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Sorption and Leaching of Bromacil and Simazine in Florida Flatwoods Soils

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Herbicides are an integral part of modern agriculture systems. A majority of the herbicides are applied directly to the soil. Bromacil [5-bromo-6-methyl-3-(1-methylpropyl)-2,4-(1H,3H) pyrimidinedione] and simazine [6-chloro-N-N'-diethyl-1,3,5-triazine-2,4-diamine] are soil-applied herbicides commonly used for weed control in Florida citrus groves. Bromacil, an acidic herbicide, has a high water solubility (815 ppm) while simazine, a basic herbicide, has a low water solubility (3.5 ppm). The sorption coefficients on organic carbon (K_{oc}) are 72 and 140 mL g^{-1} for bromacil and simazine, respectively (Rao et al. 1985).

The mobility of herbicides in soil affects their performance and ultimate dissipation. The movement of herbicides below the plant root zone depends on herbicide, soil properties, and rainfall. Soil-applied herbicides in citrus groves of Florida have a greater potential for leaching through the soil profile due to high application rates, the porous nature of soils with low organic matter content (Carlisle et al. 1989), and high annual rainfall (135 cm). Several pesticides have been detected in groundwater as a result of routine pesticide use. Residues of at least 17 pesticides have been detected in groundwater collected from 23 states (Cohen et al. 1986). Simazine has been detected in California groundwater at levels up to 3 μg L^{-1} and bromacil in Florida groundwater at levels up to 300 μg L^{-1} (Cohen et al. 1986). In a recent groundwater monitoring study, a simazine concentration of 13 μg L^{-1} and a bromacil concentration of 952 μg L^{-1} was detected in groundwater of Florida (*T. C. McDowell 1990, unpublished data*).

Physical and chemical properties of the pesticide and the soil directly influence the sorption and desorption of pesticide by soil (Bailey and White 1970). Acidic pesticides are sorbed in moderate amounts on organic matter and in relatively low amounts on clay and hydrous metallic oxides. Basic pesticides are strongly sorbed by soil organic matter and clay (Carringer et al. 1975). Herbicides are sorbed on soil by physical and

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chemical sorption mechanisms, including London-Van der Waals forces, coulombic-electrostatic forces, ligand exchange, hydrogen bonding, chemisorption, and hydrophobic bonding (Bailey and White 1970; Weber 1970; Hassett and Banwart 1989). Sorption and leaching studies are helpful in determining the fate of herbicides, especially transport in soils. Due to extensive use of bromacil and simazine in Florida citrus groves, this study was undertaken to determine their sorption and leaching patterns in seven Flatwoods soils of the southern citrus belt. The objective was to determine the influence of soil properties on sorption and leaching.

MATERIALS AND METHODS

Bulk soil samples were collected from established citrus groves (over 20 yr old) near La Belle, Hendry County, Florida. The selected groves were planted on two row raised beds with a 7.62 m row spacing. Routine herbicide application in these groves was on a band of 2.44 m on each side of the tree row. Soil sampling was done in the row middle (2.74 m wide) which received no herbicide. Soil samples were taken from 0 to 15 cm at several locations within the row middle over an area of approximately 1 ha. The two row raised bed consists of soil from drainage ditches (30 to 60 cm deep on each side of the bed) spread over the natural A horizon. The surface soil over the natural A horizon is referred to as 'disturbed soil'. Herbicide reactions with this disturbed soil is important since soil-applied herbicides are in direct contact with this layer of soil rather than the original A horizon soil. Soil samples were air-dried, ground, and sieved to pass through 2-mm sieve. Physicochemical properties of the soils are given in Table 1. Soil pH was determined on a 1:1 soil-$CaCl_2$ (0.01 M) suspension. Organic carbon content by the Walkey-Black method (Walkey and Black 1934) and cation exchange capacity by the ammonium acetate method (Chapman 1965) were determined. Clay fraction was determined by the pipette method (Day 1965).

