

Pyrithiobac Sorption on Reference Sorbents and Soils

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The paucity of information available on the behavior of the new herbicide pyrithiobac [sodium 2-chloro-6-(4,6-dimethoxypyrimidin-2-ylthio)benzoate], prompted an evaluation of the sorption of pyrithiobac on reference sorbents and cotton-producing soils from central to south Texas. Batch equilibration techniques were used to measure pyrithiobac sorption at concentrations commonly encountered in field soils. Pyrithiobac was strongly sorbed by peat, which indicated that the organic matter fraction will significantly influence sorption. The goethite sorption maximum (0.30 mmol kg⁻¹ for 0.23 mM pyrithiobac added), which represented the reference sorbent with the least sorption capacity, sorbed 1.7 times more than the soil with the greatest sorption capacity (Houston Black, 0.17 mmol kg⁻¹ for 0.23 mM pyrithiobac added). Strong correlations among measured soil properties made it difficult to identify soil components controlling pyrithiobac sorption. These results indicate that pyrithiobac was weakly sorbed by four soils due to repulsion of anionic pyrithiobac in predominantly alkaline and smectitic (negatively charged) soils.

Keywords: *Pyrithiobac; herbicide; sorption*

INTRODUCTION

Weed control programs have been hampered by the lack of a broad-spectrum postemergence over-the-top herbicide that exhibits no deleterious effects on cotton (*Gossypium hirsutum*). Pyrithiobac [sodium 2-chloro-6-(4,6-dimethoxypyrimidin-2-ylthio)benzoate], the active ingredient of Staple (DuPont, Wilmington, DE), is a new herbicide developed for postemergence control of broadleaf weeds in cotton. Pyrithiobac has shown promise in controlling obstinate broadleaf weeds in cotton (Jordan et al., 1993b) with no effect on seed cotton yield (Jordan et al., 1993a) at low application rates [0.035–0.140 kg of active ingredient (ai) ha⁻¹]. Postemergence herbicides can likely reach the soil surface following application to foliage (Reddy et al., 1994), where they would be subject to various transport, retention, and transformation processes. There are no published studies on sorption of pyrithiobac in soils because it is a new compound and has yet to be classified into a chemical family of herbicides.

The low application rates of pyrithiobac correspond to initial soil solution concentrations of ~0.05–0.20 μM in the plow layer of field soils (20 cm) prior to sorption under saturated conditions, assuming a pore space of 50%. This suggests that its potential for detection in groundwater would be reduced when compared to that of other common herbicides with greater application rates such as atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine, 1.0–4.5 kg of ai ha⁻¹] and glyphosate [*N*-(phosphonomethyl)glycine, 1.0–5.0 kg of ai ha⁻¹].

Pyrithiobac is a weakly acidic herbicide with a pK_a of 2.34 and a high aqueous solubility of 705 g L⁻¹ (2 M) at pH 7 and 264 g L⁻¹ (0.77 M) at pH 5 (DuPont Agricultural Products, 1993). The pK_a value represents

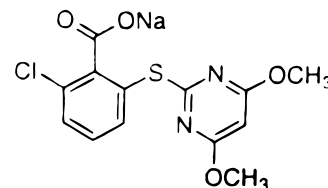


Figure 1. Chemical structure of pyrithiobac.

the pH at which the carboxyl functional group, the active site on pyrithiobac (Figure 1), has a 50% probability to be dissociated in aqueous solution. Pyrithiobac will behave as a singly charged anion at typical soil solution pH values (pH > 5).

The paucity of information concerning pyrithiobac behavior in soils prompted the initiation of this study. The objectives were to evaluate pyrithiobac sorption on reference sorbents and field soils at concentrations encountered in the field and to investigate the effects of various soil properties on the affinity of the soils for pyrithiobac.

MATERIALS AND METHODS

Reference Sorbents and Soils. The four reference sorbents that were employed for comparison purposes were Gonzales bentonite (Southern Clay Products, Gonzales, TX), Georgia kaolinite (Huber Kaolin, Macon, GA), synthetic goethite, and Michigan peat. Four soils from Texas with a wide range of physical and chemical properties were selected for this study. The soils are representative of important cotton-growing regions of Texas. The Hidalgo sandy loam (fine-loamy, mixed, hyperthermic Typic Calcicustoll) is representative of the Lower Rio Grande Valley, and the Orelia sandy clay loam (fine-loamy, mixed, hyperthermic Typic Ochraqualfs) is representative of Coastal Bend soils. The Houston Black clay (fine, montmorillonitic, thermic Udic Pellustert) and Ships silty clay (very-fine, mixed, thermic Udic Chromustert) are representative of central Texas soils.

