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Adjuvant effects on imazethapyr, 2,4-D and picloram absorption by leafy spurge (*Euphorbia esula*)¹

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Abstract:

Laboratory experiments were conducted to identify adjuvants that improve absorption of imazethapyr, 2,4-D amine, and picloram by leafy spurge. Adjuvants (0. 25% v/v) included crop oil concentrate (COC), methylated seed oil (MSO), nonionic surfactant (NIS), organosilicones (Silwet L-77[®], Sylgard[®] 309, Silwet[®] 408), 3:1 mixtures of acetylinic diol ethoxylates (ADE40, ADE65, ADE85) with Silwet L-77, ammonium sulfate (2. 5 kg ha⁻¹), and 28% urea ammonium nitrate (UAN, 2. 5% v/v). Adjuvants were combined with ¹⁴C-herbicide and commercially formulated herbicide product. Leaves were harvested 2 DAT, rinsed with 10% aqueous methanol to remove surface deposits of herbicide, and dipped in 9:1 hexane:acetone to solubilize cuticular waxes. Imazethapyr absorption increased by 38 to 68% when UAN was combined with COC, NIS, or MSO. Total absorption of imazethapyr plus COC, MSO, or NIS exceeded 86% 2 DAT when UAN was added. Urea ammonium nitrate reduced the amount of imazethapyr associated with the cuticular wax by 2. 0%. Imazethapyr absorption was similar on both the abaxial and adaxial leaf surface when UAN was not added; however, 12% more imazethapyr was absorbed from the abaxial leaf surface than from the adaxial leaf surface when UAN was combined with Sylgard 309. Uptake of 2,4-D ranged from 54 to 78% and was greatest with Silwet 408 and 3:1 mixture of ADE40:Silwet L-77. Picloram absorption ranged from 3 to 19%. Buffering picloram treatment solutions to pH 7 and including 2. 5 kg ha⁻¹ ammonium sulfate increased picloram absorption to 37%.

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Nomenclature:

2,4-D amine, (2,4-dichlorophenoxy)acetic acid dimethylamine; imazethapyr, 2- [4,5-dihydro-4-ethyl-4- (1-methylethyl) -5-oxo-1*H*-imidazol-2-yl] -5-ethyl-3-pyridinecarboxylic acid; picloram, 4-amino-3,5,6-trichloro-2-pyridinecarboxylic acid; ammonium nitrate, NH_4NO_3 ; ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$; leafy spurge, *Euphorbia esula* L. #² EPHEs.

Introduction

Introduced from Eurasia, leafy spurge is found in 26 U. S. states and six Canadian provinces (7). It is an economic threat to the northern and central Great Plains and Prairie Provinces of Canada (16). Leafy spurge displaces native species and competes with desirable forages ultimately reducing plant diversity and diminishing rangeland carrying capacity (22). Prolific vegetative reproduction promotes development of dense leafy spurge infestations, while an extensive root system with abundant energy reserves allows the plant to resist mechanical and chemical control measures.

Herbicides currently provide the most effective means to manage leafy spurge infestations (22). Annual applications of 2,4-D combined with low rates of picloram (0.28 to 0.56 kg ae ha⁻¹) are commonly recommended for leafy spurge management (19). Benefits of this treatment include increased forage yield (17, 18) and reduced leafy spurge seed production; however, these herbicides suppress desirable forbs and do not provide long-term control. Imazethapyr, which is phytotoxic to leafy spurge, translocates to roots and adventitious shoot buds (27). Also, this herbicide is tolerated by desirable warm-season grasses and legumes (23). Foliar absorption of imazethapyr by leafy spurge was limited to 20% 8 days after treatment (DAT)³ (27). Additionally, poor absorption of 2,4-D (34%) and picloram (14%) by leafy spurge has been reported (21). Increasing herbicide absorption may increase efficacy and long-term control.

Addition of adjuvants to the spray solution can increase herbicide absorption. Imazethapyr is generally applied with an adjuvant [either crop oil concentrate (COC)⁴ or nonionic surfactant (NIS)⁴] and liquid fertilizer (1). Adjuvants also may improve picloram and 2,4-D amine efficacy (2, 3). The organosilicone surfactants (36), are a newer group of adjuvants that can improve efficacy and reduce the required rain-free period after treatment for many herbicides on several weed-species (4, 28, 29, 30). Organosilicone surfactants reduce the surface tension of the spray solution, promote infiltration of the herbicide into stomata (5, 6, 37), and increase the rate of droplet spreading over the leaf

² Letters following this symbol are a WSSA-approved computer code from Composite List of Weeds. Revised 1989. Available from WSSA, 1508 West University Ave., Champaign, IL 61821-3133.

