Mobility of the Herbicide Pyrithiobac through Intact Soil Columns

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The relative mobility of pyrithiobac [sodium 2-chloro-6-(4,6-dimethoxypyrimidin-2-ylthio)benzoate], a new herbicide used for postemergence control of broadleaf weeds in cotton (*Gossypium hirsutum*), was evaluated and compared against that of bromide (Br^-) tracer on four soils representative of cotton-growing regions using intact soil columns under saturated flow conditions. Pyrithiobac breakthrough curves were asymmetrical in shape with significant tailing and displaced to the left of 1 pore volume in the Houston Black clay (fine, montmorillonitic, thermic Udic Pellustert), Orelia fine sandy clay loam (fine-loamy, mixed, hyperthermic Typic Ochraqualfs), and Ships silty clay (very-fine, mixed, thermic Udic Chromustert) soils. Breakthrough of pyrithiobac in the Hidalgo sandy loam soil (fine-loamy, mixed, hyperthermic Typic Calciustoll) was delayed and more symmetrical, with peak pyrithiobac concentration reached after 1.2 pore volumes. The immobile pore water (IPW) fractions estimated from the Br^- breakthrough curves ranged from 20 to 87% of total pore water. The IPW values demonstrated that soils with the greatest amount of IPW (Ships with IPW = 87.3%) exhibited the most rapid movement of pyrithiobac (peak concentration after 0.04 pore volume). The experimentally determined pyrithiobac breakthrough curves confirmed the high mobility of this herbicide in these alkaline and predominantly smectitic soils. These results indicate that pyrithiobac mobility was influenced by soil type and preferential flow processes when leached through intact soil columns.

Keywords: *Pyrithiobac; breakthrough; mobility; preferential flow*

INTRODUCTION

The fate of herbicides in soils is governed by myriad factors including processes in the soil environment and properties of the herbicide. The extent to which a herbicide moves vertically in soil determines its potential for groundwater contamination as well as its efficacy in weed control (Weber et al., 1986). The mobility of a particular herbicide is generally inverse to its adsorption coefficient in soil (Weber et al., 1986; Liu et al., 1995). Large differences in solute leaching patterns between intact and disturbed soil columns (Elrick and French, 1966; Cassel et al., 1974; Smith et al., 1985) are attributed to the lack of structure in disturbed soil columns (O'Dell et al., 1992; Smith et al., 1992). The use of intact soil columns for leaching studies enables researchers to maintain native soil structure and provide a better understanding of herbicide transport in the field (Locke et al., 1994) by accounting for preferential flow paths (Li and Ghodrati, 1994).

Pyrithiobac is a new herbicide developed for postemergence control of broadleaf weeds in cotton (*Gossypium hirsutum*). It is a weakly acidic herbicide (Figure 1), with a pK_a of 2.34, aqueous solubilities of 705 g L^{-1} (2 M) at pH 7 and 264 g L^{-1} (0.77 M) at pH 5, and a molecular mass of 326.4 g mol^{-1} (DuPont Agricultural Products, 1993). Pyrithiobac will behave as a singly charged anion at typical soil solution pH values (pH >5). Movement of pyrithiobac in soils should not be mitigated by sorption on the basis of previous results (Matocha and Hossner, 1998), which suggests it is potentially mobile. There are no published studies investigating the mobility of pyrithiobac in soils. The objective of this study was to evaluate the mobility of pyrithiobac compared against that of Br^- tracer through four soils representative of cotton-growing regions using intact soil columns to simulate realistic field conditions.

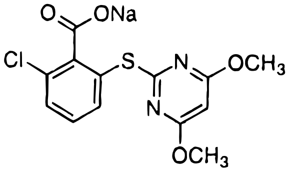

Figure 1. Chemical structure of pyrithiobac.

MATERIALS AND METHODS

Soil Column Collection/Preparation. Intact soil columns were collected from four soils that represent cotton-growing regions in central and southern Texas. The Ships soil columns were taken from a native pasture located in the flood plain of the Brazos river. Intact columns of the Orelia soil were removed from a field site under no-till management. The Hidalgo soil columns were excavated from a cultivated and irrigated field. The Houston Black soil columns were taken from a fencerow adjacent to a dryland field cultivated to corn. Characterization of the soils was described elsewhere (Matocha and Hossner, 1998).

