An Isotopic Exchange Method for the Characterization of the Irreversibility of Pesticide Sorption−Desorption in Soil

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An isotopic exchange method is presented that characterizes the irreversibility of pesticide sorption−desorption by soil observed in batch equilibration experiments. The isotopic exchange of ^{12}C- and ^{14}C-labeled triadimefon [(1-(4-chlorophenoxy)-3,3-dimethyl-1-(1*H*-1,2,4-triazol-1-yl)-2-butanone] and imidacloprid-guanidine [1-[(6-chloro-3-pyridinyl)methyl]-4,5-dihydro-1*H*-imidazol-2-amine] in Hanford sandy loam soil indicated that these systems can be described by a two-compartment model in which about 90% of sorption occurs on reversible, easily desorbable sites, whereas 10% of the sorbed molecules are irreversibly sorbed on soil and do not participate in the sorption−desorption equilibrium. This model closely predicted the hysteresis observed in the desorption isotherms from batch equilibration experiments. The isotopic exchange of triadimefon and imidacloprid-guanidine in Drummer silty clay loam soil indicated that there was a fraction of the sorbed ^{14}C-labeled pesticide that was resistant to desorption, which increased as pesticide concentration decreased and was higher for triadimefon than for imidacloprid-guanidine. In contrast, the batch equilibration method resulted in ill-defined desorption isotherms for the Drummer soil, which made accurate desorption characterization problematic.

Keywords: *Desorption; hysteresis; isotopic exchange; pesticides; sorption*

INTRODUCTION

Sorption is one of the most important processes influencing the fate of agrochemicals in soil. Laboratory equilibrium sorption data are used to predict the partitioning of organic solutes, specifically pesticides, between the soil solid and solution phases, and as indicators of pesticide mobility. This information is essential to predict pesticide efficacy and potential of groundwater contamination. However, most soil−pesticide systems are seldom, if ever, at equilibrium, so that continuous solute transfer (sorption and desorption) between the solid and solution phases occurs after pesticide application. The release (desorption) of the sorbed pesticide from soil particles is of fundamental importance in determining the final distribution of the chemical in the soil. Information on desorption, therefore, becomes particularly important in predicting the efficacy, fate, and mobility of contaminants in already contaminated soils and to develop remediation strategies (Scheidegger and Sparks, 1996).

While pesticide sorption by soil and its constituents has been extensively documented, desorption remains much less understood. Many questions remain, such as the causes of the nonsingularity (hysteresis) between the sorption and desorption isotherms frequently observed in laboratory experiments (Koskinen et al., 1979; Clay et al., 1988; Clay and Koskinen, 1990; Barriuso et al., 1994; Carton et al., 1997). The presence of nonsingle-valued sorption−desorption relationships has been attributed to a number of experimental artifacts, such as nonattainment of sorption equilibrium; removal of soil particles during desorption; formation of precipitates; or loss of pesticide due to volatilization, degradation, or both (Koskinen et al., 1979; Calvet, 1980). Changes in solution composition during the desorption experiment (i.e., removal of soluble organic material) may also contribute to hysteresis (Clay et al., 1988). However, sufficient evidence exists to suggest that hysteretic behavior can be due to a portion of pesticide that is very strongly or irreversibly bound to soil, where desorption is kinetically so slow that it would require a prohibitive experimental time to be observed (Karickhoff, 1980; Di Toro and Horzempa, 1982; Wauchope and Myers, 1985; Clay and Koskinen, 1990).

On the assumption that strongly bound pesticide would not be available for desorption, some authors have fit desorption isotherm data to equations based on two-compartment models that attributed some of the observed hysteresis to nondesorbable molecules (Di Toro and Horzempa, 1982; Barriuso et al., 1992; Benoit et al., 1996). The two-compartment model assumes that in one compartment the retention force is weak and allows easy desorption, while in the other compartment the molecules are strongly retained and are either nondesorbable (Di Toro and Horzempa, 1982) or desorbable only at high dilutions (Barriuso et al., 1992). Direct estimates of strongly bound pesticide residues can also be found in the literature, but attempts to use these estimates to explain the hysteretic behavior of the desorption isotherms are more scarce (Clay and Koskinen, 1990). Pesticide residues are usually considered bound when the chemical species cannot be extracted by methods commonly used for residue analyses or after exhaustive extraction, i.e., using organic solvents (Khan, 1982; Gilchrist et al., 1993). It follows that choice of the extraction method affects the amount of nondesorbable pesticide that remains on the soil.

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10.1021/jf980763u CCC: $18.00
Published on Web 01/28/1999

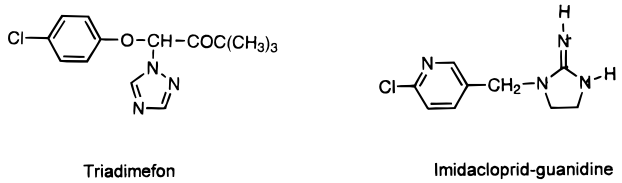

Figure 1. Chemical structures of triadimefon and imidacloprid-guanidine.

Table 1. Physicochemical Characteristics of the Soils

soil	texture	organic carbon content (%)	clay content (%)	pH
Hanford	fine sandy loam	0.41	6.90	7.8
Drummer	silty clay loam	3.95	32.1	5.9

The objective of the present study is to use an isotopic exchange method to characterize in situ the irreversibility of pesticide sorption−desorption by soil. The exchange between ^{12}C-labeled pesticide molecules and ^{14}C-labeled pesticide molecules following a 24-h preequilibration would allow characterization of the kinetics of pesticide exchange and estimation of amounts of sorbed pesticide that did not participate in the sorption equilibrium. Triadimefon [(1-(4-chlorophenoxy)-3,3-dimethyl-1-(1*H*-1,2,4-triazol-1-yl)-2-butanone] and imidacloprid-guanidine [1-[(6-chloro-3-pyridinyl)methyl]-4,5-dihydro-1*H*-imidazol-2-amine] were the test compounds selected for this study based on previous results indicating a characteristic hysteretic desorption behavior in soils (Cox et al., 1997; Celis et al., 1999). Triadimefon is a systemic fungicide that has been reported to be moderately sorbed in soils (Dell et al., 1994; Celis et al., 1999), displaying very low hysteresis in low clay and organic C content soil and increased hysteresis in soils with high clay and organic C contents (Celis et al., 1999). Imidacloprid-guanidine is one of the main metabolites of the insecticide imidacloprid [1-[(6-chloro-3-pyridinyl)methyl]-*N*-nitro-2-imidazolidinimine]. It has recently been reported to be very highly sorbed in soils with marked hysteretic behavior, especially at low pesticide concentrations (Cox et al., 1997). The information obtained from the isotopic exchange technique may help to better understand the dynamics of the pesticide sorption−desorption process in soil as well as the mechanisms responsible for hysteretic isotherms.

