Atrazine Sorption by a Mineral Soil: Processes of Labile and Nonlabile Uptake

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A microfiltration−HPLC technique which was recently introduced is applied to the study of the uptake of atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine) by a mineral soil, Green Belt BG 843. The uptake can be partitioned into labile and nonlabile contributions. Each process shows a saturation limit consistent with a "complexation site" model of atrazine binding. The indications of a definite and low stoichiometry of uptake capacity is a key result of this analysis. The labile sorption capacity, θ_c, is 0.40×10^{-6} mol g^{-1}. At 25 °C an equilibrium constant, K_1, for the labile sorption is 3.0×10^4 M^{-1}, and the apparent diffusion coefficient for nonlabile uptake is 8.8×10^{-11} cm^2 s^{-1}, corresponding to a first-order rate constant of 9.6×10^{-7} s^{-1}. Preliminary indications are that the capacity of nonlabile binding sites is $<10^{-4}$ mol g^{-1}.

Keywords: *Atrazine−soil interactions; on-line HPLC microextraction; bound residues; intraparticle diffusion; sorption capacity; sorption mechanisms*

INTRODUCTION

Pesticide−soil interactions involve several processes such as physisorption/desorption, intraparticle diffusion, chemisorption, chemical and microbiological degradation, etc. Sorption is one of the most important processes in determining the persistence and transport of pesticides in the soil subsurface environment. Considerable advances have been made in the studies of pesticide uptake by soils over the last decade (Brusseau and Rao, 1989).

Two-domain models, with a labile contribution and a nonlabile contribution to uptake kinetics, are commonly exploited (Hamaker et al., 1966; Brusseau and Rao, 1989). Labile uptake has been often treated as an instantaneous process, described by an adsorption isotherm. Where kinetics can be resolved, this uptake is usually treated as a kinetically first-order process. For nonlabile uptake recent work (Ball and Roberts, 1991a,b) has used diffusive models with a radial solution of Fick's law (Crank, 1975). Since the labile contribution is much faster, it is in pseudoequilibrium with respect to the nonlabile binding process.

A fundamental requirement for effective assessment of sorption mechanisms is an analytical chemical methodology for measuring the distribution of pesticide species between solution and suspended soil phases. Most batch methods do not distinguish between labile, presumably surface sorbed, species and bound residues which are chemisorbed or result from intraparticle diffusion. In contrast, a new on-line microfiltration−high-performance liquid chromatography, MF−HPLC, technique applied to analysis of a batch sample (Gamble and Ismaily, 1992; Gamble and Khan, 1992) meets the requirements for kinetic speciation studies of pesticide uptake in heterogeneous systems.

The objective of this study is to present a two-term physisorption/diffusion model to analyze the labile sorption and nonlabile sorption, or bound residue formation, processes which occur between the widely used herbicide atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine) and a mineral soil (GB 843). The studies cover short-term and long-term experimental periods and determine the accessible equilibrium and kinetic parameters using batch experiments combined with the MF−HPLC technique. This paper and its companion, covering *T* and particle size effects, reflect a continuation and extension of the important initiatives of Bell and Roberts (1991a,b). One important point of this paper and the previous work (Gamble and Ismaily, 1992; Gamble and Khan, 1992) is the emphasis on stoichiometry. The number of labile sites is small which forces a specific site (sometimes called "complexation") model in contrast to phase partition treatment. Gamble et al. (Gamble and Langford, 1988; Gamble and Ismaily, 1992) developed such a treatment, and it is used here.

MECHANISTIC MODEL: A TWO-STAGE MECHANISM

The two-stage surface-adsorption/intraparticle-diffusion mechanism assumes at least two kinetically distinct processes: a relatively fast labile (surface?) adsorption followed by slow diffusion into nonlabile sites. It differs in initial formalism form some other models by (1) assuming a site binding or complex formation model (Weber and Smith, 1987; Witkowski et al., 1987; Weber et al., 1991; Li et al., 1993), since the uptake by sorption is stoichiometrically limited to a small overall labile sorption capacity, and (2) treating intraparticle diffusion with a particular solution (Crank model) (Crank, 1975), where labile sorbate coverage serves as the driving force and uptake is described by a first-order rate law. The overall processes can be expressed schematically as:

$$\mathrm{SS} \underset{k_{s2}}{\overset{k_{b1}}{\rightleftharpoons}} \mathrm{LS} \underset{k_{d2}}{\overset{k_{d1}}{\rightleftharpoons}} \mathrm{NLS} \qquad (1)$$

where SS, LS, and NLS represent the dissolved species in soil solution, labile (surface?) sorbed species, and nonlabile sorbed (intraparticle diffusion trapped or

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chemisorbed) species, respectively. This latter species is one type of bound residue. LS, the labile fraction, is defined operationally as the amount of sorbed species which is "desorbed" promptly in the MF−HPLC experiment by extracting the soil with the HPLC mobile phase.

Equilibria and Kinetics of Labile Surface Adsorption/Desorption. The two-stage model uses the following equations to describe the rate behavior of surface adsorption/desorption (the first stage):

$$-\mathrm{d}M_{AT}/\mathrm{d}t = (W/V)\mathrm{d}\theta_1/\mathrm{d}t = k_{b1}M_{AT}(W/V)\theta_O - k_{s2}(W/V)\theta_L \quad (2)$$

$$-\mathrm{d}M_{AT}/\mathrm{d}t = (W/V)\mathrm{d}\theta_1/\mathrm{d}t = k_{s1}M_{AT} - k_{s2}(W/V)\theta_L \quad (3)$$

where M_{AT} (in mol L^{-1}), θ_L, and θ_O (in mol g^{-1}) represent solution phase atrazine, occupied sorption sites, and unoccupied sorption sites, respectively. k_{b1} and k_{s2} are the rate constants for adsorption (second-order, in L mol^{-1} s^{-1}) and desorption (in s^{-1}). k_{s1} is the pseudo-first-order rate constant for adsorption: $k_{s1} = k_{b1}(W/V)\theta_O$ (in s^{-1}), which is an approximation for low site coverage (i.e., θ_L being small, $\theta_O \approx$ constant); t is time (in s). The term W/V, soil weight over slurry volume, is a unit conversion factor (in g L^{-1}) which might be called soil concentration.

