

## Determining Kinetic and Nonequilibrium Sorption Behavior for Chlorpyrifos Using a Hybrid Batch/Column Experiment

STEVEN A. CRYER\*

Dow AgroSciences, LLC, 9330 Zionsville Road, Indianapolis, Indiana 46268

---

Pesticide mobility in soil is strongly coupled to the chemical's sorption characteristics. A modified soil column batch experiment was conducted to measure the transient nature of chlorpyrifos sorption and desorption from Cecil soil. This experimental system minimizes many shortcomings associated with obtaining sorption parameters by fitting soil column data to an advective–dispersive transport equation. Several chlorpyrifos formulations were investigated to determine how formulations affect soil sorption, and if this effect is adequately described using transient sorption/desorption algorithms. Both a second-order sorption with first-order desorption kinetic model and the two-site kinetic/equilibrium model were found to yield reasonable comparisons to experimental observations. In general, the formulation temporarily decreases the sorptivity of chlorpyrifos and alters the time for equilibrium to be achieved. Care must be exercised when extrapolating sorption data for a pure molecule in a laboratory setting to formulated materials used in field applications when environmental fate predictions are sought.

---

**KEYWORDS:** chlorpyrifos; sorption; kinetics; nonequilibrium

### INTRODUCTION

The transport and fate of chemical pesticides in the environment depend heavily on the sorptivity in soil (*1*). Understanding sorption–desorption of solutes in soils and the ability to mathematically approximate this behavior are important for predicting the transport of a solute in the environment. Sorption is defined as the global uptake of an organic solute into the soil solid phase, regardless of the mechanism. Many relationships describing the sorption of solutes into soils have been postulated (2–9), some of which are presented later in this article. A comprehensive review of pesticide sorption theory and experimental approaches are given elsewhere (10). However, in many cases there has not been enough experimental data to accurately assess the validity of various sorption algorithms and the assumptions on which these models were formulated.

Many investigators have studied equilibrium sorption behavior of pure solutes in soil (11–15). The sorption–desorption process can be characterized by the final equilibrium of the solute between the two phases and the time required to reach equilibrium. Experiments to quantify equilibrium sorption are only concerned with equilibrium conditions and not the transient nature of sorption–desorption as equilibrium is approached. Batch experiments are performed by combining water, soil, and pure solute, agitating, and recording the final solute equilibrium concentrations in each phase. However, actual field applications of pesticides consist of mixtures (formulations) containing the active ingredient. Little is known about the

behavior of formulated materials (formulations) containing the pure solute (the active), the longevity of the formulation, or the effects (if any) on the environmental fate of the active molecule. Several chlorpyrifos formulations were investigated to determine how formulations affect soil sorption, and if this effect could be adequately described using transient sorption–desorption mathematical models. Formulations provide a barrier around the chlorpyrifos molecule which affects the sorptivity of the active ingredient. Observed apparent sorption and desorption for chlorpyrifos formulations were quantified using various kinetic and nonequilibrium sorption–desorption algorithms.

### BACKGROUND

Laboratory soil column studies have been used to study pesticide movement through various water-saturated soils. A constant flow rate of water is typically pumped through the column to mimic groundwater or surface water movement in a saturated soil. An organic solute of known concentration is applied to the column over a specified time interval. The transport characteristics of the solute “pulse” are recorded by observing the concentration of solute in the effluent stream leaving the column.

One-dimensional mathematical models (based on conservation of mass) have been postulated to describe solute transport in laboratory soil columns. These models consider transport through the soil column by the superficial velocity of the bulk aqueous stream (volume flow of water divided by the cross-sectional area of the column) and dispersion. Attempts to account for sorption are included in these mathematical models,

---

\* To whom correspondence should be addressed. E-mail: sacryer@dow.com; telephone: 317 337-3428.

and thus various sorption algorithms can be incorporated into the model to yield predictions that closely match lab observations.

Observations of solute breakthrough in the column, along with dispersion characteristics of the pulse exiting the column, are used via an inverse problem (comparing model predictions to experimental observations) to calculate sorption parameters. By pulsing the column, both sorption and desorption can be independently characterized (4).

The mathematics used to describe (e.g., model) convection, dispersion, and accumulation of mass are rigorous and based on sound physical arguments (16). Similarly, the use of a constitutive expression for the sorption of a solute in soil is physically sound. However, the exact structure of any model attempting to describe sorption is arbitrary because the mechanisms for sorption and/or desorption are not fully known or understood at present. This has prompted researchers to propose different constitutive relationships (e.g., mathematical algorithms) to describe possible sorption mechanisms. These proposed sorption models have been used with various degrees of success in the mass conservation equation to predict solute transport through soil columns (17–19). However, the use of inverse techniques to determine sorption parameters is biased by the particular transport model and fitting procedures that are used (18).

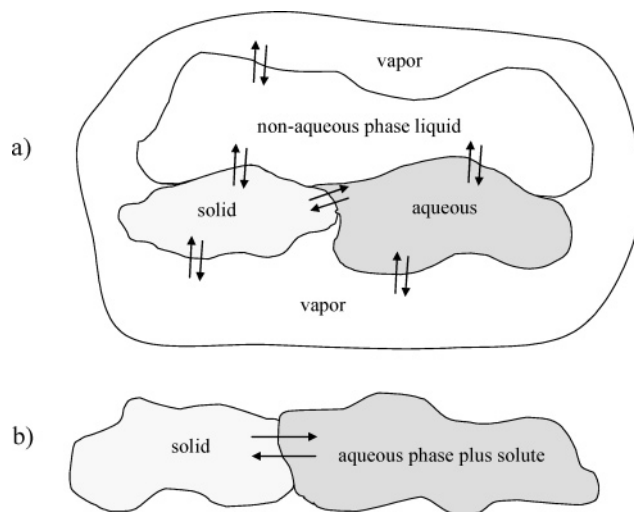
Many researchers have found good agreement between batch and column experiments for sorption parameter estimates (20–22), while others have seen the opposite (23–25). This study outlines a hybrid experimental protocol and procedure to obtain time-dependent sorption and desorption data that integrate the favorable features of batch and column experiments, thus eliminating the necessity of using a transport model for the inverse problem to determine sorption parameters. The experimental data obtained in this study is compared to various kinetic and nonequilibrium sorption models where sorption and desorption are occurring simultaneously. An exact closed form solution can be obtained for all algorithms specified in this study. The governing kinetic equations and their solutions are presented.