³ ADE, acetylinic diol ethoxylate; COC, crop oil concentrate; DAT, days after treatment; EO, ethylene oxide; MSO, methylated seed oil; NIS, nonionic surfactant; UAN, urea ammonium nitrate.

surface. This results in enhanced herbicide uptake, reduced rain-free period, and increased adhesion of spray droplets to the leaf surface (38).

Limited foliar absorption may reduce the efficacy of imazethapyr, 2,4-D, and picloram on leafy spurge. Laboratory experiments were conducted to: a) identify adjuvants to improve absorption of imazethapyr, 2,4-D amine, and picloram by leafy spurge; b) compare effects of adaxial and abaxial application of imazethapyr with organosilicone surfactants; and c) determine effects of pH and ammonium sulfate with organosilicone surfactants on picloram absorption by leafy spurge.

Materials and Methods

Plant material. Leafy spurge plants were grown in the greenhouse and growth chamber as previously described (27), with the exception that plants were watered daily with 50 ml deionized water and fertilized every 2 wk with slow-release fertilizer⁴. Experiments were conducted on leafy spurge plants that were 32 to 45 cm tall and had reached mid-bloom growth stage 14 to 18 d after being transferred to the growth chamber. The studies were conducted between July 1992 and November 1993.

Treatment solutions. Treatment solutions consisted of adjuvants combined with commercially formulated herbicides. Adjuvants included COC⁵, methylated seed oil (MSO)^{4, 6}, NIS4^{4, 7}, organosilicone surfactants (Silwet L-77⁸, Silwet 408⁹, Sylgard 309⁹), ammonium sulfate, 28% urea ammonium nitrate (UAN)⁴, and 3:1 mixtures of acetylinic diol ethoxylates (ADE's)⁴ with Silwet L-77. Surfactants at a concentration of 0.25% v/v were combined with a commercial formulation of imazethapyr, 2,4-D, or picloram applied at 0.07, 1.12, and 1.12 kg ae ha⁻¹, respectively. Calculations were based on a total delivery volume of 187 L ha⁻¹. Twenty-eight percent UAN (2.5% v/v) was applied with imazethapyr and ammonium sulfate [2.5 kg ha⁻¹ (NH₄)₂SO₄] was applied with picloram.

¹⁴C-labelled herbicides (specific activities: imazethapyr, 766 kBq mg⁻¹; picloram, 95 kBq mg⁻¹; 2,4-D, 1507 kBq mg⁻¹) were added to the treatment solutions. The amount of radioactivity applied per leaf ranged from 183 to 833 Bq, depending on the experiment. Treatments were applied to the leaf surface using a precision electronic micro-pipettor¹⁰ with application volumes varying among experiments. Five to 12 consecutive leaves were treated per plant starting 10 cm from the top of the plant and continuing downward. Applications were made within 2 h after preparing treatment solutions to avoid degradation of organosilicone surfactants (15, 26).

⁴ Sierra 17-6-10, Grace-Sierra Horticultural Products Co., Milpitas, CA 95035.

⁵ 83% paraffinic petroleum hydrocarbons, 17% emulsifier, crop oil concentrate, Cenex/Land-O-Lakes, Inver Grove Heights, MN 55077.

⁶ Sun-It II, AGSCO, Grand Forks, ND 58201.

⁷ X-77 non-ionic surfactant, United Agri-Products, Greeley, CO 80632.

⁸ OSi Specialties, Inc., 777 Old Saw Mill River Road, Tarrytown, NY 10591-6728.

⁹ Dow Corning Corp., Midland, MI 48640.

¹⁰ EDP-2 Micro 10, Rainin Instrument Co., Woburn, MA 01801.