Several stoichiometric, kinetic, and equilibrium analyses of pesticide sorption by soils (Hamaker et al., 1966; Macalady and Wolfe, 1984; Gamble and Ismaily, 1992; Gamble and Khan, 1992; Li et al., 1993) have indicated that the labile sorption has a definite capacity or saturation limit which is termed labile sorption capacity, θ_C, as shown in a mass balance expression:

$$\theta_C = \theta_L + \theta_O \quad (4)$$

θ_C is in mol g^{-1} of soil.

Analogous to the treatment for a mixed ligand system (Gamble and Langford, 1988), the sorption of atrazine to a heterogeneous mixture of n types of sorption sites can be expressed as

$$\bar{K}_1 = (K_1C_{O1} + K_2C_{O2} + ... + K_nC_{On})/(C_{O1} + C_{O2} + ... + C_{On}) \quad (5)$$

or

$$\bar{K}_1 = \sum_{I=1-n} K_iC_{Oi}/\sum_{I=1-n} C_{Oi} \quad (6)$$

where $\bar{K}_1$ is a weighted average equilibrium function (in L mol^{-1}), $K_i(I = 1-n)$ is an equilibrium binding constant for each site (in L mol^{-1}), and C_O is the concentration of vacant sorption sites (in mol L^{-1} of slurry). Experimentally,

$$\bar{K}_1 = \theta_1/\theta_O M_{AT} \text{ (or } C_1/C_O M_{AT}) \quad (7)$$

where C_1 is θ_L expressed in mol L^{-1} of slurry.

In addition, the mole fraction of covered surface sites, X_1, can be obtained as follows:

$$X_1 = \theta_1/\theta_C \quad (8)$$

In earlier hydrology models, the parameter K_d, the distribution coefficient (in L g^{-1}), is usually used

$$K_d = \theta_1/M_{AT} \quad (9)$$

The relationship between K_d and $\bar{K}_1$ can be given by combining eqs 7−9:

$$K_d = \bar{K}_1(1 - X_1)\theta_1 \quad (10)$$

K_d is a parameter developed from a phase partition model. Its limitation in describing the uptake of pesticides (especially polar or ionic ones) should be noted. The existence of the specific stoichiometric capacity θ_C is inconsistent with the definition of K_d. Equation 10 is valid only if X_1 is small and the approximate constant, K_d, lacks fundamental physical significance.

The kinetic parameters for the labile surface adsorption, k_{s1} (and k_{b1}), are evaluated by an initial rate approximation, which was cross-checked by an iterative calculation. For the initial rate method, M_{AT} vs t was fitted to a polynomial and $\mathrm{d}M_{AT}/\mathrm{d}t$ was evaluated analytically at $t = 0$.

"Bound Residue" Formation, Diffusion Equation Treatment. A number of authors have reported that an initially fast sorption of organic chemicals by soils is followed by a second stage that is much slower and apparently irreversible and have suggested that the organic chemicals slowly diffuse into the interior of the soil particles (Brusseau and Rao, 1989; Hamaker et al., 1996). This nonlabile sorption phenomenon is readily observed using the MF−HPLC technique. The fraction of atrazine not re-extracted from the particles by the HPLC mobile phase is identified as this nonlabile fraction. The possibility that the labile and nonlabile fractions are distinguished only by differing depth of diffusion into the particle will be eliminated in the accompanying paper by the result that they have radically different activation energies associated with the kinetics.

Since the initial sorption is fast and labile (i.e., recoverable with the HPLC solvent), these sites have a steady state concentration fed by the solution phase atrazine and consumed by the diffusion process. Crank (1975) has summarized solutions for the application of Fick's law. A solution for the particular case of diffusion into semi-infinite media from a steady state coverage, θ_1, is given by:

$$\theta_D = [2(\theta_1/r)(D/\pi)^{1/2}]t^{1/2} \quad (11)$$

where D is the diffusion coefficient characterizing the nonlabile uptake, θ_D is the total occupancy of nonlabile sites in units of mol g^{-1}, and r is a particle dimension appropriate to diffusion (Crank, 1975; Gamble and Langford, 1988; Gamble and Ismaily, 1992; Gamble and Khan, 1992); thus,

$$\ln(\theta_D) = \ln(A) + Z\ln(t) \quad (12)$$

In eq 12, the time independent "constant" $A = 2(\theta_1/r)(D/\pi)^{1/2}$. A plot of $\ln(\theta_D)$ versus $\ln(t)$ is a diagnostic test for intraparticle diffusion with steady state surface coverage. $Z = {}^1/_2$ is consistent with intraparticle diffusion.

The overall differential rate law for equilibration of the second stage of the mass transfer between labile sorption sites and the intraparticle-trapped state requires inward and outward transport processes. Using

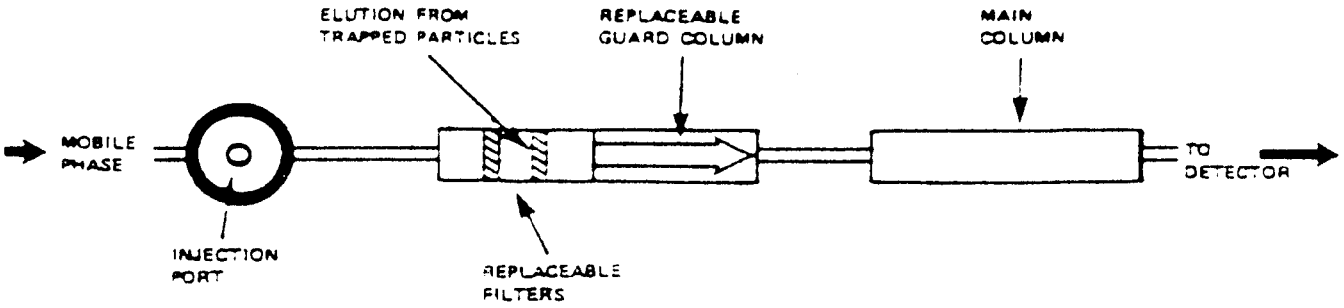

Figure 1. Experimental arrangement for the on-line HPLC microextraction of soil particles from injected slurry aliquots.

