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Herbicide Mobility Using Soil Leaching Columns

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In recent years greater environmental concern and awareness have arisen in both farm and nonfarm communities regarding the use of soil-applied herbicides. Herbicides are increasingly important production tools of commercial citrus for the control of grasses and broadleaf weeds in Florida’s 349,079 ha of commercial citrus (Florida Agricultural Statistical Service 1996). Florida’s subtropical climate, sandy soils and average annual rainfall of 127 to 178 cm favor rapid weed growth throughout much of the year but pose unique environmental concerns regarding the leaching of herbicides beyond the zone of weed seed germination and potentially into the groundwater. In 1995, samples from 303 wells in a 3-county area in Central Florida showed that 151 of the wells had detectable levels of bromacil (Power 1996). Bromacil was a commonly used citrus herbicide that has been banned from Florida’s deep sandy Entisols with sand content > 95% in the central part of the state’s citrus production region due to groundwater contamination; however, it is still used in some citrus production areas within Florida (Singh and Tucker 1997). Contamination of groundwater due to herbicide leaching is a concern throughout many major agricultural regions worldwide (Hallberg 1988). California is also confronted with many groundwater quality issues in citrus and other agricultural crops (Domagalski and Dubrovsky 1992; Ingels 1994).

Leaching of chemicals including herbicides is a major concern due to the potential loss of the chemical, which then no longer provides the needed function, as well as the environmental concerns of groundwater contamination. Any factor(s), environmental, man-made or man-influenced, that contribute to the downward movement of chemicals beyond the intended site of action can prove costly for the farmer and the environment. In most cases, this downward movement of dissolved materials is in the soil solution. The nature of the chemical, microorganisms and its reactions with the soil will regulate the mobility and the ultimate quantity available for leaching. The potential for leaching is the greatest when highly soluble chemicals are used in well-drained sandy soils with low organic matter, which is typical of many of Florida’s citrus soils (Reddy and Singh 1993; Jackson et al. 1995; Singh and Tucker 1997).

In citrus, all preemergence herbicides require soil incorporation from the site of

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application on the soil surface by either rainfall or irrigation to the zone of weed seed germination in the top several inches of soil (Tucker 1979). This is essential since mechanical incorporation has little potential use due to possible damage to citrus roots, low volume irrigation lines, or difficulties of a complete and even distribution of the herbicide to the entire under-tree canopy area of the citrus tree. Movement or incorporation of the herbicide only to the zone of weed seed germination is beneficial since this provides a mechanism that allows the herbicide to contact the germinating seedling, thus providing control of unwanted weed species, if the proper herbicide and rate were used. If the herbicides are not incorporated into the soil, their potential effectiveness is reduced by photo decomposition and/or volatilization into the atmosphere (Jain and Singh 1992).

When herbicides are leached beyond the zone of weed seed germination, the following can occur: damage to the citrus tree due to greater root contact, poor weed control due to inadequate herbicide concentration around germinating weed seeds, contamination of groundwater and monetary losses due to reduced herbicide efficiency.

A number of factors will influence leaching of soil-applied herbicides: adsorption of herbicides to soil colloids, soil texture, soil permeability, volume of water flow, water solubility of herbicides, soil pH and inorganic and organic soil colloids (Anderson 1996). While these factors play an important role in herbicide leaching, the farmer does not have full control over them or may not easily change them by agricultural practices other than irrigation scheduling or soil pH adjustment. However, by having information about the factors for a given site, the farmer can more effectively manage agricultural production practices to minimize the leaching potential of applied chemicals.

Mobility of a herbicide is dependent upon the chemical nature of the herbicide compound as well as the chemical and physical properties of the soil (Anderson 1996). The use of soil columns as a technique to simulate herbicide movement in soil is well documented (Weber et al. 1986). “Natural” and “hand-packed” soil columns are 2 types used to investigate the leaching behavior of chemicals in soils. The use of growing sensitive plant species in soils that contain toxic levels of herbicides (bioassay or bioindicator) to the chosen indicator plant can be a useful tool for both research and farm studies (Lavy and Santelmann 1986). This practice dates back over 60 years (Crafts 1935). In addition to soil columns, computer models have been developed which predicts the movement of herbicides in soils (Nofziger and Hornsby 1987).

