Atrazine Sorption by a Mineral Soil: Effects of Soil Size Fractions and Temperature

Jinhe Li,[†] Cooper H. Langford,[*,‡] and Donald S. Gamble[†]

Department of Chemistry and Biochemistry, Concordia University, 1455 de Maisonneuve Boulevard West, Montreal, Quebec H3G 1M8, Canada, and Department of Chemistry, The University of Calgary, 2500 University Drive Northwest, Calgary, Alberta T2N 1N4, Canada

Equilibrium, kinetics, and mechanism of sorption of the herbicide atrazine by a mineral soil (GB 843) have been studied with an on-line microfiltration−HPLC technique combined with a batch design. As a continuation of our previous work, this paper presents the results of a study of soil size fractionation and the effect of temperature. The experiments with soil size fractions revealed only relatively small changes in atrazine uptake. As expected, the experiments with varying temperature from 5 to 35 °C have shown a quite significant effect on the rate parameters of labile sorption (k_{s1}) and intraparticle diffusion (k_{d1} and D). However, the effect on the labile equilibrium constant was small. The resulting energetic parameters ΔH° and E_a suggested that the labile uptake of atrazine may only involve weak physisorption ($\Delta H^\circ \approx 0$ kJ mol^{-1}), while the nonlabile intraparticle diffusion was controlled by an activated process ($E_a = 89$ kJ mol^{-1}).

Keywords: *Atrazine−soil interactions; on-line HPLC microextraction; bound residues; intraparticle diffusion; soil size fractions; sorption temperature effects*

INTRODUCTION

Natural sorbents are commonly mixtures with a broad range of particle sizes, varying organic and mineralogical compositions, and diverse structural features. However, many trace organic transport and degradation models account for sorption on the bulk soil body by assuming a single equilibrium or uniform distribution of trace organics between the sorbed and mobile aqueous phases. The key equilibrium/kinetic parameters used are often estimated on the basis of bulk soil properties (Weber and Miller, 1988; Fong and Mulkey, 1990; Ball and Roberts, 1991a,b). Increasing evidence suggests that sorption often displays more complex behavior. Indeed, even some predictive modeling approaches have recognized the need to classify by fractions to better simulate the transport of pollutants.

Temperature is one of the important climatic factors in controlling pesticide−soil relationships. As well, the study of temperature effect on interactions may lead to understanding of the mechanism of trace organic sorption. Temperature dependence gives activation energies for kinetic processes which can distinguish physisorption from chemisorption.

Following the companion paper in this issue, this paper investigates the uptake of atrazine by several size fractions of the soil GB 843 and reports the effect of temperature on equilibrium and kinetic parameters. Observed phenomena will be interpreted by the two-stage adsorption/diffusion mechanism introduced in the previous paper.

MATERIALS AND METHODS

Soil Fractions and Reagents. The mineral soil GB 843 was collected from the Green Belt area of the Central Experimental Farm, Ottawa, Ontario. It had been dried and sieved so that maximum particle size was about 425 µm. Its mineralogical composition was given in the previous paper. The soil fractions were obtained by sieving with the American

† Concordia University.
‡ The University of Calgary.

Table 1. Particle Size Distribution for Soil GB 843

fractn no.	opening (mesh)	max (µm)	min (µm)	% of mass
1	40	425[a]	180	45.8
2	80	180	150	12.5
3	100	150	75	19.4
4	200	75	45	13.2
5	325	45	ND	9.1
weighted av[b]			191	100.0

[a] Initial sample maximum size. [b] Calculated by multiplying the midvalues in the ranges by the mass fraction associated with the fraction number.

standard sieve system (Gee and Bauder, 1986). Table 1 shows the particle size distribution. The mass percentages of various fractions allow calculation of weighted averages for various parameters by multiplying each parameter value by the mass fraction of that size fraction. Standard stock solutions of atrazine and other reagents and materials were prepared in the same way as previously described in the companion paper. All the atrazine concentrations used in these experiments were far below its solubility limit ($\sim 1.5 \times 10^{-4}$ M).