chemical kinetic notation:

$$d\theta_D/dt = k_{d1}\theta_L - (V/W)R_{d2} \quad (13)$$

When $d\theta_D/dt$ is given the units (mol/g)/s and θ_L is in mol/g, then k_{d1} is in s^{-1}. R_{d2} has the units (mol/L)/s, and (V/w) L/g is a units conversion factor. When the diffusional uptake of atrazine is sufficiently small, i.e., $R_{d2} \ll k_{d1}\theta_1$, this reduces to eq 14:

$$d\theta_D/dt = k_{d1}/\theta_L \quad (14)$$

While recent literature (Khan, 1973, 1982; Kearney, 1976; Wu and Gschwend, 1986) has suggested that forward uptake ($k_{d1}\theta_1$) can be approximated by first-order kinetics, no simple theoretical support has been given for this. Others (Wu and Gschwend, 1986; Ball and Roberts, 1991) use a second-order partial differential equation derived from a one-dimensional solution of Fick's law, in which two parameters, total sorbed pesticide and solution phase concentrations, are the main measurables. The MF−HPLC/batch technique can track the distinction between labile sorbed species, θ_1, and material balance loss, $\theta_L + \theta_D$. R_{d2} is little studied since it is not readily extracted from data obtained during the first 2 or 3 weeks of the reaction (Macalady and Wolfe, 1984).

The present two-stage model leads to eq 15 as the relationship between the rate constant for nonlabile uptake and the diffusion coefficient:

$$k_{d1} = (D/l^2) \quad (15)$$

where l is the distance traveled by a diffusing molecule. Due to the lack of detailed information about the particle shapes and sizes, the value of l is not known unambiguously. The radial dimension of a particle, r, therefore, is sometimes assumed to be a crude approximation. Assuming steady state site coverage, the diffusion coefficient, D, can be determined from the ln(A) term in eq 12. We will estimate k_{d1} semi-independently by initial rate methods as a cross-check.

EXPERIMENTAL PROCEDURES

Equipment. The batch setup included a reaction vessel which was a Pyrex vial, 7.3 cm high by 3.0 cm diameter, with a screw cap. A Teflon-coated stir bar and magnetic stirring base were used to keep the soil samples suspended. A thermostated circulating bath connected to double-walled Pyrex jackets was used to maintain the slurry temperature at 25.0 ± 0.1 °C. HPLC analyses were performed with a Varian Star 9010 solvent delivery system, a Varian Star 9050 UV−vis variable wavelength detector set to 220 nm, and a Model 4400 integrator. A Waters Associates LC system with a Model 441 detector and a Rheodyne Model 7125 injector was also used. The column was a Beckman C-18 Ultrasphere ODS or CSC-Chromosorb LC-7, 25 × 0.46 cm i.d. A C-18 Adsorbosphere Altech guard column cartridge with replaceable 2.0 and 0.5 μm stainless steel microfilters was used to trap solids and protect the main HPLC analytical column. In runs designed to determine solution phase atrazine only, microfiltration of the slurry prior to injection was done with disposable B-D 1 cc 26G 3/8 Tuberculin syringes and MSI Cameo Nylon 66 0.22 μm disposable microfilters. For direct injection of standards, filtrates, and whole slurries, 100 μL Hamilton 710 syringes with fixed needles were used. Figure 1 is a schematic representation of the on-line MF−HPLC device. Details have been published previously (Gamble and Ismaily, 1992; Gamble and Khan, 1992). Blank experiments have shown that atrazine adsorption on the Pyrex vial walls is not important.

Reagents and Materials. The mineral soil GB 843 was collected from a B horizon at a depth of 7.5 cm. The location was site no. 4 in field no. 8 on the Green Belt Farm of Agriculture and Agri-Food Canada in Nepean, Ontario. Its geological origins and nature are documented in detail in soil survey records. The site no. 4 is on the Dalhousie Soil Landscape Unit D3. The soil is described as "neutral (pH 6.6−7.3), fine textured marine materials, interbedded with layers of silty sediments within 2 m of the surface, 3.75% organic matter". Prior to the formation and disappearance of the Champlain sea over this location, the glaciation of the last Ice Age transported and deposited ground Precambrian Shield rock to this area. The soil was air-dried, homogenized, and sieved. Standard stock solutions of 1×10^{-4} M atrazine were freshly prepared from crystalline solid (Supelco, Inc., Bellefonte, PA) using distilled deionized water. Analytical standards were prepared by serial dilution of the stock solution. HPLC grade methanol and acetonitrile (HPLC grade, Caledon Lab. Ltd., Georgetown, Ontario, Canada) were used for the HPLC work. The use of these solvents for atrazine extraction has been demonstrated (Sheldrick, 1984; Weber and Smith, 1987; Wang et al., 1990).

General Kinetics Procedure. A 0.500 g portion of the mineral soil was suspended with stirring in approximately 15 mL of distilled deionized water for about 2 days. This is assumed to wet all the surface and sorb water into the soil particle. The kinetic run was started by the addition of a calculated aliquot of atrazine standard stock solution, with the total slurry volume being adjusted to 25.0 mL. Stirring maintained a uniform suspension of soil particles. Two different HPLC analysis sequences were used.

(1) An aliquot of the slurry was filtered with 0.22 μm filters, and then the filtrate was injected for analysis. A sequence of such measurements produced a kinetics curve for the solution phase concentration.