The primary objectives of this study were: (1) to determine and compare the mobility of selected preemergence herbicides at different application rates of water and (2) to compare the soil column data to a predictive model.

MATERIALS AND METHODS

The 7 herbicides used in the study were bromacil (5-bromo-6-methyl-3-(1-methylpropyl)-2,4(1 *H*,3*H*)pyrimidinedione), diuron(*N*'-(3,4dichlorophenyl)-*N*, *N*-dimethylurea), norflurazon (4-chloro-5-(methylamino)-2-(3-(trifluoromethyl)phenyl)-3(2*H*)-pyridazinone), oryzalin (4-(dipropylamino)-3,5-dinitrobenzenesulfonamide), oxyfluorfen (2-chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoromethyl)benzene), simazine (6-chloro-*N*,*N*'-diethyl-l,3,5-triazine-2,4-diamine) and thiazopyr (methyl2-(difluoromethyl)-5-(4,5-dihydro-2-thiazolyl)-4-(2-methylpropyl)-6-(trifluoromethyl-) 3-pyridinecarboxylate). Trade names and rates used are listed in Table 1. Application of water was equivalent to 3.2, 6.4, 9.6 and 12.8 cm of irrigation or rainfall. Experiments were replicated 3 times.

Table 1. Herbicides, trade name and irrigation/rainfall rate used

Common name	Trade name	Herbicide application rate kg/ha
bromacil	Hyvar-X 80WP	7.167
diuron	Direx 80DF	7.167
norflurazon	Solicam 80DF	8.063
oryzalin	Surflan 80DF	6.719
oxyfluorfen	Goal 1.6E	4.031
simazine	Princep-Caliber 90DF	8.869
thiazopyr	Mandate 2E	1.680
untreated control		0.000

Soil was collected in 30 cm increments to a depth of 120 cm of a Candler sand soil (Hyperthermic, uncoated Typic Quartzipsamments) at the Citrus Research and Education Center (CREC) research farm located north of Haines City, FL. This soil is typical of a well-drained ridge soil found throughout Central Florida, where citrus is a major agricultural crop. The site of soil collection was a noncrop area that had not been used for agricultural production for over 8 years. The soil was air dried and stored in large wooden containers. The average soil pH and organic matter for each of the 4 depths are shown in Table 2. The pH was determined in (1:2 Soil:Water) suspension. The organic matter content was determined by Walkley-Black method.

The soil columns were made from 10 cm polyvinyl chloride (PVC) pipes cut to a length of 150 cm. The pipe was split longitudinally for the entire length to form 2 equal halves. On the inside of each half of pipe, beginning 15 cm from the bottom and in increments 15 cm thereafter, a silicone sealer bead or ridge was placed. This ridge of silicone was to prevent water movement down the side of the pipe "edge flow" or "boundary flow" along the soil/wall interface, when tilled with soil (Weber

Table 2. Soil sample analysis data for soil used in split columns in Candler sand

Depth from soil surface (cm)	Soil pH	Organic matter %
0 to 30.5	6.5	0.9
30.5 to 61.0	5.3	0.2
61.0 to 91.5	5.1	0.2
91.5 to 122	5.0	0.3

and Peeper 1977; Weber et al. 1986). The split columns were joined using a cap on the bottom and duct tape around the pipe and down the longitudinal cuts to hold it together prior to tilling the column with soil. By using tape to join the column, the pipe could be easily split after the herbicide application to allow planting of seeds in the treated soil to determine location of herbicide movement.

The soil was uniformly packed into the leaching columns to simulate the soil profile, as collected in the field. Columns were shaken during filling and saturated with water to aid in soil compaction. Soil-tilled columns were kept in the upright position during saturation with water from the top of the column and during leaching of the herbicide. The soil was saturated with water and allowed to drain overnight prior to having the herbicides applied to the soil surface. An herbicide solution, of the proper concentration (Table 1), in a 5 mL solution was applied with a small dropper to the soil surface in each of the columns. The herbicide was allowed to equilibrate with the soil for several hours before the leaching process was initiated. Two pieces of filter paper were placed on the soil surface, inside the column, to provide a more uniform distribution of water over the soil surface. The water was allowed to drip from a 1000 mL Erlenmeyer flask mounted above the column at a rate equal to 2.5 cm per hour until the entire amount of water (3.2, 6.4, 9.6 or 12.8 cm) had been applied. The columns were allowed to drain overnight after application of water and prior to splitting the column and planting the bioindicator plant seeds.