## METHOD AND MATERIALS

**Sorption/Desorption Models. The Equilibrium Model.** Partitioning between aqueous and solid phases is generally assumed to occur instantaneously. Thus, sorption between phases is often assumed to be at equilibrium and independent of contact time. The most widely used constitutive relationship for these assumptions is given by the Freundlich isotherm where  $S$  and  $C$  are the sorbed-phase ( $\mu\text{g g}^{-1}$ ) and solution-phase ( $\mu\text{g ml}^{-1}$ ) concentrations of the sorbate, respectively (eq 1). The constants  $N$  and  $k_d$  (sorption coefficient) are obtained by curve fitting eq 1 to experimental data. Equation 1 cannot account for any desorption or transient behavior. A second Freundlich isotherm is often constructed for desorption. The time interval when equilibrium has been reached is determined by the experimenter. Equilibrium is assumed when changes in the aqueous solute concentration cease. Typical times when equilibrium has been reached are on the order of 24 hours (26–27).

$$S = k_d C^{1/N} \quad (1)$$

The Freundlich isotherm can be a poor choice for incorporation into the mass continuity equation because instantaneous sorption does not occur for many organic compounds. Only qualitative information can be elucidated from equilibrium data and the equilibrium sorption coefficient (i.e., large  $k_d$  suggests strong sorption and low soil mobility, while small  $k_d$  suggests the opposite). The equilibrium model is inadequate to describe many experimental and environmental scale studies due to the assumptions on which it is based. This may account



**Figure 1.** Typical phases in a soil system where mass transfer of a solute can occur.

for many of the poor comparisons between model predictions and soil column observations where equilibrium sorption is assumed.

**Nonequilibrium and Kinetic Models.** Laboratory observations have indicated that sorption and desorption for many compounds to soil may be a nonequilibrium process and kinetically governed. Nonequilibrium models have been postulated and used to quantify sorption for molecules that deviate from simple equilibrium approximations (26,28–32). **Figure 1a** illustrates how mass (i.e., the solute) can be transferred between different phases in the system. Four phases can exist: the solute phase (also known as the nonaqueous phase liquid (NAPL) if the water solubility is low and the solute exists as a liquid or is dissolved in a solvent other than water at ambient temperatures), the aqueous phase, the vapor phase, and the soil or solid phase. The NAPL phase can incorporate formulated solute materials, as well as the pure solute compound. Sorption and desorption can occur simultaneously between each phase as indicated by the arrows in **Figure 1a**. The rate of mass transfer between phases is assumed proportional to a rate constant “ $k$ ”. The larger the magnitude of the rate constant, the faster the speed to which equilibrium is attained.

The general rate expression describing solute mass transfer from and to the aqueous phase using traditional chemical kinetics is

$$\frac{dC}{dt} = [k_1 g_1(C) - k_2 g_2(S)] + [k_3 g_3(C) - k_4 g_4(\text{NAPL})] + [k_5 g_5(C) - k_6 g_6(\text{vapor})] \quad (2)$$

where

$C$  = concentration of solute in aqueous phase

$S$  = concentration of solute in solid phase

NAPL = concentration of solute in nonaqueous phase liquid

vapor = concentration of solute in vapor phase.

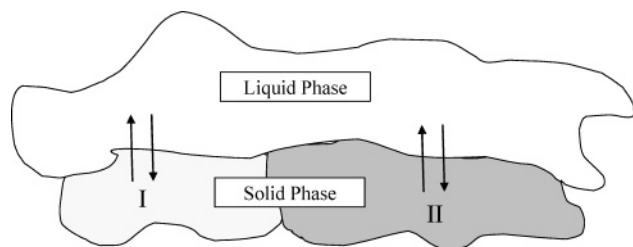
$g_i(C)$ ,  $i = 1, 3, 5$ ,  $g_2(S)$ ,  $g_4(\text{NAPL})$ , and  $g_6(\text{vapor})$  are undetermined functions of the solute concentrations in aqueous, solid, NAPL, and vapor phases, respectively, and the  $k_i$  values are the kinetic rate constants. The left-hand side of eq 2 represents the net rate of change of solute in the aqueous phase ( $C$ ) with respect to time. The first term on the right-hand side of eq 2 represents sorption–desorption between the aqueous and solid phases. Similarly, the second term of eq 2 approximates sorption–desorption between the aqueous and NAPL phases, and the third between the aqueous and vapor phases.

**Figure 1a** reduces to **Figure 1b** when the NAPL and vapor phase mass transfer are negligible. In this limit, eq 2 simplifies to

$$\frac{dC}{dt} = [k_1 g_1(C) - k_2 g_2(S)] \quad (3)$$

subject to the initial condition  $C(0) = C_0$ .

Here,  $g_1(C)$  and  $g_2(S)$  are undetermined functions of  $C$  and  $S$ , respectively.  $C_0$  is the initial concentration of solute in the aqueous



**Figure 2.** Schematic representation of the two-site kinetic/equilibrium sorption-desorption model. Type I sites are in equilibrium, type II sites are kinetically governed, and  $f_1$  equals the fraction of exchanges sites assumed to be in equilibrium.

