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# Sorption and Desorption Rates of Carbon Tetrachloride and 1,2-Dichlorobenzene to Three Organobentonites and a Natural Peat Soil

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The sorption and desorption rates of carbon tetrachloride ( $\text{CCl}_4$ ) and 1,2-dichlorobenzene (1,2-DCB) to and from three organobentonites of varying alkyl-chain length were quantified. The effects of solute structure, organobentonite structure, and solute-sorbent contact time on the rates of solute mass-transfer were investigated. For each solute, the rate of sorption was compared to the rate of desorption. In addition, the rate of 1,2-DCB sorption to a natural peat soil was quantified. The experimental data were simulated using a two-site model and a model incorporating a continuous distribution of mass-transfer rate coefficients. Based on a statistical analysis of the model simulations, the following conclusions were made: (1) The rate of 1,2-DCB sorption to the organobentonites was significantly faster than the rate of 1,2-DCB sorption to the peat soil. (2) The rate of mass-transfer during sorption and desorption was greater for  $\text{CCl}_4$  than for 1,2-DCB. (3) The alkyl-chain lengths of the organobentonites did not affect the rate of mass-transfer during sorption; however, the rate of 1,2-DCB desorption decreased as the length of the organobentonite alkyl-chain increased. (4) The rate of solute desorption was slower than the rate of solute uptake for two of the three organobentonites. (5) For most environmental applications using the organobentonites studied here, a local equilibrium assumption will satisfactorily describe  $\text{CCl}_4$  and 1,2-DCB sorption and desorption.

## Introduction

Organobentonites are produced by the exchange of organic cations (typically having a quaternary ammonium structure) for inorganic ions (e.g.,  $\text{H}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ) on the internal and external mineral surfaces of bentonite (1). The external mineral surfaces and interlamellar space of the resulting organobentonite are organophilic. Organobentonites are powerful sorbents for many organic pollutants relative to conventional bentonite (2), and the magnitude and mech-

anism of sorption are functions of the molecular structure of the exchanged organic cation (2–4), the extent of cation exchange (1, 5), the solution chemistry (6), the molecular structure of the solute (5, 7, 8), and the cation-exchange capacity of the bentonite (8). Because of their unique properties with regard to pollutant sorption from water, the number of environmental applications for organoclays has increased dramatically over the past 10 years. Organoclays have been studied and/or used as components of earthen slurry walls and landfill liners (9–11), for chromatographic applications (12, 13), in the design of groundwater remediation systems (14–16), as sorbents for air sampling (17) and wastewater treatment applications (18, 19), and for stabilization of contaminated soil (20, 21).

Although many of the above-referenced studies have focused on the equilibrium sorption of organic contaminants to organobentonites, relatively little information exists regarding the effects of the sorbent and solute properties on the rate of sorption and desorption of the solute in aqueous systems. In a series of batch sorption experiments, Nzengung et al. (22) quantified the rates of diuron and naphthalene sorption from water to two organoclays (trimethylphenylammonium-(TMPA-) and benzyldimethyltetradecylammonium-montmorillonite). Using a first-order kinetic model, these researchers found that the sorption mass-transfer coefficient varied inversely with the equilibrium sorption coefficient. Furthermore, they reported that when methanol was added as a cosolvent, the mass-transfer coefficient increased with increasing methanol fraction. This result was attributed to conformational changes to the organic matter fraction of the sorbent (and subsequent increases in intraorganic matter solute diffusion) in the presence of methanol. These researchers did not study rates of solute desorption (23). In a study of naphthalene biodegradation in water-organoclay suspensions, Crocker et al. (24) noted that the mass transfer of naphthalene between the organoclay and water was relatively fast and that organoclay particle size was related to rates of mass-transfer, with the largest particle sizes having the slowest mass-transfer rates. These researchers hypothesized that the larger clay particles were aggregates of smaller particles, and sorption rates were slowed by intraparticle diffusion limitations. These studies suggest that diffusion of the solute into the organic phase formed by the quaternary ammonium cations (both on external clay surfaces and in the interlamellar space) and diffusion into intraparticle pores of aggregates may both contribute to sorption rate limitations.

In the present work, we present the results and analyses of batch sorption experiments to quantify the rates of 1,2-dichlorobenzene (1,2-DCB) and carbon tetrachloride ( $\text{CCl}_4$ ) sorption and desorption to and from three organobentonites (decyltrimethylammonium- (DTMA-), tetradecyltrimethylammonium- (TDTMA-), and octadecyltrimethylammonium- (ODTMA-) bentonite). Previous studies have shown that solute sorption to these types of organobentonites is characterized primarily by linear sorption isotherms (or slightly concave-up isotherms at aqueous solute concentrations approaching solubility (4)), noncompetitive sorption, and relatively low isosteric heats of sorption (2). These observations are consistent with a partition mechanism wherein the solute partitions between water and the organic-matter phase of the bentonite in accord with its solubility in the two phases (2). In addition, we have quantified the rate of 1,2-DCB sorption to a natural peat soil with an organic carbon content comparable to the three organobentonites to allow for comparisons of sorption rates between organobentonites and

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natural soil. The objectives of this study are to quantitatively draw comparisons between rates of sorption and desorption for a given solute/sorbent combination, rates of sorption and desorption for different sorbents and solutes, and rates of desorption for different solute/sorbent contact times.

## Model Development

The traditional two-site equilibrium/kinetic model assumes that there are two distinct sorption regions that exhibit different mass-transfer rate characteristics. Typically, local equilibrium between the sorbed and aqueous phases is assumed to hold in one type of site, whereas the rate of mass-transfer in the other type of site is assumed to be kinetically limited. The equations governing the rate of sorption/desorption for each site are

$$\frac{dS_E}{dt} = fK_D \frac{dC}{dt} \quad (1)$$

$$\frac{dS_K}{dt} = \alpha[(1 - f)K_D C - S_K] \quad (2)$$

where  $S$  is the sorbed concentration (mg sorbed in designated type of site/kg sorbent) and the subscripts E and K represent different sorption sites or regions;  $f$  is the fraction of equilibrium sites;  $K_D$  is the distribution coefficient (L/kg),  $C$  is the aqueous solute concentration (mg/L),  $\alpha$  is the first-order mass-transfer rate coefficient (1/T), and  $t$  is time (T) (25).

