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Reduction of Norflurazon Leaching in a Sandy Soil by Adjuvants

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Citrus is cultivated in approximately 850,000 acres of Florida and contributes a significant portion of the state's agricultural revenue (Florida Agricultural Statistics Service 1996). Higher mean annual soil temperatures and the subtropical climate prevalent in Florida causes weeds to germinate and grow actively year round (Jackson 1991, Singh and Tan 1992). Weed competition adversely affects citrus yield and is economically managed using herbicides (Bridges 1992; Muraro et al. 1995). Groundwater contamination from increased pesticide usage is a concern in major agricultural regions of the world (Hallberg, 1988). Norflurazon [4-chloro-5-(methylamino)-2-(3-trifluoromethyl)phenyl)-3(*2H*)-pyridazinone], is a commonly applied herbicide for residual control of weeds in citrus. It is non-ionic, with a water solubility of 28 mg L^{-1} and K_{oc} of 248 ml g^{-1}, and a relative leaching potential index (RLPI) of 233 (Ahrens 1994, Hornsby et al. 1991).

Herbicide leaching is influenced by the physico-chemical characteristics of the soil and herbicide, and certain environmental conditions like precipitation (Alva et al. 1990, Anderson 1996, Bailey and White 1970). Leaching could be minimized through proper herbicide selection and application rate, use of controlled release formulations and through improved management practices (Singh and Tan 1996).

Adjuvants function as spreaders, stickers, antifoamers, compatibility agents, or activators of pesticidal formulations and are often known to improve the efficacy of postemergence herbicides (McWhorter, 1982). Their effects on preemergence herbicides are studied less extensively because the placement of these herbicides does not require further modification of surface related properties to enhance plant uptake. However, adjuvants modify certain physical characteristics of the spray solution like surface tension and wetting ability, which may modify the spray solution's response to move in the soil (Roberts 1992, Singh and Tan 1996, 1980). Bayer (1967) altered diuron leaching depths in a sandy clay loam by adding surfactants that either formed an impervious layer in the soil surface to resist infiltration or rapidly wetted the surface layer of soil to reduce percolation.

Surfactants can cause variable effects on herbicide movement based on soil type,

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concentration of herbicide and surfactants, and preleaching conditions (Foy 1992). Tan and Singh (1995) reported reduced leaching of norflurazon under laboratory conditions using a cationic surfactant, which had no effect on bromacil leaching. A polymer-based adjuvant was found to be specific to reduce leaching of simazine but was ineffective on bromacil, norflurazon, and diuron leaching (Jain and Singh 1992).

The objective of this experiment was to screen polymer-based adjuvants to reduce norflurazon leaching and to determine the optimum use rates of selected adjuvants to reduce herbicide leaching without compromising weed control.

MATERIALS AND METHODS

Experiments were conducted in a greenhouse at the Citrus Research and Education Center, Lake Alfred, Florida. The top 120 cm of a Candler sand (Hyperthermic, uncoated Typic Quartzipsamments), a typical well-drained, ridge soil in the citrus belt of Central Florida, was collected locally from an area known to be free of herbicide residues. The soil layers were collected in four 30-cm increments and transferred to separate bins in the greenhouse. The top 30-cm of the soil had an organic matter content of 1.1% and a pH of 6.4. Soil was air-dried for a week to ascertain uniform compaction while performing leaching experiments.

Soil leaching columns as described by Weber et al. (1986) were used to conduct experiments to determine the effect of adding adjuvants on norflurazon leaching. Columns made of PVC 135 cm long, 9.8 cm inner diameter, were cut into halves longitudinally. Silicone ridges were placed cross-sectionally at 15-cm increments along the inner wall to prevent preferential flow of solution along the soil-column interface. The halves were resealed using an adhesive tape to form a column and the bottom end was fitted with a PVC cap having a one-centimeter drainage hole. Nylon screen (8 mesh cm-‘) was placed at the bottom and columns were packed consistently by adding soil incrementally from the four bins representing the four depths of the soil profile. Bulk densities of 1.55, 1.57, 1.58, and 1.96 g cm^{-3} were determined gravimetrically for the 0 to 30, 30 to 60, 60 to 90, and 90 to 120 cm depths, respectively. The columns were secured upright on a wooden platform and were brought to field capacity and drained overnight prior to leaching.