Characterization. The cation exchange capacity (CEC) of the reference bentonite, kaolinite, and peat samples was determined using Ca²⁺–Mg²⁺ exchange (Dixon and White,

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1993). Total carbon was determined using dry combustion, and this value was taken as the organic carbon content, because no inorganic carbon was evident after reaction with HCl. Goethite (α -FeOOH) was prepared from an Fe(III) system as outlined by Schwertmann and Cornell (1991), washed with deionized H₂O, dialyzed, and freeze-dried. Bentonite, kaolinite, and goethite were characterized by XRD for diagnostic peaks and *d* spacings. The reference clays were Ca-saturated, washed with deionized water, dialyzed to remove excess salts, and freeze-dried.

The four soils were air-dried and ground to pass through a 2-mm sieve. The soil pH was measured in a 1:1 soil/H₂O ratio (McLean, 1982). The CEC of each soil was assayed according to the Polemio and Rhoades procedure (1977), and total carbon was measured by dry combustion in a tube furnace (Soil Survey Staff, 1972). Inorganic carbon (as CaCO₃) was measured manometrically using the Chittick apparatus (Dremanis, 1962). Soil organic carbon content was taken as the difference between total and inorganic carbon. Free iron oxides were determined using the DCB (sodium dithionite-citrate-bicarbonate) extraction method (Mehra and Jackson, 1960).

Particle size distribution was characterized by the pipet method (Kilmer and Alexander, 1949) and specific surface areas were estimated from the Pionke and DeAngelis (1980) equation based on the percent of various size particles. The soils were pretreated and fractionated into sand, silt, coarse clay, and fine clay as described by Dixon and White (1993). Mineralogy of the coarse (2–0.2 μ m) and fine (<0.2 μ m) clay fractions was evaluated by X-ray diffraction (XRD) analyses. Site ion solvation and other procedures were used for clay mineral identification. Oriented clay mounts were scanned with Cu-K α radiation using a Philips XRG-3000 X-ray diffractometer with a scan speed of the goniometer calibrated to 1° 2 θ per minute for all scans. The number of counts per second ranged from 2500 to 5000, depending on the particular clay fraction.

Sorption Isotherms. Pyrimidine-2-¹⁴C-labeled pyrithiobac (99% purity) with a specific activity of 2.60 MBq mg⁻¹ was provided by DuPont Co. (Wilmington, DE) and used without further treatment or purification. A stock solution was prepared containing ~455 Bq mL⁻¹, and appropriate volumes of the stock solution were diluted with 0.01 M CaCl₂ to give initial solution concentrations of approximately 0.05, 0.08, 0.10, 0.15, 0.20, and 0.23 μ M. These initial solution concentrations were chosen to approximate field application rates. Calcium chloride (0.01 M) was used as the background electrolyte in the sorption experiments to simulate natural field soil conditions and to promote flocculation when solid and solution phases were separated. Preliminary experiments were conducted to establish equilibration times of pyrithiobac on the reference sorbents and soils. Samples taken at increasing time intervals up to 36 h indicated that an apparent equilibrium was attained after 6 h in the reference sorbents and after 12 h in the soils.

Pyrithiobac degrades relatively slowly in soil, primarily by microbially mediated degradation, with an estimated half-life of 60 days based on laboratory studies (DuPont Agricultural Products, 1993). An equilibration time of 12 h in the soils would correspond to <1% of pyrithiobac degraded (assuming the maximum degradation rate), which was considered to be insignificant in our experiments.