Equipment and Kinetic Procedures. The batch setup and the on-line microfiltration (MF)−HPLC system used in this study were similar to those presented in our published work (Gamble and Khan, 1990; Gamble and Ismaily, 1992) and the previous paper. The reaction vessel was a Pyrex cylinder 7.3 cm high by 3.0 cm diameter, with a screw cap. A Teflon-coated stir bar and magnetic stirrer (Fisher Scientific) were used to keep the soil samples suspended. A thermostated circulating bath (Lauda K-2/R, Brinkmann Instruments) connected to double-walled Pyrex jackets was used to maintain the slurry at designed temperatures (25 ± 0.1 °C for soil fraction studies; 5.0, 10.0, 15.0, 25.0, and 35.0 ± 0.1 °C for temperature effect experiments). HPLC studies were performed as before. The key point is that experiments include both analysis of only solution phase atrazine after microfiltration and analysis of solution phase *plus* labile sorbed atrazine by injection of the slurry into the guard column of the HPLC and mobile phase leaching of labile sorbed atrazine.

As previously described, a 0.500 g portion of a given soil fraction was suspended with stirring in approximately 15 mL of distilled deionized water for about 2 days. This wetted all the surface and sorbed water into soil particles. The kinetic run was started by the addition of a calculated aliquot of

Soil and Temperature Effects on Atrazine Sorption

J. Agric. Food Chem., Vol. 44, No. 11, 1996 **3681**

Table 2. Basic Parameters for Soil Fraction Kinetics and Temperature Effect Experiments

fraction no.	T (± 0.1 C)	soil wt (g)	slurry vol (mL)	initial AT ($\times 10^{-6}$ M)	reaction time (days)	data points
			Soil Fraction Kinetics			
1	25.0	0.5219[a]	25.01[a]	4.02[a]	18.78[a]	101
2	25.0	0.5006	24.99	4.01	18.75	104
3	25.0	0.4988	24.90	4.02	18.71	101
4	25.0	0.5030	24.93	4.03	18.74	53
5	25.0	0.5052	24.91	4.02	18.81	53
			Temperature Effect Experiments			
	5.0	0.5031	24.96	7.99	19.23	102
	10.0	0.5038	24.97	8.00	80.07	107
bulk	15.0	0.5034	24.95	8.01	18.68	176
	25.0	0.5069	24.98	7.97	18.97	216
	35.0	0.5025	24.93	7.98	19.08	163

[a] Average values.

atrazine standard stock solution, with the total slurry volume being adjusted to 25.0 mL. Stirring maintained a uniform suspension of soil particles throughout the whole solution. Two HPLC analysis sequences, a preinjection filtration with the 0.45 μm filters followed by injection of the filtrate and a postinjection filtration which combined a guard column (2.0 μm) with 0.5 μm on-line filters, were used alternately. Methanol/H$_2$O (62.5/37.5 with 1.58 $\times$ 10^{-3} M HCl) or acetonitrile/H$_2$O (50/50 with 3.18 $\times$ 10^{-3} M HCl) was used as mobile phase with a flow rate of 1.0 mL/min. Each experiment was run in duplicate or triplicate and carried out over 3–12 weeks. To study the effect of temperature, batch experiments with bulk soil were conducted. The general experimental parameters for both soil fraction kinetics and temperature effect experiments are collected in Table 2. Blank experiments have shown that atrazine adsorption on the Pyrex vial walls was not measurable outside the measurement errors.

Characterization of Soil Fractions. Modal analyses were performed using a stereomicroscope (Wild Photomakroskop M400, Wild Leitz Canada Ltd.) with plane-polarized light (PPL) or crossed-polarized light (XPL). The sample slides (thin sections) were prepared by standard procedures (Ruthven and Loughlin, 1971). A series of samples were collected at different reaction times from the reaction vessel during a run in order to check whether or not soil particle sizes were affected by stirring of the slurry. The results indicated that there was no significant change within the first 3 weeks under the present conditions. Similar observations have been reported by Ball and Roberts (1991b) and Wu and Gschwend (1986).

Specific surface area of the different soil size fractions was measured using the EGME (ethylene glycol monoethyl ether) technique (Chiou et al., 1979). A modified Mebius method (Mortland, 1970), i.e., rapid dichromate oxidation, was used to determine the organic carbon (OC) content in the soil fractions. In addition, the labile sorption capacity (θ_C) for each of the soil fractions was determined by saturating the surface sorption sites using solutions having higher atrazine concentrations in the same way as described for the bulk soil in the previous paper. The resulting values for the specific surface area, organic carbon content, and labile sorption capacity are reported in Table 3.