(2) A second aliquot of the slurry was injected without prior filtering, directly into the instrument. An assembly of 2.0 and 0.5 μm filters on-line in the instrument trapped the solids. The mobile phase then became the extractant. The resulting chromatographic peaks consequently measured the total of the atrazine in the solution plus the atrazine that was recoverable off the solids. This sequence of measurements produced a kinetics curve for all of the atrazine that was recoverable from the whole slurry, including both solution and solids.

The two types of measurements (1 and 2) were alternated as previously reported (Gamble and Ismaily, 1992; Gamble and Khan, 1992). Methanol/H_2O (62.5/37.5 with 1.58×10^{-3} M HCl) or acetonitrile/H_2O (50/50 with 3.18×10^{-3} M HCl) was used as mobile phase with a flow rate of 1.0 mL min^{-1}. Sequence 1 determines solution phase atrazine. Sequence 2 determines the sum of solution phase plus labile sorbed.

Table 1. Basic Experimental Parameters for Bulk Soil Kinetics

init AT (10^{-6} mol L^{-1})	T (°C)	soil wt (g)	slurry vol (mL)	expt duration (days)	data points	expt no.
1.00	25	0.5040	24.95	18.76	176	7
3.32	25	0.4870	25.01	19.23	45	4
5.70	25	0.5041	24.95	19.10	47	3
7.93	25	0.5086	24.94	19.90	46	2
7.93	25	0.5084	24.94	19.90	46	14
8.00	25	0.5054	25.01	18.58	55	19
8.00	25	0.5053	25.02	18.77	56	20
20.0	25	0.5076	24.99	19.10	45	5
29.8	25	0.5335	25.16	18.72	51	6
4.08	10	0.5079	24.97	69.91	20	G5
8.00	10	0.5038	24.97	80.07	107	GT
16.0	10	0.4996	24.81	69.91	22	G6
79.9	10	0.5000	24.95	80.98	44	31
79.9	10	0.4999	24.96	81.01	44	32
100	10	0.5016	24.92	80.96	44	29
100	10	0.5008	24.92	80.98	44	30

Each batch experiment was run for 3 weeks (short-term kinetics) or 12 weeks (long-term kinetics). The basic experimental parameters for the study of soil−atrazine interactions are shown in Table 1.

Mass Balance Experiments. In an attempt to determine the amount of recoverable nonlabile atrazine, a supercritical fluid extraction (SFE) was conducted, in which a 0.5 g of GB 843 soil was slurried in 25.0 mL of solution having initial atrazine concentration 3.94×10^{-5} M. The slurry was mixed in a thermostated reaction vessel at 25 °C using a magnetic stir bar for a period of 5 weeks. At the end of this time, a 1.0 mL aliquot of the slurry was placed in a laboratory-made soil trap. The soil trap was an 85 mm length of $^1/_8$ in. (o.d.) stainless steel tube fitted with a 0.5 mm tube type stainless steel frit and two 0.22 μm membrane filters. The soil trap was fitted in place of the HPLC column, and the labile atrazine was removed by washing with mobile phase. The soil trap was placed directly into a Suprex (Pittsburg, PA) SFE/50 supercritical fluid extractor. Some of the nonlabile atrazine was extracted using a mixture of supercritical CO_2 and CH_3-OH heated to 125 °C and pressurized to 350 atm. Alternatively, the soil slurry was dispersed in an ultrasonic bath (Sonic 300 dismembrator, Fisher Scientific, Artek Systems Corp., Farmingdale, NY); then an aliquot (5.0 mL) of the slurry was centrifuged (Dynac Centrifuge, Caly Adams Co., Parsippany, NJ). The resulting residue was extracted for 2 days with acetonitrile and analyzed with the HPLC method.

Data Processing. The method of least-squares was used in the usual way, for fitting experimental data. The software used reports standard errors for the fitted function and for each of its calculated constants. For linear cases, the software also gives correlation coefficients. This was done for the slurry and filtrate analysis data, the diagnostic tests for intraparticle diffusion, the data for labile sorption capacity, and the initial rate calculations. The standard errors reported by the software were used for estimating the error limits in the mechanisms parameters. This has defined the quality of the numerical values of the parameters that have been produced as future input for risk assessment computer models.

Soil Characterization. Mineral analysis was done using a Scintag PAD V X-ray diffractometer, Scintag, Sunnyvale, CA, at the Research Branch of Agriculture Canada, Ottawa. The results are shown in Table 2.

The cation exchange capacity (CEC) for soil GB 843 was determined by saturating the cation exchange sites with a solution of 0.9 N $Ca(OAc)_2$ + 0.1 N $CaCl_2$ at pH 7.0, eluting the Ca^{2+} with a 2 N NaCl solution, and measuring the exchangeable Ca^{2+} by a AA-975 atomic absorption spectrophotometer (Varian Techtron). The result was 8.8 ± 0.2 mequiv/100 g of soil.

In order to obtain more geological information about the soil, model analyses were performed in the Geology Department of Concordia University and the Research Branch of Agriculture Canada. A stereomicroscope (Wild Photomakroskop M400, Wild Leitz Canada Ltd.) was used with plane-polarized light (PPL) or crossed-polarized light (XPL). The sample slides (thin sections) were prepared by established procedures (Steinberg et al., 1987). Briefly, thin sections are made by impregnating a soil sample powder with plastic, mounting on a glass slide, and grinding the soil layer down to 25−30 μm. Examination of soil thin sections can provide information about the size, shape, and arrangement of solid particles and voids and add information on soil mineral and organics. A series of samples were collected at different time steps from the reaction vessel during a kinetic experiment, so as to check whether or not soil particles were affected. The results indicated that there was no important change within the first 3 weeks under the present conditions. Similar observations have been reported by Wu and Gschwend (1986) and Ball and Roberts (1991). However, the considerable scatter revealed in the long-term experiments (after about 60 days, see subsequent section) resulted from the disaggregation of loosely bound fine particles to some extent under the long-term stirring conditions (Ball and Roberts, 1991). Gentle stirring appears to be important for maintaining the initial distribution of soil particle size. Ogwada and Sparks (1986) found that specific surface for a soil was relatively constant under stirring conditions for mixing rates of 0−478 rpm but increased abruptly at higher mixing rates (>2318 rpm).