Pyrithiobac sorption isotherms were determined using a batch equilibration method. Two-gram samples of each soil (oven-dry basis) and 0.5-g samples of each reference sorbent (oven-dry basis) were placed in tared centrifuge tubes with enough solution to achieve 1:10 sorbent/solution ratios. The sorption experiments were conducted in triplicate with standards and blanks included in each batch. The samples were equilibrated by mechanically mixing for predetermined times on a rotary shaker at 23 \pm 2 °C. The samples were centrifuged at 3750g for 20 min, and 1-mL aliquots of the clear supernatants were mixed with 15 mL of scintillation cocktail. Radioactivity was measured in all samples and standard solutions with a liquid scintillation counter (Beckman 7500, Beckman Instruments, Fullerton, CA) with corrections made for sample

Table 1. Physical and Chemical Properties of the Soils

soil series	clay content (g kg ⁻¹)	organic carbon (g kg ⁻¹)	iron oxides (g kg ⁻¹)	pH	surface area ^a (m ² g ⁻¹)	clay mineralogy ^b
Houston Black	533	25.4	3.8	7.9	375	Sm, Mi, K
Hidalgo	216	5.8	1.2	8.4	106	Mi, K, Sm
Orelia	313	9.7	0.2	8.0	166	Sm, Mi, K
Ships	414	25.3	5.6	8.3	357	Sm, Mi

^a Estimated from the Pionke and DeAngelis (1980) equation.

^b Sm, smectite; Mi, mica; K, kaolinite.

Table 2. Simple Correlation Coefficients (*r*) among Soils

soil property	clay	iron oxides	pH	surface area	CEC	water content
organic carbon	0.92 ^a	0.90 ^a	-0.39	0.99 ^a	0.97 ^a	0.87 ^a
clay		0.68 ^b	-0.69 ^b	0.94 ^a	0.98 ^a	0.99 ^a
iron oxides			0.04	0.88 ^a	0.81 ^a	0.59 ^b
pH				-0.44	-0.54	-0.78 ^a
surface area					0.98 ^a	0.90 ^a
CEC						0.95 ^a

^a Significant at the 1% level of probability. ^b Significant at the 5% level of probability.

Table 3. Selected Properties of Reference Sorbents

sorbent	organic carbon (g kg ⁻¹)	CEC [cmol(+) kg ⁻¹]	pH	surface area ^a (m ² g ⁻¹)
peat	439	105	6.6	56
bentonite	1.09	70	6.8	70.3
kaolinite	1.05	2.0	5.8	17
goethite		6.8 ^b	6.0	20

^a Taken from Cancela et al. (1990), Goldberg et al. (1995), and Schwertmann and Cornell (1991). ^b Represents the point of zero charge (PZC) taken from Ukrainczyk and Ajwa (1996).

quenching using an external quench correction method. Efficiencies of the liquid scintillation counter were generally >85%. The amount of pyrithiobac sorbed was calculated as the difference between the initial concentrations in the standards and final equilibrium solution concentrations in the samples. Blanks containing no sorbent indicated that sorption to the glassware was negligible. All sorption experiments were conducted at native reference sorbent and soil pH. Standard errors generally ranged from 0.007 to 0.03 μ mol kg⁻¹ in the samples and were represented by error bars in the sorption isotherms.

Sorption isotherms were normalized with respect to organic carbon, clay, and iron oxide contents to evaluate the dependence of pyrithiobac sorption on measured soil properties. This approach has been used by others (Weber et al., 1992). Collapse of the normalized isotherms to one coincident isotherm was used to qualitatively identify the most effective soil property influencing sorption in the soils. Conformity of the sorption data to a linear isotherm was operationally defined when $r^2 > 0.98$, an approach employed by other authors (Borggaard and Streibig, 1988).

RESULTS AND DISCUSSION

The four soils selected for this study have a wide range of physical and chemical properties with a narrow pH range (Table 1). Strong correlations exist between soil organic carbon, clay, and iron oxide contents (Table 2). The presence of smectite and kaolinite in the respective bentonite and kaolinite reference clays was verified by strong 1.4- and 0.722-nm XRD peaks. Review of selected properties of reference sorbents (Table 3) indicated organic carbon contents of 1.09, 1.05, and 439 g kg⁻¹ for the bentonite, kaolinite, and peat, respectively. Goethite was confirmed by sharp XRD peaks at 0.417, 0.244, and 0.268 nm, which agreed with