RESULTS AND DISCUSSION

Labile Sorption. As shown in Table 3, the measured values of θ_C for the soil fractions exhibit a clear trend: the finer the size fractions, the higher the sorption capacities, but increases are not large. A mass-weighted average for θ_C is 0.435 $\times$ 10^{-6} mol g^{-1} of soil which approximately matches the measured value for the bulk soil, 0.397 $\times$ 10^{-6} mol g^{-1} of soil.

Figure 1 shows atrazine species distribution in filtrate and slurry phases from which solution, labile sorbed, and nonlabile sorbed phases can be calculated. As discussed in our companion paper, a two-stage (surface adsorption/intraparticle diffusion) model describes the

Table 3. Specific Surface Area, Organic Carbon Content, and Labile Sorption Capacity

fraction no.	particle size (av, μm)	EGME area (m^2 g^{-1})	OC (%)	equil sorbed (θ_C) (μmol g^{-1})
1	302.5	27.3 $\pm$ 3.2[a]	0.60 $\pm$ 0.01[a]	0.370 $\pm$ 0.013[a]
2	165.0	30.2 $\pm$ 9.4	0.67 $\pm$ 0.01	0.467 $\pm$ 0.024
3	112.5	36.9 $\pm$ 1.2	0.94 $\pm$ 0.00	0.527 $\pm$ 0.014
4	60.0	41.4 $\pm$ 2.9	0.98 $\pm$ 0.04	0.581 $\pm$ 0.031
5	22.5	48.6 $\pm$ 0.4	1.26 $\pm$ 0.16	0.630 $\pm$ 0.010
weighted av		33.3	0.79	0.435
bulk soil	191.0	38.9 $\pm$ 2.3 3.90 $\pm$ 0.20[b]	0.83 $\pm$ 0.01	0.397 $\pm$ 0.036

[a] Average values. [b] BET area.
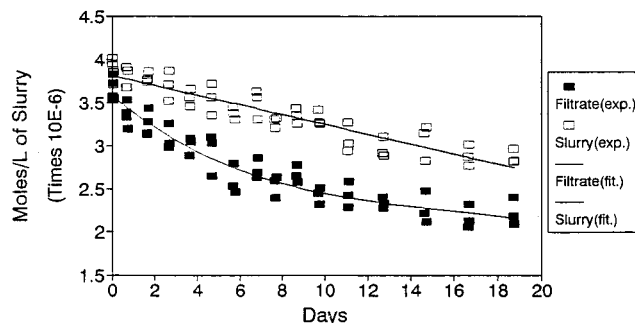
Figure 1. Slurry and filtrate measurements for the soil size fraction no. 4 (25.0 °C): □, slurry; ■, filtrate measurements; —, curves fitted by the method of least-squares to polynomials.

labile surface uptake of atrazine, including both the equilibrium aspect and the kinetic aspect, using the following expressions:

$$\bar{K} = k_{b1}/k_{s2} = \theta_1/\theta_O M_{AT} \tag{3}$$

$$\theta_C = \theta_O + \theta_1 \tag{4}$$

$$X_1 = \theta_1/\theta_C \tag{5}$$

$$K_d = \bar{K}_1 \theta_C (1 - X_1) \tag{6}$$

$$-dM_{AT}/dt = (W/V)d\theta_1/dt$$
$$= k_{b1}(W/V)\theta_O M_{AT} - k_{s2}(W/V)\theta_L \tag{7}$$

where $\bar{K}_1$ is the weighted average equilibrium function (in L mol^{-1}), K_d is the commonly used distribution coefficient (in L g^{-1}), k_{b1} is the second-order rate constant for the labile adsorption (in L mol^{-1} s^{-1}), k_{s2} is the first-order rate constant for the desorption (in s^{-1}), M_{AT} is the concentration of solution phase atrazine (in mol L^{-1}), θ_C, θ_1, and θ_O represent the labile sorption capacity, the concentration of sorption sites occupied by atrazine (in mol g^{-1} of soil), and the concentration of sites unoccupied, respectively, X_1 is the mole fraction of occupied sorption sites (dimensionless), and the term W/V is a unit conversion factor (in g L^{-1}) for the ratio of soil to solution. For low loadings of the sorption sites, $\theta_O \approx \theta_C$. Equation 7 can then be written with the pseudo-first-order rate constant $k_{s1} = k_{b1}\theta_O$. As indicated by a footnote in Table 6, $\bar{K}_1$ and K_d were estimated for that point in time at which $d\theta_L/dt = 0$. This takes into account the fact that the labile sorption and desorption rates are sufficiently fast so that they tend to maintain that equilibrium as the slower intraparticle diffusion depletes the whole labile pool.