For a batch reactor, the time rate of change of the aqueous solute concentration is given by

$$\frac{dC}{dt} = -\frac{M_s}{V} \frac{dS_T}{dt} - kC \quad (3)$$

where  $V$  is the aqueous phase volume of the reactor (L<sup>3</sup>),  $M_s$  is the mass of sorbent in the reactor (g),  $S_T$  is the total sorbed concentration (mg/Kg), and  $k$  is a first-order rate constant (1/T) that accounts for solute losses resulting from volatilization, sorption to Teflon, etc. An expression for the time derivative of  $S_T$  can be developed using the relationship  $S_T = S_K + S_E$  and eqs 1 and 2. This expression can be substituted into eq 3 to give

$$\frac{dC}{dt} = -\frac{M_s \alpha [(1 - f) K_D C - S_K]}{(V + M_s f K_D)} - \frac{kC}{(V + M_s f K_D)} \quad (4)$$

The governing system of ordinary differential equations was solved analytically with the appropriate initial conditions for both sorption and desorption.

In general, the two-site model has been unable to adequately simulate the strongly kinetic sorption and desorption data observed in laboratory and/or field-scale experiments (25–30). A fundamental limitation of the two-site model is the assumption that two regions of different mass-transfer rate characteristics can adequately describe typical sorbent heterogeneity. This is unlikely given that the physical characteristics of a sorbent can vary at the particle-scale (26, 31). To account for sorbent heterogeneity, several researchers have developed models that incorporate a continuous distribution of mass-transfer rate coefficients generated by a probability density function (PDF) (25, 28, 30, 32–34). By using a PDF to generate the distribution of rate coefficients, the distributed rate model has the same number of fitting parameters as the two-site model.

The  $\gamma$ -distribution is frequently used to obtain the distribution of mass-transfer rate coefficients for distributed rate parameter models (25, 28, 30, 32, 33). The  $\gamma$  probability density function is given by

$$p(\alpha) = \frac{\beta^{-\eta} \alpha^{\eta-1}}{\int_0^\infty x^{\eta-1} \exp(-x) dx} \exp\left(-\frac{\alpha}{\beta}\right) \quad (5)$$

where  $\eta$  (the shape parameter) and  $\beta$  (the scale parameter) are positive parameters,  $\alpha$  is the mass-transfer coefficient, and  $x$  is a dummy variable of integration. The magnitude and shape of the distribution of the mass-transfer coefficients can be varied by altering  $\eta$  and  $\beta$ .

To numerically approximate the continuous distribution of rate coefficients, the sorbent was discretized into a finite number (NK) of compartments. For this study, NK was chosen to be 100. The governing equation for the time rate of change of the sorbed concentration in an individual compartment  $i$  is given by

$$\frac{dS_i}{dt} = \alpha_i (fK_D C - S_i) \quad (6)$$

where

$$f = \frac{1}{NK} \quad (7)$$

$f$  is the fraction of sites in each compartment,  $i$  is the mass-transfer rate coefficient for compartment  $i$  (1/T), and  $S_i$  is the mass sorbed in compartment  $i$  with respect to the total mass of the soil (mg/Kg). The time rate of change of the total sorbed concentration is given by

$$\frac{dS_T}{dt} = \sum_{i=1}^{NK} \alpha_i (fK_D C - S_i) \quad (8)$$

Substitution of eq 8 into eq 3 gives the governing expression for the change in aqueous solute concentration as a function of time for a batch reactor:

$$\frac{dC}{dt} = -\frac{M_s}{V} \left[ \sum_{i=1}^{NK} \alpha_i (fK_D C - S_i) \right] - \frac{k}{V} C \quad (9)$$

Discrete values for the mass-transfer rate coefficients were determined for the NK compartments using the  $\gamma$ -distribution. The median value of the mass-transfer rate coefficient within each compartment was chosen as a representative value. The median mass-transfer rate coefficient for each compartment was determined from the cumulative probability distribution of the  $\gamma$ -function using a standard bisection search method (25). The resulting system of governing equations was solved numerically using a fourth-order Runge–Kutta integration technique.

The simulation models were fit to the experimental data, and the optimal fitting parameters were found. Confidence contours for the estimated rate parameters were developed. Details describing the criteria for determining optimal rate parameters and subsequent confidence regions are given in the Supporting Information available on microform.

## Materials and Methods

**Sorbents.** The organo-clays used in this study were synthesized in the laboratory from a base clay of Wyoming bentonite (sample TFS-81, American Colloid Co., Chicago IL) composed of 3.6% sand, 7.3% silt, and 89.1% clay. The natural organic-carbon content of the base clay is 0.1%, and its cation-exchange capacity is 78.5 milliequiv/100 g (2). Decyltrimethylammonium (DTMA) bromide was obtained from Fisher Scientific. Tetradecyltrimethylammonium (TDTMA) bromide and octadecyltrimethylammonium (ODTMA) bromide were obtained from Aldrich Chemical Co. All compounds were used as received.

**TABLE 1. Physical and Chemical Properties of the Organobentonites and the Peat Soil**

| sorbent    | mass fraction organic-carbon content | specific surface area (m <sup>2</sup> /g) | basal spacing (nm) |
|------------|--------------------------------------|---|--------------------|
| DTMA-clay  | 0.0843                               | 25.7                                      | 1.426              |
| TDTMA-clay | 0.108                                | 15.3                                      | 1.807              |
| ODTMA-clay | 0.124                                | 12.5                                      | 1.811              |
| peat soil  | 0.146                                | 2.16                                      | NA <sup>a</sup>    |

<sup>a</sup> Not applicable.

The organobentonites were prepared by exposing the Wyoming bentonite base clay to an aqueous solution containing an amount of dissolved quaternary ammonium cation corresponding to 80% of the cation-exchange capacity of the clay. Each slurry was mixed overnight to ensure complete cation exchange and then washed three times with deionized water to remove the bromide salt and loosely bound cations. Each slurry was then baked at 105 °C until dry. The dried organobentonites were ground in a jar mill, passed through a 250  $\mu$ m sieve, and stored at -5 °C.

The final organic-carbon content of each organobentonite was determined using a Carlo-Erba NA 1500 Elemental Analyzer. The surface area of the clay samples was measured by nitrogen gas adsorption using a Gemini 2360 surface-area analyzer. Analysis of the basal spacing of the organobentonites was conducted on an X-ray diffractometer (Phillips Scientific & Analytical Co.) using Ni-filtered Cu-K radiation. Samples were prepared using the glass slide method and analyzed under ambient air conditions of approximately 40% relative humidity. The organic-carbon content, the specific surface area, and the basal spacing of each organobentonite are given in Table 1. The organic-carbon content of each organobentonite was within 2% of the theoretical carbon content of each clay assuming full exchange of the organic cations. Thus, the exchanged organic cations appeared to be resistant to desorption during the washing process.