Columns, 20-cm long by 10-cm i.d., were constructed from poly(vinyl chloride) (PVC) pipe (schedule 40). Each column was beveled at one end to displace soil outward and reduce compaction (Cassel et al., 1974; Seyfried and Rao, 1987; Liu et al., 1995) as the column was pushed into the soil. During removal of the intact soil columns, efforts were made to leave the surface residue intact (Gish et al., 1991). The columns were capped on both ends, placed in plastic bags, and stored in a

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refrigerator at ~5 °C to minimize biological activity (Singh and Kanwar, 1991).

The PVC columns containing intact soil cores were placed in a 2.0 L plastic container and saturated from the bottom (subirrigated) with 0.005 M calcium nitrate [$(Ca(NO_3)_2 \cdot 4H_2O)$] solution. To ensure uniform antecedent moisture conditions and avoid air entrapment in the soil columns (Gish et al., 1991; Singh and Kanwar, 1991), the solution level in the plastic container was incrementally raised (5 cm every 6 h). It took ~24 h to saturate one column. Preliminary dye studies conducted using Brilliant Blue FCF (Flury and Flühler, 1994) to characterize flow paths of water in the intact soil columns qualitatively revealed vertical movement of soil water down channels between structural units (data not shown), suggestive of preferential flow processes. The experimental leaching setup was modified from previous investigations (McNeal and Reeve, 1964; Hill and King, 1982) by gluing a cut cylindrical piece of plastic in the center of a PVC end-cap that was fitted at the bottom of each soil column to minimize wall flow during the leaching event.

Intact Column Experiments. Leaching experiments were conducted at a temperature of 24 ± 2 °C. After prewetting, the soil columns were drained just enough to remove free water on the soil surface yet maintain saturated conditions. Pyrimidine-2-^{14}C-labeled pyrithiobac (99% purity) with a specific activity of 2.6 MBq mg^{-1} was provided by DuPont Co. (Wilmington, DE) and used without further treatment or purification. A pulse of 5 mL of ^{14}C-labeled pyrithiobac (4.6 kBq) stock solution was applied to the soil surface in each column with a pipet in a spiral pattern followed by application of a constant head (1.5 cm) of 0.01 M KBr solution that was maintained with a Mariotte bottle arrangement (Seyfried and Rao, 1987; Singh and Kanwar, 1991; Wietersen et al., 1993). These imposed experimental conditions would be representative of pyrithiobac applied to an irrigated field. A thin layer of glass wool was placed on top of each soil column to maintain the integrity of the surface during the leaching event as suggested by some authors (McNeal and Reeve, 1964; Weber et al., 1986). A constant concentration of the nonadsorbed Br^- tracer was supplied to determine the fraction of mobile pore water and to monitor the movement of small amounts of tracer because indigenous Br^- concentration in soils is generally low (Onken et al., 1977). Effluent fractions were collected in tared vials until ~2 pore volumes of water was displaced. Average flow rates through the columns ranged from 140 mL h^{-1} in the Hidalgo soil to 836 mL h^{-1} in the Houston Black soil. Triplicate soil columns were treated with ^{14}C-labeled pyrithiobac per soil type along with one control column. Effluent fractions were assayed for ^{14}C-labeled pyrithiobac by liquid scintillation techniques. Each sample was prepared for analysis by transferring a 1 mL aliquot of the effluent fraction to a 20 mL borosilicate scintillation vial and by adding 15 mL of Scinti-Verse BD cocktail (Fisher Scientific). The samples were immediately counted on a Beckman LS 7500 liquid scintillation counter with corrections made for sample quenching. Efficiencies of the liquid scintillation counter were generally >85%, and the detection limit of ^{14}C was at the nanomole level. Bromide concentrations were determined with a bromide selective ion electrode (Liu et al., 1995) with detection limits at micromole levels. After the leaching events, one column per soil type was randomly selected and stored in a freezer at −5 °C pending analysis. Pyrithiobac degradation was considered to be insignificant in our experiments as discussed previously (Matocha and Hossner, 1998).