Harvest technique. Treated leaves were harvested 2 and 8 DAT during experiment 1 and 2 DAT for all other experiments. At harvest, leaves were vortexed for 30 s in 5 ml aqueous 10% v/v methanol, 0.25% v/v Tween 20. Radioactivity of the solutions was determined by liquid scintillation spectrometry. Percent absorption was calculated by the difference between the amount of radioactivity applied and the amount recovered from the leaf surface. The amount of radioactivity applied was determined by averaging the amount of radioactivity recovered from three to five leaves that were washed immediately after application of treatment solutions.

An additional rinse was performed at harvest for experiments 1 and 3. Following the methanol rinse, leaves were dipped ten times in 3 ml 9:1 hexane:acetone to remove cuticular waxes. This solution was counted by liquid scintillation spectrometry to determine the amount of ^{14}C located within the cuticle.

Herbicide absorption experiments.

Experiment 1. The effects of COC, MSO, NIS, and 28% UAN on absorption of imazethapyr by leafy spurge was determined. Adjuvants were applied alone or combined with 28% UAN. Ten drops of 0.5 μl each, five on each side of the mid-rib, were applied to the adaxial leaf surface. Five leaves were treated per plant to replicate the treatment. A total of 833 Bq was applied per leaf. Leaves were harvested 2 and 8 DAT.

Experiment 2. Crop oil concentrate with UAN was compared to two organosilicone surfactants. Application volume was reduced because of droplet spreading as a result of the organosilicone surfactants. Crop oil concentrate, Silwet L-77, and Sylgard 309 were applied with 28% UAN in a single 0.5 μl or 1.0 μl drop per leaf. Each drop contained 833 Bq ^{14}C -imazethapyr.

Experiment 3. Effects of adjuvants on imazethapyr absorption were examined using field grown plants. Leafy spurge plants were transferred from cold storage and grown in the field for 14 to 18 d in September 1992, until they reached the mid-bloom growth stage. Plants were then transferred to the growth chamber and treated 24 h later. Herbicide treatment solutions included COC, Silwet L-77, and Sylgard 309 alone and with 28% UAN. One, 1.0 μl drop containing 833 Bq was applied per leaf. As in experiment 1, an additional hexane rinse was performed.

Experiment 4. Imazethapyr absorption by abaxial and adaxial leaf surfaces of leafy spurge was evaluated. Crop oil concentrate, Silwet L-77, and Sylgard 309 were applied alone or with UAN in a single 1.0 μl drop containing 833 Bq of ^{14}C -imazethapyr to the abaxial or adaxial leaf surface. Droplets were applied to the underside of the leaf by gently twisting the leaf, applying the treatment solution, and then carefully allowing the leaf to return to its natural position. Droplets adhered to the leaf surface without runoff.

Experiment 5. The influence of two organosilicone surfactants and three organosilicone/ADE combinations on absorption of imazethapyr, 2,4-D, and picloram was compared to COC. Surfactants included COC, Silwet 408, Silwet L-77, ADE40/Silwet L-77, ADE65/Silwet L-77, and ADE85/Silwet L-77. Adjuvants ADE40, ADE65, and ADE85 are 3:1 (v/v) mixtures of acetylinic diol ethoxylates and Silwet L-77. Ethylene oxide (EO)⁴ content in the ADE surfactants, was 40, 65, and 85% (w/w). Each surfactant was applied in combination with each herbicide. The COC imazethapyr treatment contained

28% UAN as a reference of potential imazethapyr absorption. A single 1 µl drop containing 500 Bq of ¹⁴C-herbicide was applied per leaf.

Experiment 6. Influence of pH and ammonium sulfate on picloram absorption was determined. Two surfactants that performed well in the previous experiment, ADE65 and Silwet L-77, were applied alone and with ammonium sulfate in unbuffered treatment solutions. Each treatment combination was also applied in a buffered solution at pH 5 and pH 7 (50 mM citrate buffer adjusted with hydrochloric acid or sodium hydroxide) (24). A single 1 µl drop containing 183 Bq was applied to each leaf.

Data analyses. Each treatment was replicated on five to ten leaves, each leaf on a separate plant, and the experiments were repeated. Data were analyzed as randomized complete block designs with plants as blocks. Bartlett's test for variance homogeneity indicated that the data from the trials of each experiment could be pooled (34). Mean values for parameters measured were compared using Fisher's-Protected Least Significant Difference Test ($P \leq 0.05$) (34).