In addition to the organobentonites, a peat soil collected from Picatinny Arsenal, NJ was used in this study. The peat soil was treated to remove easily solubilized soil organic matter (SOM) and floating particles (35). After the treatment, the peat was oven-dried at 105 °C for 48 h and then passed through a 0.84 mm sieve. The organic-carbon content and specific surface area of the peat soil are given in Table 1. The particle size distribution of the peat soil is given in Table S-1 of the Supporting Information.

**Solutes.** 500- $\mu$ Ci of [<sup>14</sup>C] carbon tetrachloride (CCl<sub>4</sub>) with specific activity equal to 3.4 mCi/mmol were obtained from Dupont NEN and mixed with nonradiolabeled CCl<sub>4</sub>. The resultant chemical and radiochemical purity of the CCl<sub>4</sub> stock was greater than 99%. A 250- $\mu$ Ci sample of [<sup>14</sup>C] 1,2-DCB (specific activity equal to 4.0 mCi/mmol) was obtained from Sigma Chemical Company and mixed with nonradiolabeled 1,2-DCB. The resultant chemical and radiochemical purity of the 1,2-DCB stock was greater than 98%. The structure and the chemical properties of the two solutes are shown in Table S-2 of the Supporting Information.

**Equilibrium Sorption.** Equilibrium sorption of CCl<sub>4</sub> and 1,2-DCB to each of the organobentonites was quantified using a conventional batch methodology (2). The organobentonites were combined with deionized water and radiolabeled solute in 15-mL disposable glass centrifuge tubes with Teflon-lined caps. To inhibit biological transformations, sodium azide was added to the reactors at a 200 mg/L dosage (36). Headspace was minimized (i.e., less than 0.1 mL) to avoid solute losses due to volatilization. In addition, blanks containing only deionized water, sodium azide, and radio-

labeled solute were prepared to quantify solute losses from volatilization and sorption to the glass and Teflon septa during the experiment.

After adding the contaminant, the batch reactors were rotated in the dark at 20 °C for 48 h. The tubes were centrifuged for 10 min at 2000g, and a 0.5 mL aliquot of the supernatant was transferred from each tube to a 7 mL glass scintillation vial containing 5 mL of scintillation cocktail. The radioactivity of the samples was quantified using a Packard Tri-Carb 1700TR liquid scintillation counter (LSC). The aqueous solute concentration was determined from a standard curve relating sample radioactivity to solute concentration. The sorbed concentration was calculated by difference after accounting for solute loss. This procedure was repeated to quantify 1,2-DCB sorption to the peat soil, but these batch reactors were equilibrated for 7 days instead of 48 h. In addition, the peat reactors were centrifuged for 1 h at 2000g. All sorption and desorption experiments conducted in this study were performed at the naturally occurring pH of the reactor systems. The solution pH was approximately 6.7 for all three organobentonite reactors and 6.2 for the peat soil reactors.

**Sorption Rate Experiments.** The rates of CCl<sub>4</sub> and 1,2-DCB sorption to each of the three organobentonites were quantified. For an uptake experiment, 20 15-mL batch reactors with a specified mass of organobentonite and deionized water were prepared identically. As described previously, sodium azide was added to the reactors to inhibit biological activity. In addition, 10 reactors with water but no clay were prepared to quantify solute losses during the course of the experiment. Each batch reactor was spiked with a saturated solution of the radiolabeled solute. Immediately, the clay reactors and blanks were resuspended and placed on a rotating shaker. Pairs of the clay reactors and a single blank were then removed at designated time intervals and centrifuged for 10 min at 2000g. A 0.5 mL aliquot of the supernatant was analyzed by LSC.

The rate of 1,2-DCB sorption to the peat soil was also quantified using the identical methodology. However, 36 soil reactors were prepared instead of 20 because the peat soil approached equilibrium much more slowly than the organobentonites. As with the 1,2-DCB sorption isotherm for the peat soil, the reactors were centrifuged for 1 h at 2000g. The rate of CCl<sub>4</sub> sorption to the peat soil could not be quantified because of abiotic transformation of the CCl<sub>4</sub> during the uptake experiment. Analysis of the liquid supernatant using a gas chromatograph equipped with a FID indicated that the CCl<sub>4</sub> underwent reductive dechlorination in the peat soil reactors. Reductive dehalogenation was not observed during the other experiments.

**Desorption Rate Experiments.** The rates of CCl<sub>4</sub> and 1,2-DCB desorption from the three organobentonites were quantified. For a single desorption experiment, 30 soil reactors and 15 blanks were prepared in the manner previously described. After adding the solute to the reactors, the tubes were shaken for either 7 or 56 days. Following the specified contact time minus 2 days, the 30 clay reactors were removed from the mechanical shaker, and the organobentonite was allowed to settle for 2 days. The tubes were not centrifuged because of difficulties resuspending the clay after centrifugation.

After the 2-day settling period, a 0.5 mL aliquot of the supernatant was analyzed by LSC. The remainder of the supernatant was removed by pipet and replaced with organic-free water. Immediately, the clay/water mixtures were resuspended and placed on the rotating shaker. Pairs of the reactors were then removed from the shaker and centrifuged at 2000g for 10 min at specified time intervals to generate the desorption curve. The blanks were handled identically to



TABLE 2. Calculated Distribution Coefficients with 90% Confidence Intervals (CI) and Linear Isotherm Model Correlation Coefficients

| solute               | sorbent<br>(contact time) | $K_D \pm 90\%$<br>CI (L/kg) | $K_{oc} \pm 90\%$<br>CI (L/kg) | $R^2$ |
|----------------------|---------------------------|-----------------------------|--------------------------------|-------|
| 1,2-dichlorobenzene  | DTMA-clay (48 h)          | 76.4 $\pm$ 3.81             | 905.8 $\pm$ 45.2               | 0.998 |
|                      | TDTMA-clay (48 h)         | 172.7 $\pm$ 4.28            | 1597 $\pm$ 39.6                | 0.999 |
|                      | DTMA-clay (48 h)          | 213.2 $\pm$ 9.86            | 1661 $\pm$ 79.5                | 0.995 |
|                      | peat (7 days)             | 103.4 $\pm$ 7.52            | 707.5 $\pm$ 51.4               | 0.996 |
| carbon tetrachloride | DTMA-clay (48 h)          | 4.23 $\pm$ 0.16             | 50.4 $\pm$ 1.9                 | 0.999 |
|                      | TDTMA-clay (48 h)         | 10.1 $\pm$ 0.12             | 93.6 $\pm$ 1.1                 | 0.999 |
|                      | ODTMA-clay (48 h)         | 13.5 $\pm$ 0.76             | 104.8 $\pm$ 6.1                | 0.998 |

quantify any solute losses during the experiment. Desorption rates were not measured for the peat soil.