**Table 1.** Summary of the Kinetic Algorithms Used in This Study<sup>a</sup>

algorithm	$F(C)$	$G(S)$
first-order sorption	$C$	$0$
second-order sorption	$C^2$	$0$
first-order sorption with first-order desorption	$C$	$S$
second-order sorption with first-order desorption	$C^2$	$S$

<sup>a</sup>  $F(C)$  and  $G(S)$  are concentration-dependent functions in eq 8.

phase at time zero. It is assumed that stable emulsifiable formulations (which contain surfactant around the active pesticide) can be modeled as a single solute phase. A popular nonequilibrium model is the transient extension of the Freundlich isotherm (eq 1). Equation 4 is a simplified kinetic expression for mass transfer between the aqueous and solid phases

$$\frac{dS}{dt} = k_2 \left( \frac{k_1}{k_2} C^m - S \right) \quad (4)$$

with initial condition  $S(0) = S_0 = 0$ , and

$$C(t) = C_0 - S(t) \quad (5)$$

with the initial condition  $C(0) = C_0$ .

Here,  $C$  and  $S$  represent time-dependent solute and soil concentrations, respectively.  $C_0$  and  $S_0$  are the initial concentrations of solute in the aqueous and solid phase, and  $m$  is an empirical constant. In this study, the initial concentrations for  $S$  are taken as zero (i.e., the solid phase is void of solute before the experiment has begun). Equation 4 is an “ $m$ ”-order kinetic rate expression for forward (sorption) and first-order reverse (desorption). Equation 4 is sometimes referred to as one-site kinetic adsorption. Clearly, one finds eq 4 reduces to eq 1 in the limit of time ( $t \rightarrow \infty$ ,  $m = 1/N$ , and  $k_d = k_1/k_2$ ).

From continuity of mass (eq 5), it readily follows  $dS/dt = -dC/dt$  (i.e., the rate of change of solute from the aqueous phase is equal to the rate of change in the solid phase). Two other simple kinetic models that exclude desorption are investigated. The solute concentrations in the aqueous phase are modeled using classical first- or second-order kinetics.

$$\frac{dC}{dt} = -k_m C^\sigma \quad (6)$$

subject to  $C(0) = C_0$ , and

$$S = C_0 - C(t) \quad (7)$$

subject to  $S_0 = 0$ .

Here,  $\sigma$  equals 1 or 2 for first- and second-order kinetics, respectively. A summary of the kinetic models used in this study is given in **Table 1**, with the generic form of the sorption-desorption algorithm given by eq 8.

$$\frac{dC}{dt} = k_1 F(C) - k_2 G(S) \quad (8)$$

**Two-Site Equilibrium/Kinetic Sorption Model.** **Figure 2** is a schematic representation of the two-site equilibrium/kinetic sorption model (33–35). This model assumes the solid phase consists of two individual regions (sites I and II). One region (site I) is at equilibrium with the aqueous phase (in terms of sorption), while the other (site II) is governed by first-order kinetics. These sites are also thought to represent chemical and physical restricted domains for sorption. This analysis does not attempt to deduce the actual sorption-desorption mechanisms, but rather uses inverse solution techniques to obtain pseudo coefficients that characterize the experimental observations, regardless of the exact nature of the behavior involved. The mass transfer between each phase due to sorption-desorption can be written as

$$\frac{dS_I}{dt} = f_1 k_1 \frac{dC}{dt} \quad (9)$$

$$\frac{dS_{II}}{dt} = \alpha [(1 - f_1) k_1 C - S_{II}] \quad (10)$$

subject to  $S_I(0) = S_{II}(0) = 0$ , and where

$k_1$  = rate constant for first-order sorption (dimensionless)

$k_2$  = rate constant for second-order desorption ( $\text{hr}^{-1}$ )

$\alpha = k_2/k_1$  = ratio of rate constants ( $\text{hr}^{-1}$ )

$f_1$  = fraction of type I sites

The total amount of solute sorbed into the solid phase is the sum from regions I and II.

$$S_{\text{total}} = S_I + S_{II} \quad (11)$$

The concentration of solute in the aqueous phase can be determined by conservation of mass as

$$C = C_0 - S_I - S_{II} \quad (12)$$

**Closed Form Solutions.** Equations 4–10 can be integrated directly (initial conditions are  $C(0) = C_0$ ,  $S(0) = 0$ ) to obtain analytical expressions for solute concentration in both the aqueous and solid phases (**Table 2**). Once  $C$  is known,  $S$  is easily determined by mass continuity (eq 5 or eq 12).

**Experimental Apparatus.** A general procedure for evaluating sorption models has been to curve fit lab scale soil column data with the conservation of mass model (typically a 1-D convection-dispersion model that ignores radial and azimuth convection-dispersion (17)). This can be a reasonable method of comparison if the conservation of mass model is globally correct. The mathematical model generally employed for predicting solute transport through soil columns is decoupled from the conservation of momentum equation (i.e., velocity is constant everywhere), and the physical properties of the medium remain constant and uniform over time. These assumptions exhibit various degrees of validity for an actual experimental column.

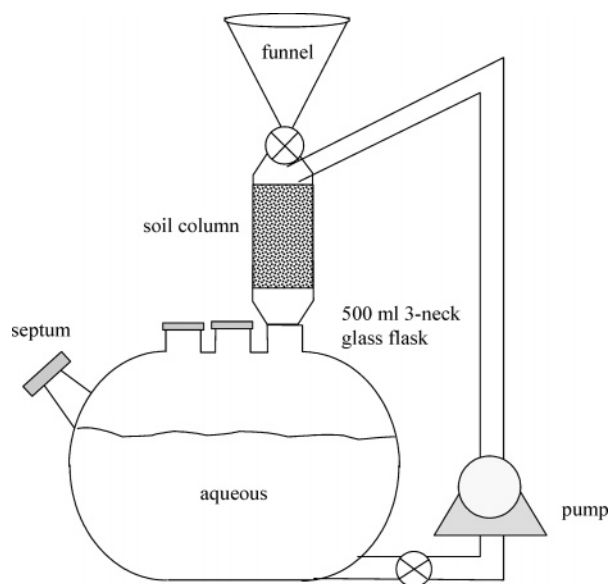
Trying to validate various sorption models via inverse use of a 1-D solute transport model and experimental column data can be misleading because of uncertainties and numerical dispersion associated with the transport model itself (irrespective of which sorption model is incorporated). Limitations include variations in column flow and/or immobile water zones, heterogeneity of the soil column due to the size and mass of soil required, the uncertainty associated with the transport model in predicting “reality”, and in the curve-fitting procedure required for the inverse problem. The 1-D transport model can and does yield quantitative information, but this information is limited by the assumptions on which the model is based.