MATERIALS AND METHODS

Soils. Two soils with markedly different physicochemical characteristics were selected for this study. Fresh soils from the 0−15 cm depth of a Hanford sandy loam and a Drummer silty clay loam were collected, air-dried, and passed through a 2-mm diameter sieve. Physicochemical characteristics of the soils are given in Table 1. Soil texture was determined by the hydrometer method (Gee and Bauder, 1986). Soil pH was measured in a 1:2 (w:w) soil/deionized water mixture. The organic C content was determined by dichromate oxidation (Nelson and Sommers, 1982).

Chemicals. Pure analytical triadimefon (chemical purity >99%) was purchased from Chem Service (West Chester, PA). The [phenyl-U-^{14}C]triadimefon was donated by Mobay Chemical Corp. (now Bayer Corp., Stilwell, KS). It was purified by HPLC, and final radiochemical purity was >98%. Pure analytical imidacloprid-guanidine (chemical purity >99%) and the [2-imidazol-^{14}C]imidacloprid-guanidine (radiochemical purity >97%) were supplied by Bayer Corp. The chemical structures of triadimefon and imidacloprid-guanidine are shown in Figure 1.

Sorption−Desorption Isotherms. Sorption−desorption isotherms on soil were obtained by the batch equilibration method using 35-mL glass centrifuge tubes with Teflon-lined caps. Initial pesticide solutions were prepared in 0.01 M $CaCl_2$ at concentrations (C_{ini}) ranging from 0.4 to 8.0 mg L^{-1} for triadimefon and from 0.1 to 3.0 mg L^{-1} for imidacloprid-guanidine. Radiolabeled chemical was added to nonradioactive solutions to give solution radioactivity of ~70 Bq mL^{-1}. Triplicate 2-g soil (triadimefon) or 0.5-g soil (imidacloprid-guanidine) samples were equilibrated with 10 mL of pesticide initial solution by shaking mechanically at 21 ± 2 °C for 24 h. These soil:solution ratios were selected to obtain sorption percentages [(pesticide sorbed/pesticide initially present) × 100] >15% and <85%. Batch kinetic studies were performed using the Drummer soil and showed that 24 h was sufficient to reach sorption equilibrium. Previous work has reported no significant degradation of triadimefon or imidacloprid-guanidine after 2 days of equilibration with soil (Cox et al., 1997; Celis et al., 1998). After equilibration, the suspensions were centrifuged at 3000 rpm for 30 min, and 5 mL of supernatant was removed for analysis. Solutions shaken in tubes without soil served as controls.

Desorption isotherms were obtained from two equilibrium points of the sorption isotherms. After sorption, the 5 mL of supernatant removed for the sorption analysis was replaced with 5 mL of 0.01 M $CaCl_2$. The suspensions were shaken at 21 ± 2 °C for 24 h and centrifuged, and 5 mL of supernatant was removed for analysis. This desorption cycle was repeated at least four times. In the case of imidacloprid-guanidine, additional desorption isotherms were obtained using free-pesticide soil extract. The soil extract was made by mixing 0.5 g of soil with 10 mL of 0.01 M $CaCl_2$ and equilibrating for 24 h, as described previously. The soil slurry was centrifuged, and the supernatant was used as the replacement solution.

Isotopic Exchange Experiments. The scheme in Figure 2 shows a typical isotopic exchange experiment performed in this study. For every equilibrium point of the sorption isotherms, additional tubes (A and B) were prepared. The amounts of soil, solution, and initial pesticide concentration in tubes A and B were exactly the same and identical to those used to obtain the equilibrium point of the sorption isotherm; however, tube A contained only ^{12}C-labeled pesticide whereas tube B contained ~70 Bq mL^{-1} of ^{14}C-labeled pesticide. Initial solutions were carefully prepared to ensure that they contained exactly the same total pesticide concentration, [^{12}C-labeled pesticide]$_{tube\ A}$ = [^{12}C-labeled pesticide + ^{14}C-labeled pesticide]$_{tube\ B}$.

The suspensions were shaken at 21 ± 2 °C for 24 h (step 1). After sorption equilibrium was reached in tubes A and B, the suspensions were centrifuged at 3000 rpm for 30 min. The supernatant of tube A (8 g) was replaced with the supernatant of tube B (8 g) and vice versa (step 2). The replacement of the supernatant is a critical operation; if not meticulously done, the results would be affected. Supernatant replacement was performed using 8-mL glass pipets, and it was verified that the amount of supernatant that remained on the walls of the glass pipets was <0.2%. It was assumed that equilibrium was not disturbed in step 2; however, after supernatant exchange, tube A contained ^{14}C-labeled pesticide only in solution phase whereas tube B contained sorbed ^{14}C-labeled pesticide plus ^{14}C-labeled pesticide in the 2 mL of initial solution that remained in the soil. The soil and solution were reequilibrated, and the kinetics of the ^{14}C-labeled pesticide exchange between the solid and solution phases was monitored by measuring the decrease in ^{14}C-labeled pesticide in solution with time in tube A and the increase in ^{14}C-labeled pesticide in solution with time in tube B (step 3). All isotopic exchange experiments were performed in triplicate.

