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Sorption of Bromacil, Diuron, Norflurazon, and Simazine at Various Horizons in Two Soils

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The impact of agricultural practices on groundwater quality is a matter of increasing public interest. Agricultural practices provide non-point sources for a variety of potential water contaminants. Sorption and microbial degradation of pesticides in soil are important factors in determining leaching behavior of pesticides and contamination of groundwater. Sorption of pesticides vary considerably depending on their chemical characteristics. Soil properties influence the degree of sorption of pesticides, which in turn determine the potential for leaching.

Several investigators have shown that the organic fraction of the soil as the single factor most highly related to herbicide sorption (Carringer et al. 1975, Hayes 1970, Kozak et al. 1983, Sheets et al. 1962, Upchurch and Mason 1962, Weber et al. 1969, Weed and Weber 1974). Grover (1974) studied the sorption of trifluralin, triallate, and diallate on several sorptive surfaces. Sorption was extremely high on activated charcoal, and least on montmorillonite. Weber et al. (1969) reported an increase in the sorption of s-triazine herbicides on soil organic matter with an increase in pH. The maximum sorption occurred at pH levels in the vicinity of the pKa values of the respective herbicides. On the other hand, sorption of herbicides with basic properties (buthidazole, VEL 3510, tebuthiuron, and fluridone; pKa values 0.6-1.7) decreased with increasing pH (Weber 1980). Soil pH, organic matter, and microbial biomass are important factors affecting herbicide sorption and degradation. The above properties vary considerably in various horizons for a given soil. Accordingly, sorption of herbicide may vary at different horizons. Therefore, sorption data determined by using only the surface soil is usually not representative of the subsoil horizon through which a herbicide has to be transported before it can contaminate the groundwater.

Bromacil [5-bromo-6-methyl-3-(1-methylpropyl)-2,4(1H,3H) pyrimidinedione], simazine [6-chloro-N-N′-diethyl-1,3,5-triazine-2,4-diamine], norflurazon [4-chloro-5-(methylamino)-2-(3-(trifluoromethyl)phenyl)-3(2H)-pyridazinone], and diuron [N′-(3,4-dichlorophenyl)-N,N-dimethylurea] are important herbicides routinely used in Florida citrus groves. The objectives of this investigation

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were: (1) To study the sorption of the above four herbicides at various horizons in two soils representative of Flatwood and Ridge soils; and (2) To examine the relationships between herbicide sorption and various properties of the above soils.

MATERIALS AND METHODS

Soil samples were obtained from 0-25-, 25-45-, 45-90-, 90-105-, and 105-150-cm depths from an uncultivated Myakka sand, siliceous, hyperthermic Aeric Haplaquods series (representative of Flatwood soils) adjacent to an abandoned citrus grove, and from 0-30-, 30-60-, 60-90-, and 90-120-cm depths from an uncultivated Candler fine sand (Hyperthermic, uncoated, Typic Quartizipsamments) series (representative of Central Florida Ridge soils). Sampling depths in the Myakka sand were chosen on the basis of distinct horizonation. However, sampling depths in the Candler fine sand were arbitrary since no distinct horizonation was noticeable. Soil samples were taken using a 10-cm diameter, core sampler. Fifteen soil cores at each depth were taken randomly from an area of 50 x 50 m. The core samples from each depth were mixed together, air-dried, ground, and sieved through a 2-mm sieve. Subsamples were taken from the bulk soil for chemical analyses and sorption study.

Bromacil, simazine, norflurazon, and diuron, were used in this study. These herbicides represent a wide range of physical and chemical properties (Table 1) and are important in Florida citrus production. Sorption of these herbicides was studied by employing the batch equilibration technique. Air-dried soil (2.5 g) was weighed into 10-mL polyethylene vials and 2.5-mL of 0.001 M $CaCl_2$ was added. To each vial, a 100-µL solution of either ^{14}C labelled or unlabelled herbicide was added. The quantity of herbicide added was 12.5 µg (5 µg/g soil), and the total radioactivity applied (in the case of labelled treatment) was approximately 10,000 DPM. A treatment without the soil was included to determine the total amount of ^{14}C applied. No loss of radioactivity in the tube without soil was evident during the equilibration period. Each treatment was replicated three times.