**Figure 3** illustrates the experimental apparatus used in this study to evaluate different sorption models. A small soil column (i.d. = 2.54 cm, length = 2.54 cm) occupies one neck of a 500 mL three-neck flask. Water is pumped continuously from the flask to the soil column using a peristaltic pump. The fluid passes through the soil and returns back to the flask. The aqueous fluid is continually agitated using a Teflon stirring bar and magnetic stirrer. The tubing connecting the flask/pump/column is 0.635 cm o.d. Teflon. All fittings and stopcocks are Teflon. A stainless steel mesh is used at the bottom of the column to

**Table 2.** General Solution of Kinetic Sorption/Desorption Equation,  $dC/dt = -k_1C^m + k_2S^n$ , with Initial Conditions of  $C(0) = C_0$ ,  $S(0) = 0$ 

description	solution
first-order sorption ( $m = 1, n = 0$ )	$\frac{C}{C_0} = \exp(-k_1t)$
second-order sorption ( $m = 2, n = 0$ )	$\frac{C}{C_0} = \frac{1}{1 - k_1C_0t}$
first-order sorption with first-order desorption ( $m = 1, n = 1$ )	$\frac{C}{C_0} = \frac{\exp[-k_1(1 - \alpha)t] + \alpha}{1 + \alpha}$
	where
	$k_2 = k_1, \alpha = \frac{C}{C_0} \frac{1 - C/C_0}{1 - C/C_0}$
	at equilibrium
second-order sorption with first-order desorption ( $m = 2, n = 1$ )	$\frac{C}{C_0} = \frac{-k_2}{2K_1} + \frac{\beta}{2K_1} \left[ \frac{\alpha_2 \exp(\beta t) - 1}{\alpha_2 \exp(\beta t) + 1} \right]$
	where
	$K_1 = k_1C_0, \beta = (k_2^2 + 4K_1k_2)^{1/2}, \alpha_2 = \frac{-2K_1 - k_2 - \beta}{-2K_1 - k_2 + \beta}$
	$k_2 = \gamma K_1, \gamma = \frac{(\frac{C}{C_0})^2}{1 - \frac{C}{C_0}}$
two-site kinetic/equilibrium model <sup>a</sup>	$\frac{S_1}{C_0} = \varphi_1 \exp(-\beta t) + \varphi_2 + 1$
	$\frac{S_{II}}{C_0} = -\frac{\varphi_1 b_2}{a_2} \exp(-\beta t) + \frac{a_1(1 - \varphi_2)}{a_2}$
	$\frac{C}{C_0} = 1 - \frac{S_1}{C_0} - \frac{S_{II}}{C_0}$
	where
	$a_1 = \frac{f_1\gamma}{1 + f_1\gamma} + b_1, a_2 = a_1 + \frac{f_1\gamma\alpha}{1 + f_1\gamma}, b_1 = \alpha(1 - f_1)\gamma$
	$b_2 = \alpha[(1 - f_1)\gamma + 1], \varphi_1 = \frac{2a_1}{b_2 - a_1}, \varphi_2 = -\varphi_1 - 1, \beta = b_2 - a_1$

<sup>a</sup> Equations 8 and 9 can be integrated directly to obtain a closed form solution for the two-site kinetic/equilibrium model. Both  $\alpha$  (ratio of rate constants) and  $f_1$  (fraction of type I sites) are free parameters.

**Figure 3.** Experimental apparatus.

keep soil from entering the flask while still passing water. This apparatus offers advantages over a traditional batch equilibrium experiment by

providing a septum port (mounted on the side) for withdrawing transient aqueous samples for analytical analysis and by providing an agitation regime more closely approximating flow in saturated porous media.

The apparatus represented in **Figure 3** eliminates many of the uncertainties associated with large-scale column studies. The smaller column volume ( $12.9 \text{ cm}^3$ ) provides a higher likelihood of obtaining a homogeneous soil medium. In addition, the time delay between water entering and exiting the column is minimized. The effluent leaving the column was not discarded, but is remixed into a bulk reservoir (i.e., the flask). Fluid from the reservoir was continually recirculated to the column. The apparatus is analogous to a chemical batch reactor (as the time delay for fluid circulating between the soil column and reservoir ( $\sim 1 \text{ min}$ ) is orders of magnitude greater than the time scale associated with the kinetic experiment (days)). The concentration of solute was known (i.e., measured) in the aqueous phase before being recirculated through the soil column (time =  $t_0$ ). As time progressed from  $t_0$ , the solute was sorbed into the soil, and this rate of sorption  $dC/dt$  was measured by samples taken at various time intervals. The rate of sorption was given by the decrease of the initial solute concentration in the aqueous phase (i.e., the amount of solute sorbed into the soil is given by the initial solute concentration in the aqueous phase ( $C_0$ ) minus the aqueous solute concentration at various times  $C(t)$ :  $dS/dt = -dC/dt$ ). Both sorption and desorption processes occur simultaneously in this batch system. Kinetic data are used to compare various sorption-desorption models presented in this article.

## EXPERIMENTAL PROCEDURE

The soil column was first saturated with 100 mL of distilled water. The water was added via the funnel on top of the column. An additional 100 mL of water was added to the flask through one of the unused flask necks. A known amount of  $^{14}\text{C}$ -labeled chlorpyrifos formulation was added to the glass flask the evening before the experiment was initiated to allow for equilibrium sorption–desorption to be reached between the solute and glass walls of the flask. The soil column contained Cecil soil (Typic Hapludult, Clayey, Kaolinitic, Thermic, silty clay loam, pH = 5.8, % organic carbon = 0.34, % sand = 70, % silt = 12, % clay = 18%).