Chemical Analysis. The amount of ^{14}C-labeled pesticide in solution was determined by scintillation counting. One milliliter aliquots of clear supernatant were mixed with 6 mL of Ecolite scintillation cocktail (ICN, Costa Mesa, CA), and the radioactivity was determined using a 1500 Packard liquid scintillation analyzer (Packard Instruments Co., Downers Grove, IL).

Data Analysis. The amount of pesticide in solution (C_e, mg L^{-1}) and sorbed to the soil (C_s, mg kg^{-1}) after the 24-h

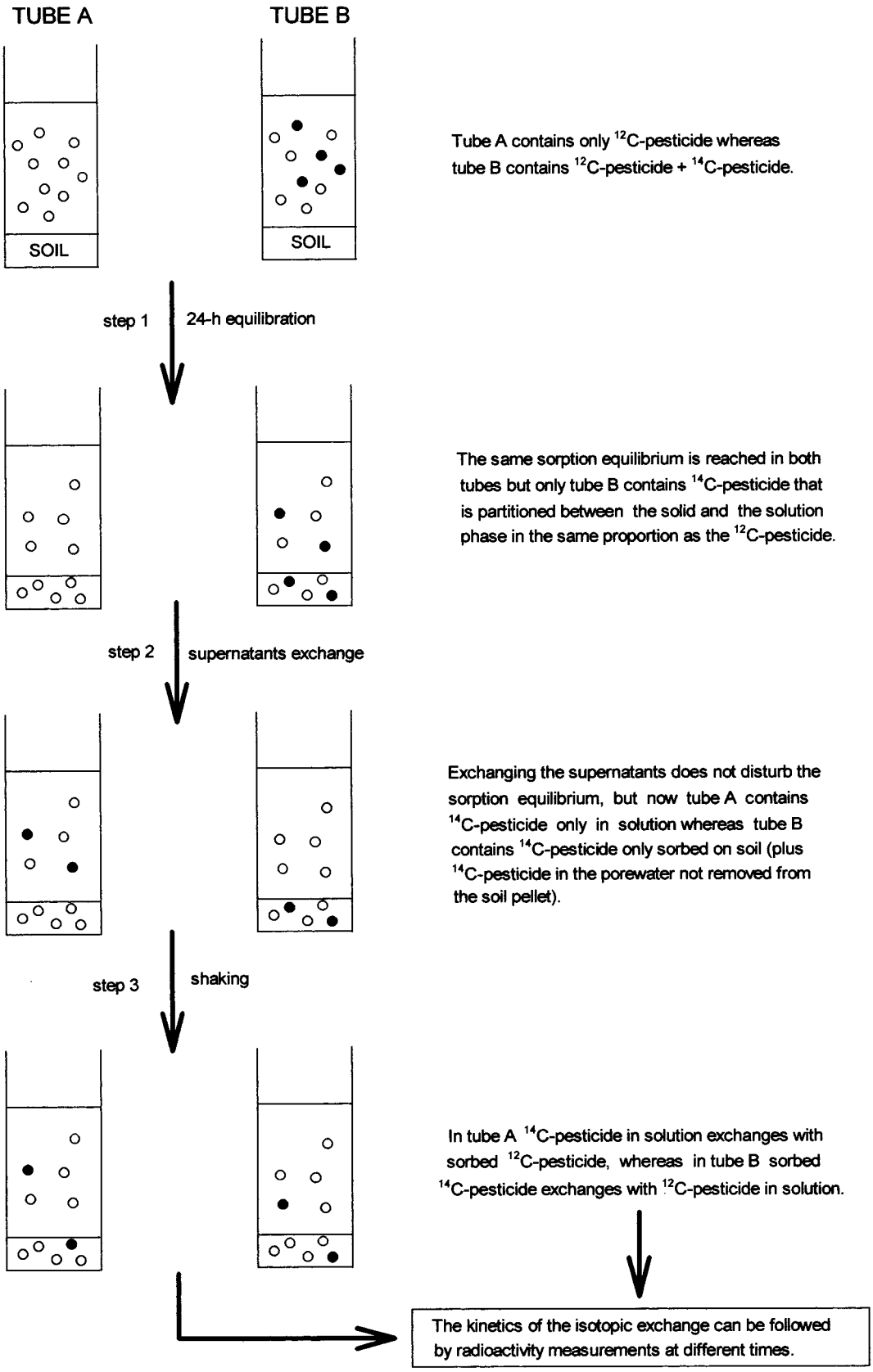

Figure 2. Diagram of the isotopic exchange experiment: ○, ^{12}C-labeled pesticide; ●, ^{14}C-labeled pesticide.

preequilibration time was calculated from the radioactivity measurements of the supernatants:

$$C_e = \frac{R_e}{SV} \quad (1)$$

$$C_s = \frac{R_s}{SM} \quad (2)$$

where R_e is the total radioactivity (Bq) in solution, R_s is the total radioactivity (Bq) in the sorbed phase, S is the specific activity (Bq mg^{-1}) of the initial pesticide solution, M is the

mass (kg) of soil, and V is the volume (L) of solution. R_s was calculated from the difference $R_i - R_e$, where R_i is the radioactivity (Bq) in the volume V of initial pesticide solution.

At any single concentration, the equilibrium between pesticide in solution and pesticide sorbed to the soil can be expressed as

$$C_e \overset{K_d \text{ or } K}{\rightleftharpoons} C_s$$

where K_d (L kg^{-1}) $= C_s/C_e$ is the distribution coefficient at the equilibrium concentration C_e. The distribution coefficient can also be expressed as a dimensionless equilibrium constant $K = R_s/R_e$, which is related to the distribution coefficient by $K_d = KV/M$.

