

Sorption and Desorption of Triadimefon by Soils and Model Soil Colloids

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Sorption–desorption of the azole fungicide triadimefon [1-(4-chlorophenoxy)-3,3-dimethyl-1-(1*H*-1,2,4-triazol-1-yl)-2-butanone] on eight soils and a series of single, binary, and ternary model soil colloids was determined using the batch equilibration technique. Regression analysis between Freundlich sorption coefficients (K_f) and soil properties suggested that both clay and organic C (OC) were important in triadimefon sorption by soils, with increasing importance of clay for soils with high clay and relatively low OC contents. Triadimefon sorption coefficients on soil were not significantly affected by the concentration of electrolyte or the presence of soluble soil material in solution, but they were highly dependent on the soil:solution ratio due to the nonlinearity of triadimefon sorption on soil. Freundlich sorption isotherms slopes were very similar for all soils (0.75 ± 0.02). Desorption did not greatly depend on the concentration at which it was determined and showed higher hysteresis for more sorptive soils. Results of triadimefon sorption on model sorbents supported that both humic acid and montmorillonite-type clay constituents contribute to triadimefon retention by soil colloids.

Keywords: *Triadimefon; sorption; desorption; soil constituents*

INTRODUCTION

Triadimefon [1-(4-chlorophenoxy)-3,3-dimethyl-1-(1*H*-1,2,4-triazol-1-yl)-2-butanone], also known as Bayleton, is a systemic fungicide with protective, curative, and eradicator action. It is used as a foliar fungicide (Wright et al., 1983) and as a soil fungicide (Hardison, 1976) in control of powdery mildews in cereals, vegetables, and fruits and in many diseases of turf (Tomlin, 1994).

Very little information has been published on the fate of triadimefon in soil. Some photolysis pathways that may result in deactivation have been reported (Clark et al., 1978; Hartmann and Schwack, 1994; Moza et al., 1995; Nag and Dureja, 1997), and losses by volatilization after field application have been evaluated (Murphy et al., 1996). However, data concerning the factors controlling triadimefon sorption in soil are even more limited. Sorption of several fungicides, including triadimefon, to thatch and a silty clay loam soil was determined (Dell et al., 1994). Because Freundlich sorption coefficients normalized to the organic C (OC) content for soil and thatch were similar, it was assumed that organic matter controlled sorption. However, there is no information available on triadimefon sorption by soils varying in their physicochemical characteristics, on the reversibil-

ity of the sorption–desorption process, or on the relative importance of the several soil constituents in triadimefon sorption–desorption by soil. This information is essential to understand the fate of an agrochemical in soil because retention processes determine the concentration of agrochemical in the soil solution, and consequently the amount that can reach the target organism and that can be leached, volatilized, and degraded.

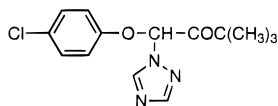
To evaluate the role of the different soil constituents in pesticide sorption, purified soil components, such as clay minerals, metal oxides, and humic acids, have been used as model sorbents (Yamane and Green, 1972; Weber, 1982; Laird et al., 1992; Pignatello and Xing, 1996). In the vast majority of the studies, the model sorbents used were single pure soil constituents that provided “clean” surfaces, whereas in natural colloids association processes between components may alter the sorbent availability for pesticide sorption (Karickhoff, 1984). Recently, there has been increased interest in the study of the behavior of model associations containing several constituents designed to simulate naturally occurring soil colloids (Fusi et al., 1993; Onken and Traina, 1997; Celis et al., 1998b).

In the present paper, the sorption–desorption of triadimefon by eight soils varying in their physicochemical properties is characterized. The effects of soil:solution ratio, electrolyte concentration, and soluble soil material on triadimefon sorption is reported. Also, a

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Table 1. Physicochemical Characteristics of the Soils

| soil | location | texture | organic C content (%) | clay content (%) | clay:organic C ratio | pH |
|-------------|----------------|-----------------|-----------------------|------------------|----------------------|-----|
| Winder | Vero Beach, FL | fine sand | 0.29 | 3.08 | 11 | 5.8 |
| Hanford | Fresno, CA | sandy loam | 0.41 | 6.90 | 17 | 6.1 |
| Tifton | Tifton, GA | sandy loam | 0.70 | 10.6 | 15 | 5.9 |
| Dundee | Benoit, MS | silty clay loam | 1.05 | 27.0 | 26 | 5.4 |
| Oska-Martin | Stilwell, KS | silty clay | 1.34 | 42.5 | 32 | 4.9 |
| Waukegan | Rosemount, MN | silt loam | 1.80 | 22.0 | 12 | 5.8 |
| Crane | Oxford, IN | silt loam | 2.50 | 26.1 | 10 | 4.6 |
| Drummer | Oxford, IN | silty clay loam | 3.95 | 32.1 | 8 | 5.3 |

**Figure 1.** Chemical structure of triadimefon.

series of single model soil constituents [clay minerals, Fe(III) oxide, humic acid] and binary and ternary associations of montmorillonite, Fe oxide, and humic acid are used to assess the relative importance of the main active soil constituents in triadimefon sorption in soil.