Bioindicator plants used in the study were winter rye grass (*Lolium perenne*) for all herbicides except simazine; sugar beet (*Beta vulgaris* L.) was used as the bioindicator plant for simazine. The columns were split longitudinally, and 3 rows of seeds were planted down the entire length of the column. The columns were lightly watered 1 to 2 times daily and fertilized as needed to maintain adequate plant growth. Visual ratings as to the depth in cm of toxic levels of herbicide movement, as indicated by plant death or lack of seed germination, were made approximately 28 d after planting for each half of the column and averaged to obtain a single observation value. Experimental design was a randomized block design which was replicated 3 times. Data were analyzed as a factorial design, and the means were separated using a Waller-Duncan statistical test.

Table 3. Chemical characteristics of herbicides[†]

Herbicide	Solubility in water at 25°C	Average partition coefficient (K_{oc})	Half-life in soil ($t_{½}$)	Relative leaching potential index[‡] ($K_{oc}/t_{½}$) x 10
	mg/L	mL/g	d	
bromacil	815	32	60	5
diuron	42	480	90	53
norflurazon	28	700	45-180	233
oryzalin	2.6	600	20	300
oxyfluorfen	0.1	100,000	35	>2000
simazine	6.2[§]	130	60	22
thiazopyr	2.5[§]	250[¶]	64	39

[†]Taken from Ahrens, 1994.
[‡]Taken from Hornsby et al., 1991.
[§]Solubility in water for simazine and thiazopyr are at 22 and 20°C respectively.
[¶]Taken from McLaren (1996).

Herbicides used in the study had a wide range of physical and chemical properties that will affect their mobility in the soil (Table 3). The relative leaching potential index (RLPI) indicates the relative potential for the chemical to leach in the soil: the lower the number, the greater the potential to leach (Hornsby et al. 1991).

RESULTS AND DISCUSSION

Leaching of all herbicides increased as the amount of water applied increased from 3.2 to 12.8 cm (Table 4). The interaction between herbicide leaching depth and water application rate was significant at the 5% level. Our data support the statement that increased water application rates significantly affect the movement of herbicides in the soil.

Based upon the findings of this study, the herbicides were divided into 3 categories based on their movement in the soil as indicated by the death of the bioindicator plants: (1) low, (2) moderate, or (3) high mobility. Herbicides in the low mobility category were oryzalin, thiazopyr, oxyfluorfen and diuron. Oryzalin moved from 1.9 to 4.14 cm as water application rates were increased from 3.2 to 12.8 cm. Thiazopyr and oxyfluorfen were in between that of oryzalin and diuron. Diuron moved from 8.36 to 16.10 cm in the soil with 3.2 to 12.8 cm water, respectively. In this category of low mobility, some statistical differences existed between oryzalin, the least mobile of the category, and diuron at the water application rates of 6.4, 9.6 and 12.8 cm; however, diuron was not different from thiazopyr and oxyfluorfen

Table 4. Depth of control of bioindicator plants by herbicide in cm at various simulated rainfall rates

	Water application rate			
Herbicide	3.2 cm	6.4 cm	9.6 cm	12.8 cm
oryzalin	1.90 m*	3.61 m	4.14 m	4.14 m
thiazopyr	3.91 m	6.30 klm	6.99 klm	7.52 j-m
oxyfluorfen	5.41 lm	6.78 klm	8.05 j-m	8.89 j-m
diuron	8.36 j-m	11.43 i-l	13.13 ijk	16.10 i
norflurazon	11.20 i-l	18.21 hi	29.21 fg	40.23 e
simazine	14.17 ij	24.13 gh	35.13 ef	50.04 d
bromacil	34.72 ef	79.17 c	99.26 b	106.68 a