Sorption−desorption data were also fit to the linearized form of the Freundlich equation:

$$\log C_s = \log K_f + 1/n_f \log C_e \quad (3)$$

where K_f and $1/n_f$ are the empirical Freundlich constants. Hysteresis coefficients, H, for the sorption−desorption isotherms were calculated according to

$$H = (1/n_{fd})/(1/n_f) \quad (4)$$

where $1/n_{fd}$ is the Freundlich $1/n_f$ constant for the desorption isotherm (O'Connor et al., 1980; Barriuso et al., 1994).

Based on the sorption kinetic results, pesticide sorption equilibrium in the isotopic exchange experiments was assumed to be reached in tubes A and B in the first 24-h period of shaking (step 1 in Figure 2). It was also assumed that sorbed and equilibrium pesticide concentrations were identical in tubes A and B, so that both tubes remained in equilibrium after supernatants were exchanged. However, after supernatant exchange, ^{14}C-labeled molecules were present only in solution in tube A and sorbed to the soil in tube B (plus amount in 2 mL of initial solution not exchanged), so redistribution of these ^{14}C-labeled molecules would occur according to

$$R_e' \overset{K'}{\rightleftharpoons} R_s'$$

where R_e' and R_s' are the amounts of ^{14}C-labeled pesticide (Bq) in solution and sorbed to the soil, respectively, at a given time after supernatant exchange.

If sorption is a reversible process and all the pesticide sorbed on soil is in equilibrium with the pesticide in solution, then redistribution of the ^{14}C-labeled pesticide will occur until the partition constant K' ($=R_s'/R_e'$) equals the equilibrium partition constant K ($=R_s/R_e$), measured in the preequilibration step, i.e.

$$R_s/R_e = R_s'/R_e' \quad (5)$$

Thus, the distribution of the ^{14}C-labeled pesticide during the isotopic exchange for reversible behavior can be predicted.

RESULTS AND DISCUSSION

Sorption Kinetics. Triadimefon sorption kinetics obtained with the Drummer soil showed that 24 h was sufficient to reach sorption equilibrium (Figure 3). More than 90% of triadimefon sorption 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. Control samples, without soil, showed no losses of pesticide due to sorption on glass or volatilization (Figure 3); therefore, differences in pesticide concentrations after the 24-h equilibration period with the soil were assumed to be sorbed. Previous research has shown that imidacloprid-guanidine sorption equilibrium on a similar soil was reached within 24 h (Cox et al., 1997). Sorption kinetics

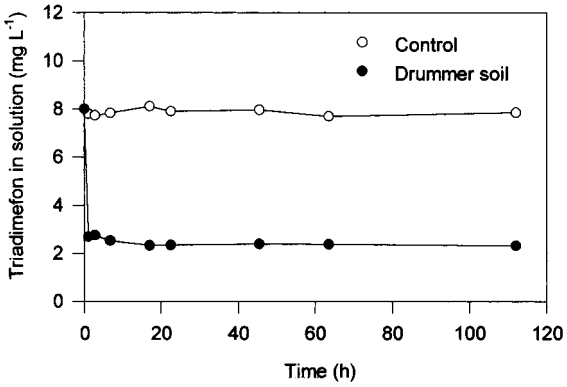

Figure 3. Triadimefon sorption kinetics on Drummer soil and control sample.

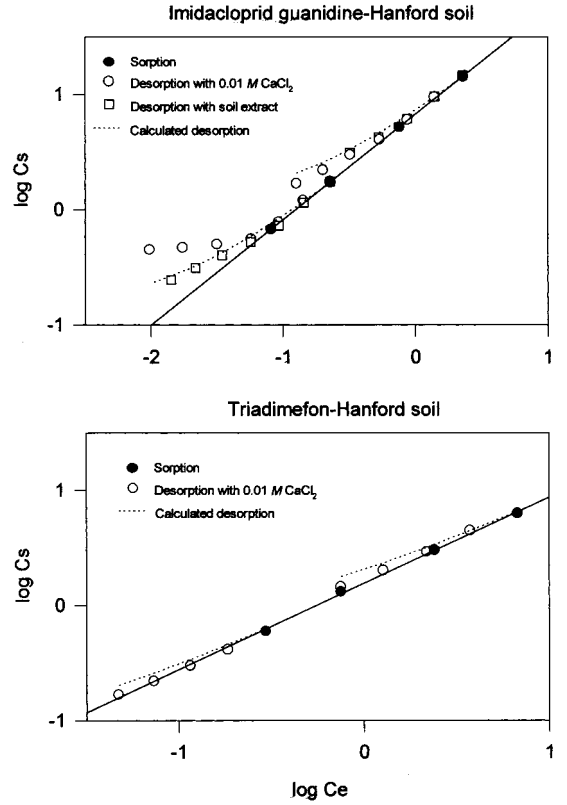

Figure 4. Imidacloprid-guanidine and triadimefon sorption−desorption isotherms on Hanford soil. Symbols correspond to experimental data, solid lines are the Freundlich-fit sorption isotherms, and dashed lines are the predicted desorption assuming that 10% of the sorbed pesticide do not participate in the sorption−desorption equilibrium.

on the Hanford soil was not obtained; however, 24 h was most likely sufficient to reach sorption equilibrium for this soil since it had much lower organic C and clay contents than the Drummer soil (Table 1). This was further supported by the very fast isotopic exchange kinetics observed for Hanford soil where equilibrium was reached within the first hour of isotopic exchange.

Sorption−Desorption Isotherms. Triadimefon and imidacloprid-guanidine sorption isotherms on Hanford and Drummer soil fit the Freundlich equation, $r^2 > 0.998$, with slopes ($1/n_f$) significantly less than 1 (Figures 4 and 5; Table 2). Imidacloprid-guanidine was sorbed by both soils to a greater extent than triadimefon; Freundlich K_f and K_{f-oc} constants for imidacloprid-guanidine sorption were 3−4 times greater than those for triadimefon. The sorptive capacity of the Drummer

Table 2. Freundlich Constants for Triadimefon and Imidacloprid-Guanidine Sorption on Hanford and Drummer Soil

	triadimefon				imidacloprid-guanidine			
soil	K_f	$1/n_f$	r^2	K_{f-oc}[a]	K_f	$1/n_f$	r^2	K_{f-oc}
Hanford	1.55 ± 0.04[b]	0.75 ± 0.02	0.998	378	6.75 ± 0.02	0.915 ± 0.002	1.000	1646
Drummer	13.3 ± 0.6	0.76 ± 0.03	0.998	337	42.2 ± 0.1	0.831 ± 0.002	1.000	1068

[a] $K_{f-oc} = (K_f/\%\text{organic C}) \times 100$. [b] Value ± standard error of the calculated coefficients.