MATERIALS AND METHODS

Chemical. Pure analytical triadimefon (chemical purity >99%) was purchased from Chem Service (West Chester, PA). The radiochemical triadimefon was donated by Mobay Chemical Corp. (now Bayer Corp., Stilwell, KS). It was purified by HPLC using a Hewlett-Packard 1090 liquid chromatograph (Hewlett-Packard Co., Cupertino, CA), and final radiochemical purity was >98%. The following HPLC conditions were used: Lichrosphere 5 RP column of 250 mm length \times 4.0 mm i.d.; flow rate, 0.4 mL min⁻¹; eluent system, 65:35 (v:v) methanol:water; UV detection, 230 nm. Molecular structure of triadimefon is shown in Figure 1.

Soils. Eight U.S. soils with different physicochemical characteristics were used. Fresh soils from the 0–15 cm depth were collected, air-dried, and ground to pass a 2-mm sieve prior to use. Physicochemical characteristics of the soils are given in Table 1.

Model Sorbents. The single model soil constituents used were Georgia kaolinite (KGa-2), Montana illite (IMt-1), calcium-saturated Wyoming montmorillonite (CaSWy), poorly crystallized ferrihydrite (Ferrih), and Fluka commercial humic acid (Fluka HA). All clays were supplied by the Clay Minerals Repository of the Clay Minerals Society. To obtain CaSWy, the <2 μ m fraction of Wyoming montmorillonite (Crook County, WY) was saturated with Ca²⁺ by five successive treatments with 1 M CaCl₂, washed with deionized water until Cl⁻ free, and freeze-dried. Ferrih was prepared by neutralizing a 0.5 M Fe(NO₃)₃ solution with NH₄OH to a pH of 7.5, washing until NO₃⁻ free, and freeze-drying (Murad and Schwertmann, 1980). Fluka HA was used as supplied by Fluka Chem. Corp. Binary and ternary associations of montmorillonite, ferrihydrite, and humic acid simulating natural occurring soil colloids were also prepared. Preparation of these colloids has previously been described in detail (Celis et al., 1998b). In brief, montmorillonite was coated with two different amounts of ferrihydrite by neutralizing with 0.1 M NaOH (final pH = 7.5) suspensions containing 100 mL of Fe(NO₃)₃ (7.5 or 15 mM) and 2 g of CaSWy. CaSWy-Ferrih binary associations were washed with deionized water, centrifuged, and freeze-dried prior to use. CaSWy was also coated with two different amounts of HA by adding 2.5 g of clay to a solution (pH 6.5) of 500 mL of HA (500 or 1000 mg L⁻¹) previously dissolved using 0.5 mL of 1 M NaOH. Suspensions were shaken for 24 h, dialyzed against deionized water, and freeze-dried. CaSWy blank samples without Ferrih or HA were also prepared to separate the effects of the presence of Ferrih or HA coatings on CaSWy from alterations produced by the additional reactions during the synthesis of the associations. Finally, a

Table 2. Physicochemical Characteristics of the Model Sorbents

| model sorbent | Fe content (%) | organic C content (%) | pH | SSA ^a (m ² g ⁻¹) |
|----------------------|----------------|-----------------------|-----|--|
| KGa-2 | <i>b</i> | | 5.4 | 18 |
| IMt-1 | | | 6.1 | 30 |
| CaSWy | | | 7.9 | 23 |
| Ferrih | | | 5.6 | 315 |
| Fluka HA | | 40.8 | 4.6 | 0 ^c |
| CaSWy (blank) | 0 | | 6.3 | 18 |
| CaSWy-Ferrih | 1.88 | | 5.8 | 45 |
| CaSWy-Ferrih | 3.43 | | 5.7 | 56 |
| CaSWy (blank) | | 0 | 7.1 | 24 |
| CaSWy-HA | | 2.4 | 5.2 | 9 |
| CaSWy-HA | | 6.8 | 5.2 | 3 |
| CaSWy-Ferrih (blank) | 3.40 | 0 | 4.9 | 55 |
| CaSWy-Ferrih-HA | 3.10 | 4.3 | 4.9 | 10 |

^a Nitrogen specific surface area. ^b Not determined. ^c <1 m² g⁻¹.

montmorillonite-ferrihydrite-HA ternary model colloid was obtained by adding 2.5 g of the CaSWy-Ferrih binary association, prepared from the 15 mM Fe(III) solution, to a solution of 500 mL of 500 mg L⁻¹ Fluka HA. After shaking for 24 h, the CaSWy-Ferrih-HA ternary model colloid and its blank sample without HA were dialyzed in deionized water and then freeze-dried. Physicochemical properties of the model sorbents used are summarized in Table 2.