The resulting values for $\bar{K}_1$, K_d, and X_1 are presented in Table 4. The trends for $\bar{K}_1$ and K_d are qualitatively consistent with those that would be expected on the basis of both specific surface area and organic matter

Table 4. Labile Sorption Results for Soil Fractions

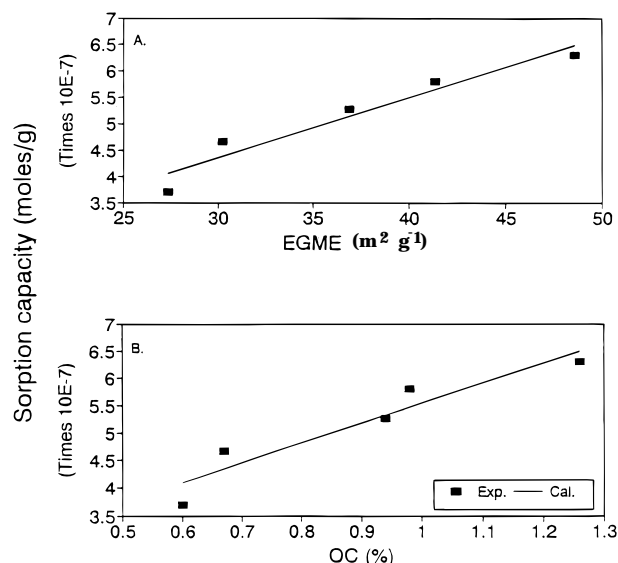|			equilibrium		
fraction no.	θ_C (10^{-6} mol g^{-1})	K_1 (10^4 M^{-1})	X_1 (10^{-2})	K_d (10^{-2} L g^{-1})	k_{s1} (10^{-6} s^{-1})
1	0.370	2.37 ± 0.43[a]	7.92 ± 1.22[a]	0.807[a]	5.21 ± 0.044[a]
2	0.467	2.79 ± 0.08	6.00 ± 0.17	1.22	6.64 ± 1.08
3	0.527	3.03 ± 0.02	6.02 ± 0.00	1.50	10.3 ± 0.04
4	0.581	4.63	6.47	2.52	13.9 ± 0.9
5	0.630	4.21	6.78	2.47	23.6 ± 1.9
weighted av	0.435	3.02	7.02	1.37	10.6
measured bulk soil	0.397 ± 0.036	3.03 ± 0.97	10.2	1.01 ± 0.35	9.62 ± 1.08

[a] Average values.
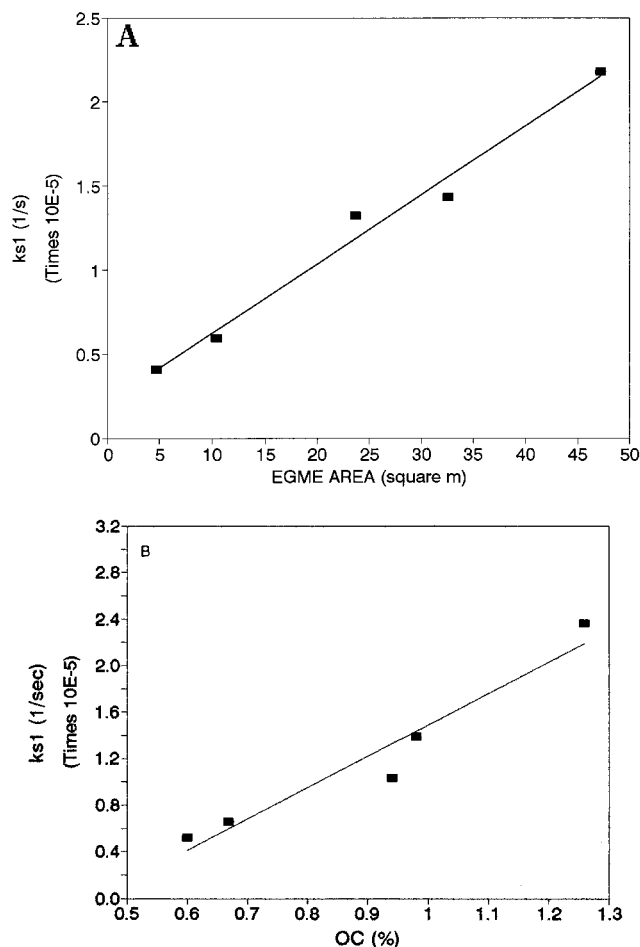
Figure 2. Labile sorption rate constant, k_{s1}: (A) as a function of EGME surface measurements and (B) as a function of organic carbon content.