Table 3. Freundlich Desorption Slopes, $1/n_{fd}$, and Hysteresis Coefficients, $H = (1/n_{fd})/(1/n_f)$, for Triadimefon and Imidacloprid-Guanidine Sorption−Desorption on Hanford and Drummer Soil

	triadimefon				imidacloprid-guanidine			
	$C_{ini} = 8$ mg L^{-1}		$C_{ini} = 0.4$ mg L^{-1}		$C_{ini} = 3$ mg L^{-1}		$C_{ini} = 0.3$ mg L^{-1}	
soil	$1/n_{fd}$	H	$1/n_{fd}$	H	$1/n_{fd}$	H	$1/n_{fd}$	H
Hanford	0.68 ± 0.02[a]	0.91 ± 0.06	0.69 ± 0.01	0.92 ± 0.04	0.74 ± 0.03	0.81 ± 0.03	0.42 ± 0.08	0.46 ± 0.09
Drummer	0.47 ± 0.05	0.62 ± 0.09	0.32 ± 0.02	0.42 ± 0.05	0.75 ± 0.02	0.90 ± 0.03	0.64 ± 0.03	0.77 ± 0.04

[a] Value ± standard error of the calculated coefficients.

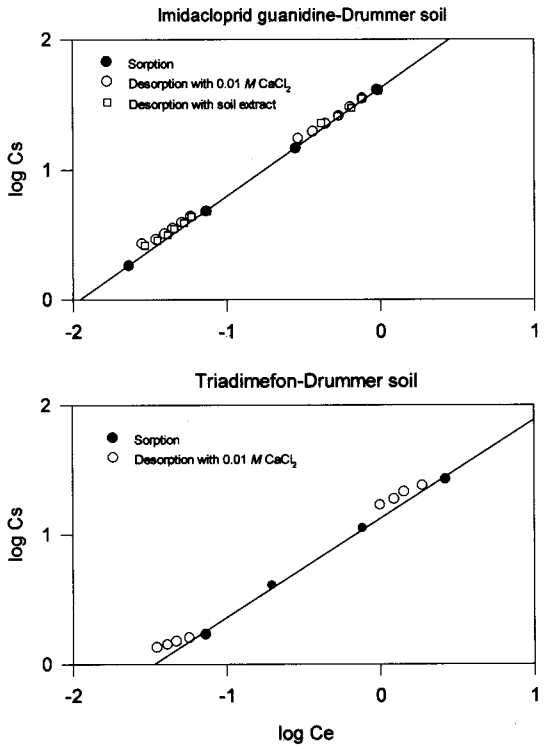

Figure 5. Triadimefon and imidacloprid-guanidine sorption−desorption isotherms on Drummer soil.

soil was almost 10 times greater than that of the Hanford soil for both chemicals, most probably due to the higher clay and organic C content of Drummer soil (Cox et al., 1997; Celis et al., 1999). Normalization of K_f values to the organic C content of the soils reduced variability between soils (Table 2).

Triadimefon desorption hysteresis coefficients, H, on Hanford soil were close to unity, indicating high reversibility of the sorption−desorption process (Table 3). Triadimefon H values for Drummer soil were lower than those for Hanford soil, especially at the lowest concentration. This indicates that desorption of triadimefon is lower in more sorptive soils and at low pesticide concentrations. H values for imidacloprid-guanidine decreased as pesticide concentration decreased for both soils; however, the lowest H values were displayed by Hanford soil. These results are in contrast to those of Cox et al. (1997), who found the opposite effect of the sorptive capacity of the soil on imidacloprid-guanidine desorption as well as a much greater influence of pesticide concentration. However, the pesticide concentrations used by Cox et al. (1997) were lower than ours, and the amount of soil in their sorption experiments were 4 times greater. When more energetic sites are assumed to be occupied first, at the low concentrations and high soil surface available in the experiments of Cox et al. (1997), sorption would have occurred preferentially on more energetic sites, making desorption more difficult especially from highly sorptive soils.

Desorption parameters obtained from highly sorptive soils should be considered with caution. At high sorption percentages, the small aqueous chemical concentrations that result from pesticide desorption during successive desorption cycles lead to poorly defined desorption isotherms with experimental points that fall very near the initial equilibrium point (Di Toro and Horzempa, 1982). This is clearly illustrated in Figures 4 and 5, where desorption behavior is much better defined in the case of Hanford soil (where sorption percentages ranged from 15 to 30%) than in the case of Drummer soil (where sorption percentages ranged from 70 to 85%). Thus, the low hysteresis observed for imidacloprid-guanidine desorption from Drummer soil may not be representative of the desorption behavior at higher dilutions. In fact, the behavior of imidacloprid-guanidine for the first desorption steps from Hanford soil does not reflect hysteresis, whereas nonsingularity of the sorption−desorption isotherms becomes evident at higher dilutions (Figure 4).

Changes in solution composition during the desorption experiment were evaluated as a cause of hysteresis for imidacloprid-guanidine by using soil extract instead of 0.01 M $CaCl_2$ in the desorption steps (Figures 4 and 5). In general, for both soils desorption with soil extract was practically identical to desorption with 0.01 M $CaCl_2$; however, imidacloprid-guanidine desorption from Hanford soil at low concentration was significantly enhanced with the use of soil extract (Figure 4). It is not evident why this effect was only observed in that particular case, but it could be due to the low amounts of chemical that remained sorbed to the soil. This chemical could correspond to the most strongly sorbed fraction and could be partially desorbable by the use of soil extract (containing dissolved organic matter) but not with 0.01 M $CaCl_2$ alone (Barriuso et al., 1992).