Characterization of Soils and Model Sorbents. Total OC measurements were performed using a Perkin-Elmer 240 C total elemental C analyzer (Perkin-Elmer Corp., Norwalk, CT). The Fe content of the binary and ternary model sorbents was determined by atomic absorption spectroscopy after oxalate extraction of the samples (McKeague and Day, 1966). For the pH measurements, 2 g of soil or 50 mg of model sorbent were equilibrated with 10 mL of 0.01 M CaCl₂ for 4 h, centrifuged, and the pH of the supernatant measured using a combination glass electrode. Specific surface areas (SSA) were obtained by N₂ adsorption at 77 K using a Carlo Erba Sorptomatic 1900 (Fisons Instruments, Milan). Samples were outgassed at 80 °C and equilibrated under vacuum for 15 h before measuring the N₂ adsorption isotherm.

Sorption. Triadimefon sorption isotherms on soil and model sorbents were obtained by the batch equilibration technique using 35 mL glass centrifuge tubes with Teflon-lined caps. Initial triadimefon solutions were prepared in 0.01 M CaCl₂ at concentrations ranging from 0.4 to 8.0 mg L⁻¹. Radiolabeled triadimefon was added to nonradioactive solutions to give a final solution radioactivity of ~70 Bq mL⁻¹. Triplicate 2-g soil or duplicate 50-mg model sorbent samples were equilibrated with 10 mL of triadimefon initial solution by shaking mechanically at 21 \pm 2 °C for 24 h. Batch kinetics studies were performed using the Drummer soil and showed that 24 h were sufficient to reach sorption equilibrium. After equilibration, the suspensions were centrifuged at 3000 rpm for 30 min, and 5 mL of supernatant were removed for analysis. Solutions shaken in tubes without solid served as controls and showed no loss of ¹⁴C from the solution during the equilibration periods.

The effect of soil:solution ratio, electrolyte concentration, and soluble soil constituents on triadimefon sorption by soil was determined at single triadimefon initial concentration 3 mg L⁻¹. Triadimefon sorption was measured at 0.5:10, 1:10,

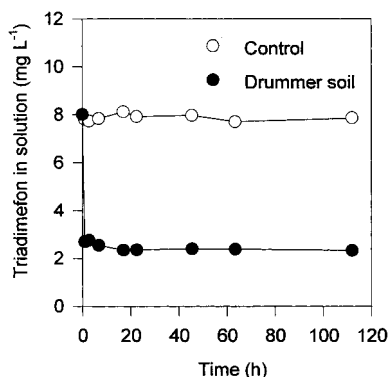


Figure 2. Triadimefon sorption kinetics on Drummer soil and control sample. Kinetics on soil were obtained at initial triadimefon concentration of 8.0 mg L⁻¹ and 2 g:10 mL soil:solution ratio.

and 2:10 soil:solution ratios (g:mL), at 0.001, 0.01, and 0.1 M CaCl₂ concentrations and in the presence of soil extract from the Drummer soil. The soil extract was obtained by shaking 100 g of soil with 100 mL of 0.01 M CaCl₂ for 4 h followed by centrifugation (30 min at 3000 rpm) and collection of the supernatant. Then, 2 mL of triadimefon stock solution (15 mg L⁻¹) was added to 8 mL of extract to obtain the 3 mg L⁻¹ triadimefon initial solution.

Desorption. Desorption was measured immediately after sorption from all the equilibrium points of the sorption isotherms of selected soils and from the highest equilibrium concentration in the case of model sorbents. The 5 mL of supernatant removed for the sorption analysis were replaced with 5 mL of 0.01 M CaCl₂. After shaking at 21 ± 2 °C for 24 h, the suspensions were centrifuged, and 5 mL of supernatant was removed for analysis. This desorption cycle was repeated four times.

Chemical Analysis. One-milliliter aliquots of the clear supernatants were mixed with 6 mL of Ecolite scintillation cocktail, and the radioactivity determined by liquid scintillation counting using a 1500 Packard Instruments liquid scintillation analyzer (Packard Instruments Co., Downers Grove, IL). The amount of triadimefon in solution was determined from the specific activity of the initial triadimefon solutions.

Data Analyses. The amount of sorbed triadimefon after equilibration was calculated from the difference between the initial and equilibrium solution concentrations. Sorption and desorption data were fit to the linearized form of the Freundlich equation

$$\log C_s = \log K_f + 1/n_f \log C_e \quad (1)$$

where C_s (mg kg⁻¹) is the amount of triadimefon sorbed at the equilibrium concentration C_e (mg L⁻¹), and K_f and $1/n_f$ are the empirical Freundlich constants.