Table 2. Results of Mineral Analyses for GB 843 Bulk Soil

mineral analysis		clay analysis	
material	% of soil	material	% of clay
plagiolase	45	mica/vermiculite	1−10
		larger interlayer spaces	
microcline	8	smaller interlayer spaces	1−10
quartz	15	chlorite	1−10
amphibole	3	mica	1−10
dolomite	2	amphiboles	1−10
clay	27	quartz	10−35
		feldspar	
		microcline	1−10
		plagioclase	1−10

For the purpose of element identifications, a scanning electron microscopy (SEM) with energy dispersive spectrometry (EDS) study was conducted at the Electron Microscopy Centre of Research Branch, Agriculture Canada, Ottawa. Samples were analyzed, using a digital scanning microscope (DSM 940A, ZEISS, Germany) equipped with a X-ray fluorescence analysis system (Tracor Northern-5500). All samples were mounted on $^1/_2$ in. spectrographically pure carbon planchets. X-ray data from five areas (each area ca. 1.8 × 1.8 mm) of each sample were collected over 60 s. Escape peaks were stripped from the spectra. Diagnostic peaks were identified at maximum sensitivity, and peak areas were calculated.

Labile Sorption Capacity. An aqueous suspension of the soil was titrated with a standard solution of atrazine at 25.0 °C. The on-line HPLC microextraction method was used to resolve the sorbed total into its labile sorbed and bound residue components. This permitted the labile sorbed component to be plotted against the solution concentration, as shown in Figure 2. The first part of the curve has a linear relationship between labile sorbed atrazine and solution phase atrazine. In the second part of the titration, the labile sorbed atrazine remained constant as the solution concentration increased. The labile sorption sites had become saturated, giving a titration end point for the total number of sites. This gave a labile sorption capacity of $(0.39_7 \pm 0.03_6) \times 10^{-6}$ mol g^{-1}.

RESULTS AND DISCUSSION

Rapid Initial Uptake. Figure 3 shows the short-term results of an experiment having an initial atrazine concentration of 1.0×10^{-6} M. The rapid early uptake in the labile sorption accounts for as much as 16% (1.56×10^{-7} mol L^{-1}) of the initial concentration but only 2% of θ_C. The data are noisy in the early stage, and it is quite possible that a more complete treatment would reveal more than one labile uptake kinetic step. However, we will see that one rate constant provides a

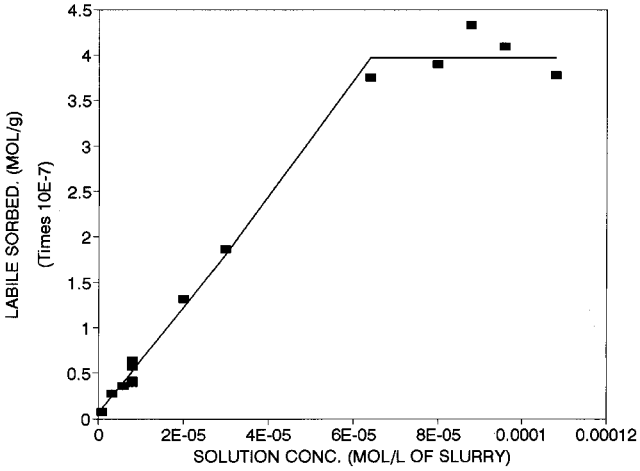

Figure 2. Measurement by titration curve of the labile sorption capacity of soil GB 843 for atrazine (25.0 °C).

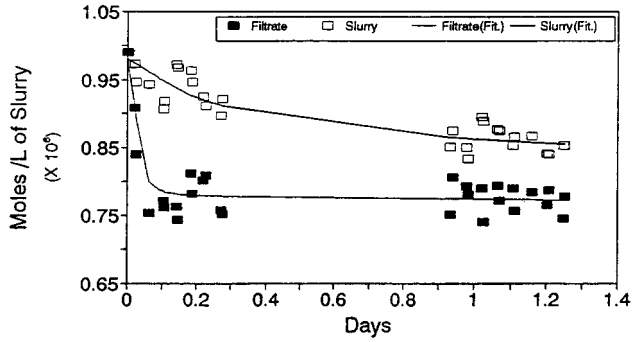

Figure 3. Slurry and filtrate measurements for the early part of experiment no. 7 (25.0 °C): □, slurry measurements; ■, filtrate measurements; −, curves fitted by the method of least-squares to polynomials.

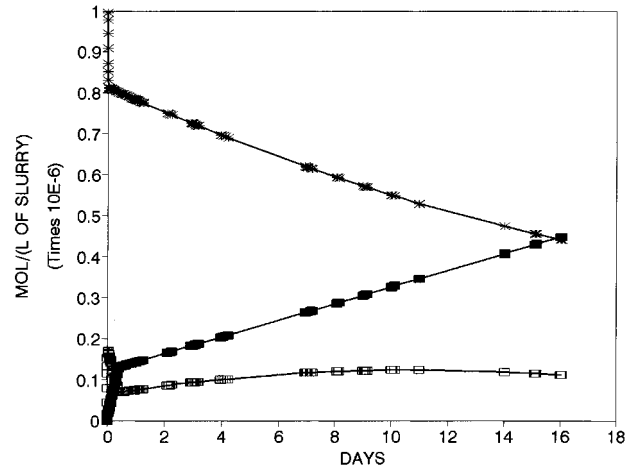

Figure 4. Kinetics curves for the atrazine species of experiment no. 7, calculated from the slurry and filtrate curves of Figure 3: *, in solution; □, labile sorbed; ■, bound residue formed by intraparticle diffusion.

satisfactory treatment of the present data and does not justify postulation of more parameters.