Adjuvants screened in the study are described in Table 1. Each adjuvant was applied with norflurazon at 1:1 wt/wt to provide the adjuvant at 8.06 kg ai ha^{-1} (8.12 mg $column^{-1}$). Herbicide and adjuvant stock solutions were prepared in distilled water at higher concentrations and were diluted sequentially to obtain the application rates. A mixture containing 2.5 ml each of the herbicide and adjuvant solution was transferred into a 20-ml vial and shaken vigorously in a vortex mixer for one minute. The adjuvants monazoline-O (oleyl imidazoline), schercozoline-C (1-H-imidazole-1-ethanol,4,5-dihydro-,2-norcocoalkyl derivative) and schercozoline-O(9-octadecenamide-N-[3-(dimethylamino)propyl]imethylamine) were viscous and required a hot water bath before they could be used in the study.

Table 1. Adjuvants screened for efficacy to reduce herbicide leaching in a Candler sand.

Adjuvant[1]	R_f[2]	Adjuvant	R_f	Adjuvant	R_f
Agridex[3]	0.86	Gum Arabic[7]	1.37	JMI-40-PR[8]	0.84
Dyne-amic[3]	1.34	Gum Ghatti[7]	1.72	JMI-90G1[8]	0.98
E-14-2[4]	1.21	Gum Guar[7]	1.01	JMI-95AT[8]	0.88
E-14-5[4]	0.96	Gum Karaya[7]	1.23	JMI-98G1[8]	0.88
E-17-2[4]	2.22	Gum locust bean[7]	1.27	JMI-Plex[8]	0.86
E-18-15[4]	1.80	Gum Storax[7]	1.30	Kinetic[3]	1.40
Emcol CC-36[5]	1.21	Gum Tragacanth[7]	1.03	Monazoline-O[9]	1.85
Emcol CC-42[5]	0.56	Gum Xanthan[7]	1.44	Monazoline-CY[9]	1.12
Emcol CC-55[5]	1.77	Impact II[8]	1.21	Monazoline-T[9]	1.98
Emcol CC-57[5]	1.24	Impact JMI[8]	0.63	Schercozoline-C[10]	1.34
Freeway[6]	1.36	Induce[8]	1.24	Schercozoline-O[10]	1.41
Gum Accroides[7]	1.27	JMI-25AT[8]	0.93	Silwet L-77[5]	1.06

[1]Adjuvants whose R_f differed by > 0.27 were significantly different using the LSD test (P = 0.05).

[2]Retardation Factor calculated as: Distance moved by the herbicide/Distance moved by herbicide + adjuvant.

[3]Helena Chem. Co., Las Vegas, NE 89118.

[4]Exxon Chem. Co., Milton, WI 53563.

[5]Witco Corp., Dublin OH 43017.

[6]Loveland Ind., Greeley, CO 80632.

[7]Sigma Chem. Co., St. Louis, MO 63178.

[8]Jay-Mar, Inc., Plover, WI 54467.

[9]Mona Ind. Inc., Paterson, NJ 07544.

[10]Scher Chem., Clifton, NJ 07012.

The soil surface in the columns was leveled, and the 5-ml herbicide-adjuvant mixture was transferred carefully over the entire soil surface with a Pasteur pipette. A 1-cm layer of silanized grade glass wool was placed on the surface to ensure proper spread and uniform solution flow through the column while leaching was being performed. Leaching treatment was carried out by dripping deionized water over the glass wool to simulate a rainfall of 12.5 cm at 2.5 cm hr^{-1}. The flow rate was monitored periodically to ensure uniform leaching. Columns remained intact for 18 hours before conducting bioassays.