Figure 3. Labile sorption capacity, θ_C: (A) as a function of EGME surface measurements and (B) as a function of organic carbon content.

content, that is, both $\bar{K}_1$ and K_d increase slightly from coarser to finer soil fractions. Similar observations have been reported by, e.g., Karickhoff et al. (1979).

Labile sorption kinetics should be inherently second order (eq 7). Applying a first-order approximation to the initial rate (i.e., $\theta_O \approx$ constant, and neglecting the desorption and intraparticle diffusion terms), an initial rate approximation (Gamble and Khan, 1990) may be used. The resulting values for the pseudo-first-order rate constant, k_{s1} ($=k_{b1}(W/V)\theta_O$), are shown in Table 4. It can be seen that the k_{s1} values consistently increase as the particle size decreases.

Figure 2 shows a linear correlation of k_{s1} with EGME measurements, and a similar correlation of k_{s1} with soil organic matter. The r^2 values are 0.948 and 0.937, respectively. Related to this are the linear plots of θ_C against EGME data and organic matter in Figure 3. There are likely three reasons why these four correlations have a common link. The first is the relationship $k_{s1} = k_{b1}\theta_O$ mentioned in the discussion of eq 7. The

next is the fact that soil organic matter has long been known to have more sorption sites per gram than soil minerals do. The third reason is that EGME measurements might actually reflect the number of sorption sites per gram that are available in the absence of sorbed water, rather than simple geometric surface area.

Nonlabile Uptake. Nonlabile atrazine species trapped show a steady increase with reaction time as we saw in the preceding paper. Phenomena which can be modeled as an initially fast sorption followed by a much slower and apparently irreversible uptake have often been observed. Most literature (Khan, 1973; Kearney, 1976; Wu and Gschwend, 1986) has treated the uptake by diffusion with first-order kinetics, but no simple theoretical support has been given for this. In the two-stage model of the previous paper, a particular diffusion model published by Crank (1975) is relevant to the intraparticle diffusion of the second stage. Crank provided solutions to the Fick's law equation for a series of similar models. Each of these models was characterized by different kinetics for labile surface site coverage. The relevant model in this case has steady state coverage, θ_1, of the labile surface sorption sites and diffusion from there into a semi-infinite sink. The simple relationship $k_{d1} = D/r^2$ was abstracted from Crank's model. k_{d1} is a first-order rate constant, and r is a mean particle radius (θ_D is the amount of atrazine trapped by intraparticle diffusion, in mol g^{-1} of soil). The initial rate calculation of k_{d1} using steady state surface coverage was described in the previous paper. Table 5 shows the resulting k_{d1} and D values.

k_{d1} is a compound parameter which depends on the apparent intraparticle diffusivity (D) and the particle

Soil and Temperature Effects on Atrazine Sorption

J. Agric. Food Chem., Vol. 44, No. 11, 1996 **3683**

Table 5. Nonlabile Uptake Kinetics for Soil Fractions

				steady state			
fraction no.	av r $(10^{-2}$ cm)	θ_L $(10^8$ mol g$^{-1})$	$d\theta_D/dt$ $(10^{-14}$ mol g^{-1} s$^{-1})$	D^a $(10^{-11}$ cm^2 s$^{-1})$	$k_{d1}{}^a$ $(10^{-6}$ s$^{-1})$	$k_{d1}{}^b$ $(10^{-6}$ s$^{-1})$
1	1.513	2.93 ± 0.45	4.31	25.8 ± 14.2	1.13 ± 0.62	1.47 ± 0.23
2	0.825	2.80 ± 0.08	3.53	6.12 ± 1.82	0.90 ± 0.28	1.26 ± 0.92
3	0.563	3.17 ± 0.00	2.92	2.15 ± 0.36	0.68 ± 0.11	0.79
4	0.30	3.76	3.02	0.699	0.78	0.80
5	0.113	4.27	2.20	0.0668	0.52	0.51
weighted av	0.955	3.19		13.1	0.91	1.16
bulk	0.955	5.30		8.75	0.96	1.16 ± 0.07