Labile Sorption. Following the rapid early uptake, an approximate dynamic steady state appears to be reached with respect to the labile sorption/desorption. Figure 4 summarizes the results of the above sorption experiment over an extended period (16 days). It is apparent that there is a plateau region on the labile curve with a weak maximum at about 9.9 days, which accounts for 15% of the total atrazine and 1.9% of the labile sorption sites θ_L. At the maximum, the curve has a singularity, $d\theta_1/dt = 0$.

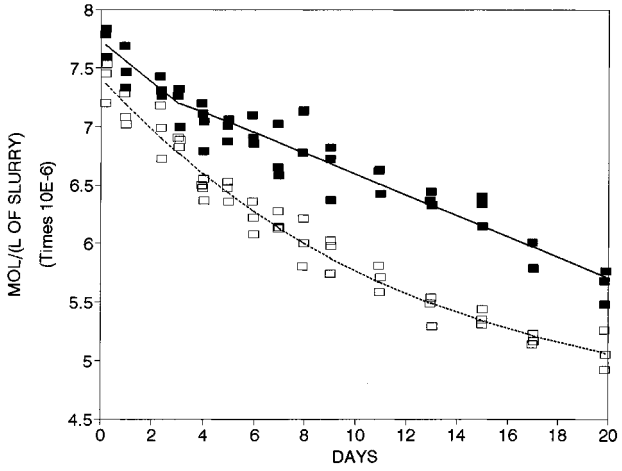

Figure 5. Slurry and filtrate measurements for experiment no. 20 (25.0 °C): ■, slurry measurements; □, filtrate measurements; −, curves fitted by the method of least-squares to polynomials.

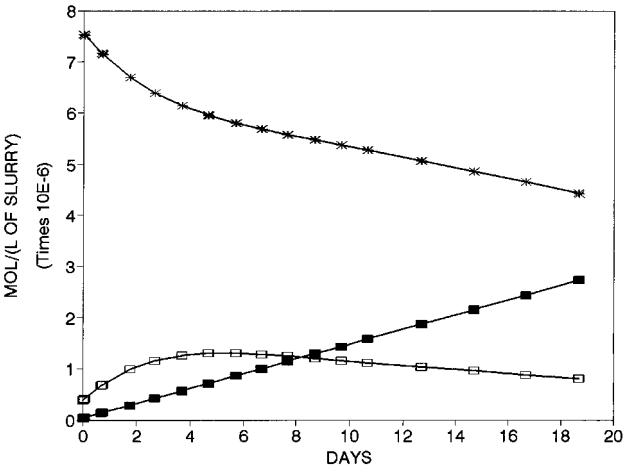

Figure 6. Kinetics curves for the atrazine species of experiment no. 20, calculated from the slurry and filtrate curves of Figure 5: *, in solution; □, labile sorbed; ■, bound residue formed by intraparticle diffusion.

In contrast, the other two atrazine species (free in solution phase and trapped in nonlabile sites) show a gradual decrease or increase with time. Inherently, the nonlabile binding curve should be nonlinear (eq 13), but departure from linearity is usually not resolvable during the first 2 or 3 weeks of the reaction. This reflects the small departure of $d\theta_1/dt$ from zero during this time period. Toward the end of the experiment, a significant portion (−45%) of atrazine is trapped in nonlabile sites, and θ_L declines.

Early in the experiment, when the amount of atrazine that has diffused into the interiors of the soil particles is still so small that diffusion out is not yet measurable, eq 1 reduces to a simpler form. The shape of the overall curve closely resembles standard kinetics for the system: $A \rightleftharpoons B \rightarrow C$. Figures 5 and 6 show similar atrazine species distribution with time for an experiment having higher initial concentration (8.0×10^{-6} mol L^{-1}).

Equilibrium Parameters. Table 3 collects the relevant approximate equilibrium parameters of labile sorption in terms of θ_C, $\bar{K}_1$, K_d, and X_1, in which the weighted average equilibrium function, $\bar{K}_1$, was calculated according to eq 7. The labile sorption capacity, θ_C, conceptually defines a saturation limit of sorbed atrazine on labile sorption sites but, also, is experimentally measurable with a properly designed batch setup as described earlier. As a key equilibrium parameter, it

Table 3. Results of Labile Sorption Equilibrium for Bulk Soil at 25 °C

no.	init concn (10^{-6} mol L^{-1})	equil sorbed (10^{-7} mol L^{-1})	K_1 (10^4 M^{-1})	K_d (10^{-2} L g^{-1})	θ_C (10^{-6}mol g^{-1})	X_1
7	1.00	1.50	3.50	1.36	0.397	0.0188
4	3.20	5.49	3.28	1.21	0.397	0.0693
3	5.70	7.24	2.17	0.783	0.397	0.0912
2	7.93	9.92	2.90	1.01	0.397	0.125
14	7.93	8.32	2.06	0.732	0.397	0.105
20	7.99	11.40	3.05	1.04	0.397	0.142
19	8.00	12.80	3.47	1.16	0.397	0.161
5	20.00	26.30	3.39		0.397	0.287
6	29.80	37.30	3.46		0.397	0.430
av			3.03 ± 0.53	1.04 ± 0.21		

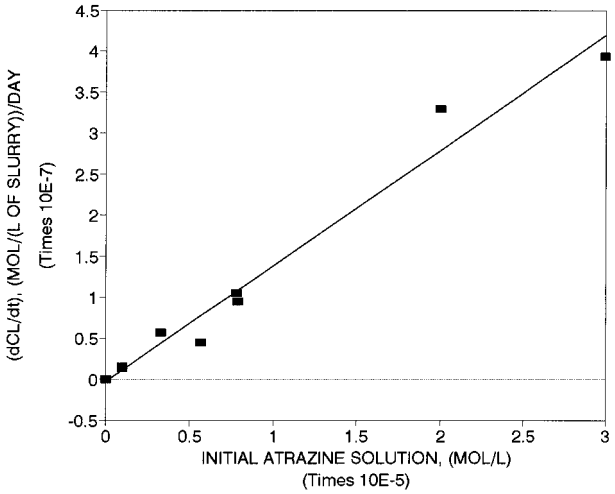

Figure 7. Calculation of k_{s1} by the initial rate method at 25.0 °C. Linear least-squares fit: slope = 0.831; standard error = 0.093; $r^2 = 0.909$.