Table 1. Physical and chemical characteristics of herbicides[a]

Herbicide	Solubility in water at 25°C	Partition coefficient Koc	Ionizability	Half-life in soil $t_{1/2}$	Leaching potential Koc/$t_{1/2}$
	(ppm)	(mg/L)	(pKa)	(day)	
Bromacil	815	72	Acidic (9.1)	90	0.8
Simazine	5	138	Basic (1.65)	75	1.9
Norflurazon	28	248	Nonionic	45	5.5
Diuron	42	400	Nonionic	100	4.0

[a] Herbicide Handbook. 1989. Weed Science Society of America, Champaign, IL (Sixth Ed.)

The suspension was shaken for 24 hr on a vibrating shaker and centrifuged for 20 min. One mL of supernatant was transferred to scintillation vials containing 10-mL of scintillation cocktail (ScintiVerse II, Fisher Scientific Co., Fairlawn, NJ). The amount of ^{14}C was quantitated in a liquid scintillation spectrometer (LS 1800, Beckman Inst. Co., Brea, CA). The supernatant used for counting ^{14}C activity was very clear, therefore, quench correction was not required. The counts from unlabelled treatments (background counts for the soil) were subtracted from the counts for the respective labelled treatments.

$$\text{Herbicide in solution (\%)} = \frac{^{14}\text{C in supernatant at equilibrium}}{^{14}\text{C applied}} \text{X } 100$$

Herbicide sorbed = (100 - Percent of herbicide in solution).

Some chemical properties of the soil samples representative for various horizons of sampling are shown in Table 2. Soil pH was measured in water and 0.001 M $CaCl_2$ at 1:1 ratio of soil:solution. Organic matter content was measured by the Walkley-Black method (Walkley and Black 1934). For measuring cations, 20 mL of Mehlich 1 extractant (Mehlich 1953) was added to 5 g of soil. The suspension was shaken for 5 min and filtered through Whatman No. 42 filter paper. The concentrations of cations were determined by inductively coupled plasma emission spectroscopy. The cation concentrations were expressed as cmol kg^{-1}.

RESULTS AND DISCUSSION

Myakka sand is very acidic with the pH ranging from 4.3-5.0 for various horizons (Table 2). The organic matter content was 3.4% in the top 25-cm of soil immediately followed by a horizon (25-45-cm) with only 0.23% organic matter. The organic matter content increased to 1.87% in the spodic horizon (45-90-cm) and decreased to 0.70% at 105-150-cm depth. Although soil pH of the spodic horizon was slightly greater (0.3 pH unit) than that of surface soil, the concentration of aluminum was 7.5-fold greater in the former than the latter horizon sample. The aluminum content was extremely low in the 25-45-cm horizon sample. The pH of the Candler fine sand decreased from 6.9 in 0-30-cm sample to 5.7 in 90-120-cm depth sample. The organic matter content also decreased from 1.13 to 0.30%. The CEC of the surface 30-cm of soil was 5.79 cmol kg^{-1} which decreased to 2.89, 2.05, and 2.03 cmol kg^{-1} in samples at 30-60-, 60-90-, and 90-120-cm, respectively.

Among the four herbicides, the fraction of herbicide sorbed decreased in the order: diuron > norflurazon > simazine > bromacil in both the soils, regardless of horizons of sampling (Fig. 1). Jain and Singh (1989) using Astatula fine sand (0-30-cm) also reported similar trends with respect to sorption of the above herbicides. In the Myakka sand, the sorption of bromacil was 62% in the top 25-cm sample, and decreased to 5% in the 25-45-cm depth. However, the sorption increased to 30% in the spodic horizon and slightly decreased to 19 and 15% at 90-105- and 105-150-cm samples, respectively. In field situations, bromacil if leached through the top 25-cm of soil is subjected to rapid leaching in the 25-45-cm horizon. However, as it reaches the spodic horizon,