*Means followed by same letter do not significantly differ (P=.05, Waller-Duncan).

except at the 12.8 cm rate. The second category consisted of moderately mobile herbicides, norflurazon and simazine, which were not different statistically from one another except at the 12.8 cm application rate with simazine moving to a depth of 50.04 cm and norflurazon moving to a depth of 40.23 cm. The third category consisted of bromacil, which moved to a significantly greater depth than all other products at all water application rates ranging from 34.72 to 106.68 cm for the 3.2 to 12.8 cm rainfall rate, respectively. For all treated columns, only the top 106.68 cm were measured; however, bromacil movement was beyond 106.68 cm at the 12.8 cm application rate as the grass was dead below the 106.68 cm measurement point. The findings for bromacil were similar to information reported by Reddy and Singh (1993) and Tan and Singh (1995). Estimated leaching of 4 herbicides in Candler fine sand (Alva and Singh 1990) and in Astatula fine sand (Jain and Singh 1992) provided a ranking of most mobile to least mobile in the order of bromacil, simazine, norflurazon and diuron, respectively.

These data also correspond fairly well to the data published as to the organic carbon adsorption coefficient (K_{oc}) values shown in Table 3. The K_{oc} describes the relative affinity or attraction of the pesticide to the soil materials and, therefore, its mobility in the soil (Hornsby et al. 1991). Generally, soil with more sand and less silt, clay, or organic matter have a greater potential for leaching of herbicides. Pesticides that are very mobile have K_{oc} values less than 100 in sandy soils, or 50 in fine-textured soils, and should be used with caution due to leaching potential (Buttler et al. 1992). From the data in Table 3, the relative leaching potential index (RLPI) defines the relative dilution of the herbicide in soil solution or the reduction in mass as it moves through the soil and, therefore, its potential to leach into groundwater sources. The smaller the RLPI value, the greater the potential for the pesticide to leach. Ranking herbicides in this study from least to greatest potential to leach would be as follows: oxyfluorfen, oryzalin, norflurazon, diuron, thiazopyr, simazine and bromacil.

In recent years computer models have been used to predict the movement of chemicals in soils. One model which was developed by the University of Florida is “Chemical Movement in Layered Soils” (Nofziger and Hornsby 1987). This program was written to serve as a management tool and decision aid. The Chemical Movement in Layered Soils (CMLS) model estimates the location of peak concentrations of nonpolar organic chemicals as they move through soils in response to downward movement of water.

When using CMLS model to predict the movement of herbicides in the soil, differences between the computer model and the soil columns existed and are presented in Table 5. The soil used for estimating the herbicide movement was a Candler fine sand and can be found in the program data base as S53-22-(1-4). Bulk density and soil organic matter is similar to soil used in the soil column studies. The estimate of water movement was added for the computer model to indicate at the 6.4-, 9.6- and 12.8-cm application rate that water moved beyond the entire 122-cm length of the soil column.

In all cases, the soil column results indicated that the herbicides moved to a greater depth in the column at all water application rates than was predicted by CMLS model.

Differences between the two may be attributed to the following: (1) The soil was saturated when the herbicide was applied. (2) The computer model is making predictions based upon a natural soil profile, whereas the soil column has been hand packed, thus making the soils somewhat different in soil profile, compaction and composition. Differences between soil column and CMLS data may be less if this study had used a natural soil column which did not disturb or mix the soil profile; however, to collect columns to a depth of 122 cm in a natural state would be extremely difficult. (3) The model is predicting the peak concentration of the herbicide, whereas the bioindicator plants indicate where toxic level of the herbicide exist, to the plant species used. Peak concentration and the presence of the herbicide are 2 different concepts. (4) The model is making predictions based upon the average K_{oc} for the selected herbicide. Herbicides will have a range of K_{oc} values based upon the different soil types. As an example, oryzalin has a published average K_{oc} of 600 but ranges from 93 to 2700 mL/g (Ahrens 1994) depending on soil type. When you change the K_{oc} value from 600 to 93 or 2700, the predicted movement of the herbicide is profoundly changed (Table 6). The lower K_{oc}, value of 93 indicates movement of the herbicide 5 to 6 times further than the average K_{oc} value of 600 and 21 to 31 times further when comparisons are made for a K_{oc} value of 2700. Additionally, the label for oxyfluorfen contains a statement about the need for at least one-quarter inch of irrigation or rainfall within 3 to 4 wk of application. However, when a K_{oc} value of 100,000 is used (Table 3), the model predicts that oxyfluorfen did not move from the soil surface even at 12.8 cm of applied water (Table 5). If this