^{a} Calculated from the diffusion equation and particle radius. ^{b} Calculated from the initial rate.
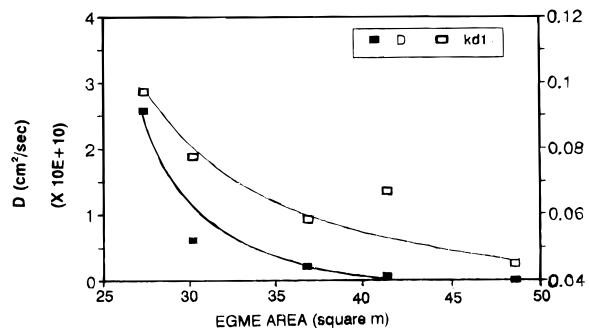
Figure 4. Effects of EGME "surface" on intraparticle diffusion: ■, diffusion coefficient, D; □, rate constant, k_{d1}.
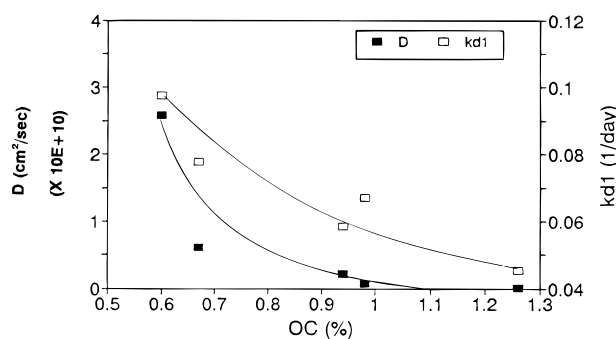
Figure 5. Effects of organic carbon content on intraparticle diffusion: ■, diffusion coefficient, D; □, rate constant, k_{d1}.

radius (r). Both D and r values vary in the same direction with particle size. Therefore, the overall effect will depend upon their relative magnitudes as shown in Table 5. For comparison, k_{d1} can be determined from the initial diffusion rate (dθ_D/dt) and the labile surface coverage (θ_L). The coarser fractions have larger dθ_D/dt values and smaller θ_1 values (resulting in larger k_{d1}). It is important to note that k_{d1} values calculated both ways have approximately the same magnitude (the weighted averages being 0.91 and 1.16 × 10^{-6} s^{-1}) and decrease slightly with decreasing particle sizes. Note that, to date, there is no reliable method to estimate the size parameter connecting D and k_{d1}. The relation to particle size (r) is postulated. Therefore, the agreement with the initial rate calculation is reassuring.

Figures 4 and 5 show plots for D and k_{d1} against specific surface area and organic carbon content. It can be seen that, in contrast to k_{s1} that shows linear correlation to specific surface area and organic carbon content (Figure 2), D and k_{d1} drop more sharply with both surface area and organic content. Again, we cannot tell which parameter of the soil is more significant. There is nothing about the increase of EGME surface area that has any obvious relation to reduced rates of trapping in "bound residue" sites. Thus, it is attractive to speculate that the slow uptake into bound sites is connected to organic matter. Gilchrist et al. (1993) found no slow uptake term in an organic free clay.

Table 6. Temperature Effect on Labile Sorption Kinetics

		steady state			
T (°C)	θ_L $(10^{-8}$ mol g$^{-1})$	$\bar{K}_1$ $(10^4$ M$^{-1})$	k_{s1} $(10^{-6}$ s$^{-1})$	X_1 at K_d equil^a	K_d $(10^{-2}$ L g$^{-1})$
5	5.64	2.95 ± 0.82	5.76 ± 0.42	0.142	1.00 ± 0.25
10	5.60	3.35	6.35 ± 0.19	0.141	1.14
15	5.75	3.75 ± 0.90	6.82 ± 0.37	0.145	1.27 ± 0.28
25	5.30	3.03 ± 0.97	9.62 ± 1.08	0.102	1.01 ± 0.35
35	4.66	3.32 ± 1.38	14.4 ± 2.0	0.149	1.11 ± 0.40

^{a} i.e., dθ_1/dt = 0.

Table 7. Temperature Effect on Nonlabile Uptake

|		final	
T (°C)	θ_D $(10^{-8}$ mol g$^{-1})$	D $(10^{-11}$ cm^2 s$^{-1})$	k_{d1} $(10^{-7}$ s$^{-1})$
5	7.52^a	1.26 ± 0.53	1.38 ± 0.58
10	9.39	1.87	2.05
15	7.46^a	3.37 ± 2.78^a	3.69 ± 3.05^a
25	5.52	10.5	11.5
35	4.74^a	54.0 ± 2.00^a	59.3 ± 21.9^a

^{a} Average values of several runs.