## Results

**Isotherm Results.** The sorption of 1,2-DCB to the three organobentonites and to the peat soil was linear over the range of aqueous concentrations quantified. The sorption of  $\text{CCl}_4$  to the three organobentonites was also linear. The  $\text{CCl}_4$  and 1,2-DCB isotherms for the organobentonites and the peat soil are shown in Figure S-1 of the Supporting Information. Given the linearity of the isotherms, the linear/partition model was used to quantify the magnitude of solute sorption (Table 2). For the organobentonites, equilibrium was reached during the 48-h incubation period. The value of  $K_D$  obtained for each isotherm was used in the kinetic simulation models. Unlike the organobentonites, the sorption of 1,2-DCB to the peat was at approximately 94% of equilibrium after the 7-day incubation (see peat uptake results). Therefore, the equilibrium  $K_D$  of the peat soil was estimated by calculating a single-point value of  $K_D$  from the last data point collected during the sorption uptake experiment.

**Sorption and Desorption Rate Results.** The two-site model and the  $\gamma$ -model both fit the organobentonite uptake data well (Figure 1); however, the percent errors obtained from the  $\gamma$ -model were lower in all but one instance (Table 3). The sorption of  $\text{CCl}_4$  to the DTMA-clay was the exception. The true optimal set of fitting parameters for the  $\gamma$ -model was not obtainable for  $\text{CCl}_4$  sorption to the DTMA-clay because of computer floating point memory limitations. In contrast to the organobentonite simulations, only the  $\gamma$ -model was able to adequately simulate the rate of 1,2-DCB sorption to the peat soil (Figure 1). The percent error for the two-site model was roughly three times higher than the percent error for the  $\gamma$ -model (Table 3).

The two-site model and the  $\gamma$ -model both fit the organobentonite desorption data well (Figure 2); however, the two-site model provided better fits than the  $\gamma$ -model for six of the nine desorption experiments (Table 3). Overall, the percent errors obtained from the  $\gamma$ -model were lower than the percent errors obtained from the two-site model for nine of the 16 sorption and desorption data sets.

Ninety percent confidence regions for the model parameters were developed for the sorption and desorption experiments. Given that the experimental data were better simulated by the  $\gamma$ -model in the majority of cases, the conclusions presented in this article are based on the modeling results obtained from the  $\gamma$ -model simulations. The exception to this statement is for  $\text{CCl}_4$  sorption to the DTMA-clay. Confidence regions for the  $\gamma$ -model parameters were not attempted for  $\text{CCl}_4$  sorption to the DTMA-clay because the optimal set of parameters was not obtained. For this set of data and for any data set directly compared to  $\text{CCl}_4$  sorption to the DTMA-clay, the confidence regions obtained from the two-site model were used in the rate analysis. With

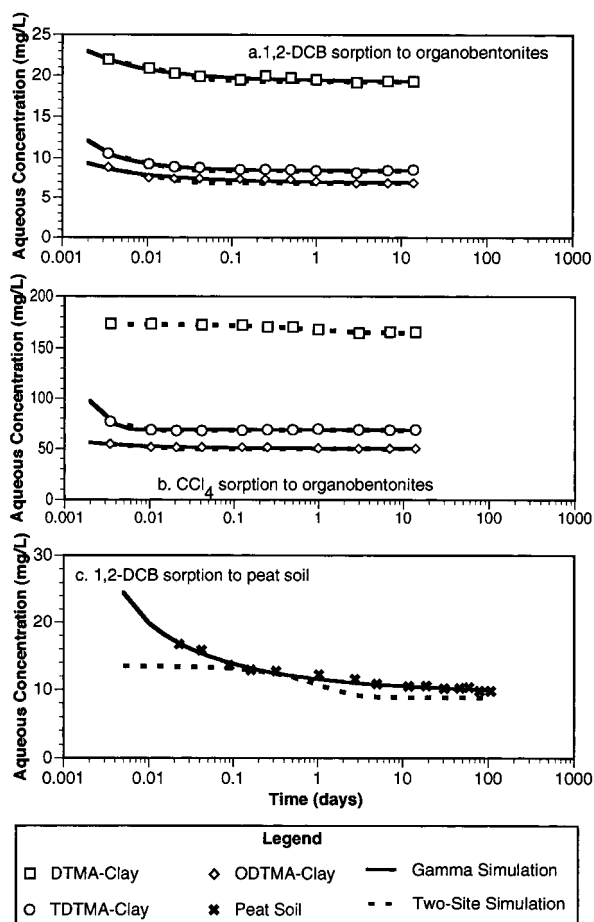


FIGURE 1. Measured aqueous concentrations and optimal model simulations for (a) 1,2-DCB sorption and (b) carbon tetrachloride sorption to the three organobentonites. Measured aqueous concentrations and optimal model simulations for (c) 1,2-DCB sorption to the peat soil.

only a few exceptions, the two modeling approaches yielded similar conclusions.

## Discussion

Based on the subsequent analysis, the following conclusions were made: (1) The rate of 1,2-DCB sorption to the organobentonites was significantly faster than the rate of 1,2-DCB sorption to the peat soil. (2) The rate of mass-transfer during sorption and desorption was greater for  $\text{CCl}_4$  than for 1,2-DCB. (3) The alkyl-chain length of the organobentonite did not affect the rate of mass-transfer during sorption; however, the rate of 1,2-DCB desorption decreased as the alkyl-chain length increased. (4) The rate of solute desorption was slower than the rate of solute uptake for the ODTMA-clay experiments and for 1,2-DCB desorption from the TDTMA-clay following the 56-day incubation. (5) The