The value of 1 pore volume for each soil was calculated by sacrificing two columns per soil type and determining dry bulk density in 4 cm increments. Total soil porosity was calculated by assuming a mean particle density of 2.65 Mg m^{-3} (Kissel et al., 1973; Smith et al., 1985; Marshall and Holmes, 1988). One pore volume for each column was calculated as the product of total soil porosity and total soil volume (Singh and Kanwar, 1991). Total soil volume based on column dimensions was ~1300 cm^3 in most cases. The difference between the weight of the saturated soil column and its dry weight was also used to estimate the value for 1 pore volume in each soil, and these values were averaged with the calculated pore volumes. This approach has been used by others (Thomas and Swoboda, 1970; Brooks et al., 1998).

Table 1. Physical and Chemical Properties of the Soils[a]

soil series	clay content (g kg^{-1})	organic carbon (g kg^{-1})	iron oxides (g kg^{-1})	pH	clay mineralogy[b]
Houston Black	533	25.4	3.8	7.9	Sm, Mi, K
Hidalgo	216	5.8	1.2	8.4	Mi, K, Sm
Orelia	313	9.7	0.2	8.0	Sm, Mi, K
Ships	414	25.3	5.6	8.3	Sm, Mi

[a] Taken from Matocha and Hossner (1998). [b] Sm, smectite; Mi, mica; and K, kaolinite.

The amount of ^{14}C remaining in the soils at each depth was determined by sectioning the frozen intact columns of each soil type in 2 cm sections. Efforts were made to keep the columns in a near frozen state using dry ice. The PVC casing was removed from each sectioned soil sample, and the soil was placed in polyethylene ziploc bags and stored at −5 °C. Prior to analysis, the sectioned soil samples were thawed, weighed, and mixed thoroughly, and subsamples were removed to determine gravimetric moisture content. Each soil sample was air-dried, ground with mortar and pestle, and mixed thoroughly. Duplicate 0.15 g subsamples were taken from each sectioned soil sample, placed in paper cone cups with cellulose powder, and combusted with a Packard B306 Tri-Carb sample oxidizer. The combusted $^{14}CO_2$ was trapped in a strong base of CarboSorb, mixed with Permafluor, and radioactivity was measured using a Beckman LS 7500 liquid scintillation counter. The efficiency of the oxidizer was ~92%, and micromole levels could be measured.

Data Analyses. Breakthrough curves (BTCs) were generated by plotting relative analyte concentration (C/C_0) versus relative pore volume (V/V_0) for Br^- and ^{14}C-labeled pyrithiobac, where C is the measured concentration, C_0 the initial concentration, and V the sample volume collected relative to 1 pore volume (V_0). Mobile and immobile pore water fractions were estimated from the Br^- BTCs. A least significant difference (LSD) test was used to determine significance at the 0.05 level of probability.

RESULTS AND DISCUSSION

Bromide BTCs. Nonadsorbed Br^- anion was used as a tracer to compare with the movement of pyrithiobac and to calculate the mobile and immobile pore water fractions through the intact soil columns after 2 pore volumes of effluent was collected. The Br^- BTCs were all asymmetric, characterized by early appearance of Br^- tracer in the effluent reaching a relative concentration (C/C_0) of 0.5 well before 1 pore volume, particularly in the well-structured Houston Black, Orelia, and Ships soils when compared to the Hidalgo soil (Figure 1). The extent of asymmetry observed in the Br^- BTCs generally increased with increasing soil clay content (Table 1). The asymmetric shape of Br^- BTCs is indicative of preferential flow through macropores (Singh and Kanwar, 1991; O'Dell et al., 1992). The effects of soil structure on creating preferential flow paths for water and dissolved solutes in undisturbed (intact) soil columns has been well established (Jury et al., 1991).