Sorption of bromacil and simazine was studied using the ^{14}C-labelled herbicides in a batch-equilibrium technique. A 2.5 g sample of air-dried soil was weighed into a 6-mL polyethylene vial. The solution containing ^{14}C-labelled and technical grade herbicide in 3.1 mL water was added to each vial. Final herbicide rate was 6.19 μg bromacil or simazine per g soil. Total radioactivity applied was approximately 11,000 dpm g^{-1} soil. A treatment without soil was included to determine the amount of radioactivity applied. Samples were equilibrated by shaking on an orbit shaker for 24 hr and centrifuged for 20 min. A one mL supernatant was pipetted into a vial containing 10 mL scintillation cocktail (ScintiVerse II, Fisher Scientific Company, 711 Forbes Avenue, Pittsburgh, Pennsylvania) and radioactivity was quantified by liquid scintillation counter (LS 1800, Beckman Instruments Company, Brea, California). Scintillation counts were corrected for background and quenching. Amount of herbicide

Table 1. Physicochemical properties of soils (0 to 15 cm depth).

Soils	Texture	Classification	pH ($CaCl_2$)	Organic carbon	Clay	CEC[a]
				%	%	$cmol_c\ kg^{-1}$
Riviera	Fine sand	Arenic Glossagualfs	6.20	0.94	5.1	4.11
Wabasso	Sand	Alfic Haplaquods	6.62	0.61	2.4	2.54
Holopaw	Fine sand	Grossarenic Ochraqualf	6.10	0.50	1.3	2.03
Basinger	Fine sand	Spodic Psammaquents	5.75	0.61	1.9	1.52
Pineda	Fine sand	Arenic Glossaqualfs	7.11	1.22	0.5	8.40
Chobee	Fine sandy loam	Typic Argiaquolls	7.18	1.39	16.1	8.10
Boca	Fine sand	Arenic Ochraqualf	7.05	1.67	3.5	10.79

[a]CEC = Cation exchange capacity.

sorbed was calculated as the difference between total radioactivity applied and the radioactivity in soil solution. The results are expressed as actual amount of herbicide sorbed per g soil and as distribution coefficient (K_d), which is the ratio of concentration of ^{14}C-herbicide in the soil to the aqueous phase at equilibrium. K_d values were normalized for soil organic carbon content by the equation $K_{oc} = (K_d \times 100)/\%$ organic carbon (Hassett et al. 1981). The experiment was conducted in a randomized complete block design with four 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).

Leaching behavior of bromacil and simazine was studied in soil leaching columns for two of the seven soils which showed extreme sorption values. Soils used in the leaching studies were Holopaw fine sand and Chobee fine sandy loam. Leaching was evaluated using clear acrylic columns 8-cm long with 7-cm inner diameter. The bottom of the column was constructed using a thin nylon mesh above the acrylic plate with holes. 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. After packing each column, the soil bulk density was determined (≈ 1.5 g cm^{-3}) and used in calculating porosity. Each column was saturated with deionized water from bottom of the column by capillary force and allowed to drain for 18 hr. ^{14}C-labelled herbicide was mixed with commercial herbicide and applied in 1 mL of water to the soil surface uniformly as several drops. Herbicide rate was 5 kg ha^{-1} with a radioactivity of approximately 30,000 dpm per column. 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 2.3 cm/hr. The leachate was collected at each pore volume up to a total of six pore volumes. Each pore volume of Holopaw fine sand and Chobee fine sandy loam was equivalent to 130 (= 3.4 cm rainfall) and 150 mL (= 3.9 cm rainfall), respectively. One mL of leachate in duplicate for each pore volume was used to quantify radioactivity as described in the sorption study. The radioactivity at each pore volume was expressed as percent of ^{14}C-herbicide applied. Experimental design, replications, and statistical analyses were as described in the sorption study.

RESULTS AND DISCUSSION

The seven soils studied were light textured with over 90% sand except Chobee fine sandy loam. They were low in organic carbon (0.50 to 1.67%) with acidic to neutral pH (Table 1). The soils had a cation exchange capacity of 1.52 to 10.79 $cmol_c$ kg^{-1}. These soils are extensively found in the southern citrus belt of Florida.

Table 2. Sorption and distribution coefficient of bromacil and simazine in soils[a].