Columns were split open longitudinally by removing the tape on one side and slicing the sand along the center, starting from the column bottom. Three shallow furrows were made on the soil surface with 3 cm between each furrow, using a ruler. Barnyardgrass seed, the bio-indicator used in this study, was placed uniformly in each furrow and covered with adjacent soil. The bioassay columns were mist-irrigated at regular intervals to keep the surface moist. Herbicide leaching was determined from injury symptoms to seedlings growing in soils contaminated with norflurazon. Injury symptoms were manifested as bleached appearance, due to lack of chlorophyll, of the entire plant or leaves (Devine et al. 1993). Distances moved by the herbicide were measured on the basis of symptoms exhibited. Retardation Factor (R_f) values were calculated as follows to determine the efficacy of each adjuvant to reduce herbicide leaching:

$$R_f = D_0 / D_a$$

where, D_0 = Distance moved by the herbicide alone
D_a = Distance moved by herbicide with adjuvant

Adjuvants exhibiting higher R_f values on the basis of statistical analysis were chosen to conduct further studies. The rate of application of selected adjuvants was adjusted to 50, 25, 12.5 and 6.25% by weight of the herbicide to determine the effect on R_f values.

Petri dish bioassays were conducted to determine the effect of different concentrations of norflurazon on the exhibition of injury symptoms by the bioassay species, barnyardgrass, used in this study. A stock solution of 8.0 µ g ml^{-1} norflurazon was prepared using distilled water. Sequential dilutions were carried out to prepare solutions of concentrations ranging from 4.0 µ g ml^{-1} to 0.004 µ g ml^{-1}. One milliliter of each dilution was mixed thoroughly with 10 ml distilled water and transferred to petri dishes containing 50 g top soil. After mixing the solution with soil, 25 barnyardgrass seeds were placed in each petri dish and covered with adjacent soil. Petri dishes were transferred to an incubator to simulate temperature and light conditions of the greenhouse. Seedlings were observed for injury symptoms due to norflurazon.

Weed control studies were conducted in a greenhouse with an average day/night temperatures of 32/25 C, ambient light level at mid-afternoon of approximately 1000 µ $mol.m^{-2}sec^{-1}$, and an average photo period of 12 h. Plastic containers (500 ml) were filled with a Candler fine sand (O-30 cm). Approximately 50 seeds of pigweed, velvetleaf, barnyardgrass, and yellow foxtail were placed on top of the soil surface and covered with a 1 cm layer of the same soil. Norflurazon was applied either alone or with the selected adjuvants as a tank mix at 2.8 kg ai ha^{-1} (Allen track sprayer, Allen Machine Works, 607 E. Miller Rd., Midland, Mich. 48640) with adjuvant rates ranging from 0.08 to 2.8 kg ai ha^{-1}. Containers were sprayed with the respective herbicide/adjuvant mixture treatment followed by a 10-mm irrigation. All herbicide formulations were applied using flat fan nozzles (Teejet 8002 flat fan spray nozzles, Spraying Systems Co., North Ave., Wheaton, IL 60788) delivering 230 L/ha with water as the carrier. Seedlings were allowed to germinate and establish for three weeks. Weed control ratings and shoot fresh weights were recorded three weeks after treatment.

Studies were designed as Randomized Complete Block with three replications for each treatment. Data were subjected to Analysis of Variance (ANOVA) with mean separations using Fisher's Protected Least Significant Difference (LSD) test at P = 0.05 (PRM, Gylling Data Management Inc., Brooklings, SD 57006). The R_f values were regressed against different rates of application of each adjuvant to predict their effect on herbicide leaching (Freund et al. 1986).

RESULTS AND DISCUSSION

Petri dish studies indicated that barnyardgrass seedlings were capable of detecting norflurazon concentrations of 500 µg g^{-1} in the soil by exhibiting injury symptoms caused by the herbicide. The adjuvants monazoline-O(oleyl imidazoline), monazoline-T (tall oil imidazoline), and E-17-2 (dihydroxyethylisotridecyloxypropylamine) reduced leaching of norflurazon by approximately 50% compared to the control (Table 1). These adjuvants had higher R_f values compared to that of other adjuvants screened. Adjuvants with R_f values > 1.7 included E-17-2, E-18-15 (ethoxylated alkylamine, chemical name not available; CAS 61790-82-7), Emcol CC-55 (polyoxypropylenediethyl-12-hydroxyethyl ammonium acetate), Gum Ghatti (chemical name not available, CAS 9000-28-6), monazoline-O, and monazoline-T. Reduction of herbicide leaching as a result of adding adjuvants was described by other investigators (Foy 1992, Tan and Singh 1995). Tan and Singh (1995) reported reduction of norflurazon leaching with imidazoline based cationic adjuvants. Monazoline-O, monazoline-T, and E- 17-2 were selected to carry out further experiments due to their high R_f values.