The Br^- BTCs were further analyzed by estimating BTC parameters such as the mobile and immobile pore water fractions. Several researchers (Nielsen and Biggar, 1961; Kissel et al., 1973; Singh and Kanwar, 1991) have estimated the mobile pore water (MPW) fraction for leaching columns as the number of pore volumes required to reach a relative chloride (Cl^-) concentration of 0.5. The amount of MPW was subtracted from 1 pore volume to obtain the immobile pore water (IPW) fraction

Table 2. Selected Physical Characteristics of the Intact Soil Columns

soil series	bulk density (g cm^{-3})	total porosity (%)
Houston Black	1.10	58.5
Hidalgo	1.45	45.2
Orelia	1.25	52.8
Ships	1.20	54.7

Table 3. Pore Volumes and Leachate Parameters Measured from Intact Soil Columns[a]

soil series	1 pore vol (mL)	IPW[b]	bromide[c]	pyrithiobac[c]
Houston Black	780.1 a	84.5 a	97.2 a	28.0 b
Hidalgo	614.8 b	20.0 b	100.0 a	73.2 a
Orelia	738.2 a	72.2 a	99.3 a	43.0 b
Ships	759.0 a	87.3 a	99.0 a	32.1 b

[a] Mean values within each column with the same letter are not significantly different at the 0.05 level of probability according to the least significant difference (LSD) test. [b] Represents the percent of total pore water. [c] Recovery in 2 pore volumes expressed as percent of applied.

or “stagnant” water. A direct relationship exists between the estimated amount of IPW and the degree of preferential flow (Singh and Kanwar, 1991). The amount of water in 1 pore volume was influenced by soil type, with the Hidalgo soil having a significantly lower amount of water in 1 pore volume compared to the other three soils (Table 2). The deeper than predicted movement of surface-applied chemicals in the field has given rise to the mobile−immobile soil pore water description (Clothier et al., 1992).

The estimated amount of IPW was >3-fold greater in the Houston Black, Ships, and Orelia soils, when compared to the Hidalgo soil (Table 3). This behavior implied that the amount of IPW, used as a relative measure of preferential flow, was strongly influenced by soil type and decreased in the following order: Ships > Houston Black > Orelia > Hidalgo. These results further indicate that the total volume of soil pore water active in moving Br$^-$ through the column ranged from 12.7% in the Ships soil to 80% in the Hidalgo soil.

The amount of IPW in each soil type was not attributed solely to preferential flow because the effects of anion exclusion need to be considered (Dyson and White, 1987; Singh and Kanwar, 1991), particularly in soils with predominantly smectitic (negatively charged) mineralogy. Pronounced exclusion of Cl$^-$ was reported in the Houston Black (Thomas and Swoboda, 1970) soil using salt concentrations (0.01 M) similar to those in this study. The estimated specific exclusion volume of 0.30 cm^3 g^{-1} of clay reported by Elprince and Day (1977) was used to calculate the total exclusion volume for the four soils based on the assumption that this volume was entirely due to exclusion of Br$^-$. The total anion exclusion volumes for the Ships, Houston Black, Orelia, and Hidalgo soils were 40, 38, 28, and 23% of the total pore water, which was related to the clay content in each soil (Table 1). Singh and Kanwar (1991) reported an anion exclusion volume of ∼19% in a loam soil containing 25% clay. Therefore, the estimated effective amounts of IPW caused by preferential flow through macropores were approximately 47, 47, and 44% in the Ships, Houston Black, and Orelia soils, respectively. The negative effective IPW volume obtained in the Hidalgo soil (−3%) apparently indicated (i) preferential flow was less influential than initially estimated by the Br$^-$ BTC, (ii) the anion exclusion volume was overestimated, or (iii) experimental variability.

