactants as glyphosate rainfastness adjuvants. *Pestic. Sci.* 38: 272-273.
- Wales, D.J. and Griffiths, P.L., 1995. A study examining relationships between physiochemical properties and bioefficacy of tank added surfactant adjuvants

- with IPA glyphosate. Pp. 11-19. *In*: Proc. of Fourth Int. Symp. on Adjuvants for Agrochemicals, R.E. Gaskin, (Ed), Melbourne, NZFRI Bulletin No.193.
- Zabkiewicz, J.A., Forster, W.A., Steele, K.D. and Liu, Z.Q., 1995. Comparison of uptake into field bean (*Vicia faba*) and wheat (*Triticum aestivum*) of organosilicone and non-silicone surfactants. Pp. 219-224. *In*: Proc. of Fourth Int. Symp. on Adjuvants for Agrochemicals, R.E. Gaskin, (Ed), Melbourne, NZFRI Bulletin No.193.