When sorption was evaluated at single initial concentration, a distribution coefficient, K_d ($K_d = C_s/C_e$), was calculated. Sorption coefficients normalized to OC (K_{f-oc} or K_{oc}) were calculated by dividing the K_f or K_d values by the fraction of OC in the sorbent. Hysteresis coefficients, H , for the sorption-desorption isotherms were calculated according to

$$H = (1/n_{fd})/(1/n_f) \quad (2)$$

where $1/n_f$ and $1/n_{fd}$ are the Freundlich constants obtained for the sorption and desorption isotherms, respectively (O'Connor et al., 1980; Barriuso et al., 1994).

RESULTS AND DISCUSSION

Triadimefon Sorption-Desorption on Soils. Sorption kinetics obtained with the Drummer soil (Figure 2) showed that sorption equilibrium for triadimefon was reached very rapidly; more than 90% of the sorption

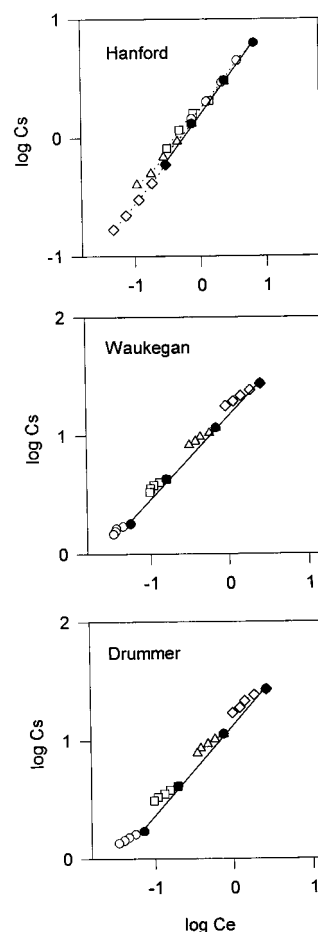


Figure 3. Triadimefon sorption-desorption isotherms on selected soils. Closed symbols are equilibrium sorption points, whereas open symbols are successive desorption points.

occurred within the first hour of shaking. A slight sorption took place from 1 to 17 h, and no difference in equilibrium concentration was measured during the next 95 h. Therefore, 24 h were considered sufficient to reach the sorption equilibrium for triadimefon. This was most likely true also for the other soils, since they usually had significantly lower organic C and clay contents than the Drummer soil. Control samples, without soil, showed no losses of fungicide due to sorption on glass, precipitation or volatilization (Figure 2), so differences in triadimefon concentrations after equilibration with the soil were assumed to be sorbed. No significant degradation was detected by HPLC after a 3-day period of shaking.

Triadimefon sorption isotherms for all eight soils showed marked curvature with Freundlich slopes ($1/n_f$) that were significantly less than 1 and very similar for all soils (Figure 3; Table 3). Dell et al. (1994) reported a value of $1/n_f = 0.73$ for triadimefon sorption on a Chalmers silty clay loam soil, that is also within the range of 0.71–0.77 obtained for our soils. The significance of $1/n_f < 1$ on triadimefon sorption is a high dependence of sorption on initial solution concentration, with higher sorption percentages at lower concentrations (Cox et al., 1997). It usually occurs when high-energy binding sites are limited, and progressive saturation of those sites occurs as the solute concentration increases (Weber and Miller, 1989; Dell et al., 1994).

The fact that Freundlich slopes, $1/n_f$, were not significantly different for all soils allowed comparison of the Freundlich K_f constants as a measure of the extent

Table 3. Triadimefon Freundlich Sorption Coefficients for the Different Soils

| soil | K_f ($\text{mg}^{1-1/n_f} \text{L}^{1/n_f}$) | K_{f-oc} | $1/n_f$ | r^2 |
|-------------|--|------------|-----------------|-------|
| Winder | 1.33 ± 0.15^a | 459 | 0.74 ± 0.13 | 0.970 |
| Hanford | 1.55 ± 0.04 | 378 | 0.75 ± 0.02 | 0.998 |
| Tifton | 1.96 ± 0.16 | 280 | 0.77 ± 0.09 | 0.987 |
| Dundee | 22.0 ± 2.7 | 2095 | 0.76 ± 0.05 | 0.995 |
| Oska-Martin | 16.5 ± 1.1 | 1231 | 0.73 ± 0.03 | 0.998 |
| Waukegan | 14.6 ± 0.6 | 811 | 0.71 ± 0.02 | 0.998 |
| Crane | 9.76 ± 0.55 | 392 | 0.75 ± 0.04 | 0.998 |
| Drummer | 13.6 ± 0.6 | 344 | 0.76 ± 0.03 | 0.998 |

