

Surfactant Effects on Glyphosate Efficacy¹

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Abstract. Field and greenhouse studies were performed to examine the influence of various surfactants with glyphosate on whole plant efficacy. Relationships were examined between glyphosate phytotoxicity and surfactant properties, including ionic form, degree of ethoxylation, and hydrophobe composition. Cationic tertiary amine surfactants enhanced glyphosate performance in both field and greenhouse studies. Nonionic allinol and octoxynol surfactants were not effective in combination with glyphosate. In field studies, glyphosate efficacy increased with increasing surfactant ethylene oxide (EO) content. Soybean and velvetleaf responded similarly to glyphosate-surfactant spray applications, as both demonstrated significant linear and quadratic relationships between increasing surfactant ethoxylation and phytotoxicity, while common lambsquarters showed a significant linear relationship only. Cationic surfactants were evaluated in the greenhouse and a significant quadratic regression of glyphosate phytotoxicity to common lambsquarters on increasing surfactant ethoxylation indicated an optimum surfactant EO content of about 10 moles. Both tertiary and quaternary ethoxylated fatty amines were effective with glyphosate in decreasing common lambsquarters' fresh weight. Fatty amine hydrophobe composition did not correlate with glyphosate phytotoxicity to common lambsquarters. **Nomenclature:** Glyphosate, *N*-(phosphonomethyl)glycine; common lambsquarters, *Chenopodium album* L. #³ CHEAL; velvetleaf, *Abutilon theophrasti* Medicus # ABUTH; soybean, *Glycine max* (L.) Merr. 'Elgin'. **Additional index words:** Adjuvant, cationic surfactant, ethylene oxide, nonionic surfactant.

INTRODUCTION

Surfactants have been shown to increase phytotoxicity of glyphosate (1, 4, 5, 10). However, variability among surfactant effects on glyphosate efficacy have been reported (6, 11). The literature suggests that cationic (polyethoxylated tertiary fatty amine) surfactants are more effective than nonionics in enhancing glyphosate activity (2, 8, 9, 11), and that increasing the degree of surfactant ethoxylation (increasing hydrophile-lipophile balance (HLB)) also increases glyphosate efficacy. Wyrill and Burnside (11) found that ethoxylated stearyl ether and

amine surfactants with HLBs ranging from 16 to 20 optimized glyphosate phytotoxicity to common milkweed (*Asclepias syriaca* L.) and hemp dogbane (*Apocynum cannabinum* L.). To date, however, the effect of ethoxylation within several series of nonionic and cationic surfactants on glyphosate whole plant toxicity has not been reported.

The objectives of this study were to further examine surfactant influence on glyphosate by comparing various classes of ethoxylated nonionic and cationic surfactants (see Figure 1 for structures). Nonionic surfactants⁴ included the ethoxylated octoxynols and allinols. Cationic surfactants⁵ included tertiary and quaternary ethoxylated fatty amines. MON 0818,^{6,7} the surfactant included in the commercial formulation of glyphosate (Roundup^{6,7}), was also included for comparison purposes. Within each surfactant class the impact of surfactant ethoxylation on glyphosate efficacy was evaluated.

MATERIALS AND METHODS

Field experiment. Soybeans were planted in 76-cm rows at the Agronomy South Farm Research Center in Urbana, IL in 1991 and 1992. Plots were 3 m by 9 m with a 2.3-m

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³Letters following this symbol are a WSSA-approved computer code from Composite List of Weeds, Revised 1989. Available from WSSA, 1508 W. University Ave., Champaign, IL 61821-3133.

⁴Triton X series, Rohm and Haas Co., Philadelphia, PA 19105; Trycols, Henkel Corp. (Emery Group), Cincinnati, OH 45249.

⁵Ethomeens and Ethoquads, Akzo Chemicals, Inc., McCook, IL 60525.

⁶Monsanto Agric. Products Co., St. Louis, MO 63167.

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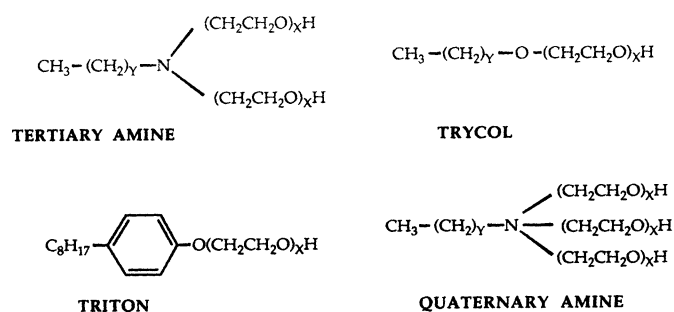