Isotopic Exchange. Figure 6 shows the kinetics of the isotopic exchange of imidacloprid-guanidine (sorption of ^{14}C-labeled pesticide from solution in tube A and desorption of ^{14}C-labeled pesticide from soil in tube B) in 24-h preequilibrated suspensions of Hanford and

Table 4. Dimensionless Equilibrium Partition Coefficients, K ($=R_s/R_e$), Partition Constants after 24 h of Isotopic Exchange, K' ($=R_s'/R_e'$), and Percentages of Irreversibly Bound Pesticide, $\%R_{s-irr}$ [$(R_{s-irr}/R_s) \times 100$], for Imidacloprid-Guanidine and Triadimefon on Hanford Soil

		from preequil step	from ^{14}C sorption (tube A)		from ^{14}C desorption (tube B)	
	initial concn (mg L^{-1})	K ($\times$1000)	K' ($\times$1000)	$\%R_{s-irr}$	K' ($\times$1000)	$\%R_{s-irr}$
imidacloprid-guanidine	3.0	314 ± 4[a]	289 ± 3	8 ± 1	355 ± 2	8 ± 1
	1.0	347 ± 8	292 ± 10	7 ± 2	387 ± 5	7 ± 2
	0.3	380 ± 2	331 ± 19	13 ± 5	419 ± 6	7 ± 1
	0.1	419 ± 2	365 ± 9	13 ± 2	477 ± 16	10 ± 3
triadimefon	8.0	210 ± 7	192 ± 10	9 ± 4	269 ± 18	13 ± 4
	0.4	438 ± 13	382 ± 7	13 ± 2	510 ± 2	12 ± 1

[a] Mean ± standard error of triplicate samples.

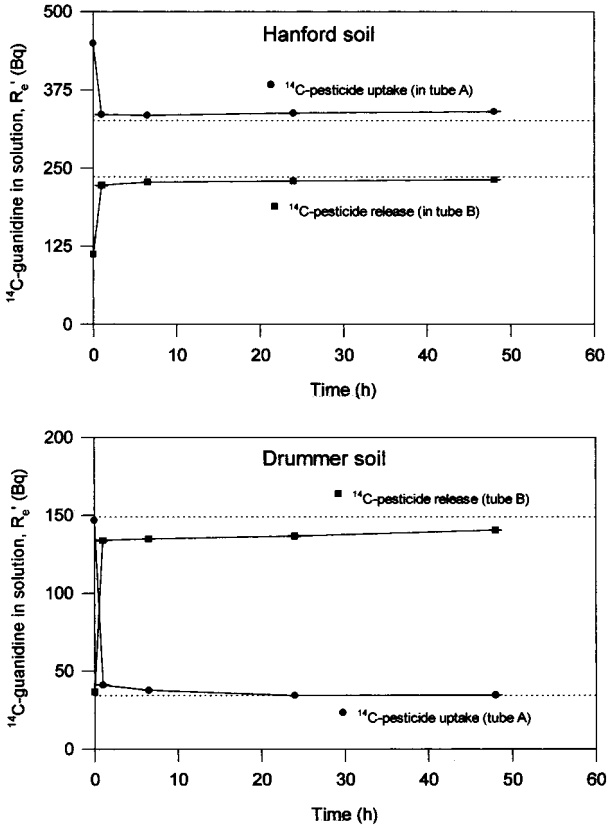

Figure 6. Kinetics of the isotopic exchange of imidacloprid-guanidine in 24-h equilibrated soil suspensions (C_{ini} = 0.3 mg L^{-1}). Dashed lines are the radioactivities expected from the equilibrium partition constant, K, measured in the preequilibration step (eq 5).

Drummer soils. In Hanford soil, the kinetics of the isotopic exchange was very fast and mixing was probably the rate-limiting step; however, the distribution of ^{14}C-labeled pesticide between the soil and solution phases never matched the pesticide distribution observed in the preequilibration step (Figure 6). Table 4 reports the partition constants, K', for ^{14}C-labeled imidacloprid-guanidine after 24 h of isotopic exchange in tubes A and B as compared to the equilibrium partition constants, K, at different pesticide concentrations. The fact that $K' < K$ in tubes A and $K' > K$ in tubes B is indicative that isotopic exchange occurred to a lesser extent than predicted by the partition constant measured at equilibrium. Very similar results were found in the experiments performed with triadimefon (Table 4).

The fact that isotopic exchange did not occur to the extent predicted by the preequilibration partition constant could be due to a fraction of the sorbed pesticide in the preequilibration step that was irreversibly bound and did not actually participate in the reversible sorption−desorption equilibrium. Thus, we assumed that equilibrium was reached after preequilibration, but only a fraction of the sorbed pesticide participated in that equilibrium. The rest of the sorbed molecules were assumed to be irreversibly bound and not to participate in the reversible sorption−desorption process.

On the basis of the above assumption, the extent of the isotopic exchange would be given by a modified form of eq 5 that subtracts from the total amount of sorbed ^{14}C-labeled pesticide the amount of ^{14}C-labeled pesticide that is not participating in the equilibrium:

$$\frac{R_s - R_{s-irr}}{R_e} = \frac{R_s'}{R_e'} \text{(in tube A)} \qquad (6)$$

$$\frac{R_s - R_{s-irr}}{R_e} = \frac{R_s' - R_{s-irr}}{R_e'} \text{(in tube B)} \qquad (7)$$

where R_{s-irr} is the ^{14}C-labeled pesticide (Bq) sorbed on irreversible sites during the preequilibration step.

In eqs 6 and 7, the left-hand term represents the "reversible" equilibrium partition constant for the ^{14}C-labeled pesticide in the preequilibration step, whereas the right-hand terms represent the "reversible" equilibrium partition constant for the ^{14}C-labeled pesticide after the isotopic exchange step in tubes A and B.