Results and discussion

Experiment 1. Imazethapyr absorption was rapid. Greater than 85% of the total absorption occurred by 2 DAT (Table 1). Imazethapyr absorption by leafy spurge was greatest with MSO in the absence of UAN (Table 1). Imazethapyr absorption with COC or NIS was similar to that previously reported for Tween-20 (27). Imazethapyr absorption improved 38 to 68% with the addition of UAN and was greatest with COC or MSO (Table 1). Ammonium salts increased efficacy (12, 41) and absorption (9) of imazethapyr in other weed species.

Table 1. ¹⁴C-imazethapyr absorption by leafy spurge as affected by surfactant and UAN^a at 2 and 8 d after application.

Surfactant ^c	Absorption ^b			
	2 DAT		8 DAT	
	0% UAN	2.5% UAN ^a	0% UAN	2.5% UAN ^a
	% of applied			
COC	25	93	33	97
MSO	59	97	57	98
NIS	22	86	33	83
LSD (0.05)		6		

^a 2.5% v/v 28% urea ammonium nitrate.

^b Percent absorption calculated by difference between amount applied and amount recovered in leaf wash.

^c COC, crop oil concentrate; MSO, methylated seed oil (Sun-It II); NIS, nonionic surfactant (X-77).

In addition to the 10% methanol leaf wash, a hexane:acetone rinse was performed to remove cuticular waxes from the leaf surface in experiments 1 and 3 (Table 2). Consistently less ¹⁴C was recovered from the hexane:acetone washes when 28% UAN was present in the treatment solution. The amount of ¹⁴C-imazethapyr recovered in the hexane:acetone wash was minimal when compared to the amount absorbed into the leaf tissue, regardless of UAN usage. Nevertheless, there was a clear distinction that UAN reduced the amount of ¹⁴C-imazethapyr recovered from within the cuticle.

In experiment 1, only the main effect of UAN influenced accumulation of ¹⁴C-imazethapyr in the cuticular waxes. Urea ammonium nitrate reduced cuticular accumulation of ¹⁴C-imazethapyr from 2.5% to 0.5% of applied ¹⁴C (Table 2). In experiment 3, there was an interaction between the effects of UAN and surfactant that was attributed to the larger influence of UAN when applied with COC (Table 2). With COC alone, 8.8% of applied ¹⁴C-imazethapyr resided in the cuticular waxes compared to 0.5% when UAN was included with COC. Mean cuticular accumulation of experiment 3 was 0.9% and 4.7% of applied, with and without UAN, respectively (Table 2).

Table 2. ¹⁴C-imazethapyr accumulation in the cuticle of leafy spurge as affected by urea ammonium nitrate and surfactant.

Experiment/ Surfactant ^b	¹⁴ C-imazethapyr in cuticle ^a	
	0% UAN	2.5% UAN
	—% of applied—	
Experiment 1		
Mean	2.5	0.5
LSD (0.05)		0.3
Experiment 3		
COC	8.8	0.5
309	2.7	1.0
L-77	2.5	1.2
LSD (0.05)		1.0
Mean	4.7	0.9
LSD (0.05)		0.6

^a Cuticular waxes were removed with a 9:1 hexane:acetone rinse.

^b COC, crop oil concentrate; 309, organosilicone surfactant (Sylgard 309). L-77, organosilicone surfactant (Silwet L-77).

^c 2.5% v/v 28% urea ammonium nitrate.

Reduced cuticular accumulation of imazethapyr could be an indirect effect of UAN acting at the plasma membrane, a barrier for herbicide absorption and possible site for adjuvant action (40). Research conducted by Gronwald *et al.* (9) indicates that ammonium sulfate increases absorption of imazethapyr by cell suspension cultures. Ammonium sulfate may indirectly acidify the cell wall, protonating imazethapyr. Uncharged imazethapyr then diffuses across the plasma membrane, dissociates, and becomes trapped

within the cell. A concentration gradient is maintained across the cuticle by enhancing absorption into underlying tissues. Without ammonium, the concentration gradient could dissipate, limiting further diffusion across the cuticle and increasing accumulation within the cuticle. Our results support such a hypothesis (Table 2).

