Bull. Environ. Contam. Toxicol. (1993) 50:449–457

Environmental Contamination and Toxicology

Effect of Acrylic Polymer Adjuvants on Leaching of Bromacil, Diuron, Norflurazon, and Simazine in Soil Columns

Krishna N. Reddy and Megh Singh

University of Florida, Institute of Food and Agricultural Sciences, Citrus Research and Education Center, 700 Experiment Station Road, Lake Alfred, Florida 33850, USA

The temperate to subtropical climate of Florida is an ideal environment for weed growth. Herbicides have been and will continue to be used for effective and economical weed control in citrus. The majority of herbicides are applied directly to the soil for residual weed control. Bromacil [5-bromo-6-methyl-3-(1-methylpropyl)-2,4-(1H,3H) pyrimidinedione], diuron [N'-(3,4-dichlorophenyl)-N,N-dimethylurea], norflurazon [4-chloro-5-(methylamino)-2-(3-(trifluoromethyl)phenyl)-3(2H)-pyridazinone], and simazine [6-chloro-N-N'-diethyl-1,3,5-triazine-2,4-diamine] are soil-applied herbicides widely used for weed control in Florida citrus groves. Bromacil, an acidic herbicide, has high water solubility (815 mg L^{-1}), while simazine, a basic herbicide, has low water solubility (3.5 mg L^{-1}). The distribution coefficient on organic carbon (K_{oc}) is 72 and 140 mL g^{-1} for bromacil and simazine, respectively (Rao *et al.* 1985; Hornsby *et al.* 1990). Diuron and norflurazon are nonionic herbicides with a water solubility of 42 and 28 mg L^{-1} and K_{oc} of 480 and 248 mL g^{-1}, respectively (Rao *et al.* 1985; Hornsby *et al.* 1990).

Movement of herbicides below the plant root zone depends on the nature of soil, including inorganic and organic components, as well as the chemical nature of the herbicide (Bailey and White 1970). Herbicide mobility in soil is both an agronomic and an environmental concern. Soil-applied herbicides that readily move in the soil can fail to control target weeds due to dilution effect or can become a potential groundwater contaminant due to leaching through the soil profile. Soil-applied herbicides in citrus groves of Florida have a greater potential for leaching through the soil profile due to high application rates, porous nature of soils with low organic matter content (Carlisle *et al.* 1989), and high annual rainfall (135 cm). Several herbicides have been detected in groundwater as a result of normal herbicide use. In a 1990 groundwater monitoring study, simazine concentration of 13 μg L^{-1} and bromacil concentration of 952 μg L^{-1} has been detected in groundwater of Florida (T. C. McDowell, Florida Dept. Agric. and Consumer Services, Tallahassee).

Send reprint requests to Dr. Megh Singh at the address above.

Controlled release technology has some potential to prolong herbicide efficacy for weed control and to minimize leaching of soil-applied herbicides. With a controlled release formulation, the herbicide is either chemically attached to or physically entrapped within another substance such as a polymer to modify herbicide release. Controlled release formulations include various shapes of porous and nonporous monoliths, pliable beads, coated granules, microcapsules, water insoluble mixtures, films, salt mixtures, and adjuvants (Schreiber *et al.* 1987; Riggle and Penner 1990). A pine kraft lignin (PC940C) effectively controlled the release of metribuzin and alachlor (Riggle and Penner 1988). Starch encapsulation of EPTC (Schreiber *et al.* 1988), trifluralin (Trimnell *et al.* 1981), and chloramben (Raboy and Hopen 1982) resulted in slow release of herbicides. Activated charcoal and humic acid substances have been used as adjuvants to modify herbicide release (Madhun *et al.* 1986; Alva and Singh 1991). Surfactants such as Aliquat 204 (dilauryl dimethyl ammonium chloride) and Aliquat 221 (dicoco dimethyl ammonium chloride) reduced diuron mobility (Bayer 1967). Synthetic polymers have also been used as adjuvants for controlled release of herbicides. Hydrosorb (Alva and Singh 1991) and STAY-TEC (Jain and Singh 1992) polymers have increased the sorption and decreased the mobility of simazine.