The adjuvant E-17-2 was most efficient for reducing norflurazon leaching (Fig. 1). Observed values indicated an increase in R_f values by approximately 15% as a result of adding this compound to norflurazon compared to monazoline-O and monazoline-T. The model, based on significant linear regression, also predicted a similar response with other rates tested. Both observed and predicted values indicated a similar rate of increase in R_f values with increases in adjuvant ratios in the tank mix. The response of monazoline-O and monazoline-T to reduce norflurazon leaching was similar for most rates tested. Although adjuvant rates in the tank mix were increased geometrically, the R_f values did not change so drastically. This unique behavior was exhibited by all three adjuvants.

E- 17-2 decreased herbicide leaching by 58%, when applied at equal proportions by weight with norflurazon, compared to the herbicide applied alone (Fig. 2). A 15% decrease in leaching efficiency was noted when adjuvant rate was lowered to 50% of that of the herbicide. At the lowest rate of E-17-2 used in the tank mix 0.78% herbicide by weight, the resultant decrease in norflurazon leaching was about 10%. Based on the model, norflurazon leaching could be halved by mixing E- 17-2 at 75% by weight of the herbicide, and be reduced by one-fourth by adding the adjuvant at 10% by weight of the herbicide. Reddy and Singh (1993) reported approximately 35% reduction in norflurazon leaching and 10% reduction in bromacil leaching using acrylic polymer based adjuvants based on a different model.

E- 17-2 applied at equal proportions with norflurazon had a slight but insignificant effect on control of pigweed and barnyardgrass by the herbicide (Table 2). At lower rates, weed control was not affected by adding the adjuvant to the herbicide solution. Monazoline-O and monazoline-T did not affect weed control at any of

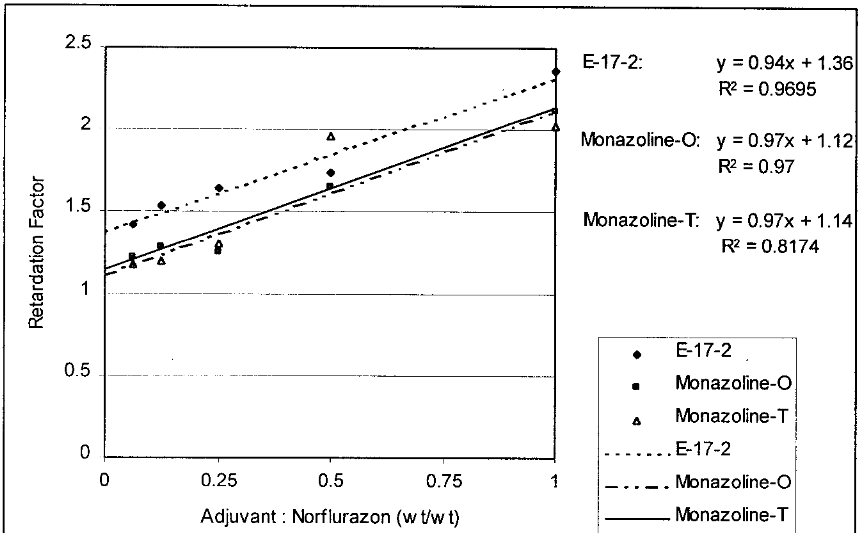

Figure 1. Effect of adjuvants E-17-2, monazoline-O, and monazoline-T on norflurazon leaching in a sandy soil using soil leaching column bioassays.

the application rates tested. These results indicate that the adjuvants did not cause herbicide binding at levels sufficient to affect weed control.