Figure 1. Generalized chemical structures of surfactants used in field and greenhouse studies.

by 9-m treated area. The remaining 0.7-m wide untreated area in each plot served as a check and aided in the visual estimation of soybean injury or weed control. Treatments were applied with a CO_2 backpack sprayer delivering 187 L/ha at 345 kPa with 8002 flat fan nozzles. The isopropylamine (IA)⁸ salt of glyphosate formulated without surfactant (Rodeo)^{6,7} was applied at a rate of 0.43 kg ai/ha. Surfactants were included in the spray mix at 0.5% (v/v). Treatments were applied to soybean plants having six trifoliolate leaves (30 to 40-cm tall), 30 to 40-cm tall velvetleaf, and 40 to 60-cm tall common lambsquarters (1992 only). Soybean injury and weed control ratings were determined 7 and 21 DAT, and were based on percent visual injury (0 = no apparent injury, 100 = plant death) (Tables 1 and 2).

Treatments were arranged in a randomized complete block design with three replications. Data were subjected to a repeated-measures analysis of variance using GLM (7) and the LSD test was used to separate treatment means. A repeated-measures analysis over time was used because visual injury ratings were recorded on each experimental plot at two different times (7 and 21 DAT). Data were pooled over 1991 and 1992. Analysis of variance of transformed percent injury data (square root of arc sin) and nontransformed percent injury data were similar, so statistics performed on the nontransformed data are presented. A single degree of freedom orthogonal contrast was performed for nonionic vs. cationic surfactants, and polynomial regression analysis was performed to examine the effect of surfactant ethoxylation on glyphosate efficacy for each plant species.

⁸Abbreviations: EO, ethylene oxide; IA, isopropylamine.

⁹Chevron Chemical Co., Ortho Consumer Products Division, San Ramon, CA 94583.

Greenhouse experiments. Common lambsquarters plants were grown in plastic tubes containing vermiculite. Plants were watered daily and fertilized once a week with RapidGro^{®7,9} fertilizer (23-19-17). Natural sunlight was supplemented with metal halide lamps to maintain a 14-h photoperiod, with a maximum intensity reaching 1800 $\mu\text{E}/\text{m}^2/\text{s}$ at plant level. Temperatures ranged between 26 C day and 19 C night.

Glyphosate-IA (Rodeo) at 0.56 kg ai/ha with 0.5% (v/v) surfactant was applied to 13 to 18-cm tall common lambsquarters plants with a pneumatically-driven laboratory cabinet sprayer delivering 187 L/ha at 207 kPa. Reduction in shoot fresh weight was measured 10 DAT by comparison with untreated plants. Two separate studies were performed, and each was repeated twice. The first experiment compared cationic surfactants with nonionics and was arranged in a completely randomized design with five replications (Table 3). The second experiment compared cationics only and was arranged in a completely randomized design with eight replications (Table 4). Data were pooled over experiments within each study and subjected to analysis of variance, and the LSD test was used to separate treatment means. Regression analysis was performed to examine the effect of surfactant ethoxylation on glyphosate phytotoxicity to common lambsquarters.

RESULTS AND DISCUSSION

Field experiment. The ability of various surfactants to enhance glyphosate phytotoxicity in the field is demonstrated in Table 1. The effect of surfactant ionic form is shown more clearly in Table 2. For each plant species, at each time, cationic surfactants enhanced glyphosate phytotoxicity.

The three plant species differed in their response to glyphosate during the ratings period (Table 2). Velvetleaf injury increased from the early to the late rating for both ionic forms, while soybean injury decreased over time for the cationic surfactants and showed no change for the nonionic surfactants. At the herbicide rate used, soybean demonstrated the ability to overcome the initial damage caused by the herbicide, while velvetleaf required a longer period to develop maximal visual injury symptoms. Common lambsquarters injury did not change significantly for either ionic form during the ratings period, which suggests that this species cannot overcome the rapid initial damage incurred by glyphosate application.

The effect of surfactant EO⁸ content on glyphosate

Table 1. Effect of surfactants (0.5% v/v) on glyphosate injury 7 DAT (early) and 21 DAT (late) to velvetleaf, soybean, and common lambsquarters with glyphosate applied as the isopropylamine salt at 0.43 kg/ha. Values are averaged over 1991 and 1992 (velvetleaf, soybean) or 1992 only (common lambsquarters) at Urbana, IL.