Soils	Bromacil				Simazine			
	Sorbed				Sorbed			
	Amount	Percent[b]	K_d	K_{oc}	Amount	Percent[b]	K_d	K_{oc}
	$\mu g\ g^{-1}$	%	$mL\ g^{-1}$	$mL\ g^{-1}$	$\mu g\ g^{-1}$	%	$mL\ g^{-1}$	$mL\ g^{-1}$
Riviera	1.71 c	28 c	0.47 c	50	2.00 d	32 d	0.59 d	63
Wabasso	1.95 b	32 b	0.57 b	93	2.44 bc	39 bc	0.80 bc	131
Holopaw	1.30 d	21 d	0.33 d	66	1.17 e	19 e	0.29 e	58
Basinger	1.94 b	31 b	0.57 b	93	2.30 c	37 c	0.73 c	119
Pineda	1.94 b	31 b	0.57 b	47	1.91 d	31 d	0.55 d	45
Chobee	2.35 a	38 a	0.76 a	55	2.85 a	46 a	1.06 a	76
Boca	2.35 a	38 a	0.76 a	46	2.52 b	41 b	0.85 b	51

[a]Means within a column followed by the same letter are not significantly different at the 5% level as determied by Fisher's protected LSD Test.

[b]As percent of herbicide applied. Amount of bromacil or simazine applied was 6.19 $\mu g\ g^{-1}$ soil.

Among the soils, amounts of herbicides sorbed ranged from 1.30 to 2.35 μg g^{-1} soil for bromacil and 1.17 to 2.85 μg g^{-1} soil for simazine (Table 2). The differences in amounts of herbicide sorbed were significant among the soils. A similar trend was observed when the amount of herbicide sorbed was expressed as percent of herbicide applied (Table 2). Sorption values of this magnitude are similar to the values reported for bromacil and simazine in other sandy soils of Florida (Alva and Singh 1990; Singh et al. 1985). Simazine, a basic herbicide, sorbed in higher amounts relative to bromacil, an acidic herbicide, except in Holopaw fine sand and Pineda fine sand. In Holopaw and Pineda fine sand, both herbicides sorbed in similar amounts. Among the soils, sorption of both herbicides was lowest in Holopaw fine sand and highest in Chobee fine sandy loam due, in part, to differences in organic carbon content, clay content, and cation exchange capacity (Table 1). Boca fine sand had higher organic carbon and cation exchange capacity than Chobee fine sandy loam. Nevertheless, bromacil sorption was unaffected and simazine sorption decreased significantly in Boca fine sand (Table 2). Chobee fine sandy loam had over four times greater clay than Boca fine sand and perhaps simazine, a basic herbicide, had stronger affinity for clay (Weber 1970).

The distribution coefficient (K_d) ranged from 0.33 to 0.76 mL g^{-1} for bromacil and 0.29 to 1.06 mL g^{-1} for simazine. Such a narrow range of K_d values suggests weak binding of these herbicides to soil. A significant linear relationship was observed between K_d (y) and organic carbon content (x) for bromacil ($y = 0.31 + 0.27x$; $r^2 = 0.64$; $P > 0.03$). In simazine, absence of a significant relationship between K_d and soil properties studied suggests that other soil components may play a role in determining the sorption of simazine. Sorption coefficient (K_{oc}) ranged from 46 to 93 mL g^{-1} (mean 64) for bromacil and 45 to 131 mL g^{-1} (mean 78) for simazine (Table 2). Mean K_{oc} value for bromacil is similar to the value reported in the literature (Rao et al. 1985) indicating a role of organic carbon in sorption. In simazine, mean K_{oc} value is below the value reported in the literature (Rao et el. 1985), suggesting that sorption mechanism is perhaps related to some other soil properties besides organic carbon content.