TABLE 3. Minimum Percent Error and Corresponding Simulation Parameters for the Gamma and Two-Site Models

| experiment type                 | solute                        | $\gamma$ -model |                      |         | two-site model |                      |         |
|---------------------------------|-------------------------------|-----------------|----------------------|---------|----------------|----------------------|---------|
|                                 |                               | $\eta^a$        | $\beta^b$            | % error | $f^c$          | $\alpha^d$           | % error |
| sorption to DTMA                | CCl <sub>4</sub> <sup>e</sup> |                 |                      |         | 0.910          | 1.131                | 0.307   |
| sorption to DTMA                | 1,2-DCB <sup>f</sup>          | 0.542           | 5708                 | 0.865   | 0.797          | 47.24                | 1.260   |
| sorption to TDTMA               | CCl <sub>4</sub>              | 1.297           | 230.5                | 0.751   | 0.022          | 267.4                | 0.752   |
| sorption to TDTMA               | 1,2-DCB                       | 1.106           | 410.9                | 1.295   | 0.674          | 87.63                | 1.788   |
| sorption to ODTMA               | CCl <sub>4</sub>              | 0.578           | 14280                | 0.894   | 0.841          | 118.8                | 1.294   |
| sorption to ODTMA               | 1,2-DCB                       | 0.461           | 4780                 | 2.587   | 0.673          | 71.66                | 4.326   |
| sorption to Peat                | 1,2-DCB                       | 0.309           | 244.3                | 2.666   | 0.594          | 0.594                | 7.190   |
| desorption from DTMA (7 days)   | CCl <sub>4</sub>              | 350.6           | 1.280                | 1.047   | 0.0395         | 168.6                | 1.043   |
| desorption from DTMA (7 days)   | 1,2-DCB                       | 0.117           | $9.5 \times 10^{17}$ | 1.252   | 0.0277         | 398.6                | 1.430   |
| desorption from DTMA (56 days)  | 1,2-DCB                       | 0.295           | $3.5 \times 10^5$    | 1.861   | 0.929          | 1.398                | 1.765   |
| desorption from TDTMA (7 days)  | CCl <sub>4</sub>              | 7.290           | 23.99                | 1.262   | 0.300          | 1.237                | 1.237   |
| desorption from TDTMA (7 days)  | 1,2-DCB                       | 0.237           | 40620                | 1.686   | 0.798          | 0.878                | 1.395   |
| desorption from TDTMA (56 days) | 1,2-DCB                       | 0.092           | $5.1 \times 10^7$    | 1.781   | 0.736          | 0.152                | 1.579   |
| desorption from ODTMA (7 days)  | CCl <sub>4</sub>              | 1.636           | 73.01                | 0.972   | 0.267          | 69.44                | 0.869   |
| desorption from ODTMA (7 days)  | 1,2-DCB                       | 87.71           | 0.248                | 1.586   | 0.0001         | 22.07                | 1.596   |
| desorption from ODTMA (56 days) | 1,2-DCB                       | 2.112           | 18.33                | 1.340   | 0.840          | $4.1 \times 10^{-7}$ | 1.517   |

<sup>a</sup>  $\eta$  is the shape factor parameter for the gamma distributed rate parameter model. <sup>b</sup>  $\beta$  is the scale factor parameter for the gamma distributed rate parameter model. <sup>c</sup>  $f$  is the fraction of equilibrium sites for the two-site model. <sup>d</sup>  $\alpha$  is the mass-transfer rate coefficient (d<sup>-1</sup>) for the two-site model. <sup>e</sup> Carbon tetrachloride. <sup>f</sup> 1,2-Dichlorobenzene.

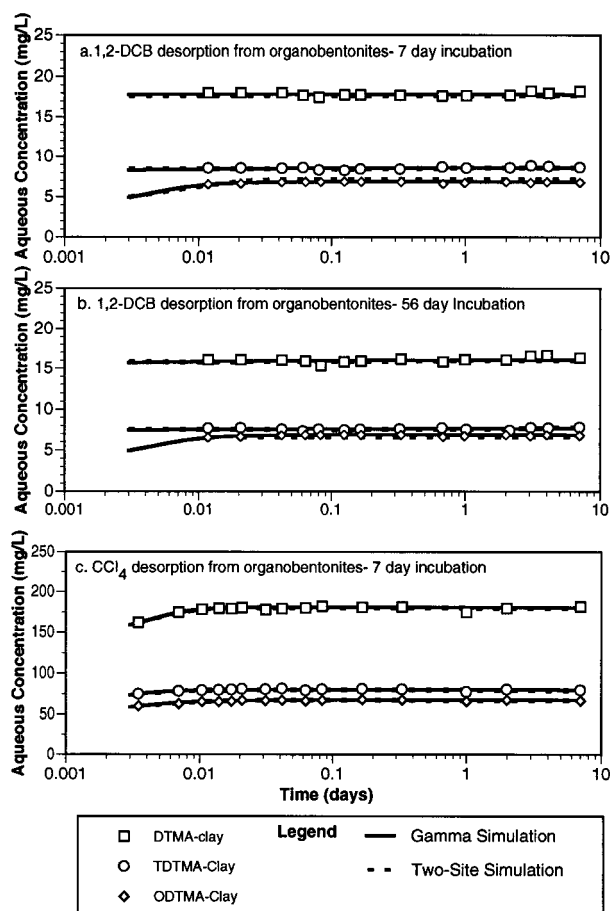


FIGURE 2. Measured aqueous concentrations and optimal model simulations for 1,2-DCB desorption from the three organobentonites after 7-days (a) and 56-days (b) incubations. Measured aqueous concentrations and optimal model simulations for carbon tetrachloride desorption from the three organobentonites after a 7-days (c) incubation.

solute-sorbent contact time did not significantly alter the rate of 1,2-DCB desorption from the organobentonites. (6) For most environmental applications using the organobentonites studied here, a local equilibrium assumption will

satisfactorily describe CCl<sub>4</sub> and 1,2-DCB sorption and desorption.

**Organobentonite Sorption vs Peat Sorption.** The rate of 1,2-DCB sorption to the peat soil was statistically different from the rates of 1,2-DCB sorption to the organobentonites (Figure 3). Although the separation between the confidence regions is evident, the difference among the simulated rates of uptake is not obvious. In general, the following relationships between  $\eta$  and  $\beta$  the rates of sorption hold: as  $\eta$  and  $\beta$  increase, the rate of mass-transfer increases; as  $\eta$  and  $\beta$  decrease, the rate of mass-transfer decreases; the previous two observations hold if one parameter is held constant and the other parameter varied. For example, the rate of 1,2-DCB sorption to the DTMA-clay was faster than the rate of 1,2-DCB sorption to the peat soil. This is true because the peat soil's confidence region lies below and to the left of the DTMA-clay's parameter confidence region (Figure 3). To confirm this observation, the optimal distributions of the mass-transfer rate coefficients and their respective confidence boundaries for the peat soil and the DTMA-clay were compared (Figure 4). As depicted in Figure 4, the sites characterized by mass-transfer rate coefficients higher than 1000 d<sup>-1</sup> are numerically treated as instantaneous sorption sites. Analysis of modeling simulations (data not shown) indicated that this numerical assumption did not affect the model predictions within the time domain of interest. The mass-transfer rate coefficients for the peat soil are approximately 2–3 orders of magnitude lower than the rate coefficients that describe 1,2-DCB sorption to the DTMA-clay. As a result, the incubation time necessary to reach equilibrium was much longer for the peat soil (i.e., months) than for the DTMA-clay (i.e., minutes to hours). Similarly, 1,2-DCB sorption to the TDTMA- and ODTMA-clays occurred more rapidly than 1,2-DCB sorption to the peat soil.