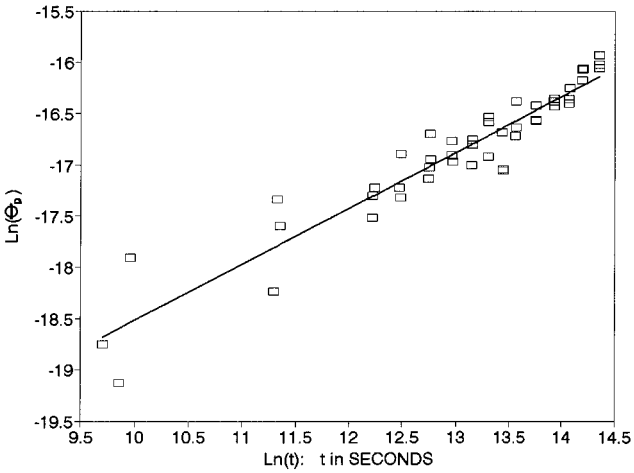

Figure 8. Diagnostic test for intraparticle diffusion with steady state surface site coverage. See Table 4.

determines the chemical stoichiometry of the prompt reaction. Unfortunately, there are few reference values available for comparison. Wang et al. (1990) have studied the interactions of atrazine with Laurentian humic substances and reported the binding capacity values of 8.8 μmol g^{-1} for FA, 15.3 μmol g^{-1} for HA, and 0.37 μmol g^{-1} for the Laurential podzol soil, respectively. The soil number is close to the value measured here, which is perhaps fortuitous given the difference in organic matter content of the two soils.

Rate Parameters. M_{AT} vs t was fitted to a polynomial which could be analytically differentiated to give the initial rate (dM_{AT}/dt at $t = 0$). This gives the pseudo-first-order rate constant (k_{s1}) for each initial value of M_{AT}. It can be seen that the labile sorption pseudo-first-order rate constant is directly proportional to the initial atrazine concentration (M_{AT} at $t = 0$). Figure 7 is a plot of $(dC_1/dt)_{t=0}$ (proportional to dM_{AT}/dt) against initial solution phase atrazine. The uptake rate varies linearly with initial concentration. This is the exact behavior for first-order kinetics. The straight line has a slope (k_{s1}) = $9.62 \times 10^{-6} \pm 1.08 \times 16^{-6}$ (s^{-1}) (statistical test $r^2 = 0.909$). The second-order rate constant, k_{b1}, is calculated as the k_{s1} divided by the sorption capacity giving a value of 1.22 ± 0.14 x L mol^{-1} s^{-1}.

Relatively few and very scattered reference k_{s1} data have been reported, in part because the labile adsorption process has simply been approximated as a rapid equilibrium with no attempt to resolve kinetics. Gamble and Khan (1992) reported a k_{s1} value of 5.81×10^{-7} s^{-1} for the atrazine sorption by an organic soil (Mesisol peat, 37.7% organic matter), which is 15 times lower than the value observed here. Gilchrist et al. (1993) have studied atrazine interactions with pure clay minerals and reported a greater k_{s1} value of about 8×10^{-4} s^{-1}, comparably faster than the present value. No uptake into nonlabile sites was observed in the clay. Adsorption onto sites which remain labile to extraction by the HPLC solvent must involve the pore structure of the particle since these values are not as high as fast physisorption on only the outer geometrical surface of a nonporous particle would produce in stirred samples.

Nonlabile Uptake. In the absence of chemical reactions (e.g., hydrolysis) and microbiological degradation, for a well-mixed and closed-batch system the mass difference between the initial atrazine and the slurry analyses can be attributed to the loss by intraparticle diffusion. To test this, chemical analysis was done for reaction products. None were found. On the other hand, 18.5 ± 1.5% of the atrazine-bound residue was recovered by supercritical fluid extraction. As seen in Figures 4 and 6, the experimental method monitored the kinetics of bound residue formation. When these kinetics curves were subjected to diagnostic test plots like those in Figures 8 and 9, the results anticipated by diffusion theory were obtained. All of the evidence obtained is consistent with the kind of intraparticle diffusion that has been suggested by other authors.

Diagnostic test plots for intraparticle diffusion were made according to eq 12, by plotting $\ln(\theta_D)$ against ln-(t). Figure 8 shows an example, and Table 4 gives the results of nine such tests. They are generally in agreement with Crank's diffusion model that has steady state surface coverage. The model can be subjected to an additional experimental test. The diffusion rate ($d\theta_D/dt$) should be a linear function of the labile surface coverage, θ_L. Figure 9 and Table 5 give additional experimental support for the model.

Within a reaction period of about 3 weeks, the intraparticle diffusion clearly does not approach equilibrium. As shown in Figures 4 and 6, the nonlabile atrazine exhibits a continuous, nearly linear, increase. An initial rate type of calculation gave k_{d1} = (1.16 ±

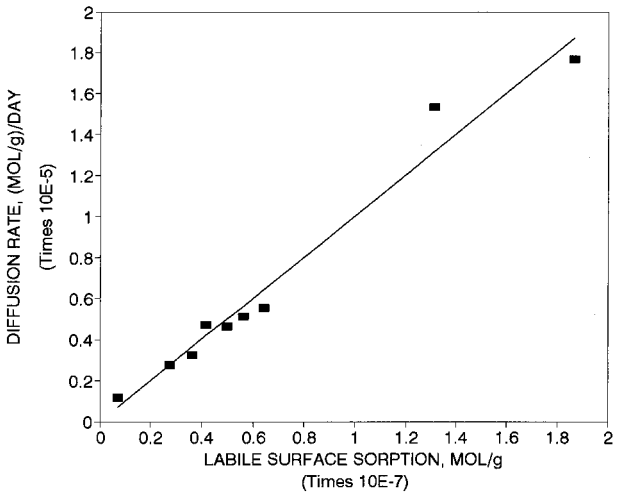

Figure 9. First-order kinetics test for intraparticle diffusion with steady state surface coverage. Linear least-squares fit: slope = 0.0999; standard error = 0.0064; $r^2 = 0.972$.