Three 50  $\mu\text{L}$  aliquot samples were withdrawn (the following morning) after equilibrium between the radio labeled solute and glass reactor had been attained. The flask stopcock was then opened, and the pump was activated ( $t = t_0$ ). The flow rate of the pump was 0.9  $\text{mL min}^{-1}$ , which is faster than representative water infiltration rates in soil. Three 50  $\mu\text{L}$  aliquots were withdrawn at each sampling interval, and the radioactive readings from scintillation counting were measured (variance of less than 1%). The time difference relative to  $t_0$  for each sample aliquot was recorded. The experiment was concluded when the concentration of solute in the aqueous phase remained constant with time (i.e., the system attained equilibrium). The total amount of mass (volume) withdrawn for samples was insufficient to necessitate any corrections to the results. In addition, it was assumed that no chlorpyrifos degradation occurred over the time interval of the experiment.

Three different chlorpyrifos formulations were used. Two of the three formulations are commercially available (Lorsban 4E insecticide and Lorsban R insecticide). The third is an experimental formulation (XRM) containing polymeric surfactant. Both Lorsban 4E insecticides as well as XRM are formulations of chlorpyrifos, while Lorsban R insecticide is near pure (99%) chlorpyrifos.

**Determination of Rate Constants from Experimental Data.** The parameters in eqs 4–12 were determined by curve-fitting the analytical solutions to the experimental data. A linear least-squares approach was employed which sought to minimize the sum of the squared residuals (eq 13).

$$\epsilon^2 = \sum_{i=1}^W (C_{\text{model}} - C_{\text{experiment}})^2 \quad (13)$$

where

$C_{\text{model}}$  = concentration of solute in aqueous phase predicted by kinetic model

$C_{\text{experiment}}$  = actual concentration of solute in aqueous phase observed experimentally.

$W$  = number of experimental data points available

Rate constants were adjusted in an iterative fashion to obtain the minimal value of eq 13. The sum of the squared errors ( $\epsilon^2$ ) and kinetic parameters for various models obtained by this method are tabulated in Tables 3 and 4.

## RESULTS

Experimental data from a typical run are represented in Figure 4a,b along with several sorption–desorption algorithm predictions. This experiment consisted of using Lorsban 4E insecticide at an initial concentration of 61  $\mu\text{g mL}^{-1}$ . This concentration is above the chlorpyrifos solubility limit in water (0.94–2.0  $\mu\text{g mL}^{-1}$  in water (36)). It is postulated that the stable emulsion remains intact over the time interval of the experiment, and thus formulation components are not separated within the soil column. The solute was found to readily sorb during the first 6 h of the experiment, which was followed by a slower asymptotic approach to equilibrium. The first-order kinetic model for sorption overestimates the sorptivity seen experimentally (i.e., Table 3). A closer match to experimental data is obtained when the model considers both sorption and desorption as first-order processes. However, a second-order sorption model

**Table 3.** Summary of Kinetic Parameters and Residuals for Kinetic Algorithms<sup>a</sup>

formulation	first	second	first/first	second/first
XRM				
$k_1^b$	$3.57 \times 10^{-2}$	2.90	$4.55 \times 10^{-2}$	3.06
$k_2^b$	—	—	$1.32 \times 10^{-2}$	$3.54 \times 10^{-3}$
$\epsilon^2$	$4.40 \times 10^{-2}$	$4.14 \times 10^{-2}$	$4.07 \times 10^{-2}$	$5.69 \times 10^{-2}$
Lorsban 4E Insecticide				
$k_1^b$	0.354	37.9	0.384	38.5
$k_2^b$	—	—	$2.45 \times 10^{-2}$	$2.36 \times 10^{-3}$
$\epsilon^2$	$6.18 \times 10^{-2}$	$5.64 \times 10^{-2}$	$2.71 \times 10^{-2}$	$3.46 \times 10^{-3}$
Lorsban R Insecticide				
$k_1^b$	0.481	42.5	0.693	67.0
$k_2^b$	—	—	0.173	$3.12 \times 10^{-2}$
$\epsilon^2$	0.257	0.181	0.194	0.293

<sup>a</sup> Here,  $k_1$  and  $k_2$  are the rate constants for sorption and desorption, respectively. Column headings are for sorption–desorption algorithms. <sup>b</sup> Units for  $k$  with first-order kinetics are ( $\text{hr}^{-1}$ ). Units for  $k$  with second-order kinetics are ( $\mu\text{g mL}^{-1} \text{hr}^{-1}$ ).

**Table 4.** Summary of Kinetic Parameters and Residuals for the Two-Site Kinetic/Equilibrium Model Employed in This Study