^a Value \pm standard error.

of sorption for the different soils in the range of concentrations used. Regression analysis between the K_f values and selected soil properties showed that triadimefon sorption was poorly correlated with OC content ($R^2 = 0.19$) and pH ($R^2 = 0.28$) and slightly correlated with clay content ($R^2 = 0.68$). It appears that both clay and OC may have been important in triadimefon sorption on the soils and that the role of clay became even more evident for Dundee and Oska-Martin soils, most likely because their high clay content (>20%) was accompanied with a relatively low OC content (<2%). The high K_f values measured for Dundee and Oska-Martin soils as well as their high OC-normalized constants, K_{f-oc} , should be noted (Table 3). When these soils were not considered in the regression analysis a better correlation of K_f with both OC ($R^2 = 0.71$) and clay ($R^2 = 0.82$) was observed, probably due to the high correlation between clay and OC ($R^2 = 0.94$).

Mineral contributions to sorption may be significant or even dominate when the polarity of the sorbate is high or when the OC content of the sorbent is low, especially with coincident high clay content (Karickhoff, 1984). Mingelgrin and Gerstl (1983) proposed a clay:organic C ratio of 25–60 as “threshold” for mineral contributions in the case of neutral organics with polar functional groups. Our results indicate that mineral contributions to triadimefon sorption are evident for Dundee and Oska-Martin soils, which have clay:organic C ratios > 25 (Table 1). For soils with clay:organic C ratio < 25, a decrease in K_{f-oc} with increasing OC (Table 3) may indicate that OC have obscured the role of the mineral surfaces in triadimefon sorption. Decreases in K_{oc} as the OC content increases have been previously reported and attributed to some contribution of mineral surfaces to sorption at low OC fractions (Onken and Traina, 1997; Celis et al., 1998a). Onken and Traina (1997) pointed out that processes such as sorption or condensation of organic molecules on the mineral constituents could take place when the fractional OC is low, but they may be limited when the fractional OC is high.

When distribution coefficients were obtained for Drummer soil at different soil:solution ratios, an increase in K_d with increasing soil:solution ratio was observed (Table 4). This is usually attributed to an effect of a soluble soil component, such as salt concentration (Cox et al., 1998). However, experiments performed at different CaCl_2 concentrations, and in the presence of soil extract, showed no significant effect of these variables on triadimefon sorption (data not shown). Therefore, the increase in K_d with increased soil:solution ratio should be exclusively attributed to the nonlinearity of triadimefon sorption on soil. The values of $1/n_f < 1$ are indicative of a limited number of high-energy sorption sites, which makes sorption higher at low surface

Table 4. Triadimefon Sorption Distribution Coefficients on Drummer Soil Obtained at Different Soil:Solution Ratios

| soil:solution ratio (g:mL) | K_d^a (L kg^{-1}) |
|----------------------------|--------------------------------|
| 1:10 | 14.7 ± 0.7 |
| 2:10 | 16.9 ± 0.5 |
| 4:10 | 19.1 ± 0.3 |

^a Distribution coefficient ($K_d = C_s/C_e$) determined at single initial concentration of 3 mg L^{-1} .

coverage. At high soil:solution ratios, the number of sorption sites relative to the amount of triadimefon present increases, which results in higher sorption.

Triadimefon desorption isotherms determined for selected soils (Hanford, Waukegan, and Drummer) from all the sorption equilibrium points showed little dependence on the initial solution concentration (Figure 3, Table 5). For every equilibrium point, triadimefon desorption from the Hanford fine sandy loam soil was almost completely reversible, with hysteresis coefficients H close to unity. In the more sorptive Waukegan and Drummer soils, some hysteresis was observed, as indicated by the low $1/n_{fd}$ and H values (Table 5). Lower desorption in more sorptive systems has been attributed to irreversibility of strongly bound chemical to soil colloidal components, especially soil organic matter (Cox et al., 1997). For these two soils, desorption was not greatly dependent on the equilibrium concentration from which it was determined (Figure 3), although the decrease in the hysteresis coefficients with decreasing concentrations observed for Drummer soil (Table 5) may indicate that desorption from organic matter becomes even more difficult at low fungicide concentrations.