Surfactant	Ionic form ^a	Moles EO	Velvetleaf		Soybean		Common lambsquarters	
			Early	Late	Early	Late	Early	Late
			----- % visual injury -----					
Trycol 5993	N	3	15	17	16	12	28	22
Trycol 5940	N	6	22	31	23	18	43	28
Trycol 5949	N	8	20	32	24	20	37	32
Trycol 5943	N	12	28	29	36	25	57	48
Trycol 5874	N	14	25	36	35	34	67	68
Trycol 5946	N	18	25	50	38	42	70	77
Triton X-100	N	9.5	20	37	21	25	72	68
Triton X-165	N	16	24	33	36	33	77	77
Triton X-305	N	30	18	29	28	35	68	60
Ethomeen C12 ^b	C	2	29	53	44	41	77	82
Ethomeen C15	C	5	40	58	59	43	78	88
Ethomeen C20	C	10	41	61	63	50	80	85
Ethomeen C25	C	15	43	50	65	49	87	83
Ethomeen S12 ^c	C	2	31	68	64	54	72	88
Ethomeen S15	C	5	38	71	63	58	77	82
Ethomeen S20	C	10	42	78	68	53	80	93
Ethomeen S25	C	15	46	78	71	61	83	96
MON 0818	C	15	40	63	64	53	82	90
No surfactant	—	—	15	15	19	15	22	12
Check	—	—	0	0	0	0	0	0
LSD (0.05)			18	16	12	16	11	8

^aIonic form—N = nonionic, C = cationic.

^bEthomeen C series are tertiary amines containing 12 carbon alkyl hydrophobes.

^cEthomeen S series are tertiary amines containing 18 carbon alkyl hydrophobes.

efficacy was examined by performing polynomial regression analyses for each plant species. For velvetleaf ($y = 35.15 + 1.154x - 0.0505x^2$) and soybean ($y = 36.16 + 1.227x - 0.0437x^2$), regression analysis indicated both linear and quadratic terms were significant. For common lambsquarters ($y = 63.93 + 0.51x$), only the linear term was significant. These results demonstrate that for velvetleaf and soybean, increasing surfactant ethoxylation increases glyphosate efficacy until an optimum EO content is reached (soybean optimum = 14.0 moles EO, velvetleaf optimum = 11.4 moles EO), then declines as EO content

continues to increase. For common lambsquarters it appears that glyphosate efficacy continues to increase with increasing surfactant ethoxylation.

Greenhouse experiments. The effect of a cationic, polyethoxylated fatty amine surfactant for promoting glyphosate efficacy is demonstrated in Table 3. Glyphosate alone or with nonionic surfactants in either class, with the exception of Trycol 5946, did not significantly reduce common lambsquarters fresh weight. However, all cationic surfactants in combination with glyphosate significantly reduced fresh weight. Although surfactants within each

Table 2. Comparison of surfactant form on glyphosate injury 7 DAT (early) and 21 DAT (late) to velvetleaf, soybean, and common lambsquarters with surfactants shown in Table 1.

Ionic form	Velvetleaf		Soybean		Common lambsquarters	
	Early	Late	Early	Late	Early	Late
	----- % visible injury -----					
Cationic	39	64	62	51	79	87
Nonionic	23	33	31	30	61	58
Prob. > F	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001

Table 3. Effect of surfactants (0.5% v/v) on common lambsquarters shoot fresh weight in the greenhouse with glyphosate-isopropylamine applied at 0.56 kg/ha. Shoot fresh weights were taken 10 DAT, and represent the means of five replications in each of three separate experiments.

Surfactant	Ionic form	Moles EO	Fresh weight g/plant
Trycol 5993	Nonionic	3	3.04
Trycol 5940	Nonionic	6	3.07
Trycol 5949	Nonionic	8	3.44
Trycol 5943	Nonionic	12	2.82
Trycol 5874	Nonionic	14	2.92
Trycol 5946	Nonionic	18	2.69
Triton X-114	Nonionic	7.5	3.85
Triton X-100	Nonionic	9.5	3.04
Triton X-102	Nonionic	13	3.02
Triton X-165	Nonionic	16	3.20
Triton X-305	Nonionic	30	3.25
Ethomeen C12 ^a	Cationic	2	1.73
Ethomeen C15	Cationic	5	1.23
Ethomeen C20	Cationic	10	1.02
Ethomeen C25	Cationic	15	1.01
MON 0818	Cationic	15	1.33
Glyphosate—no surfactant			3.45
No herbicide control			3.42
LSD (0.10)			0.70

^aEthomeen C series are tertiary amines containing 12 carbon alkyl hydrophobes.

class (Trycols, Tritons, Ethomeens) performed similarly, (i.e., effective or not effective), a trend was observed between surfactant ethoxylation and reduction in fresh weight. This trend was further examined by performing a regression analysis of EO content on plant fresh weight. A significant linear or quadratic fit was not observed for the nonionic surfactants. However, significant linear and quadratic terms were fitted for the cationic surfactants, indicating increasing fresh weight reduction as surfactant EO content increased. MON 0818 (15 moles EO), the cationic surfactant included in the Roundup formulation of glyphosate, was also an effective surfactant and was similar to the cationic tertiary amines (Ethomeens) in enhancing glyphosate efficacy.