Table 2. Important chemical properties of soils used for sorption of four herbicides

Horizons (cm)	pH (water)	pH (1 mM $CaCl_2$)	Organic matter (%)	Mehlich 1 extractable cations [cmol kg^{-1}]					
				Ca	Mg	K	Na	Al	Σ cations
				Myakka sand					
0-25	4.3	3.1	3.40	0.39	0.21	0.16	0.05	0.72	1.53
25-45	4.4	3.5	0.23	0.06	0.03	0.01	0.03	0.17	0.30
45-90	4.6	3.7	1.87	0.09	0.03	0.01	0.06	5.38	5.57
90-105	5.0	4.0	1.20	0.21	0.07	0.02	0.04	5.65	5.99
105-150	4.9	3.9	0.70	0.14	0.08	0.02	0.06	4.63	4.93
				Candler fine sand					
0-30	6.9	6.4	1.13	4.17	0.60	0.02	0.03	0.97	5.79
30-60	6.6	5.8	0.43	1.16	0.33	0.02	0.01	1.37	2.89
60-90	5.8	4.9	0.40	0.52	0.17	0.02	0.01	1.33	2.05
90-120	5.7	4.7	0.30	0.43	0.15	0.02	0.02	1.41	2.03

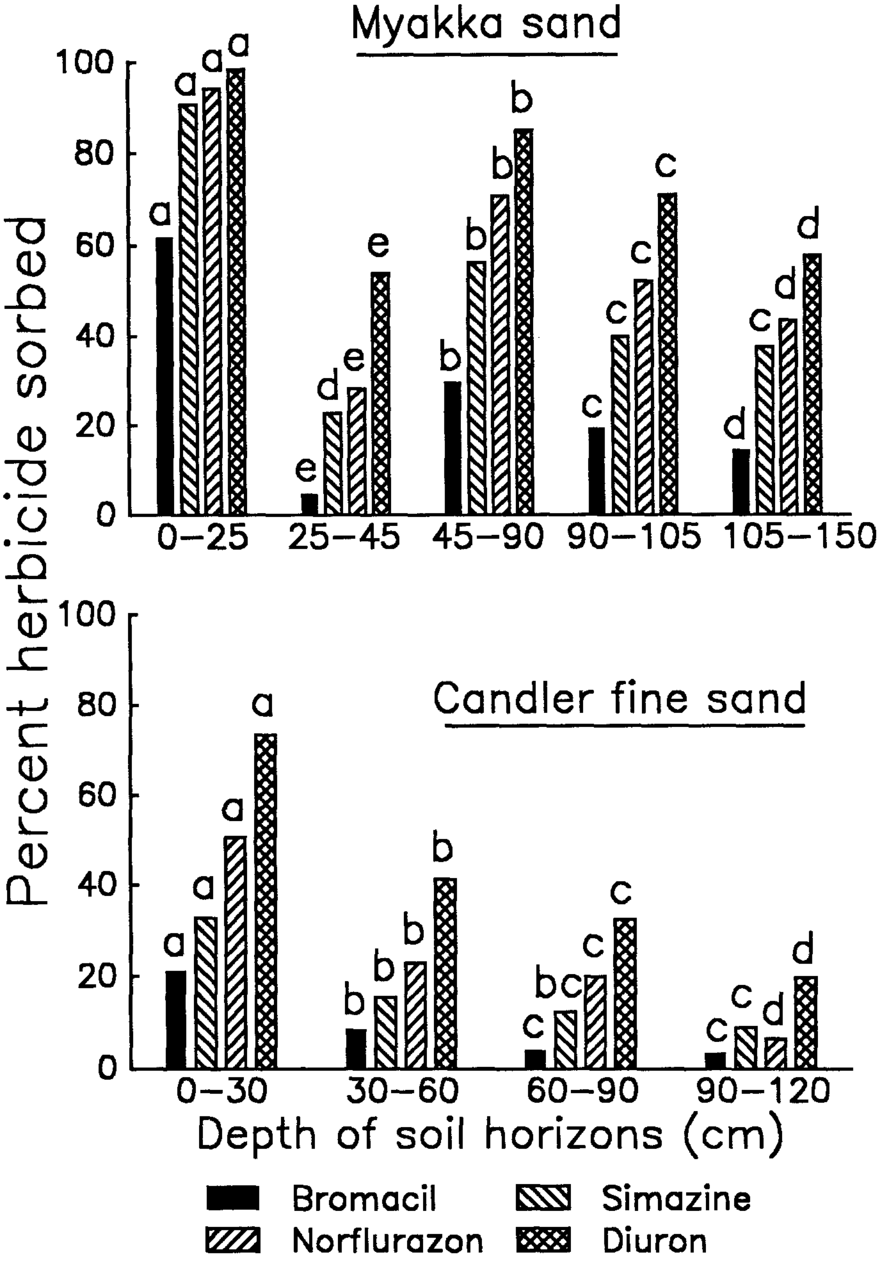

Figure 1. Sorption of bromacil, simazine, norflurazon, and diuron in two soils at various horizons. The letters "a" through "e" indicate relative sorption at different depths for a given soil, with "a" indicating the depth at which sorption was highest, etc. Means followed by similar letters for each herbicide for a given soil are not significantly different at P = 0.05.

an increased sorption would minimize the downward movement of bromacil. The results clearly reveal that the leaching potential of bromacil is strongly dependent on properties of the soil at various horizons. The sorption trend with soil horizons was very similar for simazine, norflurazon, and diuron as discussed above for bromacil. The greatest difference in sorption of various herbicides was evident in the 25-45-cm depth sample. Accordingly, in this horizon sample, sorption of diuron was 54% while that of bromacil was only 5%. The sorption of all four herbicides was lower in the Candler fine sand than in the Myakka sand. This could be partly due to the difference in organic matter content (Table 2). The organic matter content of top 30-cm of Candler fine sand (1.13%) was very similar to that at 90-105-cm depth sample of Myakka sand (1.20%). The sorption of bromacil, simazine, norflurazon, and diuron were 21, 33, 51, and 73%, respectively, in