Experiment 2. Droplet size and application volume can have profound effects on herbicide absorption (14). Ninety-four percent of ¹⁴C-imazethapyr was absorbed when applied with COC and UAN in a 1 µl drop, but only 74% was absorbed when applied in a 0.5 µl drop (Table 3). Absorption of imazethapyr with COC and UAN at the 1 µl application volume (Table 3) was similar to that observed where the application volume was ten, 0.5 µl drops (Table 1). Imazethapyr absorption with Sylgard 309 and Silwet L-77 was less than 35% for a 1 µl application and 8 to 17% for a 0.5 µl volume.

Reduction in herbicide absorption between 1 and 0.5 µl application volume is probably due to rapid droplet desiccation. The spreading ability and very low surface tension of the organosilicone surfactants may have actually reduced imazethapyr absorption. A 0.5 µl drop of solution containing organosilicone surfactant would spread and dry within 30 s.

Table 3. ¹⁴C-imazethapyr absorption by leafy spurge as influenced by application volume and surfactant.

Surfactant ^b	Absorption ^a	
	Application volume	
	0.5 µl	1.0 µl
	% of applied	
COC	74	94
309	8	33
L-77	17	34
LSD (0.05)	8	

^aPercent absorption was calculated by difference between amount applied and amount recovered in leaf wash.

^bCOC, crop oil concentrate; 309, organosilicone surfactant (Sylgard 309); L-77, organosilicone surfactant (Silwet L-77). Treatments contained 2.5% v/v 28% UAN and leaves were harvested 2 d after application.

Experiment 3. Environment can influence the structure and crystallization of the epicuticular waxes, which can affect herbicide absorption (14). Foliar absorption and herbicide efficacy may differ between plants grown in the field and greenhouse (13). Leafy spurge plants grown outdoors were used to evaluate adjuvant performance and estimate whether imazethapyr absorption was similar to that from experiments performed with plants grown in the growth chamber (Table 4). COC with UAN provided 90% absorption of imazethapyr by the field-grown leafy spurge. Usage of the organosilicone surfactants, Sylgard 309 and Silwet L-77 combined with UAN, resulted in 36 and 28% imazethapyr absorption, respectively. Imazethapyr absorption by field-grown plants (Table 4) appeared similar to that of plants grown in the growth chamber (Table 3, column 2). Imazethapyr absorption without UAN was poor for leafy spurge plants grown outdoors or in a growth chamber.

Experiment 4. Applying imazethapyr to the abaxial leaf surface of leafy spurge generally did not improve imazethapyr absorption (Table 5). The exception was Sylgard 309 applied with UAN. This adjuvant combination increased imazethapyr absorption by 12% on the abaxial leaf surface compared to the adaxial leaf surface (Table 5).

Because the stomatal density is greater on the abaxial leaf surface (3 1), one would expect organosilicone surfactants to provide greater absorption of the herbicide than adaxial application (5, 6, 26, 37). However, no difference in imazethapyr absorption between leaf surfaces was observed when imazethapyr was applied with COC, Sylgard 309, or Silwet L-77 to leafy spurge (Table 5).

Since no data were taken on the status of stomatal apertures, it is possible that the stomata were closed at treatment. Plants were well watered at the time of treatment and were treated near mid-day, so stomata should have been open. Similar imazethapyr absorption from abaxial and adaxial leaf surfaces with the organosilicones suggests that either the stomata were closed or the majority of absorption was not by stomatal infiltration.

Experiment 5. The acetylinic diol ethoxylates do not interfere with the physical properties of the organosilicone surfactant and improve the dynamic surface tension and spreading properties of the herbicide solution (25). The ADE surfactants could be used in formulated products that are intended to be applied with trisiloxane based organosilicone surfactants; however, none of the organosilicones or ADE mixtures provided absorption of imazethapyr comparable to the application with COC and UAN (Figure 1). The ADE40/Silwet L-77 mixture and Silwet 408 surfactant provided greater than 75% absorption of 2,4-D amine by leafy spurge (Figure 1). Absorption of 2,4-D was twice that previously reported by Lym and Moxness (21).

Imazethapyr absorption decreased with surfactants of high EO content. The ADE65/Silwet L-77 and ADE85/Silwet

Table 4. ¹⁴C-imazethapyr absorption by field-grown leafy spurge plants, at 2 d after application.

Surfactant ^b	Absorption ^a	
	0%	2. 5%
	UAN	UAN ^c
	----- % of applied -----	
COC	41	90
309	17	36
L-77	31	28
LSD (0. 05)	6	

^a Percent absorption calculated by difference between amount applied and amount recovered in leaf wash.