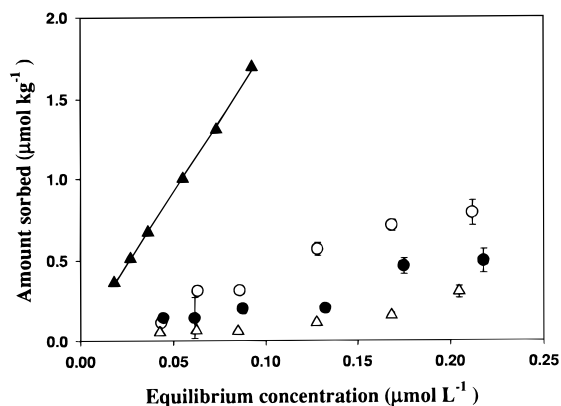


Figure 2. Pyriithiobac sorption isotherms for peat (▲), bentonite (○), kaolinite (●), and goethite (△) samples expressed on a total weight basis. Error bars represent the standard error of each mean value.

published *d* spacings. The preparation method produced a goethite with a surface area of $\sim 20 \text{ m}^2 \text{ g}^{-1}$ (Schwertmann and Cornell, 1991). No phyllosilicate mineral impurities were present in the H_2O_2 -treated peat on the basis of XRD analyses.

Reference Sorbent Sorption. The slopes of the sorption isotherms indicate that the affinity of pyriithiobac for the reference sorbents was in the order peat > bentonite > kaolinite > goethite when expressed on a total weight basis (Figure 2). The sorption capacity of the peat ($1.70 \mu\text{mol kg}^{-1}$) exceeded that of the bentonite, kaolinite, and goethite by 5-, 8-, and 28-fold at an equilibrium concentration (C_e) of $\sim 0.09 \mu\text{M}$. Strong sorption by the peat indicates that the organic matter fraction significantly influenced sorption of pyriithiobac. Sorption of pyriithiobac by the peat was linear over the concentration range studied and was fitted to a linear isotherm equation

$$q = 17.7C_e + 0.035 \quad r^2 = 0.999 \quad (1)$$

by the method of least squares where *q* is the amount of pyriithiobac sorbed ($\mu\text{mol kg}^{-1}$), C_e is the equilibrium pyriithiobac concentration ($\mu\text{mol L}^{-1}$), and r^2 is the regression coefficient. The slope of the linear regression line gave the sorption coefficient K_d (L kg^{-1}) of 17.7. This trend resembled the C-shaped (linear) isotherm described by Giles et al. (1960) characterized by a slope that is independent of solution concentration produced by a constant partitioning between the sorbent and solution phases (Sposito, 1989). Existence of a linear isotherm as proof of partitioning has been criticized (Mingelgrin and Gerstl, 1983) and would not likely be operative at pH 6.6 because pyriithiobac would exist as a negatively charged (anionic) species and is highly water soluble at pH 7 (2 M) and pH 5 (0.77 M) (DuPont Agricultural Products, 1993). The linearity of the sorption isotherm for the peat could represent the linear portion (low concentration range) of a Langmuir isotherm.

The low-affinity (nonlinear) pyriithiobac sorption isotherms in the kaolinite and goethite samples exhibited a steep increase in sorbed pyriithiobac at $C_e > 0.15 \mu\text{M}$. The greater sorption capacity of bentonite when compared to kaolinite and goethite on a total weight basis was probably due to favorable interactions between the saturating cation (Ca^{2+}) on bentonite and the carboxyl functional group on pyriithiobac. However, additional

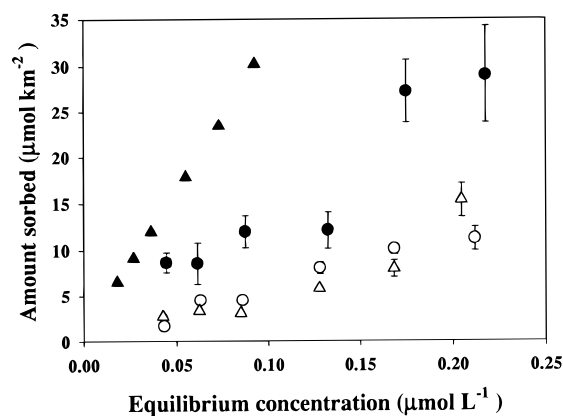


Figure 3. Pyriithiobac sorption isotherms for peat (▲), bentonite (○), kaolinite (●), and goethite (△) samples expressed on a surface area basis. Error bars represent the standard error of each mean value.