The slow approach to equilibrium for 1,2-DCB sorption to the peat soil relative to the rapid rates of 1,2-DCB sorption to the organobentonites is likely a result of the complex and heterogeneous nature of the peat's organic matter. For the peat soil, the sorption rate limitation is attributed to diffusional resistances encountered by the 1,2-DCB within the SOM. Researchers have hypothesized that the outer region of the SOM is an amorphous polymer-like structure (31, 37, 38). The reported molecular weights of humic substances can range from 300 to 200 000 (39). The flexible outer region reacts to environmental changes such as pH, ionic strength, and temperature (40, 41). The inner region

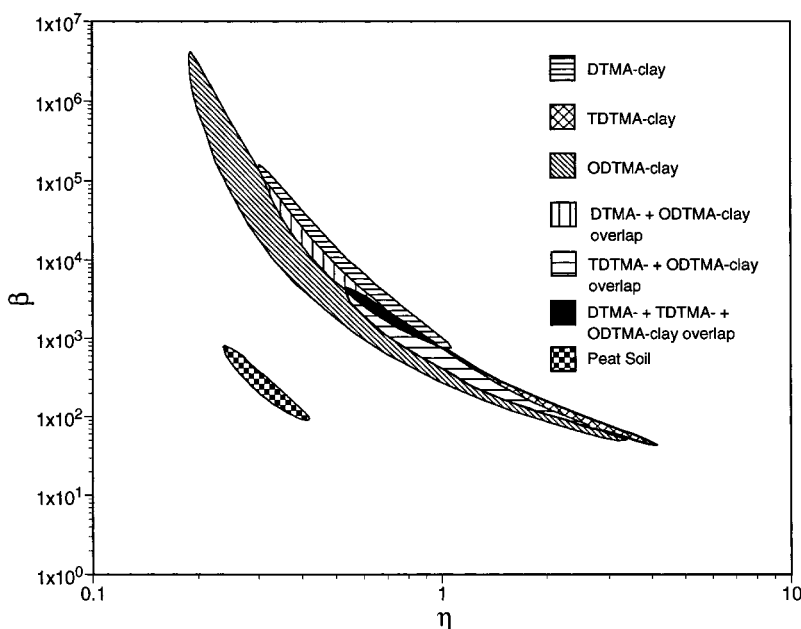


FIGURE 3. Comparison of the confidence regions of the  $\gamma$ -model parameters for 1,2-DCB sorption to the three organobentonites and the peat soil.  $\eta$  is the shape parameter and  $\beta$  is the scaling parameter for the  $\gamma$ -model.

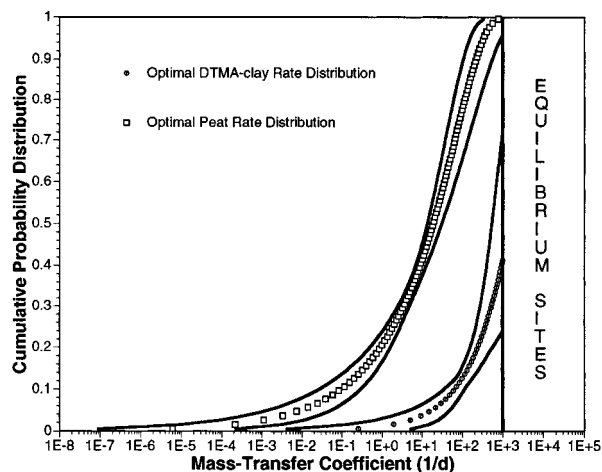


FIGURE 4. Optimal distributions of the mass-transfer rate coefficients used to simulate 1,2-DCB sorption to DTMA and the peat soil. The solid lines represent the 90% confidence intervals for the mass-transfer rate coefficient for the optimal rate coefficient distribution.

of the SOM is described as a “condensed, glasslike humic polymer phase” (38) and is the result of the diagenetic alteration over time of the amorphous humic phase (42). The condensed region and, to a lesser extent, the amorphous region of SOM have been assumed to contribute to the diffusive resistances encountered by a solute during sorption ((43), and references cited within). It is likely that the slow sorption of 1,2-DCB to the peat soil can also be attributed to rate-limited diffusion of the solute through the peat’s intraparticle pore network (27, 44).

The organobentonites were synthesized in the laboratory from specific quaternary ammonium cations, and thus the structures and molecular weights (139–251) of the different alkyl chains are known. Therefore, the organic-carbon fraction of each organobentonite is composed of numerous small alkyl chains of the same size. Unlike the peat soil, the organic carbon fraction of each organobentonite is relatively homogeneous and less complex. Therefore, the reduced rate of sorption for the peat soil relative to the organobentonites may result from greater diffusional resistances encountered within the peat soil due to the more complex and hetero-

geneous nature of the peat soil’s SOM. In addition, the relative amounts of “condensed” organic-matter present in the peat soil and the organobentonites may contribute to the observed differences in the rates of sorption for 1,2-DCB.

**Solute Effect.** For the DTMA-clay, the rates of uptake for  $\text{CCl}_4$  and 1,2-DCB were statistically different at the 90% confidence level (Figure 5a). The fraction of sorption sites acting in an equilibrium manner for  $\text{CCl}_4$  and for 1,2-DCB was not statistically different. However, the mass-transfer rates associated with the nonequilibrium sites are considerably lower for  $\text{CCl}_4$  sorption than for 1,2-DCB sorption. When the sorption of  $\text{CCl}_4$  is simulated using the parameter sets from 1,2-DCB’s confidence region, the model is unable to simulate the behavior of the data between 4 h and 3 days (Figure S-2 of Supporting Information). In contrast, the rates of 1,2-DCB sorption to the TDTMA- and ODTMA-clays were significantly slower than the rate of  $\text{CCl}_4$  sorption (Figure 5b,c). It is not immediately clear as to why the inconsistency among the  $\text{CCl}_4$  and 1,2-DCB sorption rates exists among the three organobentonites.

For the DTMA- and TDTMA-clays, there was no statistical difference between the rates of 1,2-DCB and  $\text{CCl}_4$  desorption (Figure S-3a,b of the Supporting Information). For the TDTMA-clay, the majority of the 1,2-DCB confidence region lies to the left of the  $\text{CCl}_4$  confidence region. The relative placement of the two confidence regions indicates that the rate of 1,2-DCB desorption is probably slightly slower than the rate of  $\text{CCl}_4$  desorption, although the difference is not statistically significant. For the ODTMA-clay, the rate of 1,2-DCB desorption was significantly slower than the rate of  $\text{CCl}_4$  desorption (Figure S-3c of Supporting Information). The slower desorption rates of 1,2-DCB compared to  $\text{CCl}_4$  from the TDTMA- and ODTMA-clays are consistent with the observation that the rate of 1,2-DCB uptake was slower than  $\text{CCl}_4$  uptake for the same 2 clays.