The objectives of this research were: 1) to examine the leaching characteristics of bromacil, diuron, norflurazon, and simazine in a sandy soil under citrus production and 2) to evaluate the effectiveness of three acrylic polymer adjuvants for minimizing leaching of these herbicides in soil leaching columns.

MATERIALS AND METHODS

Soil from 0-30, 30-60, 60-90, and 90-120 cm depth was collected from abandoned citrus groves at the Davenport Research Farm of the Citrus Research and Education Center, Lake Alfred, Florida. The soil used in the study was Candler fine sand (Typic Quartzipsamment). This soil represents a typical deep, well-drained, ridge soil in the citrus belt of central Florida. The physicochemical properties for the four depths of Candler fine sand have been reported by Alva and Singh (1990). Briefly, the top 30 cm soil had 97% sand and 1.1% organic matter with a pH 6.4.

Leaching behavior of bromacil, diuron, norflurazon, and simazine was studied in soil leaching columns. Soil from only surface 30 cm was used in the leaching studies. Leaching was evaluated using clear acrylic columns of 8-cm long and 7-cm inner diameter. The bottom of the column was constructed using a thin nylon mesh above the perforated acrylic plate. This allowed free water movement while maintaining soil column integrity. The columns were packed by adding small amounts of soil to the column while it was agitated on a vortex shaker. The columns were packed to attain a bulk density of 1.5 g cm^{-3}. Each column was saturated with deionized water from the bottom of the column by capillary force and allowed to drain for 18 hr. Herbicide solutions were prepared in distilled water using 33.8% water soluble liquid formulation of bromacil, 80% dispersible granular formulation of diuron and norflurazon, or a 41.9% liquid formulation of simazine. Herbicide solutions were then spiked with ^{14}C-herbicide. The ^{14}C-herbicides used were [Carbononyl-2-^{14}C] bromacil (specific activity = 7.1 $\mu Ci/\mu mole$, purity = 98%), [Phenyl (U)- ^{14}C] diuron (specific activity = 10.3 $\mu Ci/\mu mole$, purity = 99%), [4,5- ^{14}C] norflurazon (specific activity = 41.1 $\mu Ci/\mu mole$, purity = 99.8%), and [Δ-^{14}C] simazine (specific activity = 4.56 $\mu Ci/\mu mole$, purity = 97.1%). A one mL aliquot of final treatment solution contained 1.925 mg of herbicide with a radioactivity of 50,000 dpm. One mL treatment solution per column was applied to the soil surface uniformly as several drops. This was equivalent to a herbicide rate of 5 kg ai ha^{-1}. Immediately after herbicide application, a filter paper was placed on the soil surface and deionized water was applied using a peristaltic pump at a rate of 2.5 cm hr^{-1}. The leachate was collected at each pore volume up to a total of 10 pore volumes. Each pore volume was equivalent to 117 mL (= 3.0 cm rainfall). One mL of leachate in duplicate for each pore volume was pipetted into a vial containing 10 mL scintillation cocktail (ScintiVerse II, Fisher Scientific Company, 711 Forbes Avenue, Pittsburgh, Pennsylvania) and radioactivity quantified by a liquid scintillation counter (LS 1800, Beckman Instruments Company, Brea, California). Scintillation counts were corrected for background and counting efficiency by the external standard method. The radioactivity at each pore volume was expressed as a percent of ^{14}C-herbicide applied. The experiment was conducted in a randomized complete block design with four replications. The data was subjected to analysis of variance and means were separated at the 5% level of significance using Fisher's protected LSD test (Little and Hills 1978).