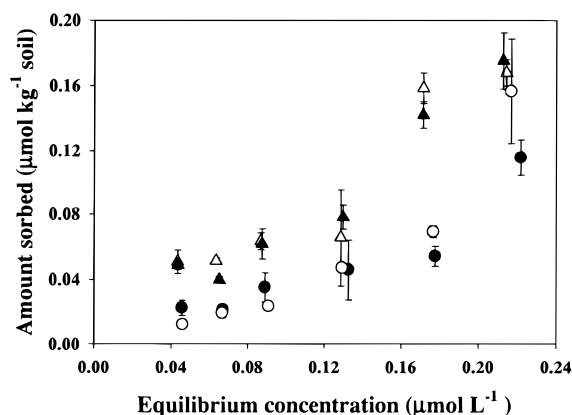


Figure 4. Pyriithiobac sorption isotherms for the Houston Black (▲), Hidalgo (○), Orelia (●), and Ships (△) soils expressed on a total weight basis. Error bars represent the standard error of each mean value.

experiments are needed with variable reaction conditions before further statements can be made regarding the pyriithiobac sorption mechanism.

The comparison of sorption capacity among reference sorbents was different when presented on an external surface area basis (Figure 3). The order of pyriithiobac sorption capacity changed to peat > kaolinite > bentonite \approx goethite. This implied that the kaolinite had a greater pyriithiobac sorption level per unit of surface area in comparison to the bentonite. Kaolinite develops a small positive charge under acidic conditions, which increases in magnitude when the pH is lowered (McBride, 1994). At pH 5.8, kaolinite probably developed sufficient positive charge to sorb pyriithiobac, which would be predominantly in anionic form. Similarly, Schofield and Samson (1953) observed that Cl^- was sorbed by kaolinite suspensions at a pH below 6.5 and was repelled at a higher pH.

Sorption of Pyriithiobac on Soils. Sorption capacity of the soils on a total weight basis generally increased with increasing organic carbon, clay, and iron oxide content (Figure 4 and Table 1). The pronounced increase in sorbed pyriithiobac that occurred at large C_e gave rise to nonlinear isotherms, resembling the S-shape curve described by Giles et al. (1960). These nonlinear isotherms indicate unfavorable sorption (Weber et al., 1991). Weak sorption was ascribed to repulsion of anionic pyriithiobac in predominantly alkaline and smectitic (negatively charged) soils.

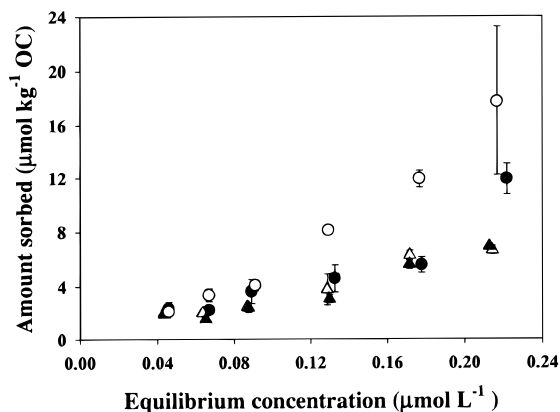


Figure 5. Pyrithiobac sorption isotherms for the Houston Black (\blacktriangle), Hidalgo (\circ), Orelia (\bullet), and Ships (\triangle) soils expressed on an organic carbon content basis. Error bars represent the standard error of each mean value.

Nonlinear sorption behavior reported at low concentrations for organic pollutants was attributed to sorption mechanisms having different concentration-dependent relationships which may control sorption over different concentration ranges as described by McGinley et al. (1993). Their modeling results indicated that nonlinear sorption behavior at low concentrations results from reactively heterogeneous solids (soils) having limited sorption capacity in different regions of reactivity. This model treats soil as an assemblage of discrete components, each of which exhibits a distinct sorption capacity.

Sorption isotherms for other low-use-rate, weakly acidic herbicides, such as the sulfonylureas, are generally linear at such low initial concentrations as used here (0.05–0.23 μM). Linear sorption isotherms were shown for primisulfuron [methyl 2-[[[[[4,6-bis(difluoromethoxy)-2-pyrimidinyl]amino]carbonyl]amino]sulfonyl]benzoate] (Ukrainczyk and Ajwa, 1996; Werkheiser and Anderson, 1996) on soils, whereas others reported strongly nonlinear sorption isotherms for primisulfuron at greater solution concentrations (Stehouwer et al., 1994).