^b COC, crop oil concentrate; 309, organosilicone surfactant (Sylgard 309); L-77, organosilicone surfactant (Silwet L-77).

^c 2. 5% v/v 28% urea ammonium nitrate.

Table 5. ¹⁴C-imazethapyr absorption 2 d after application by the abaxial or adaxial leaf surface of leafy spurge.

Surfactant ^c	Absorption ^a			
	0% UAN		2. 5% UAN ^b	
	Adaxial	Abaxial	Adaxial	Abaxial
	----- % of applied -----			
COC	55	52	88	95
309	28	30	45	57
L-77	43	44	66	72
LSD (0. 05)	9			

^a Percent absorption calculated by difference between amount applied and amount recovered in leaf wash.

^b 2. 5% v/v 28% urea ammonium nitrate.

^c COC, crop oil concentrate; 309, organosilicone surfactant (Sylgard 309); L-77, organosilicone surfactant (Silwet L-77).

L-77 reduced imazethapyr absorption compared to ADE40/Silwet L-77, Silwet 408 or Silwet L-77 alone. Absorption of 2,4-D amine ranged from 54 to 78% and was also inversely related to the EO content among ADE/Silwet L-77 mixtures.

A combination of mechanisms may be responsible for the results observed with imazethapyr and 2,4-D. The surfactants may have been absorbed into the cuticle (33), developing hydrophilic channels (39). The hydrophilic head group of the surfactants then behaved as a selective pore for the herbicide, with absorption dependent upon the physicochemical properties of the herbicide (8). Absorption of polar herbicides such as difenzoquat (1,2-dimethyl-3,5-diphenyl-1*H*-pyrazolium) (11) and glyphosate (*N*-(phosphonomethyl)glycine) (8) would be greatest with higher EO contents, while more hydrophobic compounds such as imazethapyr and 2,4-D would require shorter EO chains.

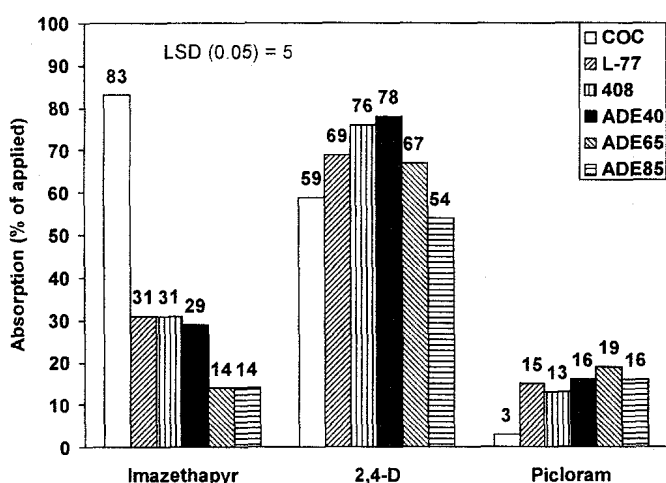


Figure 1. Percent of absorption of ¹⁴C-imazethapyr, ¹⁴C-2,4-D, and ¹⁴C-picloram by leafy spurge 2 DAT. Surfactants evaluated included COC, Silwet L-77, Silwet 408, and the following 3:1 mixtures of acetylinic diol ethoxylates with Silwet L-77, ADE40/L-77, ADE65/L-77, ADE85/L-77. For imazethapyr, 2.5% v/v 28% UAN was combined with the COC.

Consistent with this hypothesis, the ADE40/Silwet L-77 mixture (shorter EO chains, less polar) provided more absorption of imazethapyr and 2,4-D than the ADE65/Silwet L-77 and ADE85/Silwet L-77 surfactants which had longer EO chains and were more polar (Figure 1). The higher EO contents of the ADE65 and ADE85 surfactant mixtures with Silwet L-77 could be anticipated to overcome the antagonism of glyphosate absorption in grasses caused by Silwet L-77. These ADE's should also be considered in combination with Silwet 408, since Silwet 408 itself can improve glyphosate absorption (8, 32). Picloram absorption was consistently low regardless of the surfactant used. Excluding COC, picloram absorption ranged from 13 to 19% (Figure 1). Similar values have been reported by Lym and Moxness (21, 24) for picloram absorption by leafy spurge. Picloram absorption with COC averaged only 3%.