Triadimefon Sorption–Desorption on Model Sorbents. Among the single model sorbents studied, montmorillonite and HA were found to have the highest sorption capacity for triadimefon. Kaolinite did not sorb triadimefon, and the amounts sorbed by ferrihydrite and illite were lower than 10% of the chemical initially present in solution. Triadimefon sorption isotherm on CaSWy showed a high S-character (Giles et al., 1960) with $1/n_f > 1$. This has been traditionally attributed to competition with water molecules for sorption sites and interactions of the sorbed species at high surface coverage (Giles et al., 1960). From the molecular structure of triadimefon (Figure 1), it is very likely that sorption on the hydrophilic surfaces of montmorillonite occurred through the hydrophilic part of the molecule (carbonyl group and heterocyclic ring), so that interactions between the aromatic rings of the sorbed triadimefon species at high surfaces coverage could have taken place. In contrast, the value of $1/n_f < 1$ for HA may indicate that, as found for soils, binding sites are limited and progressive saturation of those sites occurs as the solute concentration increases (Weber and Miller, 1989; Dell et al., 1994).

In binary systems, greater sorption was observed on the CaSWy-Ferrih associations than on CaSWy alone, even though triadimefon was only slightly sorbed by Ferrih (Table 6). This effect has been previously observed for pesticides containing groups that can be protonated and attributed to sorption of the pesticide as cationic species as a result of either low pH or enhanced surface acidity of the montmorillonite surfaces coated with iron species (Celis et al., 1998b). In agreement with this hypothesis, triadimefon sorption on montmorillonite was found to greatly increase with

Table 5. Freundlich Desorption Constants, $1/n_{fd}$, and Hysteresis Coefficients, $H = (1/n_{fd})/(1/n_f)$, for Triadimefon Sorption–Desorption by Soils

| soil | initial concentration point for desorption | | | | | | | |
|----------|--|------|----------------------|------|----------------------|------|------------------------|------|
| | 8 mg L ⁻¹ | | 3 mg L ⁻¹ | | 1 mg L ⁻¹ | | 0.4 mg L ⁻¹ | |
| | $1/n_{fd}$ | H | $1/n_{fd}$ | H | $1/n_{fd}$ | H | $1/n_{fd}$ | H |
| Hanford | 0.68 ± 0.02 | 0.91 | 0.62 ± 0.03 | 0.83 | 0.62 ± 0.03 | 0.83 | 0.69 ± 0.01 | 0.92 |
| Waukegan | 0.42 ± 0.01 | 0.55 | 0.41 ± 0.03 | 0.54 | 0.46 ± 0.08 | 0.61 | 0.36 ± 0.08 | 0.47 |
| Drummer | 0.47 ± 0.05 | 0.62 | 0.45 ± 0.03 | 0.60 | 0.39 ± 0.02 | 0.51 | 0.32 ± 0.02 | 0.42 |

Table 6. Freundlich Sorption Constants, K_f and $1/n_f$, and Hysteresis Coefficients, H , for Triadimefon on Model Sorbents

| model sorbent | K_f (mg ^{1-1/n_f} kg ⁻¹ L ^{1/n_f}) | $1/n_f$ | H |
|--------------------------|--|-------------|------|
| IMt-1 | 15 ± 4 ^a | 1.03 ± 0.22 | |
| CaSWy | 92 ± 7 | 1.55 ± 0.08 | 0.43 |
| Ferrih | 7 ± 2 | 1.07 ± 0.22 | |
| Fluka HA | 610 ± 9 (1500) ^b | 0.89 ± 0.01 | 0.52 |
| CaSWy (blank) | 389 ± 16 ^c | | |
| CaSWy-Ferrih (1.88% Fe) | 410 ± 5 ^c | | |
| CaSWy-Ferrih (3.43% Fe) | 472 ± 23 ^c | | |
| CaSWy (blank) | 410 ± 1 ^c | | |
| CaSWy-HA (3.4% C) | 382 ± 1 ^c (11000) | | |
| CaSWy-HA (6.8% C) | 392 ± 6 ^c (5800) | | |
| CaSWy-Ferrih (blank) | 658 ± 10 | 1.31 ± 0.01 | 0.44 |
| CaSWy-Ferrih-HA (4.3% C) | 555 ± 25 (13000) | 1.17 ± 0.04 | 0.63 |

^a Value ± standard error. ^b Values in parentheses are C-normalized sorption coefficients (K_{oc}). ^c Distribution coefficient obtained at single initial concentration 8 mg L⁻¹.

Table 7. Effect of pH on Triadimefon Sorption by CaSWy

| initial pH | final pH | K_d (L kg ⁻¹) | % triadimefon sorbed |
|------------|----------|-----------------------------|----------------------|
| 6.7 | 6.9 | 119 ± 1 | 37 |
| 3.5 | 6.7 | 144 ± 11 | 42 |
| 3.0 | 3.6 | 754 ± 80 | 79 |
| 2.5 | 2.9 | 1956 ± 310 | 91 |