Effect of acrylic polymer adjuvants on movement of bromacil, diuron, norflurazon, and simazine was studied in soil leaching columns. The adjuvants tested were ASE-95 (Primal ASE-95 with 18% acrylic copolymer), ASE-108 (Acrysol ASE-108 with 18% acrylic copolymer), and G-110 (Acrysol G-110 with 22% ammonium salt of acrylic polymer). The adjuvants were supplied by Rohm and Haas Company, Independence Mall West, Philadelphia, Pennsylvania. PVC columns of 130-cm long and 10-cm diameter were split longitudinally into two equal halves. At every 15 cm from bottom, a ridge of silicone (clear, 100% silicone rubber, General Electric Company, Waterford, New York) was placed on the inside wall of each half to prevent 'edge flow' of water along the soil-wall interface. The two halves were joined by waterproof tape to form a column. A PVC end-cap with a small drain hole was fitted to the bottom of the column. Columns were packed with soil from respective four depths of soil profile. Soil packed columns were kept in an upright position on a specially made wooden frame. Soil in the columns was saturated with water from the top and allowed to drain for 18 hr. Treatments consisted of commercial formulations of herbicides (5 kg ai ha^{-1} or 3.928 mg/column) alone, herbicide + ASE-95 or ASE-108 or G-110 (5 kg ai ha^{-1} or 3.928 mg/column), and untreated control. Herbicide solutions were prepared in distilled water using commercial formulations as described above. A 2-mL aliquot of final treatment solution contained 3.928 mg of herbicide alone or in combination with 3.928 mg of adjuvant. Two mL solution of each treatment was applied per column uniformly on the soil surface as several drops using a pasteur pipet. Columns were leached by applying deionized water at 2.5 cm hr^{-1} flow rate over filter paper placed on the soil surface. The filter paper was used to ensure uniform distribution of water on soil surface. The amount of water used for leaching was equivalent to 5 cm rainfall for bromacil and 12.5 cm rainfall for diuron, norflurazon, and simazine. After leaching, the columns were allowed to drain about 18 hr and split longitudinally into two halves. Each half was planted with ryegrass in rows 5 cm apart. Shoot fresh weight for each 15 cm interval (3 rows) was recorded 3-4 weeks after planting. Data from two halves was combined. Data are presented as percent shoot fresh weight reduction for each herbicide compared to untreated control. The experiment was conducted in a randomized complete block design with three replications. Analysis of variance was performed separately for each herbicide. Means were separated at the 5% level of significance using Fisher's protected LSD test (Little and Hills 1978).

RESULTS AND DISCUSSION

Leaching of bromacil was rapid and significantly higher than that of simazine, norflurazon, and diuron (Figure 1). The amount of bromacil leached increased from 30% in the first pore volume to a peak of 43% in second pore volume and sharply decreased thereafter. Over 97% of bromacil leached within the first four pore volumes and 100% in a total of five pore volumes. The amount of simazine leached ranged from 9% in the first pore volume to a peak of 33% in the second pore volume. Over 77% was leached in the first four pore volumes. Norflurazon and diuron leaching was slow and the amounts leached in the first pore volume were negligible. Norflurazon and diuron leaching was maximum in the third pore volume. Overall, in the first four pore volumes, the amount of norflurazon (58%) and diuron (51%) leached was considerably lower than that of either bromacil or simazine. An early peak of leaching for bromacil and simazine compared to either norflurazon or diuron indicates higher mobility of bromacil and simazine. Bromacil was much more mobile than simazine. Norflurazon was more mobile than diuron.

Differences in amounts leached in a total of five pore volumes (equivalent to 15.2 cm rainfall) were significant among the herbicides (Figure 2).

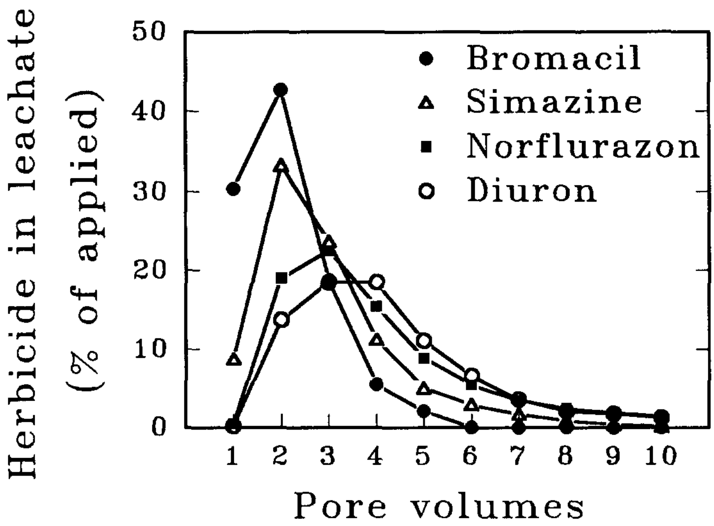

Figure 1. Herbicide in leachate at each pore volume. Leached continuously with 10 pore volumes of deionized water. Fisher's LSD values for comparing herbicide means within each pore volume are 11.0, 13.3, 3.1, 1.9, 1.9, 1.4, 1.0, 0.6, 0.4, and 0.4 for pore volumes 1 to 10, respectively.