Experiment 6. Picloram absorption varies among species (10, 35) and is dependent upon temperature (10, 20, 35) and relative humidity (24, 35). Spray additives and solution pH also are important factors influencing picloram absorption (24). Temperature and humidity cannot be easily controlled under field conditions, however spray solution pH and additives can be manipulated to optimize herbicide absorption.

Picloram absorption by leafy spurge ranged from 12% for Silwet L-77 unbuffered without ammonium sulfate to 37% for Silwet L-77 with ammonium sulfate and buffered

with trisodium citrate at pH 7. Buffering the treatment solutions at pH 5 or 7 and including ammonium sulfate had a greater effect on picloram absorption than did either treatment alone (Table 6). Moxness and Lym (24) found that the addition of 2.5 kg ha⁻¹ ammonium sulfate increased picloram absorption by leafy spurge from 18 to 46%. However, for unbuffered solutions, our results indicate ammonium sulfate did not improve picloram absorption when applied with Silwet L-77 or ADE65/Silwet L-77 (Table 6).

Table 6. ¹⁴C-picloram absorption by leafy spurge when applied in buffered solutions at pH 5 and pH 7 and in combination with ammonium sulfate.

Adjuvant ^b	Absorption ^a		
	Unbuffered ^c	pH 5	pH 7
	—% of applied—		
ADE65	18	18	27
ADE65 + AS	20	30	34
L-77	12	19	18
L-77 + AS	14	25	37
LSD (0.05)		9	

^a Percent absorption calculated by difference between amount applied and amount recovered in leaf wash. Leaves were harvested 2 d after application.

^b ADE65, 3:1 mixture of acetylinic diol ethoxylate (65% ethylene oxide) with L-77; L-77; organosilicone surfactant (Silwet L-77); AS, 2.5 kg/ha ammonium sulfate.

^c pH of unbuffered treatment solutions with and without ammonium sulfate was 6.7 and 9.0, respectively.

Picloram absorption in leafy spurge (24) and broom snakeweed [*Gutierrezia sarothrae* (Pursh) Britt. & Rusby] (35) has been reported to reach a maximum between pH 4 and 5 in buffered treatment solutions. Raising or lowering the pH resulted in decreased picloram absorption. In contrast, our results indicate that buffered treatment solutions at pH 7 provided greater picloram absorption than those at pH 5. Our results may have differed from results previously reported because of differences between application methods, surfactants, and buffers.

Buffering treatment solutions at a lower pH may improve diffusion of picloram through the cuticle by increasing the proportion of undissociated molecules (picloram, pK_a 2.3 at 22° C). Ammonium sulfate, as previously discussed with imazethapyr (9), could then facilitate movement of picloram from the apoplast into the cytoplasm. Assuming this is correct, then it would also be true that unbuffered solutions would provide less picloram diffusion across the cuticle and the effects of ammonium sulfate would be negligible because of limited availability of picloram in the apoplast. Our results support the hypothesis that both the cuticle and plasma membrane are major barriers to picloram absorption. Picloram absorption was unaffected by ammonium sulfate when applied in unbuffered treatment solutions, but was improved by the addition of ammonium sulfate to treatment solutions buffered at pH 5 (Table 6). Picloram absorption with ammonium sulfate also increased with buffering at pH 7, which is well beyond the pK_a of picloram. Thus, increases in picloram absorption may be due to unknown factors associated with

the buffer and not solely dependent upon increasing the concentration of undissociated herbicide molecules.

Urea ammonium nitrate improves imazethapyr absorption by leafy spurge and is most effective when combined with COC or methylated seed oil. UAN reduced the amount of imazethapyr that accumulated within the cuticle of leafy spurge, which suggests that UAN facilitates imazethapyr movement through the cuticle. Ammonium sulfate improved picloram absorption, but only when applied in buffered treatment solutions. Our results support findings from other studies that suggest ammonium salts act at the plasma membrane and increase weak-acid herbicide movement from the apoplast into the cytoplasm via ion-trapping (9).

Organosilicone surfactants increased 2,4-D absorption by leafy spurge and provided greater picloram absorption than did COC. Although the organosilicones were not the most effective surfactants for imazethapyr in this study, their ability to reduce the rain-free period and increase droplet adhesion and spreading should be considered.

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