The values of R_{s-irr} calculated after 24 h of isotopic exchange using eqs 6 and 7 and expressed as percentages of the total radioactivity sorbed in the preequilibration step were very consistent for all the equilibrium points of the sorption isotherm and ranged from 7 to 13% for imidacloprid-guanidine and from 9 to 13% for triadimefon (Table 4).

On the basis of the above results, it follows that, at every equilibrium point of the imidacloprid-guanidine and triadimefon sorption isotherms on Hanford soil (Figure 4), there is about 10% of the sorbed pesticide that is irreversibly bound which did not participate in the sorption equilibrium, whereas the remaining 90% is reversibly bound. Using this model, we can closely predict the hysteresis in experimental desorption isotherms for Hanford soil (Figure 4). In the case of imidacloprid-guanidine desorption at lower concentration, the model accounts for the portion of hysteresis that remained after using soil extract as the desorbing solution in the desorption steps.

The kinetics of the isotopic exchange in the Drummer soil followed a different pattern than in the Hanford soil. While ^{14}C-labeled pesticide in solution exchanged with the ^{12}C-labeled pesticide on soil (tube A) as predicted by the sorption partition constant, K, significantly less

Table 5. Dimensionless Equilibrium Partition Coefficients, K ($=R_s/R_e$), Partition Constants after 24 h of Isotopic Exchange, K' ($=R_s'/R_e'$), and Percentages of Irreversibly Bound Pesticide, $\%R_{s-irr}$ [$(R_{s-irr}/R_s) \times 100$], for Imidacloprid-Guanidine and Triadimefon on Drummer Soil

		from preequil step	from ^{14}C sorption (tube A)		from ^{14}C desorption (tube B)	
	initial concn (mg L^{-1})	K ($\times$100)	K' ($\times$100)	$\%R_{s-irr}$	K' ($\times$100)	$\%R_{s-irr}$
imidacloprid-guanidine	3.0	213 $\pm$ 2[a]	213 $\pm$ 6	0 $\pm$ 3	225 $\pm$ 2	14 $\pm$ 3
	1.0	261 $\pm$ 1	252 $\pm$ 2	4 $\pm$ 1	283 $\pm$ 5	23 $\pm$ 1
	0.3	327 $\pm$ 2	326 $\pm$ 2	0 $\pm$ 1	366 $\pm$ 6	34 $\pm$ 4
	0.1	399 $\pm$ 2	400 $\pm$ 10	0 $\pm$ 3	437 $\pm$ 16	34 $\pm$ 3
triadimefon	8.0	266 $\pm$ 1	262 $\pm$ 3	2 $\pm$ 1	286 $\pm$ 2	21 $\pm$ 2
	0.4	614 $\pm$ 8	593 $\pm$ 22	3 $\pm$ 3	688 $\pm$ 8	50 $\pm$ 3

[a] Mean $\pm$ standard error of triplicate samples.

^{14}C-labeled pesticide was released from soil (tube B), even after 48 h of shaking (Figure 6). This resulted in values of $K' \approx K$ for ^{14}C-labeled sorption (tube A), but $K' > K$ for ^{14}C-labeled desorption (tube B), after a 24-h period of isotopic exchange (Table 5). The assumption that only a fraction of the sorbed pesticide is participating in the sorption equilibrium (eqs 6 and 7) resulted in $\%R_{s-irr}$ values derived from ^{14}C-labeled sorption that were close to zero but in percentages derived from ^{14}C-labeled desorption that ranged from 14 to 34% in the case of imidacloprid-guanidine and from 21 to 50% in the case of triadimefon (Table 5). It appears, therefore, that all sorption sites in Drummer soil were readily available for ^{14}C-labeled pesticide sorption (tube A) but that only a fraction of the sorbed ^{14}C-labeled pesticide was desorbed easily (tube B).

Slow desorption kinetics for ^{14}C-labeled desorption from Drummer soil is evident in Figure 6. A number of authors have ascribed slow desorption reaction to diffusion of the chemical out of micropores of organic matter and inorganic soil components (Steinberg et al., 1987; Scheidegger and Sparks, 1996). This explanation is also reasonable in our case, since this effect was only observed for Drummer soil with the high clay and organic C contents.

The lack of agreement between the $\%R_{s-irr}$ values derived from ^{14}C-labeled sorption (tube A) and from ^{14}C-labeled desorption (tube B) in the isotopic exchange experiment for Drummer soil is intriguing and may suggest that a "true equilibrium" was not attained during the preequilibration step. In tube A, the isotopic exchange equilibrium is reached because ^{12}C-labeled pesticide molecules have been desorbed from soil, leaving the ^{14}C-labeled pesticide molecules to reach equilibrium. Therefore, there is not diffusional resistance for the desorption of ^{12}C-labeled pesticide molecules from the results of tube A. In contrast, ^{14}C-labeled pesticide concentration in solution in tube B never reached the expected value, suggesting some resistance to desorption of the sorbed molecules.

One possible explanation for the above results is that the sorption of ^{14}C-labeled pesticide molecules on sites resistant to desorption during the isotopic exchange was accompanied by the release of molecules from more easily desorbable sites. In other words, all sorption sites would be equivalent for sorption, but desorption would preferentially occur from easily desorbable sites. This hypothesis implies a "pseudo-equilibrium" where a net increase in strongly bound pesticide occurs with time. Di Toro and Horzempa (1982) reported a similar effect when applying a two-compartment model to PCB sorption−desorption by sediment. They observed that the fraction of strongly bound PCB seemed to increase with time and this was accompanied by an equal and opposite decrease in the magnitude of the reversibly bound fraction. Transformation of reversible bonding sites to strong sites (metastable complex → stable configuration) was suggested to conceivably explain this behavior. An interesting feature in Table 5 is the increase in the "resistant to desorption" fraction as triadimefon and imidacloprid-guanidine concentrations decreased. This would indicate that the number of strong sites is limited and saturation of these sites occurs as pesticide concentration increases.