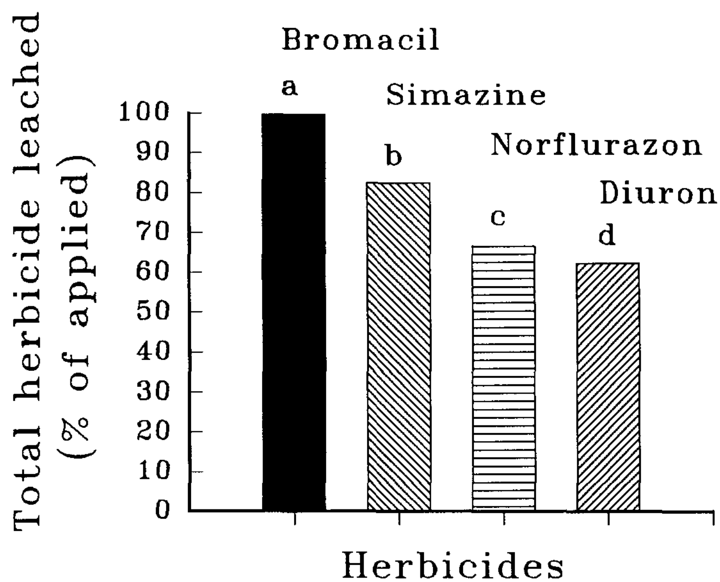

Figure 2. Total amount of herbicide leached in five pore volumes (equivalent to 15.2 cm rainfall). Means followed by different letter are significant at the 5% level as determined by Fisher's LSD test.

Bromacil completely leached followed by simazine (82%), norflurazon (67%), and diuron (62%) in a total of five pore volumes. A similar trend was observed when leaching continued up to 10 pore volumes. Leaching of simazine, norflurazon, and diuron in 10 pore volumes was 88, 81, and 78%, respectively (data not shown). The relative leaching of herbicides in decreasing order was: bromacil > simazine > norflurazon > diuron. Alva and Singh (1990) have proposed a similar ranking of leachability of these four herbicides in previous herbicide sorption studies. Differences in herbicide leaching were due, in part, to differences in water solubility and distribution coefficient on organic carbon (K_{oc}). Obviously, the lower the herbicide sorption on soil, the greater the amount available for leaching. The relative sorption of these herbicides in decreasing order was: diuron > norflurazon > simazine > bromacil in several sandy soils of Florida (Alva and Singh 1990; Reddy and Singh 1992a; 1992b; Jain and Singh 1992). Bromacil is the most mobile among the four herbicides studied.

The results indicate that leaching potentials of bromacil and simazine would be considerably greater than that of norflurazon and diuron. A rainfall of 3 cm following herbicide application would leach over 30% of bromacil below 8 cm of the soil surface as compared to less than 9% of simazine and negligible amounts of norflurazon and diuron.

As ryegrass shoot fresh weight was inversely proportional to the herbicide concentration in the soil, a greater percent of shoot fresh weight reduction would indicate higher concentration of herbicide. Overall, adjuvants reduced movement of herbicides in soil columns as evident from smaller shoot fresh weight reduction in the presence of adjuvants compared to herbicide alone (Figure 3). In the absence of adjuvants, the distance herbicides moved in soil columns ranged from 30 cm for diuron to 105 cm for bromacil. When water equivalent to 5 cm rainfall was applied, bromacil moved to a depth of 105 cm; however, amount of bromacil moved was significantly reduced in the presence of adjuvants. ASE-95 and ASE-108 reduced bromacil movement to 90 cm compared to 105 cm in bromacil alone columns. Since simazine, norflurazon, and diuron were less mobile than bromacil (Figures 1 and 2) a higher amount of water (12.5 cm) was used for leaching. Simazine with 12.5 cm water moved to a depth of 60 cm. ASE-108 and G-110 reduced the amount of simazine moved compared to simazine alone. Norflurazon, like simazine, also moved up to 60 cm depth with 12.5 cm water. ASE-95 and ASE-108 reduced the movement of norflurazon. Diuron, relatively less mobile than the three herbicides, moved to a depth of 30 cm and the adjuvants had no significant effect on movement.