After establishing that cationic surfactants are effective in promoting glyphosate efficacy on common lambsquarters, a second study was performed in the greenhouse to determine if differences existed among various types of cationic surfactants. Surfactants in this study (Table 4) included polyethoxylated tertiary and quaternary fatty amines. Surfactants differed in degree of ethoxylation and in length of the carbon chain in the hydrophobic portion of the molecule. Soya amines (S series) contain 18 carbon alkyl hydrophobes, coco amines (C series) contain 12

Table 4. Effect of surfactants (0.5% v/v) on common lambsquarters shoot fresh weight in the greenhouse with glyphosate-isopropylamine applied at 0.56 kg/ha. Shoot fresh weights were taken 10 DAT, and represent the means of eight replications in each of three separate experiments.

Surfactant	Amine type	Moles EO	Fresh weight g/plant
Ethomeen S12 ^a	Tertiary	2	2.33
Ethomeen S15	Tertiary	5	1.65
Ethomeen S20	Tertiary	10	1.27
Ethomeen S25	Tertiary	15	1.46
Ethomeen C12 ^b	Tertiary	2	1.94
Ethomeen C15	Tertiary	5	1.53
Ethomeen C20	Tertiary	10	1.38
Ethomeen C25	Tertiary	15	1.82
Ethoquad C12 ^b	Quaternary	2	1.63
Ethoquad C25	Quaternary	15	1.93
Ethoquad O12 ^c	Quaternary	2	1.95
Ethoquad O25	Quaternary	15	1.92
MON 0818	Tertiary	15	1.99
Glyphosate—no surfactant			4.97
No herbicide control			5.69
LSD (0.10)			0.59

^aEthomeen S series contain 18 carbon alkyl hydrophobes.

^bEthomeen and Ethoquad C series contain 12 carbon alkyl hydrophobes.

^cEthoquad O series contain oleic acid (18 carbon) hydrophobes.

carbon alkyl hydrophobes, and oleyl amines (O series) contain oleic acid (18 carbons) as the principal hydrophobe. All surfactants tested demonstrated an ability to increase glyphosate phytotoxicity to common lambsquarters compared to both the no surfactant treatment and no herbicide control. Although not significantly different from the majority of the other cationic surfactants tested, the tertiary fatty amines with a high degree of ethoxylation (Ethomeen C20, S20, S25) consistently ranked near the top in reducing fresh weight throughout the three experiments. A regression analysis demonstrated a quadratic relationship between cationic surfactant ethoxylation and fresh weight, with a R^2 value of 0.58 (Figure 2). Surfactant effectiveness with glyphosate tended to increase with increasing degree of ethoxylation (2 to 10), then declined as EO content increased from 10 to 15. The effect of carbon chain length in the hydrophobic portion of the surfactant molecule was variable and did not correlate well with glyphosate efficacy. Quaternary fatty amines were effective, but with the exception of Ethoquad C12 did not perform as well as the most effective tertiary fatty amine, Ethomeen S20.

The results of this study confirm previously reported results that highly-ethoxylated tertiary fatty amine surfac-

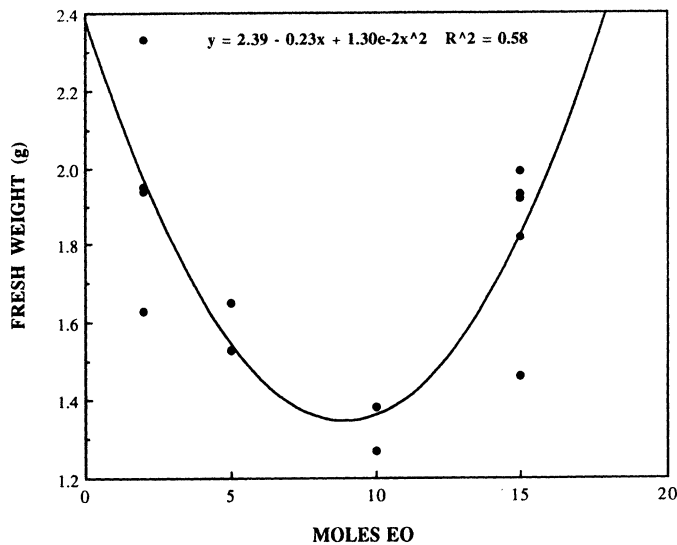


Figure 2. Effect of increasing cationic surfactant ethylene oxide (EO) content on reduction of common lambsquarters shoot fresh weight. Plants were sprayed in the greenhouse with 0.56 kg/ha glyphosate-isopropylamine plus 0.5% (v/v) surfactant. Values plotted represent all surfactant treatments listed in Table 4.