Nonlinearity in sorption isotherms can lead to inaccurate determination of partition or distribution coefficients (K_d values) (Singh et al., 1990). Failure to consider isotherm nonlinearity has recently been reported to lead to considerable error in the estimation of transport parameters for herbicide experimental breakthrough curves (Spurlock et al., 1995). Linear fits of the sorption data for all of the soils resulted in $r^2 < 0.98$ (data not shown). Thus, the nonlinearity in pyrithiobac sorption isotherms for the soils precluded the calculation of a linear K_d value.

The high affinity of pyrithiobac for organic matter based on its sorption by the peat makes it reasonable to expect some dependence on soil organic carbon. Organic carbon normalization of the sorption data approximately collapsed the soil isotherms on each other, particularly at small C_e , and they spread apart at greater concentrations, with the Hidalgo soil exhibiting the greatest sorption capacity beyond 0.12 μM (Figure 5). The fact that the isotherms for the two highest organic carbon soils (Houston Black and Ships) were reasonably coincident with one another throughout the entire concentration range was expected because they both contain similar organic carbon contents and sorbed similar amounts of pyrithiobac on a total weight basis (see Figure 4).

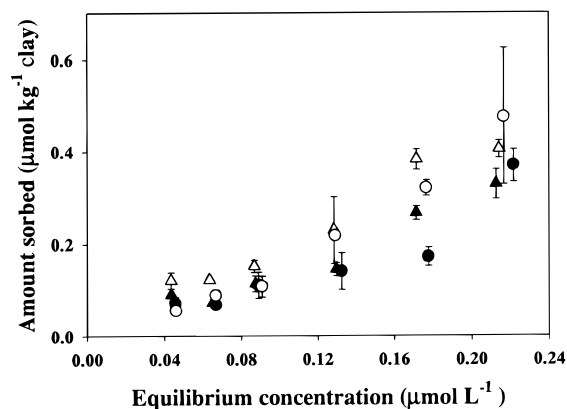


Figure 6. Pyrithiobac sorption isotherms for the Houston Black (\blacktriangle), Hidalgo (\circ), Orelia (\bullet), and Ships (\triangle) soils expressed on a clay content basis. Error bars represent the standard error of each mean value.

The strong nonlinearity of the organic carbon-normalized isotherms at greater C_e values was most pronounced for the Hidalgo and Orelia soils, which both contain $< 1\%$ organic carbon. Two possible reasons for this trend include the presence of different forms of organic matter with a continuous range of reactivities that are concentration dependent (Weber et al., 1992). In addition, previous work has shown that clay minerals may be controlling sorption of weak acid herbicides when soil organic carbon is low ($< 1\%$) and at pH values at which the herbicide was exclusively anionic (Goetz et al., 1986), which resembled conditions in the Hidalgo and Orelia soils. Partition theory, which assumes organic carbon to be the primary sorbent, did not predict pyrithiobac sorption (data not shown) in the alkaline soils, which could be expected because of pyrithiobac's greater water solubility at high pH values (pH 7.9–8.4). According to Green and Karickhoff (1990), partition theory should be used to predict sorption only if a herbicide's water solubility is < 1 mM.

Significant pyrithiobac sorption by the inorganic fraction of the soils would make it reasonable to expect some dependence on clay content. The clay content-normalized sorption isotherms for the four soils were more compressed than the organic carbon-normalized isotherms (Figure 6). However, these qualitative results limit the conclusions that can be drawn because soil organic carbon and clay content were highly correlated with each other ($r = 0.92$, $p < 0.001$), making it difficult to separate contributions from each to pyrithiobac sorption. Nonetheless, the nonlinearity in the low organic carbon soils (Hidalgo and Orelia) was apparently reduced more effectively in the clay content-normalized isotherms than in the organic carbon-normalized isotherms.