Table 5. Estimation of peak concentration and observed movement of herbicides in centimeters in response to downward movement of water using CMLS and soil columns

	Water application rate per acre (cm)							
	3.2 cm		6.4 cm		9.6 cm		12.8 cm	
Herbicide	Predicted	Observed	Predicted	Observed	Predicted	Observed	Predicted	Observed
oryzalin	0.51	1.91	1.02	3.61	1.27	4.14	1.78	4.14
thiazopyr	1.02	3.91	2.03	6.30	3.05	6.98	4.32	7.52
oxyfluorfen	0.00	5.41	0.00	6.78	0.00	8.05	0.00	8.89
diuron	0.51	8.36	1.02	11.43	1.78	13.13	2.29	16.10
norflurazon	0.51	11.20	0.76	18.21	1.27	29.21	1.52	40.23
simazine	2.03	14.17	4.06	24.13	5.84	35.13	7.87	50.04
bromacil†	7.11	34.72	13.97	79.17	53.85	96.72	98.81	106.68
water	71.12		154.43		219.71		283.97	

†Bromacil was measured to a depth of 106.68 cm; however, movement was below that depth.

Table 6. Effect of changing K_{oc} values on the predicted movement of oryzalin in Candler fine sand

	K_{oc} value		
	93	600	2700
Rainfall rates	Predicted movement in cm		
3.2 cm	2.79	0.51	0.00
6.4 cm	5.33	1.02	0.25
9.6 cm	8.13	1.27	0.25
12.8 cm	10.92	1.78	0.51

predicted movement of 0.0 cm was correct, then the herbicide would offer little herbicidal properties and be broken down by light and other factors, thus reducing effectiveness of oxyfluorfen.

Since the program uses the average K_{oc} and not a specific value for the given soil type, the use of the model could incorrectly predict the herbicide movement for a specific soil in which the K_{oc} is different than the average K_{oc} value. However, the model does provide a quick method to compare different potential movements of herbicides using average K_{oc} values. If specific estimates of herbicide movement are needed, K_{oc} values should be obtained for the soil in question and reliance based upon average values should be avoided.

The herbicides in this study can be divided into 3 basic categories of low, moderate and high mobility based upon their movement in the soil columns. Low mobility herbicides were oryzalin, thiazopyr, oxyfluorfen and diuron which moved in the soil from 1.91 to 16.10 cm at 3.2 to 12.8 cm, respectively. Moderately mobile herbicides were norflurazon and simazine and moved to a depth of 11.20 cm for norflurazon at 3.2 cm and 50.04 cm for simazine at 12.8 cm. Bromacil was the most mobile herbicide in the study at all water application rates and moved beyond a depth of 106.68 cm when 12.8 cm of water was applied.

Ranking herbicides based upon mobility in the soil columns in the order of least mobile to greatest would be as follows: oryzalin, thiazopyr, oxyfluorfen, diuron, norflurazon, simazine and bromacil with the ranking of diuron, norflurazon, simazine and bromacil being in the same order as published by Jain and Singh (1992).

When using computer models to estimate herbicide movement for a specific soil, input parameters should be clearly understood. As with the CMLS program, adjusting the K_{oc} value from the average to a specific K_{oc} for the soil can profoundly change the predicted movement. Computer models offer a quick way to estimate and compare mobility of different herbicide products using the same conditions; however, caution should be used in making statements about how this predicted mobility would occur in a field situation unless the program uses specific K_{oc} for the soil type under study.

Citrus growers should be aware of the leaching potential of herbicides and select those herbicides that will minimize potential groundwater contamination problems, especially if the grove contains soils that are sandy and have low organic matter content.

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