tants are required to optimize glyphosate performance. The reasons behind this specificity for surfactant chemical structure with glyphosate spray applications have been studied by several researchers. Sherrick et al. (8) noted differences in glyphosate phytotoxicity to field bindweed (*Convolvulus arvensis* L.) between MON 0818 and Tween 20 surfactant treatments, and suggested that increased activity of the cationic surfactant MON 0818 was attributable to increased uptake of glyphosate. de Ruiter et al. (2) correlated differential glyphosate phytotoxicity to winter wheat (*Triticum aestivum* L.) to an enhancement of glyphosate absorption by the cationic surfactant Ethomeen T25 and inhibition of glyphosate absorption by the non-ionic surfactant Renex 688. Gaskin and Holloway (3) examined the interaction of surfactant structure and concentration on enhancement of glyphosate foliar uptake. They reported that surfactant hydrophobe composition and ethoxylation significantly affected foliar uptake of glyphosate. Their results correlate well with the whole plant responses presented in this paper, in that primary aliphatic amines with a high degree of ethoxylation generally exhibited the greatest enhancement of glyphosate foliar uptake, in comparison with nonionic allinol or nonoxynol surfactants with equivalent EO content. They also observed a quadratic relationship between surfactant-induced uptake of glyphosate and increasing EO content for both amine

and allinol classes. We conclude from these studies that enhancement of foliar glyphosate uptake by cationic amine surfactants is responsible for preferentially increasing glyphosate efficacy when compared to its use with non-ionic surfactants.

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LITERATURE CITED

- Buhler, D. D. and O. C. Burnside. 1983. Effect of spray components on glyphosate toxicity to annual grasses. *Weed Sci.* 31:124-130.
- de Ruiter, H., M.A.M. Verbeek, and A.J.M. Uffing. 1988. Mode of action of a nonionic and a cationic surfactant in relation to glyphosate. p. 44-55 in B. Cross and H. B. Scher, eds. *Pesticide Formulations: Innovations and Developments*. ACS Symp. Ser. No. 371, Am. Chem. Soc., Washington, DC.
- Gaskin, R. E. and P. J. Holloway. 1992. Some physicochemical factors influencing foliar uptake enhancement of glyphosate-mono(isopropylammonium) by polyoxyethylene surfactants. *Pestic. Sci.* 34:195-206.
- Jordan, T. N. 1981. Effects of diluent volumes and surfactant on the phytotoxicity of glyphosate to bermudagrass (*Cynodon dactylon*). *Weed Sci.* 29:79-83.
- McWhorter, C. G. and W. R. Azlin. 1978. Effects of environment on the toxicity of glyphosate to johnsongrass (*Sorghum halepense*) and soybeans (*Glycine max*). *Weed Sci.* 26:605-608.
- O'Sullivan, P. A., J. T. O'Donovan, and W. M. Hamman. 1981. Influence of non-ionic surfactants, ammonium sulphate, water quality and spray volume on the phytotoxicity of glyphosate. *Can. J. Plant Sci.* 61:391-400.
- SAS Institute. 1990. *SAS/STAT User's Guide*, Version 6. p. 265-291. Chap. 8, Repeated-measures analysis of variance. SAS Inst., Cary, NC.
- Sherrick, S. L., H. A. Holt, and F. D. Hess. 1986. Effects of adjuvants and environment during plant development on glyphosate absorption and translocation in field bindweed (*Convolvulus arvensis*). *Weed Sci.* 34:811-816.
- Sherrick, S. L., H. A. Holt, and F. D. Hess. 1986. Absorption and translocation of MON 0818 adjuvant in field bindweed (*Convolvulus arvensis*). *Weed Sci.* 34:817-823.
- Sprinkle, P., W. F. Meggitt, and D. Penner. 1975. Absorption, action, and translocation of glyphosate. *Weed Sci.* 23:235-240.
- Wyrill III, J. B. and O. C. Burnside. 1977. Glyphosate toxicity to common milkweed and hemp dogbane as influenced by surfactants. *Weed Sci.* 25:275-287.