It is apparent from Figure 1 that leaching of bromacil was not only rapid but also greater than that of simazine. The amount of bromacil leached in both Holopaw fine sand and Chobee fine sandy loam was similar and reached a peak in the third pore volume of leachate. Leaching of simazine gradually increased and reached a peak at the fourth and the fifth pore volume in Holopaw fine sand and Chobee fine sandy loam, respectively. Leaching of simazine in Chobee fine sandy loam was somewhat lower than in Holopaw fine sand. Perhaps, higher organic carbon and clay in Chobee fine sandy loam resulted in sorption-induced retardation. An early peak of leaching of bromacil as compared to simazine indicates increased mobility

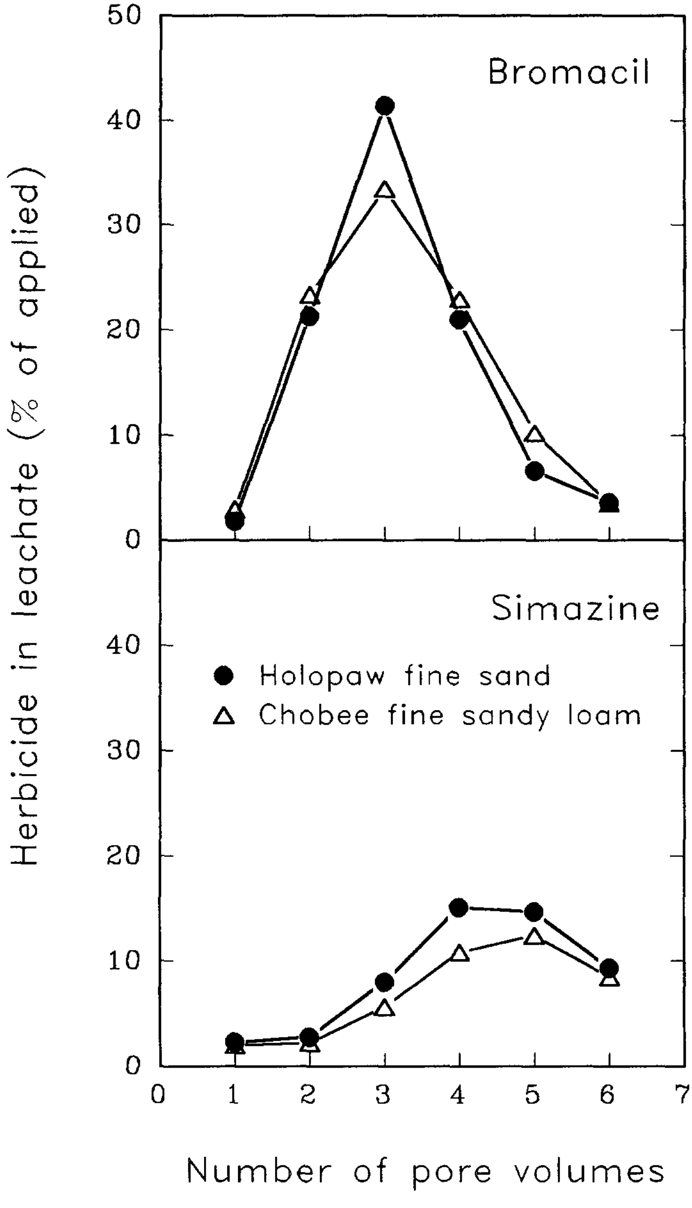

Figure 1. Bromacil and simazine in leachate from Holopaw fine sand and Chobee fine sandy loam soil leached continuously with six pore volumes of deionized water. Means for soils within herbicide at each pore volume are not significantly different at the 5% level as determined by Fisher's protected LSD Test.

of bromacil relative to simazine (Figure 1). Cumulative leaching of bromacil in six pore volumes (equivalent to 20 to 23 cm rainfall) was over 96% of that applied in both soils. The percent of simazine leached in the six pore volumes was 42% in Holopaw fine sand and 52% in Chobee fine sandy loam. A similar ranking of leachability of bromacil and simazine has been reported by Alva and Singh (1991) in Candler fine sand.

The study indicates that, at the most, 38% of bromacil and 46% of simazine applied was sorbed in these low organic matter soils. A rainfall of 20 to 23 cm can displace over 96% of bromacil and over 42% of simazine in these soils. Bromacil has greater mobility than simazine. Due to limited sorption and rapid leaching of bromacil and simazine in these soils, the potential exists for groundwater contamination by these herbicides during their routine applications in citrus groves planted on raised beds.

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