Given that 1,2-DCB is a larger molecule than  $\text{CCl}_4$ , the previous results are consistent with the observation that as the size of the sorbing solute increases, its mass-transfer rates are reduced (45). The difference between the two solutes’ mass-transfer rates may be attributed to diffusional resistances caused by the organobentonite alkyl chains. It is reasonable that 1,2-DCB diffusion through the organic-cation alkyl chains may be more restricted than  $\text{CCl}_4$  diffusion

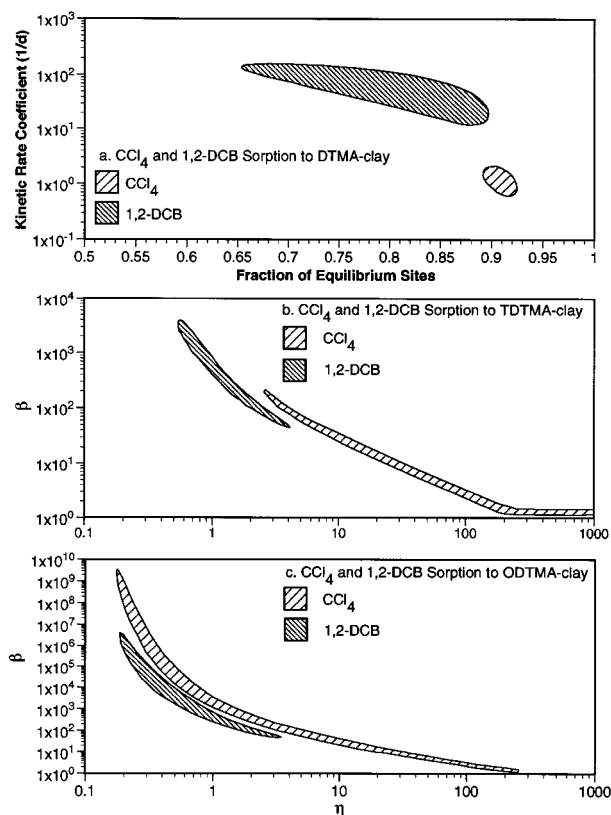


FIGURE 5. Comparison of the confidence regions of the model parameters for 1,2-DCB and carbon tetrachloride sorption to (a) DTMA-clay, (b) TDTMA-clay, and (c) ODTMA-clay.  $\eta$  is the shape parameter and  $\beta$  is the scaling parameter for the  $\gamma$ -model.  $f$  is the fraction of equilibrium sites and  $\alpha$  is the mass-transfer rate coefficient for the two-site model.

through the same alkyl chains because of 1,2-DCB's larger molecular size. However, the alkyl chain lengths for the organobentonites are short when compared to natural soil, thus the sorption rate differences between solutes are not as pronounced for organobentonites as for natural soils.

**Organo-Clay Effect.** For the three organobentonites of varying alkyl-chain length, the rates of 1,2-DCB sorption were not statistically different from one clay to another (Figure 3). The same was true for  $\text{CCl}_4$  (confidence regions not shown). Thus, the length of the organobentonite's alkyl chain did not affect the rate of sorption for either 1,2-DCB or  $\text{CCl}_4$ . For 1,2-DCB desorption following the 7-day incubation, the rates of desorption from the DTMA- and TDTMA-clays were not statistically different. However, the rate of 1,2-DCB desorption from the ODTMA-clay was significantly slower than the rates of desorption from the DTMA- and TDTMA-clays (Figure 6a). Following the 56-day incubation, the rates of 1,2-DCB desorption from the TDTMA- and ODTMA-clays were significantly slower than the rate of 1,2-DCB desorption from the DTMA-clay. There was no statistical difference between the rates of 1,2-DCB desorption from the TDTMA- and ODTMA-clays (Figure 6b). For  $\text{CCl}_4$ , the rates of desorption were not significantly different for the three organobentonites (Figure S-4 of Supporting Information).

The length of the alkyl chain can affect the basal spacing (see Table 1) of the organobentonites as well as the configuration of the alkyl chains within the interlamellar spaces. It is speculated that the diffusive resistances encountered by a solute within the alkyl chains of the organobentonites should be affected by the length of the alkyl chain. The results of the  $\text{CCl}_4$  sorption and desorption experiments do not support this hypothesis. Likewise, the

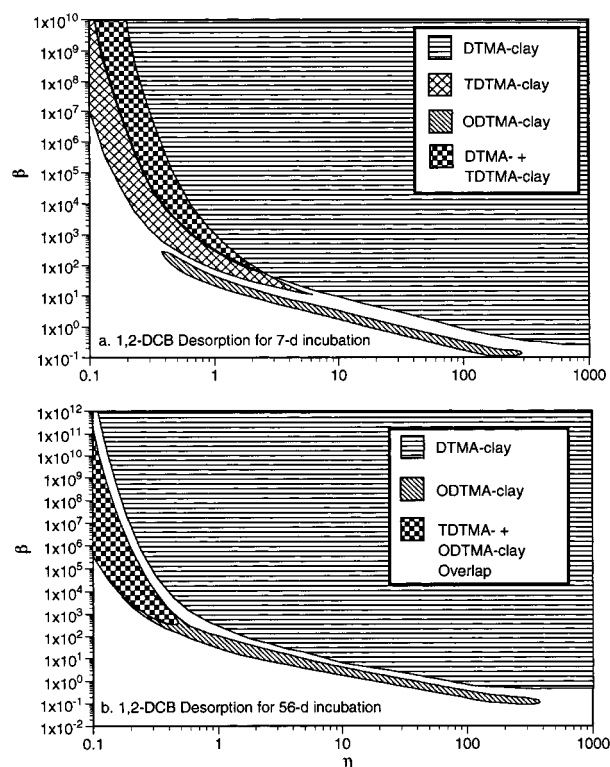


FIGURE 6. Comparison of the confidence regions of the  $\gamma$ -model parameters for 1,2-DCB desorption from the three organobentonites following 7-day (a) and 56-day (b) incubations.  $\eta$  is the shape parameter and  $\beta$  is the scaling parameter for the  $\gamma$ -model.

structure of the alkyl chains did not affect the rate of 1,2-DCB sorption to the organobentonites. However, the anticipated result was observed during the 56-day 1,2-DCB desorption experiments and, to an extent, during the 7-day 1,2-DCB desorption experiments. In light of these results it is difficult to determine to what degree the alkyl-chain structure affects the rates of sorption and desorption.