Table 4. Diagnostic Tests for Bulk Soil Intraparticle Diffusion at 25 °C (See Figure 8)

no.	θ_L at $d\theta_2/dt = 0$ (10^{-8} mol g^{-1})	In(A)	Z
7	0.743	−25.18 ± 0.27	0.488 ± 0.103
4	2.82	−24.29 ± 0.11	0.465 ± 0.106
3	3.58	−23.91 ± 0.01	0.471 ± 0.030
14	4.16	−23.59 ± 0.05	0.506 ± 0.027
2	4.96	−25.46 ± 0.04	0.719 ± 0.013
20	5.68	−23.69 ± 0.08	0.516 ± 0.016
19	6.41	−23.36 ± 0.19	0.488 ± 0.027
5	13.20	−22.52 ± 0.07	0.556 ± 0.031
6	18.70	−22.57 ± 0.15	0.519 ± 0.025
av			0.525 ± 0.042

Table 5. Results of Nonlabile Uptake Kinetics for Bulk Soil at 25 °C (by Eqs 12 and 15)

no.	θ_L (mol g^{-1})	D (cm^2 s^{-1})	k_{d1} (s^{-1})
7	7.50×10^{-9}	1.71×10^{-10}	1.88×10^{-6}
4	2.75×10^{-8}	7.53×10^{-11}	8.25×10^{-7}
3	3.62×10^{-8}	9.32×10^{-11}	1.02×10^{-6}
14	4.16×10^{-8}	1.34×10^{-10}	1.47×10^{-6}
2	4.96×10^{-8}	2.24×10^{-12}	2.45×10^{-8}
20	5.68×10^{-8}	5.88×10^{-11}	6.45×10^{-7}
19	6.41×10^{-8}	8.93×10^{-11}	9.79×10^{-7}
5	1.32×10^{-7}	1.13×10^{-10}	1.24×10^{-6}
6	1.87×10^{-7}	5.11×10^{-10}	5.60×10^{-6}
av		$8.8 \pm 4.6 \times 10^{-11}$	$9.6 \pm 5.1 \times 10^{-7}$

0.074) × 10^{-6} s^{-1}. This agrees well with the average value in Table 5. The diffusion coefficient (D) and the first-order rate constant (k_{d1}) have been evaluated subject to the limit on k_{d1} imposed by the approximation of the particle dimension, r. Table 5 shows the results, in which both D and k_{d1} were calculated from eqs 12 and 15, respectively. The diffusion coefficient (D) has a magnitude of ∼1 × 10^{-10} cm^2 s^{-1}, and the first-order rate constant (k_{d1}) has an average value of ∼1 × 10^{-6} s^{-1}.

Finally, it should be noted that none of the experimental methods used in this research can be guaranteed to give the appropriate value of cross sectional area, a, for use in eq 15. As is commonly done, the particle mean radius ($r = 0.96 \times 10^{-2}$ cm for the bulk soil) has been taken for the calculations. Remarkably, results cross-check. The assumption is shown to be reasonable. Apparently, the overall particle size correlates an apparent D and an empirical pseudo-first-order rate constant that is not dependent on a measure of size for its evaluation.

Wu and Gschwend (1986) have reported D values in close agreement with these results, which is probably partly fortuitous given the differences in the systems. Ball and Roberts (1991) used alternative but related models to evaluate a rate constant in a system with significantly different components. Nevertheless, the value was of a similar order of magnitude to those reported here. Earlier data for both D and k_{d1} can be derived from Karickhoff and Morris' study (Karickhoff and Morris, 1985) of the sorption of hydrophobic pollutants in sediment suspensions by viewing their k_2 as a first-order diffusive rate constant. Their results (on the order of 10^{-11}–10^{-13} cm^2 s^{-1} for D) approach the order of magnitude reported here.

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APPENDIX: CALCULATION OF k_{b1} BY THREE METHODS

Table i. Chemical Species (Data from LIGL7.WK1)

no.	soln (×10^{-1} mol L^{-1})	rev sorbed (mol L^{-1})	irrev sorbed (mol L^{-1})	reaction time (days)
1	9.9581	0.0000	0.0000	0.000
2	9.7778	1.1895×10^{-8}	1.0321×10^{-8}	0.001
3	9.4509	4.3776×10^{-8}	1.1138×10^{-8}	0.004
4	9.1009	7.7755×10^{-8}	1.2158×10^{-8}	0.008
5	8.7091	1.1550×10^{-7}	1.3586×10^{-8}	0.012
6	8.5310	1.3250×10^{-7}	1.4402×10^{-8}	0.015

Table ii. Constants for Iterative Calculations

constant	value	unit
C_T	1.000×10^{-6}	mol L^{-1}
W/V	20.00	g L^{-1}
θ_O (mean)	3.950×10^{-7}	mol g^{-1}
K_1	3.760×10^4	L mol^{-1}
k_{d1}	0.135	$days^{-1}$
Q	8.640×10^4	s $days^{-1}$
t_1	0.000	days

Table iii. Calculation Results of k_{b1}

method	k_{b1} ± SE (× 10^6 L mol^{-1} $days^{-1}$)
initial rate approximation	1.38 ± 0.20
iterative calculation with labile sorption curve (θ_L) (eqs 22 and 23)	1.59 ± 0.05
iterative calculation with solution phase curve (M_{AT}) (eqs 24 and 25)	1.08 ± 0.16
av	1.35 ± 0.20

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