the former soil, while 19, 40, 52, and 71%, respectively, in the latter soil. Thus, except for simazine, sorption of other herbicides was very similar in the above two samples. Therefore, organic matter content plays a major role in determining sorption of herbicides regardless of differences in soil series, pH, and horizon of sampling.

In the Candler fine sand, the sorption of bromacil was only 21% in the top 30-cm of soil. The sorption decreased to 9, 4, and 3%, respectively, in the 30-60-, 60-90-, and 90-120-cm depth samples. The sorption of simazine, norflurazon, and diuron at the 90-120-cm depth decreased by 23, 44, and 53% of the respective sorption in the top 30-cm of soil. Therefore, in the Candler fine sand, sorption of all four herbicides consistently decreased along with a decrease in organic matter content as the depth of sampling increased. Walker et al. (1989) also reported a decrease in sorption of chlorsulfuron and metsulfuron-methyl at 40-60- than at 0-20-cm depth samples of eight different soils. Since a decrease in sorption of herbicide partly contributes to a greater potential for its leaching, the determination of sorption using only the top soil is likely to underestimate the leaching potential of a given herbicide.

In the case of Myakka soil, although the horizon (25-45-cm) immediately below the top 25-cm soil is extremely permeable, the spodic horizon (45-90-cm) and the underlying soil down to 150-cm are likely to restrict the leaching of herbicides because of an increased sorption.

The sorption of bromacil increased by 7-23% and 3-7% in the Myakka sand and Candler fine sand, respectively, when pH of the suspension was increased to 6.5 prior to addition of bromacil (Fig. 2). Increase in pH may increase negative charges in the soil, thus resulting in increased sorption of bromacil.

Organic matter content of soil was highly correlated with sorption of all four herbicides (Fig. 3). The relationship was linear for bromacil and simazine ($R^2 = 0.94$ to 0.99), while curvilinear for norflurazon and diuron ($R^2 = 0.84$ to 0.94).