**Uptake vs Desorption Rate Comparisons.** For the DTMA-clay, the rates of desorption for 1,2-DCB and  $\text{CCl}_4$  were not statistically different from the corresponding rates of sorption to the DTMA-clay. The confidence regions for 1,2-DCB sorption and desorption (7-day incubation) to and from the DTMA-clay are shown in Figure S-5 of the Supporting Information. Similar to the DTMA-clay, the rates of 1,2-DCB and  $\text{CCl}_4$  desorption from the TDTMA-clay following the 7-day contact time were not significantly different from the corresponding rates of uptake (confidence regions not shown). In contrast, the rate of 1,2-DCB desorption following the 56-day contact time was significantly slower than the rate of 1,2-DCB sorption to the TDTMA-clay (Figure 7a). This result indicates that the extended contact time reduced the rate of 1,2-DCB desorption from the TDTMA-clay. In contrast to the DTMA- and TDTMA-clays, the rates of desorption from the ODTMA-clay were significantly slower than the rates of uptake for 1,2-DCB (Figure 7b) and  $\text{CCl}_4$  (Figure S-6 of Supporting Information) desorption experiments.

Several researchers have hypothesized that rate-limited desorption of NOCs from natural soils may be caused by rearrangement of the flexible humic polymer chains of the SOM after solute sorption (29, 40, 46). Rearrangement of the humic polymer chains could potentially obstruct diffusion pathways that were originally unobstructed during the sorption process causing diffusional resistances during the desorption process. The observed organobentonite desorption data compared to the corresponding uptake data can



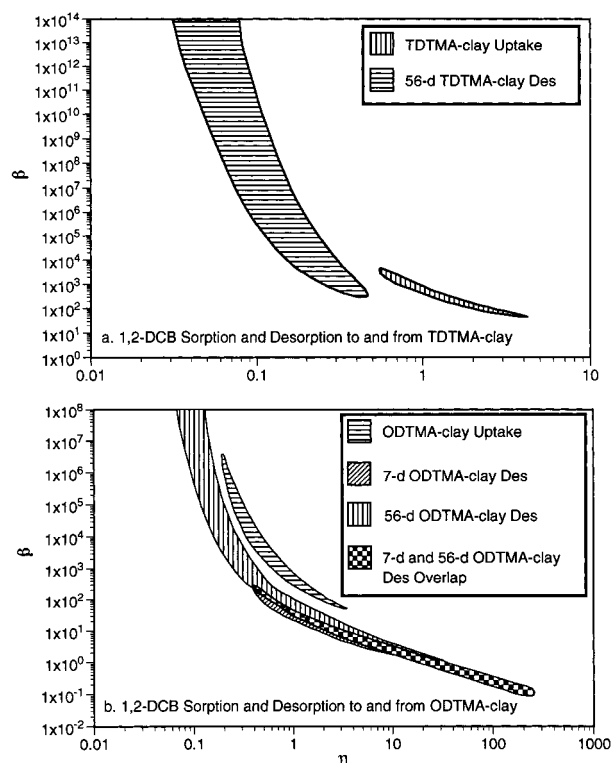


FIGURE 7. (a) Confidence regions of the  $\gamma$ -model parameters for 1,2-DCB sorption to TDTMA-clay and 1,2-DCB desorption from TDTMA-clay after a 56-day incubation. (b) Confidence regions of the  $\gamma$ -model parameters for 1,2-DCB sorption to ODTMA-clay and 1,2-DCB desorption from ODTMA-clay after 7-day and 56-day incubations.  $\eta$  is the shape parameter and  $\beta$  is the scaling parameter for the  $\gamma$ -model.

be interpreted within this hypothesis. Rearrangement of the alkyl chains within the interlamellar space of the organobentonite may have occurred as a result of the mechanical agitation from the mixing during the incubation. In addition, it is speculated that sorption of the solute into the interlamellar spaces of the organobentonites may cause conformational changes of the alkyl chains.

For the DTMA-clay there was no observed differences between uptake and desorption for either solute. However, the alkyl chain length of the DTMA-clay only has 10 carbon atoms. The alkyl chains of the DTMA-clay are likely to be less flexible than the alkyl chains of the TDTMA- and ODTMA-clays that possess 14 and 18 carbon atoms, respectively. As a result, rearrangement of the DTMA-clay's alkyl chains may be significantly less than the rearrangement of the alkyl chains of the TDTMA- and ODTMA-clays.

For the TDTMA-clay, there was no statistical difference between uptake and desorption for either  $\text{CCl}_4$  or 1,2-DCB 7-day desorption. The 14 carbon alkyl chains of the TDTMA-clay do not reduce the rate of desorption following a 7-day incubation relative to uptake for either solute. However, during the 56-day incubation, sufficient rearrangement of the TDTMA-clay's alkyl chains appears to have occurred causing the rate of 1,2-DCB desorption to be significantly slower than the rate of 1,2-DCB uptake. For the ODTMA-clay, the rates of desorption were slower than the rates of uptake for both solutes at the tested incubation times. The additional four carbon atoms in the ODTMA-clay's alkyl chains compared to the TDTMA-clay's alkyl chains appear to have added a sufficient degree of flexibility to allow significant rearrangement of the alkyl chain configurations. These results indicate that the ability of an alkyl chain to rearrange over time increases as the length of the alkyl chain increases.

**Contact Time.** The rate of 1,2-DCB desorption from the organobentonites was not affected by the contact time. Further discussion is provided in the Supporting Information.

**Implications for Organobentonite Environmental Applications.** As stated previously, many environmental applications for organobentonites have been proposed. For many of these applications, knowledge of the rates of pollutant sorption and desorption may be an important design parameter. For the class of organobentonites studied here, the rates of mass-transfer during sorption and desorption occur over short time scales. Although slight, yet statistically significant differences exist among the rates of mass-transfer for different organobentonite and solute combinations, the magnitude of these differences would not be an important design consideration. Based on the rates of mass-transfer observed during this study, the assumption of equilibrium sorption and desorption may be appropriate for most environmental applications.

## Acknowledgments

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## Supporting Information Available

Tables of particle-size distribution of the peat soil and structure and chemical properties of 1,2-DCB and  $\text{CCl}_4$  and figures of sorption isotherms for  $\text{CCl}_4$ , boundaries of  $\gamma$ -model simulations, and confidence regions of the  $\gamma$ -model parameters (10 pages). Ordering information is given on any current masthead page.

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