The results of this study indicate adjuvant specificity for specific herbicides. Among the four herbicides studied, the effect of the adjuvant for decreasing leaching was more apparent for bromacil and least for diuron. Several

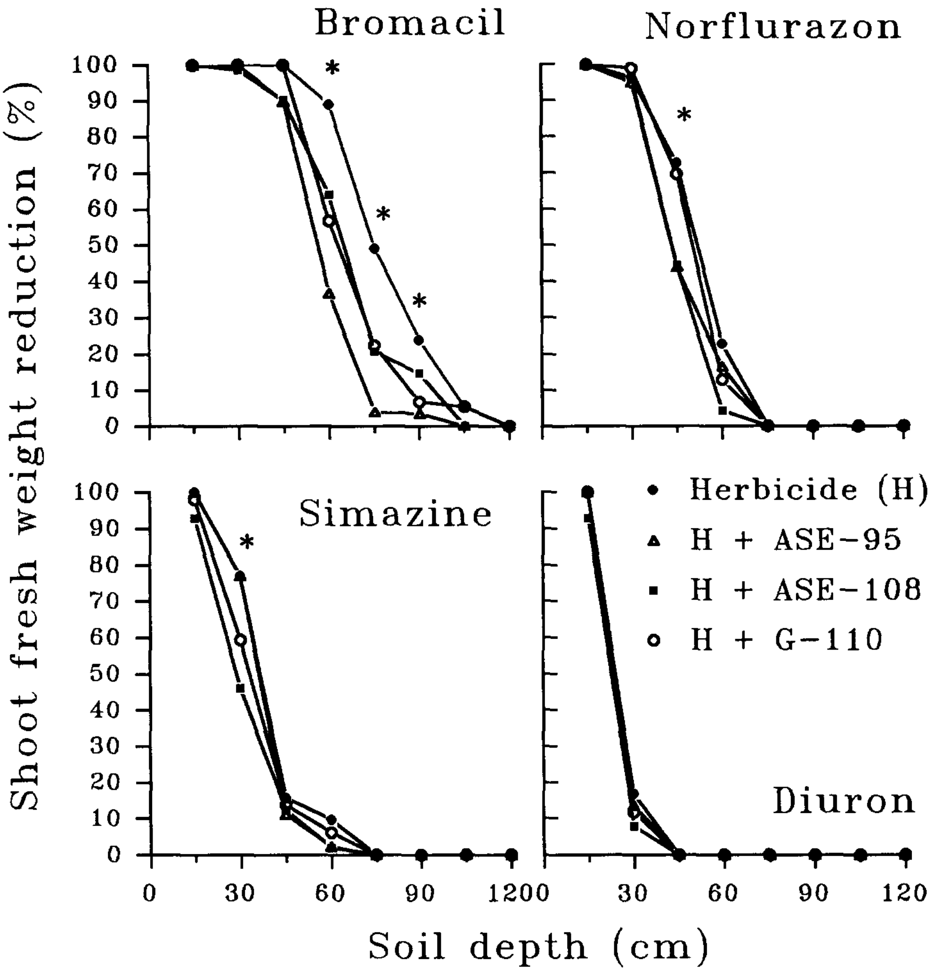

Figure 3. Effect of acrysol adjuvants on movement of bromacil, diuron, norflurazon, and simazine in soil columns as determined by ryegrass bioassay. Columns leached with water equivalent to 5 cm rainfall for bromacil and 12.5 cm rainfall for diuron, norflurazon, and simazine. Shoot fresh weight recorded at 3 weeks after planting for bromacil, norflurazon, and diuron and at 4 weeks after planting for simazine. Data are presented as percent shoot fresh weight reduction compared to untreated control. * = Fisher's LSD test significant within the depth. The LSD for bromacil: at 60 cm, 20; at 75 cm, 22; at 90 cm 16; for simazine: at 30 cm, 14; for norflurazon: at 45 cm, 24.