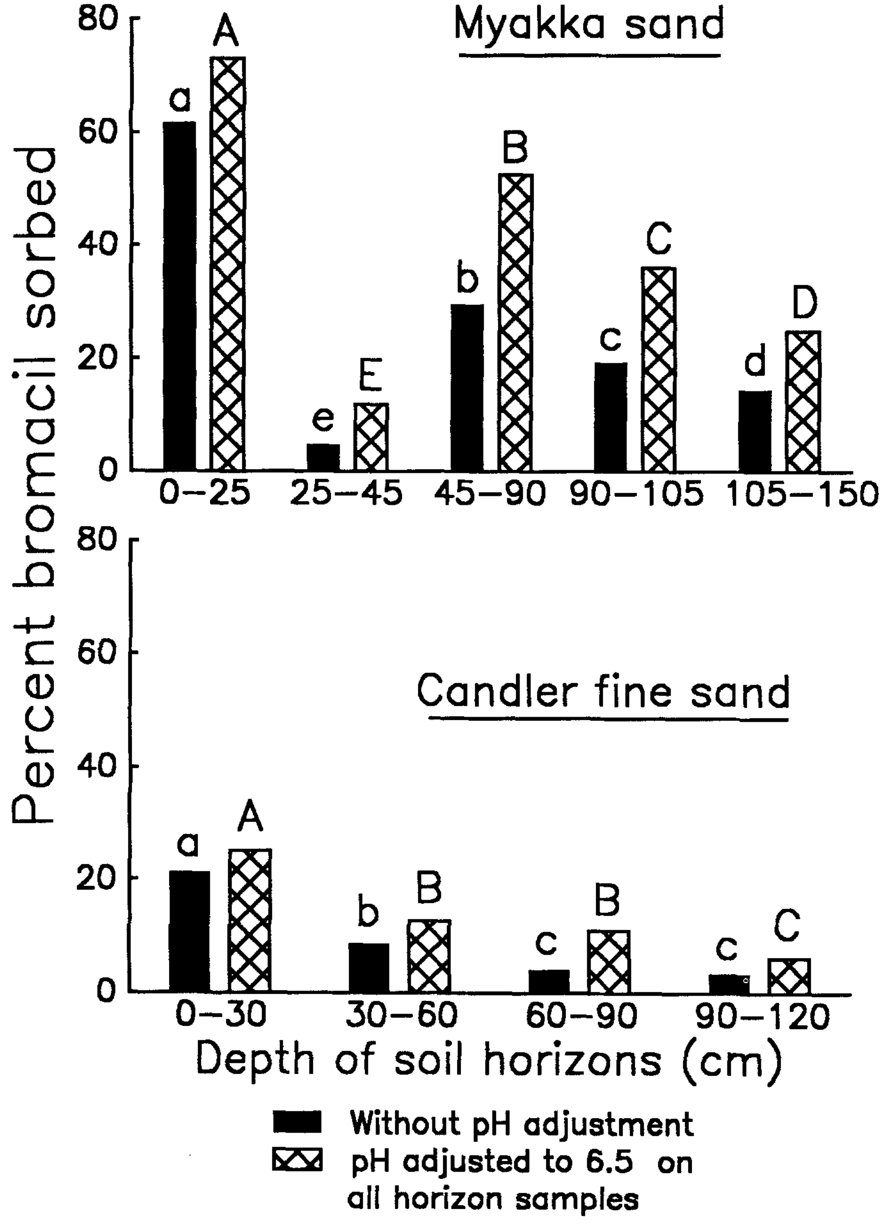

Figure 2. Sorption of bromacil without the pH adjustment and with pH adjusted to 6.5 in two soils at various horizons. Means followed by similar letters are not significantly different at P = 0.05. (Mean comparisons between horizon samples without the pH adjustment and with pH adjusted to 6.5 are shown by lower case and upper case letters, respectively.)