Another explanation for the different behavior observed in tubes A and B is the possibility of slow sorption processes. A small amount of additional sorption during the second 24-h equilibration would result in accumulation of ^{14}C-labeled pesticide in soil in tube B. Slow sorption has been described in terms of diffusion from readily accessible sites to restricted sites, so that new accessible sites become available for pesticide in solution (Karickhoff and Morris, 1985; Xue and Selim, 1995). If some slow sorption took place during the second 24-h equilibration step of our experiments, it would affect ^{14}C-labeled pesticide molecules presorbed on soil in tube B but not the freshly transferred ^{14}C-labeled pesticide molecules in solution in tube A. Accumulation of ^{14}C-labeled pesticide molecules in soil would, therefore, be evident in the experiments with tubes B.

It should be noted that, in contradiction to the existence of slow sorption process, an apparent equilibrium was reached for Drummer soil within 24 h, with no statistically significant change in solution concentration after a 5-day equilibration period (Figure 3). However, it has been recently demonstrated that the onset of the slow sorption stage is not easily identified and may not be analytically detectable until several days beyond the apparent equilibrium (DiVicenzo and Sparks, 1997). DiVicenzo and Sparks (1997) have also demonstrated the effect of initial concentration on the slow sorption process. The higher the concentration, the faster the rate of slow sorption and the sooner its onset. Our higher concentration samples may have experienced a faster slow kinetic phase and, therefore, could have been closer to a "true" equilibrium at the time when desorption was initiated. This may result in less irreversible behavior than the low concentration samples (Table 5).

The high percentages of irreversibly bound triadimefon obtained from the isotopic exchange experiment on the Drummer soil agree with the low hysteresis coefficients of the sorption−desorption isotherms, although desorption isotherms were not very well defined (Table 3; Figure 5). The resistance to desorption observed for imidacloprid-guanidine in the isotopic exchange experiments, however, was not evident in the desorption

isotherms (Figure 5, Table 3). As mentioned above, the small pesticide concentrations that result from pesticide release from Drummer soil during successive desorption cycles require a prohibitive number of experimental data points and lead to ill-defined desorption isotherms that make desorption characterization problematic (Di Toro and Horzempa, 1982; Barriuso et al., 1994). In this regard, the isotopic exchange experiment seems to be a useful tool for the characterization of the irreversibility of pesticide sorption−desorption in highly sorptive soil−pesticide systems.

SUMMARY AND CONCLUSIONS

The isotopic exchange method described in the present paper is an easy and useful tool to characterize the irreversibility of the sorption−desorption of organics by soil and its components. Using triadimefon and imidacloprid-guanidine as test compounds, we have shown that analysis of the exchange of ^{14}C-labeled pesticide molecules in a equilibrated soil suspension allows a direct in situ characterization of the dynamics of pesticide sorption−desorption equilibrium in soil. This method eliminates inherent experimental artifacts of other methods, such as changes in solution composition during successive desorption cycles or the specific effectiveness of the extracting method used to evaluate the amounts of strongly bound pesticide.

The isotopic exchange of triadimefon and imidacloprid-guanidine in Hanford sandy loam soil suspensions indicated that these systems can be described by a two-compartment model in which about 90% of sorption occurs on reversible easily desorbable sites whereas 10% of the sorbed molecules are irreversibly sorbed on soil and do not participate in the sorption−desorption equilibrium. This model closely predicted the small hysteresis for the batch desorption isotherms even after correcting for changes in solution composition during the successive desorption cycles.

The isotopic exchange of triadimefon and imidacloprid-guanidine in Drummer silty clay loam soil suspensions suggested differences between the accessibility and desorbability of sorption sites on soil. A fraction of the sorbed pesticide was resistant to desorption (or otherwise desorbed very slowly). This fraction was higher for triadimefon than for imidacloprid-guanidine and increased as pesticide concentration decreased, suggesting that saturation of sites resistant to desorption occurred as pesticide concentration increased. However, "nonanalytically detectable" slow sorption of the chemicals through micropores of the organic matter and inorganic components could have contributed to the results observed in the experiments with the Drummer soil. The isotopic exchange technique used was especially useful in the case of the Drummer soil because its high sorption capacity for triadimefon and imidacloprid-guanidine led to ill-defined batch desorption isotherms, which made desorption characterization problematic.

ABBREVIATIONS USED

C_{ini}, initial pesticide concentration in the sorption step (mg L^{-1}); C_e, pesticide equilibrium concentration after the sorption step (mg L^{-1}); C_s, sorbed pesticide after the sorption step (mg kg^{-1} soil); H, hysteresis coefficient; K_f, $1/n_f$, Freundlich sorption constants; K_{fd}, $1/n_{fd}$, Freundlich desorption constants; K_{f-oc}, C-normalized K_f constant; K_d ($=C_s/C_e$), equilibrium distribution coefficient at single concentration (L kg^{-1}); K ($=R_s/R_e$), dimensionless equilibrium partition constant; K' ($=R_s'/R_e'$), dimensionless partition constant for the ^{14}C-labeled pesticide at any time after supernatants exchange in the isotopic exchange experiment; M, mass of soil (kg); R_i, total radioactivity in the volume V of initial pesticide solution (Bq); R_e, radioactivity in solution after 24-h equilibration with the soil (Bq); R_s, radioactivity in soil after 24-h equilibration with the soil (Bq); R_e', radioactivity in solution at a given time after supernatants exchange in the isotopic exchange experiment (Bq); R_s', radioactivity in soil at a given time after supernatants exchange in the isotopic exchange experiment (Bq); R_{s-irr}, radioactivity in soil that does not participate in the sorption equilibrium (Bq); V, volume of solution (L).

ACKNOWLEDGMENT

We thank Bayer Corp. for kindly supplying the radioactive chemicals.

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Received for review July 15, 1998. Revised manuscript received December 7, 1998. Accepted December 8, 1998. Mention of a company or trade name is for information only and does not imply recommendation by USDA-ARS. R.C. thanks the Spanish Ministry of Education and Culture for his PFPI fellowship.

JF980763U