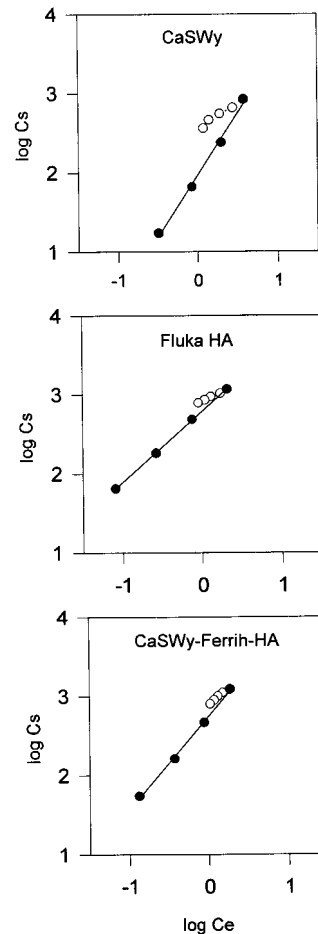
decreasing pH (Table 7) and became nearly 100% sorbed on Fe³⁺-saturated Wyoming montmorillonite (not shown). For pH associated with FeSWy (pH = 2.9), triadimefon is almost completely sorbed by CaSWy, most probably as protonated triadimefon cation (Table 7).

When CaSWy was coated with HA, the increase in sorption coefficient expected from the high triadimefon sorption on pure HA and low pH of the associations was not observed (Table 6). K_{oc} decreased as the OC in the association increased, thus becoming closer to the value obtained for pure HA. It seems that the association of HA with CaSWy reduced the availability of the mineral surfaces to sorb triadimefon. This effect was very similar to that observed in soils. A similar effect was also observed for CaSWy-Ferrih-HA ternary association. It should be noted, however, that the high K_{oc} value and the shape of the sorption isotherm (with $1/n_f > 1$) for CaSWy-Ferrih-HA ternary association indicated that much of triadimefon sorption took place on montmorillonite surfaces.

Desorption of triadimefon from the model sorbents was found to be hysteretic (Figure 4). The highest hysteresis (lowest H coefficients) was measured for CaSWy and could be due to intermolecular attraction between sorbed molecules on montmorillonite which should make desorption kinetically less favorable, especially at high surface coverage.

CONCLUSIONS

Triadimefon sorption isotherms on a number of soils and model soil colloidal sorbents simulating naturally

**Figure 4.** Triadimefon sorption–desorption isotherms on selected model sorbents. Closed symbols are equilibrium sorption points, whereas open symbols are successive desorption points.

occurring soil colloids have shown that both organic matter and soil clay are important in determining the sorption equilibrium for triadimefon in soil. The role of clay was particularly evident for soils with high clay contents and relatively low OC percentages (clay:organic C ratio > 25). A decrease in K_{oc} as the OC increased could be indicative of progressive coating of the mineral surfaces by the soil OC. The marked curvature of the sorption isotherms, with Freundlich slopes ($1/n_f$) significantly less than 1 for every soil, indicated binding sites for triadimefon were limited and resulted in higher sorption coefficients at low surface coverage. Lower desorption for more sorptive soils might indicate some irreversible binding of triadimefon to soil surfaces. The role of clay in the sorption of triadimefon was confirmed by the sorption results on model sorbents. Besides humic acid, montmorillonite showed a very high sorptive capacity for triadimefon, not only as single sorbent but also in binary and ternary associations containing montmorillonite as the most abundant component.

ABBREVIATIONS USED

CaSWy, calcium-saturated Wyoming montmorillonite; Ferrih, poorly crystallized ferrihydrite; HA, humic acid; IMt-1, Montana illite; KGa-2, Georgia kaolinite.