workers have reported adjuvant specificity. STAY-TEC, a polymer adjuvant, was specific to simazine rather than to bromacil, diuron, and norflurazon (Jain and Singh 1992). Activated charcoal and humic acid substances were specific to simazine than bromacil or dicamba (Alva and Singh 1991). Overall, adjuvants had marked effects in reducing movement of bromacil, the most mobile of the four herbicides studied. ASE-95 and ASE-108 may have some potential to reduce movement of these herbicides in soil. However, mere reduction in movement of these herbicides is unacceptable unless herbicides bound to the adjuvant are slowly released for effective weed control. These adjuvants need to be tested under field conditions for their efficacy in reducing herbicide movement without compromising weed control.

Acknowledgments. The authors thank E. I. duPont de Nemours and Company for ^{14}C-bromacil and ^{14}C-diuron, Sandoz Crop Protection Corporation for ^{14}C-norflurazon, and CIBA-GEIGY Corporation for ^{14}C-simazine. Gratitude is also expressed to Rohm and Haas Company for providing acrysol polymers. Florida Agricultural Experiment Station Journal Series No. R-02332.

REFERENCES

Alva AK, Singh M (1990) Sorption of bromacil, diuron, norflurazon, and simazine at various horizons in two soils. Bull Environ Contam Toxicol 45:365-374

Alva AK, Singh M (1991) Use of adjuvants to minimize leaching of herbicides in soil. Environ Manag 15:263-267

Bailey GW, White JL (1970) Factors influencing the adsorption, desorption, and movement of pesticides in soil. Res Rev 32:29-92

Bayer DE (1967) Effect of surfactants on leaching of substituted urea herbicides in soil. Weeds 15:249-252

Carlisle VW, Sodek F, Collins ME, Hammond LC, Harris WG (1989) Characterization data for selected Florida soils. University of Florida, Soil Sci Res Rep No 89-1 p 307

Hornsby AG, Butler TM, Tucker DPH, Knapp JL, Noling JW (1990) Managing pesticides for crop production and water quality protection. Florida Grower and Rancher 83:34-38

Jain R, Singh M (1992) Effect of a synthetic polymer on adsorption and leaching of herbicides in soil. In: Foy CL (ed) Adjuvants and Agrochemicals, CRC Press, Boca Raton, Florida, p. 329-348

Little TM, Hills FJ (1978) Agricultural experimentation: design and analysis. John Wiley and Sons, New York

Madhun YA, Freed VH, Young JL (1986) Binding of ionic and neutral herbicides by soil humic acid. Soil Sci Soc Am J 50:319-322

Raboy V, Hopen HJ (1982) Effectiveness of starch xanthide formulations of chloramben for weed control in pumpkin (Cucurbita moschata). Weed Sci 30:169-174

Rao PSC, Hornsby AG, Jessup RE (1985) Indices for ranking the potential for pesticide contamination of groundwater. Proc Soil Crop Sci Soc Fla 44:1-8

Reddy KN, Singh M (1992a) Sorption and desorption of diuron and norflurazon in Florida citrus soils. Water Air and Soil Pollution (in press)

Reddy KN, Singh M (1992b) Sorption and leaching of bromacil and simazine in Florida flatwoods soils. Bull Environ Contam Toxicol 48:662-670

Riggle BD, Penner D (1988) Controlled release of three herbicides with the kraft lignin PC940C. Weed Sci 36:131-136

Riggle BD, Penner D (1990) The use of controlled release technology for herbicides. Rev Weed Sci 5:1-14

Schreiber MM, Shasha BS, Trimnell D, White MD (1987) Controlled release herbicides. Pages 177-191. In: McWhorter CG, Gebhardt MR (eds) Methods of Applying Herbicides, Monograph 4, Weed Sci Soc Am, Champaign, Illinois

Schreiber MM, White MD, Wing RE, Trimnell D, Shasha BS (1988) Bioactivity of controlled release formulations of starch-encapsulated EPTC. J Controlled Release 7:237-242

Trimnell D, Shasha BS, Doane WM (1981) Release of trifluralin from starch xanthide encapsulated formulations. J Agric Food Chem 29:637-640

Received May 9, 1992; accepted September 11, 1992.