Clay mineral type may be more influential in separating differences in soil sorption capacities than clay content. The influence of soil kaolinite in sorption of other weak acid herbicides in soils has been discussed previously (Goetz et al., 1986; Che et al., 1992). Although all four soils contained predominantly smectitic clay mineralogy, three of the four contained discrete kaolinite on the basis of XRD analyses (Table 1). The Ships soil likely contained kaolinite, but its identification was precluded by the presence of the 14 Å chlorite peak. Relative contributions of soil kaolinite to pyrithiobac sorption could be described by normalizing sorption data to kaolinite content. Unfortunately, the

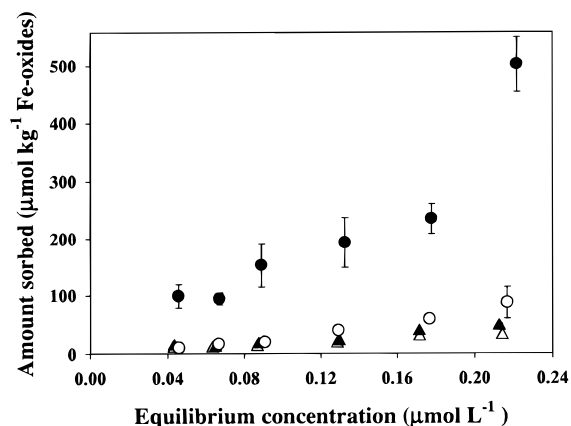


Figure 7. Pyriithiobac sorption isotherms for the Houston Black (▲), Hidalgo (○), Orelia (●), and Ships (△) soils expressed on an iron oxide content basis. Error bars represent the standard error of each mean value.

amount of kaolinite was not quantified in this study. Nonetheless, the high pyriithiobac sorption density on the reference kaolinite (see Figure 3) suggests the possible influence of small quantities of soil kaolinite in pyriithiobac sorption. The low iron oxide content in the Orelia soil explained the inflated pyriithiobac sorption capacity in this soil when sorption data were scaled to iron oxide content and indicated that iron oxides cannot control sorption in this soil (Figure 7). The high correlation between soil iron oxide and organic carbon contents ($r = 0.90$, $p < 0.001$) would likely explain the effective collapse of the iron oxide-normalized isotherms for the other three soils.

All reference sorbents exhibited greater sorption capacity than the soils. For instance, the goethite sorption maximum ($0.30 \mu\text{mol kg}^{-1}$ for $0.23 \mu\text{M}$ pyriithiobac added), which represented the reference sorbent with the least sorption capacity, sorbed 1.7 times more than the soil with the greatest sorption capacity (Houston Black, $0.17 \mu\text{mol kg}^{-1}$ for $0.23 \mu\text{M}$ pyriithiobac added). Previous studies with primisulfuron reported stronger sorption on pure minerals than soils, which was attributed to the masking of pH-dependent positively charged sites by soil organic matter coatings (Ukrainczyk and Ajwa, 1996). The effect of more positive charge per gram for kaolinite and goethite due to their pH-dependent charge surface properties probably would explain their significant pyriithiobac sorption capacity when compared to the alkaline soils, which are predominantly negatively charged due to the presence of smectite.

The small set of soils employed in this study with highly correlated physical and chemical properties limits the mechanistic inferences that can be made. To elucidate the sorption isotherm, a much larger set of soils with noncorrelated characteristics needs to be studied over a larger concentration range. In addition, more variation in reaction conditions (pH, ionic strength, Ca^{2+} concentration, temperature) coupled with spectroscopic evidence could shed some light on possible pyriithiobac sorption mechanisms such as inner sphere complexation, outer sphere complexation, or Ca -pyriithiobac ion pair partitioning (Jafvert et al., 1990).

Conclusions. There are no published studies on the sorption behavior of pyriithiobac on reference sorbents or field soils. This study was undertaken to evaluate pyriithiobac sorption on several reference sorbents and representative soils at concentrations encountered in the

field. Pyriithiobac was strongly sorbed by peat, which indicated that the organic matter fraction significantly influenced sorption of the anionic pyriithiobac compound. Reference kaolinite exhibited a greater pyriithiobac sorption density when compared to bentonite, which suggested that clay mineral type may be more influential in describing soil sorption capacities than clay content despite strong correlations among soil properties. However, pyriithiobac was weakly sorbed in all soils on the basis of low-affinity sorption isotherms on a total weight basis. Normalized pyriithiobac sorption isotherms revealed the importance of phyllosilicate minerals in pyriithiobac sorption in low organic carbon soils (<1%). The low sorption capacity in all four soils was ascribed to repulsion of anionic pyriithiobac in predominantly alkaline and smectitic (negatively charged) soils.

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