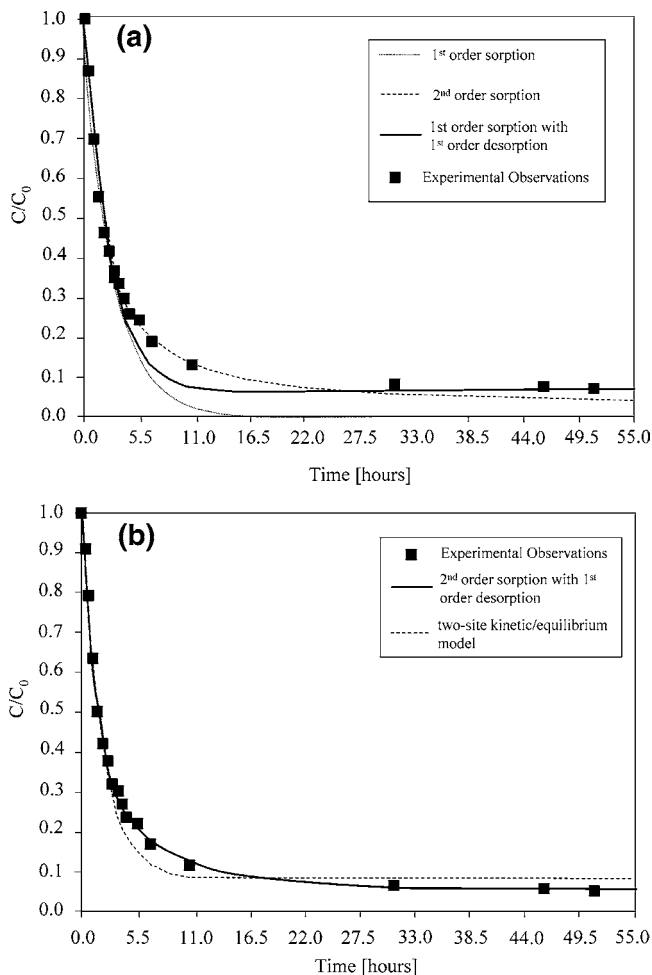
material	$f_1$	$\alpha$ ( $\text{hr}^{-1}$ )	$\epsilon^2$
XRM	0.450	0.027	$3.29 \times 10^{-2}$
Lorsban 4E insecticide	0.524	0.253	$1.88 \times 10^{-2}$
Lorsban R insecticide	0.600	2.03	0.276

(with no desorption) is seen to provide a better agreement with experimental results.

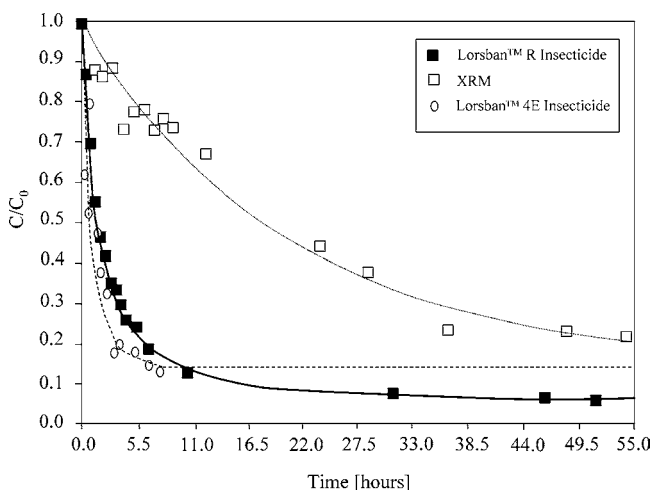
Figure 4b illustrates the comparison of experimental observations for the Lorsban 4E insecticide to the more advanced algorithms employed in this study. As expected from the results represented in Figure 4a, a second-order sorption with a first-order desorption algorithm gave excellent comparisons with experiment. Similarly, the two-site kinetic/equilibrium model gave good comparisons. Parameters characterizing these algorithms, based upon experimental observations, are summarized in Table 4. It should be noted that the two-site model is more robust than the other models chosen simply because of the additional parameter in this model (i.e., the fraction of equilibrium sites “ $f_1$ ”).

Figure 5 represents the experimental results obtained for three chlorpyrifos formulations at approximately the same initial chlorpyrifos concentrations ( $C_0 = 50\text{--}61 \mu\text{g mL}^{-1}$ ). These initial starting concentrations are within the range of a dilute tank mix spray solution for Lorsban 4E insecticide. Figure 5 clearly indicates that the formulation plays a significant role in the sorptivity of a pesticide. The general trend appears to be a decrease in the sorptivity as the stability (i.e., formulation integrity before being separated into components) of the formulation increases. Emulsions can possibly create a stable boundary layer around the chlorpyrifos/cosolvent phase which inhibits sorption or provide a competition for sorption sites between the active ingredient and formulation components. Determining the sorption of various pesticides has generally been confined to pure compounds. Undoubtedly, formulated materials require further study to establish relationships between the pure solute and the solute that is stabilized in a formulation.

Extrapolating kinetic data for a pure molecule to a molecule in a formulated mixture can lead to errors in predicting environmental fate. Clearly, the results for XRM indicate a much slower sorption rate than for Lorsban 4E insecticide and pure chlorpyrifos (Lorsban R insecticide). Under identical transport conditions and assuming chromatographic separation of formu-



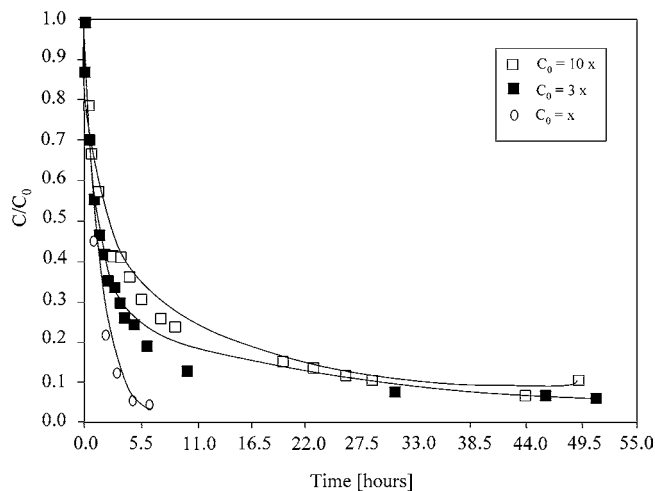
**Figure 4.** (a) Comparison of different model algorithms with experimental observations for Lorsban 4E insecticide,  $C_0 = 61 \text{ mg mL}^{-1}$ . (b) Comparison of the second-order sorption with first-order desorption and the two-site kinetic/equilibrium algorithm with experimental observations for Lorsban 4E insecticide,  $C_0 = 61 \text{ mg mL}^{-1}$ .