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LITERATURE CITED

- Barriuso, E.; Laird, D. A.; Koskinen, W. C.; Dowdy, R. H. Atrazine desorption from smectites. *Soil Sci. Soc. Am. J.* **1994**, *58*, 1632-1638.
- Celis, R.; Barriuso, E.; Houot, S. Sorption and desorption of atrazine by sludge-amended soil: dissolved organic matter effects. *J. Environ. Qual.* **1998a**, *27*, 1348-1356.
- Celis, R.; Cornejo, J.; Hermosin, M. C.; Koskinen, W. C. Sorption of atrazine and simazine by model associations of soil colloids. *Soil Sci. Soc. Am. J.* **1998b**, *62*, 165-171.
- Clark, T.; Clifford, D. R.; Deas, A. H. B.; Gendle, P.; Watkin, A. M. Photolysis, metabolism and other factors influencing the performance of triadimefon as a powdery mildew fungicide. *Pestic. Sci.* **1978**, *9*, 497-506.
- Cox, L.; Koskinen, W. C.; Yen, P. Y. Sorption-desorption of imidacloprid and its metabolites in soils. *J. Agric. Food Chem.* **1997**, *45*, 1468-1472.
- Cox, L.; Koskinen, W. C.; Yen, P. Y. Influence of soil properties on sorption-desorption of imidacloprid. *J. Environ. Sci. Health* **1998**, *B33*, 123-134.
- Dell, C. J.; Throssell, C. S.; Bischoff, M.; Turco, R. F. Estimation of sorption coefficients for fungicides in soil and turfgrass thatch. *J. Environ. Qual.* **1994**, *23*, 92-96.
- Fusi, P. P.; Arfaioli, L.; Calamai, L.; Bosetto, M. Interactions of two acetanilide herbicides with clay surfaces modified with Fe(III) oxyhydroxides and hexadecyltrimethylammonium. *Chemosphere* **1993**, *27*, 765-771.
- Giles, C. H.; MacEwan, T. H.; Nakhwa, S. N.; Smith, D. Studies in sorption. Part XI. A system of classification of solution desorption isotherms, and its use in diagnosis of desorption mechanisms and in measurement of specific surface areas of solids. *J. Chem. Soc. London* **1960**, 3973-3993.
- Hardison, J. R. Control of stripe and flag smut in Kentucky blue grass by a new systemic fungicide BAY MEB 6447. *Crop Sci.* **1976**, *14*, 769.
- Hartmann, M.; Schwack, W. Fungicides and photochemistry from model to field experiments. In *Book of Abstracts*, 8th IUPAC International Congress of Pesticide Chemistry, Washington, July 4-9, 1994; Vol. 1, p 350.
- Karickhoff, S. W. Organic pollutant sorption in aquatic systems. *J. Hydraul. Eng.* **1984**, *110*, 707-735.
- Laird, D. A.; Barriuso, E.; Dowdy, R. H.; Koskinen, W. C. Adsorption of atrazine on smectites. *Soil Sci. Soc. Am. J.* **1992**, *56*, 62-67.
- McKeague, J. A.; Day, J. H. Dithionite- and oxalate-extractable Fe and Al as aids in differentiating various classes of soils. *Can. J. Soil Sci.* **1966**, *46*, 13-22.
- Mingelgrin, U.; Gerstl, Z. Reevaluation of partitioning as a mechanism of nonionic chemicals adsorption in soils. *J. Environ. Qual.* **1983**, *12*, 1-11.
- Moza, P. N.; Hustert, K.; Feicht, E.; Kettrup, A. Comparative rates of photolysis of triadimefon in aqueous solution in the presence of humic and fulvic acid. *Chemosphere* **1995**, *30*, 605-610.
- Murad, E.; Schwertmann, U. The Mössbauer spectrum of ferrihydrite and its relations to those of other iron oxides. *Am. Miner.* **1980**, *65*, 1044-1049.
- Murphy, K. C.; Cooper, R. J.; Clark, J. M. Volatile and dislodgeable residues following triadimefon and MCPP application to turfgrass and implications for human exposure. *Crop Sci.* **1996**, *36*, 1455-1461.
- Nag, S. K.; Dureja P. Photodegradation of azole fungicide triadimefon. *J. Agric. Food Chem.* **1997**, *45*, 294-298.
- O'Connor, G. A.; Wierenga, H. H.; Cheng, H. H.; Doxtader, K. G. Movement of 2,4,5-T through large soil columns. *Soil Sci.* **1980**, *130*, 157-162.
- Onken, B. M.; Traina, S. J. The sorption of pyrene and anthracene to humic acid-mineral complexes: Effect of fractional organic carbon content. *J. Environ. Qual.* **1997**, *26*, 126-132.
- Pignatello, J. J.; Xing, B. Mechanisms of slow sorption of organic chemicals to natural particles. *Environ. Sci. Technol.* **1996**, *30*, 1-11.
- Tomlin, C. *The Pesticide Manual*; British Crop Protection Council: Surrey, U.K., The Royal Society of Chemistry: Cambridge, U.K., 1994.
- Weber, J. B. Ionization and adsorption-desorption of tricyclazole by soil organic matter, montmorillonite clay and Cape Fear sandy loam soil. *J. Agric. Food Chem.* **1982**, *30*, 584-588.
- Weber, J. B.; Miller, C. T. Organic Chemical Movement over and through Soil. In *Reactions and Movement of Organic Chemicals in Soils*; Sawhney, B. L., Brown K., Eds.; SSSA Spec. Publ. 22; ASA, CSSA, and SSSA: Madison, WI, 1989; pp 305-334.
- Wright, F. E.; Verser, J. W.; Gipson, R. D. Selective control of various foliar pathogens in wheat using fungicides. *Phytopathology* **1983**, *73*, 802.
- Yamane, V. K.; Green, R. E. Adsorption of ametryne and atrazine on Oxisol, montmorillonite, and charcoal in relation to pH and solubility effects. *Soil Sci. Soc. Am. Proc.* **1972**, *36*, 58-64.

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