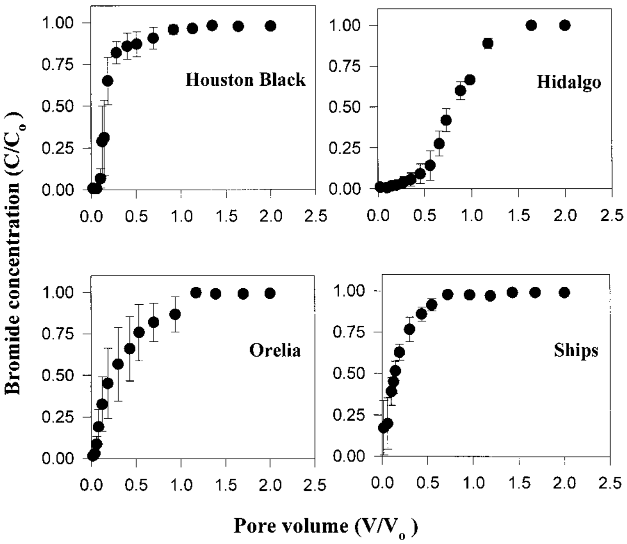

Figure 2. BTCs for bromide through intact columns of Houston Black, Hidalgo, Orelia, and Ships soils. Some points were omitted for clarity, and symbol size may exceed error bars in some cases. Error bars represent one standard error from the mean.

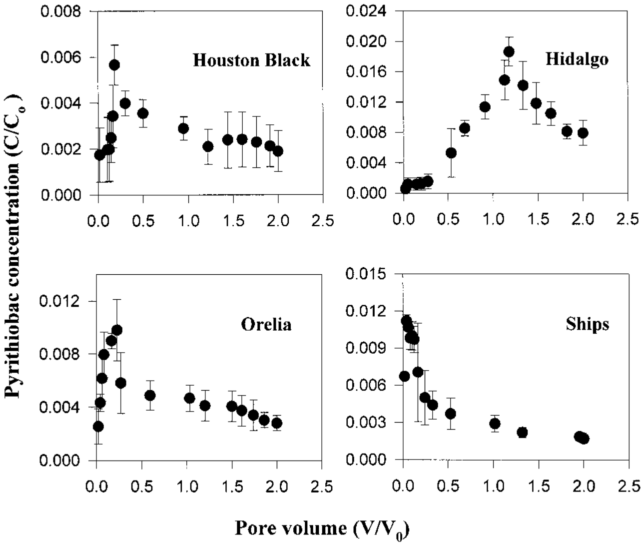

Figure 3. BTCs for pyrithiobac through intact columns of Houston Black, Hidalgo, Orelia, and Ships soils. Some points were omitted for clarity, and symbol size may exceed error bars in some cases. Error bars represent one standard error from the mean.

The amount of Br$^-$ collected after 2 pore volumes was not significantly influenced by soil type, with nearly 100% recovered in all of the soils (Table 2). The slower approach to a relative Br$^-$ concentration of 1.0 for the Houston Black, Orelia, and Ships soils provided additional evidence in support of preferential flow in these soils.

Pyrithiobac BTCs. Rapid breakthrough of pyrithiobac in the Houston Black, Orelia, and Ships soils was indicated by early appearance of pyrithiobac in the initial volumes of effluent giving rise to asymmetrical BTCs displaced well to the left of 1 pore volume (Figure 2). Breakthrough of pyrithiobac in the Hidalgo soil was delayed and more symmetrical compared to the other soils (Figure 3). Peak pyrithiobac concentrations in the effluent were reached after 1.2, 0.23, 0.19, and 0.04 pore volumes in the Hidalgo, Orelia, Houston Black, and Ships soils.

The asymmetrical shape and significant tailing of the pyrithiobac BTCs in the structured Houston Black, Orelia, and Ships soils corresponded to the large IPW values for these soils and suggested that preferential flow processes were operative (Jury et al., 1991). Additional studies have attributed enhanced movement of herbicides to preferential flow processes when using undisturbed soil columns (Rao et al., 1974; O'Dell et al., 1992), particularly in structured clay soils (White et al., 1986) and in soils from no-till sites (Steenhuis et al., 1990). Experimental evidence suggests that preferential flow occurs frequently under field conditions (Flury, 1996), and models have been developed to describe preferential flow phenomenon (Nijssen et al., 1991; Li et al., 1998; Wallach and Steenhuis, 1998).