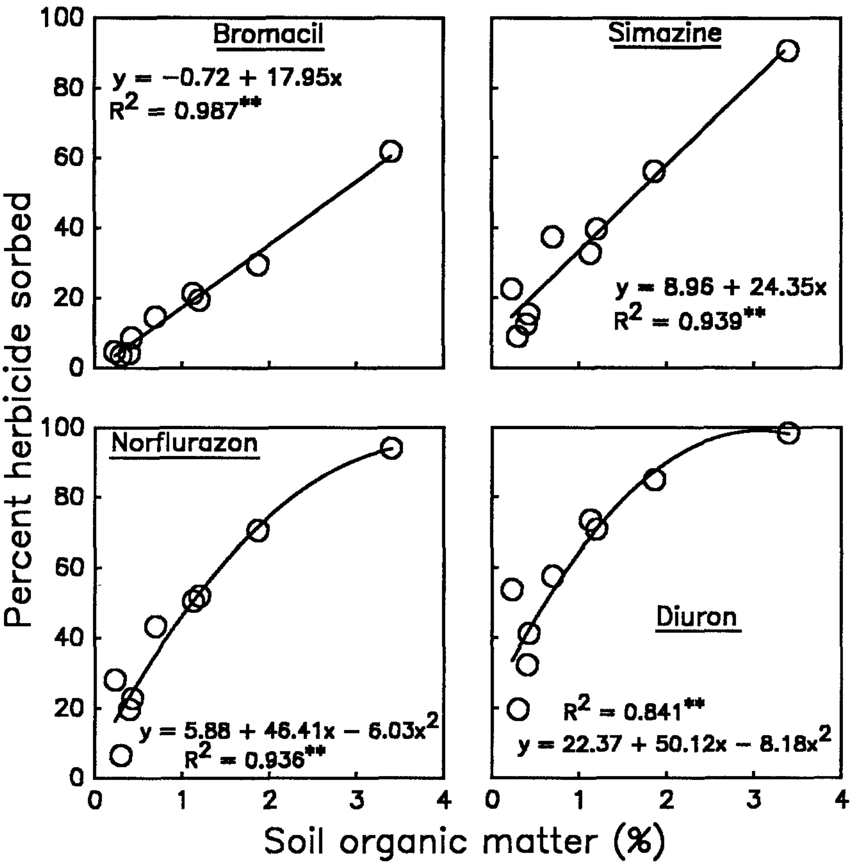

Figure 3. Sorption of bromacil, simazine, norflurazon, and diuron in two soils as a function of soil organic matter.

The ultimate objective of a herbicide sorption study is to evaluate the potential of a given herbicide for leaching through the soil profile and finally contamination of groundwater. In the absence of microbial degradation and uptake by weeds, sorption by soil components is the main factor determining the leaching of a herbicide in question. In the present study, the amounts of bromacil, simazine, norflurazon and diuron leached below the depth of sampling in the two soils were estimated. For the sake of convenience, the fractions of herbicide subjected to degradation and uptake by weeds were considered to be negligible. The estimation of leaching was based on the application of herbicide on the surface of soil at 5 µg/g soil rate, and the amount which was not sorbed in the first sampling depth was considered as leached below this depth of sampling. Considering 5 µg/g soil each of bromacil, simazine, norflurazon and diruon applied on the surface of Myakka sand, approximately 1.92, 0.47, 0.30 and 0.08 µg/g soil respective herbicides were not sorbed in the top 25-cm horizon of soil (Fig. 4), therefore, considered as potentially leachable. Drawing on the data presented in Figure 2, the remaining points