**Figure 5.** Formulation effects on the global sorptivity of chlorpyrifos ( $C_0$  for XRM =  $53 \text{ } \mu\text{g mL}^{-1}$ ,  $C_0$  for Lorsban 4E insecticide =  $61 \text{ } \mu\text{g mL}^{-1}$ ,  $C_0$  for Lorsban R insecticide =  $50 \text{ } \mu\text{g mL}^{-1}$ ).

lation components does not occur, the chlorpyrifos XRM formulation will move farther through the soil before becoming sorbed than the other two formulations used in this study.

The effects of different initial chlorpyrifos concentrations are presented in **Figure 6**. These experimental runs are for Lorsban



**Figure 6.** Effects of initial concentration on the global sorptivity of chlorpyrifos ( $x = 61 \text{ } \mu\text{g mL}^{-1}$ ).

4E insecticide, and the solid curves are computer-generated spline fits. These curves approach the same equilibrium value. However, the lower initial concentration trial sorbs slightly faster than the higher concentration trials, which indicates that higher-order kinetic approximations (second-order) may be required.

## CONCLUSIONS

Transport of pesticides and sorption to the soil are strongly coupled in determining their chemical mobility. This work has shown that sorption for chlorpyrifos formulations (using Cecil soil) is not an equilibrium process. However, simple kinetic models can be employed to approximate the transient sorption behavior that occurs in a soil system. Both second-order sorption with first-order desorption and the two-site kinetic/equilibrium model did a reasonable job of modeling bench scale experimental observations. The two-site model was the most versatile, simply because of the addition of another free parameter.

Some reservations regarding the validity of the two-site model still need to be addressed. Experiments using the same soil type under the same flow characteristics yield different values for “ $f_1$ ” when various formulations are employed (i.e., **Table 3**). The parameter “ $f_1$ ” is assumed to be a physical property of the medium and thus should remain constant under identical transport conditions. Although the two-site model can give excellent agreement between experiment and model predictions, this may just be a consequence of the additional free parameter that can be used to “curve fit” the solution to experimental data. If this is true, the two-site model may not be representing the actual physical and chemical mechanisms involved in the problem. Eliminating unnecessary free parameters helps distinguish any ambiguity between a general sorption–desorption model representation with a model that more closely describes the actual mechanisms involved in soil sorption. Knowing the kinetic sorption–desorption behavior of a solute in soil will give quantitative insight into the validity and applicability of the convective–dispersion equation and the assumptions on which it was formulated. Future mathematical models describing environmental transport of pesticides will be refined as a result.

It was observed that formulations can strongly affect the global sorption behavior of chlorpyrifos. In general, the formulation decreases the sorptivity of the active ingredient as witnessed by the increased time required until equilibrium is reached. Care must be exercised when extrapolating sorption data for pure chlorpyrifos to field applied formulated materials

when environmental fate predictions are sought. Any mechanistic model used to predict environmental fate of active materials under environmental conditions must account for the behavior of the formulation, at least in early days following a pesticide application when the formulation is still "intact". This article illustrates that appropriate algorithms for predicting the behavior of chlorpyrifos emulsions can be found.