Temperature Effect. The pseudo-first-order rate constant (k_{s1}) was calculated for each temperature using the initial rate approximation. The results are shown in Table 6. It can be seen that k_{s1} increased with increasing temperature, whereas the equilibrium surface sorbed atrazine varied little. The reverse reaction must increase in rate similarly. Note that this work did not cover the effect of temperature on the sorption capacity (θ_C) which was assumed to be a constant value (0.397 × 10^{-6} mol g^{-1}) in all cases (Gamble and Khan, 1990; Gamble and Ismaily, 1992). But, this parameter could vary slightly as a function of temperature.

In order to determine the effect of temperature on the kinetics of nonlabile uptake, both the diffusion coefficient (D) and the first-order diffusion rate constant (k_{d1}) were calculated. The results are shown in Table 7. The diffusion coefficient D (and the rate constant k_{d1}) increased as the temperature rose from 5 to 35 °C, by a factor of up to 40.

van't Hoff and Arrhenius equations have been used to treat the equilibrium and kinetic data obtained in the temperature effect experiments. The fit for K_1 gives a near zero value of $\Delta H°$ (0.8 ± 3 kJ mol^{-1}), and the fitted data for activation energies from k_{s1} and k_{d1} are 22 ± 2.4 and 89 ± 7 kJ mol^{-1}, respectively (see Figures 6 and 7). Low E_a values (<42 kJ mol^{-1}) usually indicate diffusion-controlled processes (typically, 17−21 kJ mol^{-1} for the film diffusion and 21−42 kJ mol^{-1} for the particle diffusion), whereas higher E_a values suggest chemical reaction activation barriers (Moore, 1962).

CONCLUSIONS

The observed labile uptake rate constant (k_{s1}) for the finest fraction differed from the coarsest by a factor of

3684 *J. Agric. Food Chem.,* Vol. 44, No. 11, 1996

Li et al.
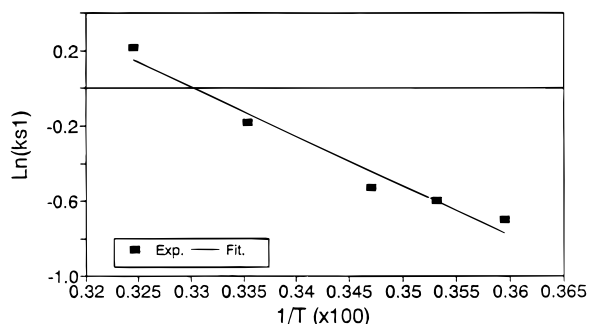
Figure 6. Arrhenius plot for the labile sorption rate constant, k_{s1}.
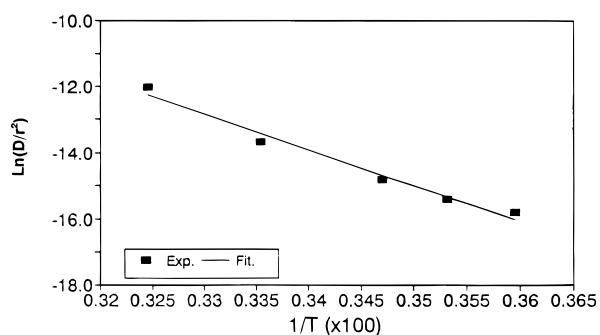
Figure 7. Arrhenius plot for the intraparticle diffusion rate constant, $k_{d1} = D/r^2$.

~4. Both θ_C and k_{s1} have been shown to be linearly correlated to specific surface area and organic carbon content. These might be important factors in the labile sorption process. However, a factor of 4 is not a large change. This emphasizes that labile sites are not all on a geometrically simple spherical surface. The measured surface area (Table 2) is *only* weakly dependent upon particle size (r). If particles were spheres, surface area would vary as r^2. Since most parameters vary slowly as r increases, it is evident that surface area is determined as an interior, perhaps gel-like, phase and relates more closely to mass than "size". This means that all particles are very similar internally. Perhaps they are nearly "self-similar" (i.e., fractal geometry).

The nonlabile uptake characterized by the effective diffusion coefficient (D) or rate constant (k_{d1}) exhibited a nonlinear behavior: both D and k_{d1} decreased rapidly with decreasing particle size. It is quite interesting that it is the smaller particles with shorter bulk diffusion paths that are penetrated more slowly. The attractive speculation connects this to increasing organic matter content.