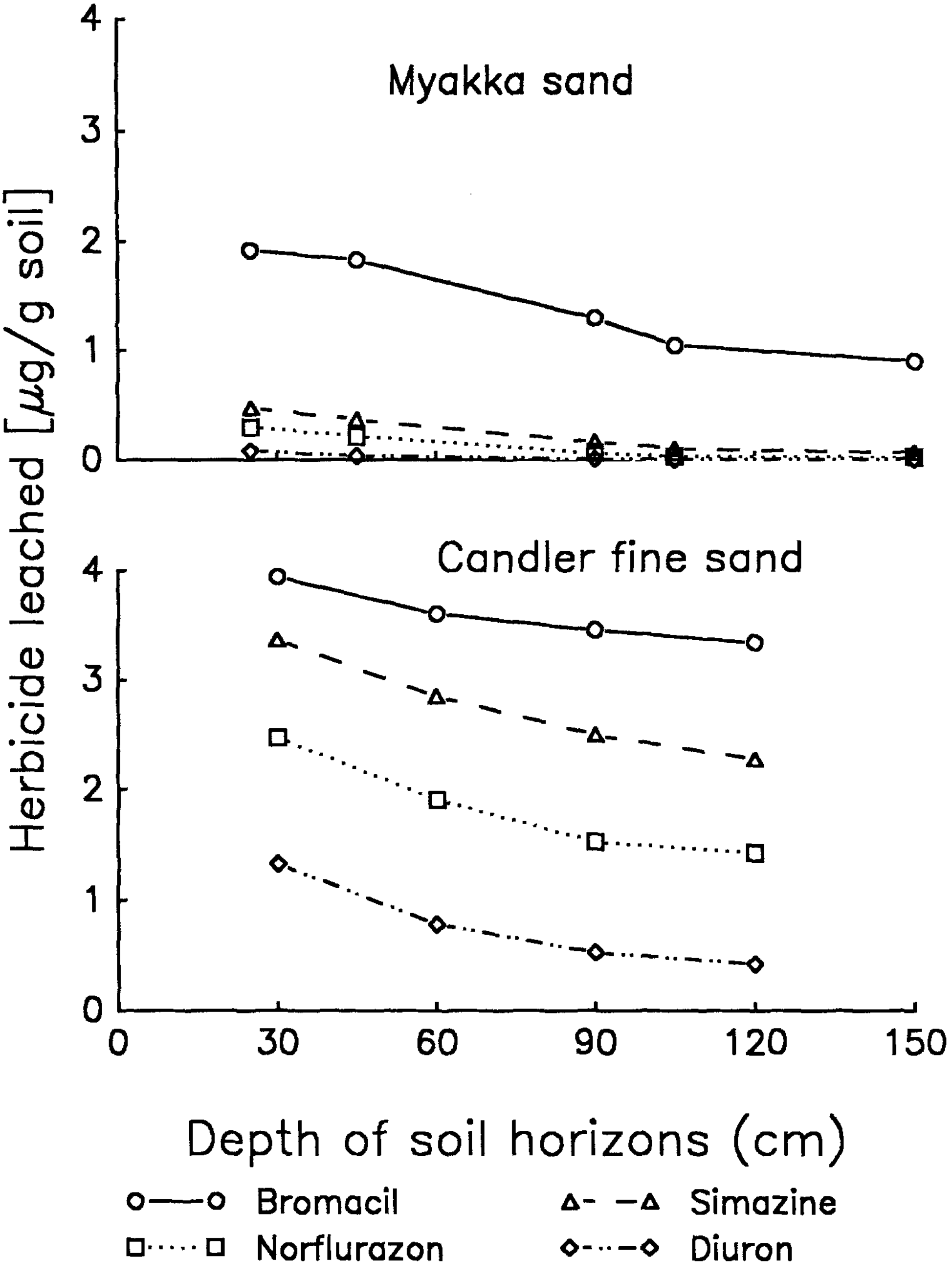

Figure 4. Estimated amounts of bromacil, simazine, norflurazon, and diuron leached through 150- and 120-cm depth of Myakka sand and Candler fine sand, respectively. The rate of each herbicide applied on the surface of soil is 5 μg/g soil.

in Figure 4 were estimated in a similar fashion. However, the potentially leachable quantities of the respective herbicides below 150-cm horizon are 0.89, 0.06, 0.02 and 0.0007 µg/g soil. The fractions of potentially leachable herbicides in the Candler fine sand were much greater than those in the Myakka sand. It appears that 3.34, 2.27, 1.43 and 0.43 µg/g soil bromacil, simazine, norflurazon and diuron, respectively, is leachable below 120-cm depth of soil in the Candler fine sand.

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