E- 17-2, an alkyl amine, monazoline-O and monazoline-T, tertiary amines, are all are cationic by nature. Norflurazon is a neutral molecule, hence, the possibility of reduced herbicide leaching due to covalent binding with the adjuvant could be eliminated. This is further clarified by their disability to affect weed control of norflurazon. The complex interaction between herbicides, adjuvants and soil system makes it difficult to explain the effect of adjuvants on herbicide leaching. The cationic adjuvants used in this study may have led to the formation of neutral species by binding to certain anionic molecules in the soil system. The resultant complex may have dissolved the herbicide rendering it less mobile in soil. The effect of adjuvants and wetting agents on soil hydrology to affect water infiltration and percolation were reported quite early (Bayer 1967, Pelishek et al. 1962). The adjuvants used in this study may have modified some of properties of the soil that governed water infiltration and movement in the profile. Adjuvants are also capable of altering the surface tension and wetting ability of the herbicide solution which in turn could influence its movement in soil (Walker 1980). Weed control experiments also suggest that residual activity of norflurazon may increase as a result of reduced herbicide loss from leaching and insignificant herbicidal tie-up from adjuvants.

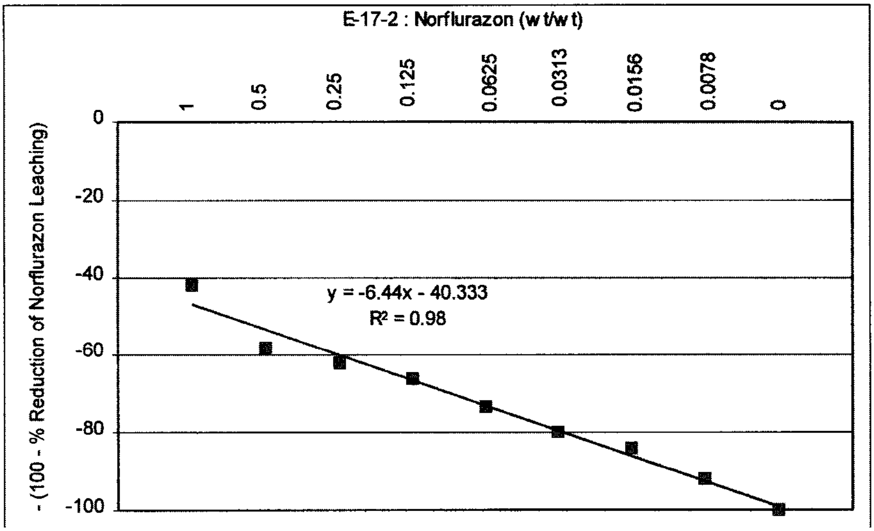

Figure 2. Effect of E-17-2 on the norflurazon leaching in a sandy soil profile based on percent reduction of herbicide movement using soil leaching column bioassays.

The economics of application of adjuvants at the use rates tested under greenhouse conditions are yet to be studied by conducting field trials. Extending weed control by minimizing losses due to leaching could also reduce application

Table 2. Effect of adjuvant application rates on pigweed and barnyardgrass control when mixed with 2.8 kg ha^{-1} of norflurazon in a greenhouse study.

Adjuvant	Adjuvant: Herbicide Ratio	Pigweed			Barnyardgrass		
		Weed Count	S.F.W (g)	% Control	Weed Count	S.F.W (g)	% Control
E-17-2	1.0	3	0.02	98	4	0.10	97
E-17-2	0.50	0	0.00	100	0	0.00	100
E-17-2	0.25	0	0.00	100	0	0.00	100
E-17-2	0	0	0.00	100	0	0.00	100
Monazoline-O	1.0	0	0.00	100	0	0.00	100
Monazoline-O	0.50	0	0.00	100	0	0.00	100
Monazoline-O	0.25	0	0.00	100	0	0.00	100
Monazoline-O	0	0	0.00	100	0	0.00	100
Monazoline-T	1.0	0	0.00	100	0	0.00	100
Monazoline-T	0.50	0	0.00	100	0	0.00	100
Monazoline-T	0.25	0	0.00	100	0	0.00	100
Monazoline-T	0	0	0.00	100	0	0.00	100
Control	--	62	1.61	0	28	3.51	0
LSD (P= 0.05)	--	12	0.30	--	3	0.23	--

rates and the cost of chemicals used. The effect of tank mixing adjuvants at higher rates along with herbicides on spray equipment is also unknown, although greenhouse studies with the pressure chamber did not cause clogging of the lines. Further research is required to verify these results under field conditions and also to determine the spectrum and duration of weed control under such conditions. If found effective, this technique may be an useful tool to reduce herbicide movement into the groundwater and to manage weeds more efficiently.

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