The BTCs for the soils with significant macroporosity (Houston Black, Ships, and Orelia) would be more sensitive to the ponding application method employed in this study on the basis of the results obtained by Kluitenberg and Horton (1990). This could explain the rapid breakthrough of both pyrithiobac and Br^-. It is intriguing to note the rapid breakthrough of pyrithiobac, which eluted ahead of the Br^- tracer in the Houston Black, Orelia, and Ships soils. Despite the low affinity of pyrithiobac for alkaline and predominantly smectitic soils, one would expect the Br^- tracer to breakthrough ahead of pyrithiobac if preferential flow was the only operative transport process as seen by others (O'Dell et al., 1992; Veeh et al., 1994). Other mechanisms could be influencing mobility of pyrithiobac.

Recent studies reported that both transport-related nonequilibrium (preferential flow) and sorption-related nonequilibrium processes are important when describing atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine] transport in naturally structured soils of relatively high pore water velocities (Gaber et al., 1995). In addition, slightly nonlinear sorption isotherms observed for pyrithiobac on these soils (Matocha and Hossner, 1998) could have profound influences on BTC shape as shown by Spurlock et al. (1995) for fenuron (1,1-dimethyl-3-phenylurea) and monuron [1,1-dimethyl-3-(*p*-chlorophenyl)urea]. Another possible explanation for the rapid movement of pyrithiobac relative to that of Br^- could be extreme effects of numerous slickenslides (Dixon, 1991) present in the shrinking and swelling Houston Black and Ships soils. These planes of weakness provide passageways for water around soil structural units and significantly enhance movement of nutrients (Ritchie et al., 1972). Also, there is a possibility that Br^- may behave as a reactive tracer under some conditions based on recent studies (Brooks et al., 1998). Regardless of the mechanisms involved, the BTCs confirmed the high mobility of pyrithiobac in these alkaline and smectitic soils. It should be pointed out that additional work is necessary before further statements can be made regarding the exact mechanisms responsible for pyrithiobac transport.

The effect of tillage also contributed to the observed differences in pyrithiobac BTCs among all four soils. The Houston Black, Orelia, and Ships soil columns were removed from no-till sites where native structure was maintained. The Hidalgo soil was taken from a cultivated field where some structure was likely destroyed (Flury, 1996), thereby increasing the pore volumes of water required to move pyrithiobac a fixed distance through the column.

The more symmetrical pyrithiobac BTC in the Hidalgo soil followed the lower IPW value and resulted in significantly greater pyrithiobac recovery in the effluent after 2 pore volumes when compared to the other soils (Table 2). Mass balance estimates indicated that 76−105% of the applied pyrithiobac was recovered in all soils and effluents. The variation in recoveries apparently resulted from the heterogeneity of intact soil columns (O'Dell et al., 1992; Li and Ghodrati, 1994), which gives rise to irregularities and inconsistencies in herbicide concentrations down the soil profile (Smith et al., 1992).

Conclusions. The relative movement of pyrithiobac and bromide through intact soil columns under saturated flow conditions was influenced by soil type. Pyrithiobac was eluted considerably ahead of 1 pore volume, and BTCs exhibited significant tailing in the well-structured Ships, Houston Black, and Orelia soils, with peak concentrations reached after the passage of 0.04, 0.19, and 0.23 pore volumes. The breakthrough of pyrithiobac in the Hidalgo soil was more delayed and symmetrical, with a peak concentration reached after 1.2 pore volumes. The IPW fractions, estimated from the bromide BTCs, revealed that soils with the greatest amount of IPW exhibited the most rapid movement of pyrithiobac. The experimentally determined pyrithiobac BTCs confirmed the high mobility of this herbicide in these alkaline and predominantly smectitic soils. Additional research is needed to explain breakthrough patterns of pyrithiobac, which eluted ahead of the nonreactive bromide tracer in the Houston Black, Orelia, and Ships soils. These results indicate that pyrithiobac mobility was influenced by soil type and preferential flow processes when leached through intact soil columns.

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