A most important point about D and k_{d1} is that temperature dependence indicates a process with high activation energy. If the indications of extraction experiments reported in the companion paper and the long-term equilibration study on nonlabile adsorption do imply that atrazine does not undergo chemical modification, the high activation energy must be associated with "chemical" perturbation of the soil matrix which creates the trap sites which take up the atrazine. Since the saturation levels in the long-term experiments are not large, the number of nonlabile binding sites may also not be large, that is, the nonlabile adsorption sites are suggested to be special sites which undergo chemical reorganization to accept atrazine. This may be exactly the behavior expected in micropores where pore diameters are not many times the atrazine radius. One of the remaining questions is whether or not it would be possible for smaller particles to have narrower pores. One can only speculate until there is more information about interactions with particular soil components such as soil organic matter.

LITERATURE CITED

Ball, W. P.; Roberts, P. V. Long-Term Sorption Of Halogenated Organic Chemicals By Aquifer Material. 1. Equilibrium. *Environ. Sci. Technol.* **1991a**, *25*, 1223−1237.

Ball, W. P.; Roberts, P. V. Long-Term Sorption Of Halogenated Organic Chemicals By Aquifer Material. 2. Intraparticle Diffusion. *Environ. Sci. Technol.* **1991b**, *25*, 1237−1249.

Chiou, C. T.; Peters, L. J.; Freed, V. H. A Physical Concept Of Soil−Water Equilibria For Nonionic Organic Compounds. *Science* **1979**, *206*, 831−832.

Crank, J. *The Mathematics of Diffusion*, 2nd ed.; Oxford University Press: Oxford, 1975; p 26.

Fong, F. K.; Mulkey, L. A. Comparison Of Numerical Schemes For Solving A Spherical Diffusion Equation. *Water Resource Res.* **1990**, *26*, 843−853.

Gamble, D. S.; Khan, S. U. Atrazine In Organic Soil: Chemical Speciation During Heterogeneous Catalysis. *J. Agric. Food Chem.* **1990**, *38*, 297−308.

Gamble, D. S.; Ismaily, L. A. Atrazine In Mineral Soil: The Analytical Chemistry of Speciation. *Can. J. Chem.* **1992**, *70*, 1590−1596.

Gee, G. W.; Bauder, J. W. Particle Size Analysis. In *Methods of Soil Analysis, Part 1-Physical and Mineralogical Methods*, 2nd ed.; Klute, A., Ed.; Soil Sci. Soc. Am.: Madison, WI, 1986; Chapter 15.

Gilchrist, G. F. R.; Gamble, D. S.; Kodama, H.; Khan, S. U. Atrazine Interactions With Clay Minerals: Kinetics And Equilibria Of Sorption. *J. Agric. Food Chem.* **1993**, *41*, 1748−1755.

Hague, R. *Dynamics, Exposure, and Hazard Assessment of Toxic Chemicals*; Ann Arbor Science: Ann arbor, MI, 1980.

Karickhoff, S. W.; Brown, D. S.; Scott, T. A. Sorption Of Hydrophobic Pollutants On Natural Sediments. *Water Res.* **1979**, *13*, 241−248.

Kearney, P. C. Summary Of Soil Bound Residue Sessions. *ACS Symp. Ser.* **1976**, *29*, 378−382.

Khan, S. U. Equilibrium and Kinetic Studies Of The Adsorption of 2,4-D And Picloram On Humic Acid. *Can. J. Soil Sci.* **1973**, *53*, 429−434.

Moor, J. W. *Physical Chemistry*, 3rd ed.; Prentice Hall: Englewood Cliffs, NJ, 1962; p 180.

Mortland, M. M. Clay-Organic Complexes And Interactions. *Adv. Agron.* **1970**, *22*, 75−117.

Ruthven, D. M.; Loughlin, K. F. Effects Of Crystallitev Shape And Size Distribution On Diffusion In Molecular Sieves. *Chem. Eng. Sci.* **1971**, *26*, 577−584.

Weber, W. J., Jr.; Miller, C. T. Modeling The Sorption Of Hydrophobic Contaminants By Aquifer Materials. 1. Rates And Equilibria. *Water Res.* **1988**, *22*, 457−464.

Wu, S.-C.; Gschwend, P. M. Sorption Kinetics Of Hydrophobic Organic Coumpounds To Natural sediments And Soils. *Environ. Sci. Technol.* **1986**, *20*, 717−725.