#### LITERATURE CITED

- (1) Karickhoff, S. W. Sorption kinetics of hydrophobic pollutants in natural sediments. In *Contaminants and Sediments: Analysis, Chemistry, Biology*; Baker, R. A., Ed.; Ann Arbor Science: Ann Arbor, MI, 1980; Vol. 2, pp 193–205.
- (2) *Organic Chemicals in the Soil Environment*; Goring, C. A. I., Hamaker, J. W., Eds.; Marcel Dekker: New York, 1972.
- (3) van Genuchten, M. Th.; Davidson, J. M.; Wierenga, P. J. An Evaluation of Kinetic and Equilibrium Equations for the Prediction of Pesticide Movement through Porous Media. *Soil Sci. Soc. Am. Proc.* **1974**, *38*, 29–35.
- (4) Brusseau, M. L.; Rao, P. S. C.; Jessup, R. E.; Davidson, J. M. Flow interruption: a method for investigating sorption nonequilibrium. *J. Contam. Hydrol.* **1989**, *4*, 223–240.
- (5) Hance, R. J. Speed of attainment of sorption equilibria in some systems involving herbicides. *Weed Res.* **1967**, *7*, 29–36.
- (6) Khan, S. U. Equilibrium and kinetic studies on the adsorption of 2,4-D and picloram on humic acid. *Can. J. Soil Sci.* **1973**, *53*, 429–434.
- (7) Haque, R.; Lindstrom, F. T.; Freed, V. H.; Sexton, R. Kinetic study of sorption of 2,4-D on some clays. *Environ. Sci. Technol.* **1968**, *2*, 207–211.
- (8) Szecsody, J. E.; Bales, R. C. Sorption kinetics of low-molecular-weight hydrophobic organic compounds on surface-modified silica. *J. Contam. Hydrol.* **1989**, *4*, 181–203.
- (9) McCall, P. J.; Agin, G. L. Desorption kinetics of picloram as affected by residence time in the soil. *Environ. Toxicol. Chem.* **1985**, *4*, 37–44.
- (10) Wauchope, R. D.; Yeh, S.; Linders, J.; Kloskowski, R.; Tanaka, K.; Rubin, B.; Katayama, A.; Kordel, W.; Gerstl, Z.; Lane, M.; Unsworth, J. B. Pesticide soil sorption parameters: theory, measurement, uses, limitations and reliability. *Pestic. Manage. Sci.* **2002**, *58*, 419–445.
- (11) LaFleur, K. S. Sorption of metribuzin by model soils and agronomic soils: rates and equilibria. *Soil Sci.* **1979**, *127*, 51–55.
- (12) McCall P. J.; Laskowski, D. A.; Swann, R. L.; Dishberger, H. J. Measurement of sorption coefficients of organic chemicals and their use in environmental fate analysis, in Test protocols for environmental fate and movement of toxicants. Proceedings of the 94th Annual Meeting of the American Association of Official Analytical Chemists, Oct 21–22, 1980, Zweig G., Beroza, M., Eds.; AOAC: Arlington, VA, 1981; pp 89–109.
- (13) Fontaine, D. D.; Lehmann, R. G.; Miller, J. R. Organic chemicals in the environment: soil adsorption of neutral and anionic forms of a sulfonamide herbicide, flumetsulam. *J. Environ. Qual.* **1991**, *20*, 759–762.
- (14) Means, J. C.; Wood, S. G.; Hassett, J. J.; Banwart, W. L. Sorption of amino- and carboxy-substituted polynuclear aromatic hydrocarbons by sediments and soils. *Environ. Sci. Technol.* **1982**, *16*, 93–98.
- (15) Savage K. E.; Wauchope, R. D. Fluometuron adsorption-desorption in soil. *Weed Sci.* **1974**, *22*, 106–110.
- (16) Bird, R. B.; Stewart, W. E.; Lightfoot, E. N. *Transport Phenomena*; Wiley: New York, 1960.
- (17) Parker, J. C.; van Genuchten, M. Th. Determining transport parameters from laboratory and field tracer experiments. Virginia Agricultural Experiment Station Bulletin 84-3, Virginia Agricultural Experiment Station: Blacksburg, VA, 1984.
- (18) Addiscott, T.; Smith, J.; Bradbury, N. Critical evaluation of models and their parameters. *J. Environ. Qual.* **1995**, *24*, 803–807.
- (19) Altfelder, S.; Streck, T.; Maraqa, M. A.; Voice, T. C. Nonequilibrium Sorption of Dimethylphthalate-Compatibility of Batch and Column Techniques. *Soil Sci. Soc. Am. J.* **2001**, *65*, 102–111.
- (20) Lee, L. S.; Rao, P. S. C.; Brusseau, M. L.; Ogwanda, R. A. Nonequilibrium sorption of organic contaminants during flow through columns of aquifer materials. *Environ. Toxicol. Chem.* **1988**, *7*, 779–793.
- (21) MacIntyre, W. G.; Stauffer, T. B.; Antworth, C. P. A comparison of sorption coefficients determined by batch, column, and box methods on a low organic carbon aquifer material. *Ground Water* **1991**, *29*, 908–913.
- (22) Gaber, H. M.; Comfort, S. D.; Inskip, W. P.; El-Attar, H. A. A test of the local equilibrium assumption for adsorption and transport of picloram. *Soil Sci. Soc. Am. J.* **1992**, *56*, 1392–4000.
- (23) Bilkert, J. N.; Rao, P. S. Sorption and leaching of three non-fumigant nematicides in soils. *J. Environ. Sci. Health, Part B* **1985**, *20*, 1–26.
- (24) MacIntyre, W. G.; Stauffer, T. B. Liquid chromatography applications to determination of sorption on aquifer materials. *Chemosphere* **1988**, *17*, 2161–2173.
- (25) Piatt, J. J.; Backhus, D. A.; Capel, P. D.; Eisenreich, S. J. Temperature-dependent sorption of naphthalene, phenanthrene and pyrene to low organic carbon aquifer sediments. *Environ. Sci. Technol.* **1996**, *20*, 751–760.
- (26) Boesten, J.; van der Pas J.; Smelt, J. J. Field test of a mathematical model for nonequilibrium transport of pesticides in soil. *Pestic. Sci.* **1989**, *25*, 187–203.
- (27) Green, R. E.; Karickhoff, S. W. Sorption estimates for modeling. In *Pesticides in the soil environment: processes, impacts and modeling*; Cheng, H. H., Ed.; Soil Science Society of America Book Series, No. 2; Soil Science Society of America: Madison, WI, 1990; pp 79–102.
- (28) Leenher J. A.; Ahrlichs, J. L. A kinetic and equilibrium study of the adsorption of carbaryl and parathion upon soil organic matter surfaces. *Soil Sci. Soc. Am. Proc.* **1971**, *35*, 700–705.
- (29) Brusseau, M. L.; Rao, P. Sc. Sorption non-ideality during organic contaminant transport in porous media. *CRC Crit. Rev. Environ. Control* **1989**, *19*, 33–99.
- (30) Quinodoz, H. A. M.; Valocchi, A. J. Stochastic analysis of the transport of kinetically sorbing solutes in aquifers with randomly heterogeneous hydraulic conductivity. *Water Resour. Res.* **1993**, *29*, 3227–3240.
- (31) Wu, S.; Gschwend, P. M. Sorption kinetics of hydrophobic organic compounds to natural sediments and soils. *Environ. Sci. Technol.* **1986**, *20*, 717–725.
- (32) Wu, S.; Gschwend, P. M. Numerical modeling of sorption kinetics of organic compounds to soil and sediment particles. *Water Resour. Res.* **1988**, *24*, 1373–1383.
- (33) van Genuchten, M. Th.; Wagenet, R. J. Two-site/two-region models for pesticide transport and degradation: theoretical development and analytical solutions. *Soil Sci. Soc. Am. J.* **1989**, *53*, 1303–1310.
- (34) Pignatello, J. J. Sorption dynamics of organic compounds in soils and sediments. In *Reactions and movement of organic chemicals in soils*; Sawhney, B. L., Brown, K., Eds.; Soil Science Society of America Special Publication 22; Soil Science Society of America and American Society of Agronomy: Madison, WI, 1989; pp 45–80.
- (35) Maraqa, M. L.; Zhao, X.; Wallace, R. B.; Voice, T. C. Retardation coefficients of nonionic organic compounds determined by batch and column techniques. *Soil Sci. Soc. Am. J.* **1998**, *62*, 142–152.
- (36) Racke, K. D. Environmental Fate of Chlorpyrifos. *Rev. Environ. Contam. Toxicol.* **1993**, *131*, 1–151.

Received for review February 1, 2005. Revised manuscript received March 17, 2005. Accepted March 18, 2005.