

HYDROPHOBICITY OF CLAY SURFACES: SORPTION OF 1,2-DIBROMOETHANE AND TRICHLOROETHENE

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Abstract—Sorption and desorption of two neutral, nonpolar organic compounds, 1,2-dibromoethane (EDB, a soil fumigant) and trichloroethene (TCE, an industrial solvent and common ground-water contaminant), by pyrophyllite, kaolinite, illite, and smectite were investigated. For sorption, vapors of the compounds in a stream of dry N₂ gas were passed through columns of the powdered clay minerals for different periods of time. The compounds retained by the clays were extracted with methanol and analyzed by gas chromatography (GC). For desorption, N₂ was passed through the treated samples, and the desorbed compounds were collected in hexane traps and analyzed by GC.

Initially sorption was rapid for several hours but then proceeded at a slower rate for many hours. Surprisingly, the clays sorbed large quantities of these neutral compounds; for example, the pyrophyllite, kaolinite, illite, and smectite sorbed about 3, 5, 6, and 9% EDB, respectively, by weight. The amounts of TCE sorbed, which is more volatile than EDB, were somewhat less. Only a portion of the compounds sorbed over a period of time were desorbed in the same period of time. Desorption was rapid initially but then proceeded at a slow rate; slow desorption continued for over 100 hr from samples which had undergone sorption for only 1–2 hr. A two-compartment efflux model was used to describe the sorption behavior. A rapidly desorbing component was considered to be present on the outer surfaces of the clay aggregates and a slowly desorbing component, in the interior pores of the aggregates.

Key Words—Diffusion, Halocarbons, Illite, Kaolinite, Pyrophyllite, Smectite, Sorption-desorption.

INTRODUCTION

Nonpolar organic molecules contain no functional groups; hence, their retention by clays is expected to be limited to physical sorption on the outer surfaces, involving van der Waals forces. Consequently, the sorbed molecules should be only weakly held, and sorption should be readily reversible. The results reported here on the sorption of two volatile nonpolar halocarbons, 1,2-dibromoethane (EDB), a soil fumigant, and trichloroethene (TCE), a common industrial solvent, by several clay minerals show that large quantities of these chemicals are sorbed and that the sorption is not readily reversible.

Concern with ground-water contamination by organic chemicals applied to soils or disposed in industrial wastes has prompted numerous investigations of their reactions and movement in soils, recently reviewed by Sawhney and Brown (1989). Most investigations have been carried out in aqueous systems, and uptake and retention of organic compounds has been generally attributed to partitioning into soil organic matter (Karickhoff *et al.*, 1979; Weber *et al.*, 1983; Chiou *et al.*, 1983). The term "partitioning" is analogous to extraction of an organic compound from aqueous solution into an organic solvent. When nonpolar organic compounds are partitioned into solid soil organic matter their distribution is considered homogeneous throughout the volume of the solid phase. In contrast, they are assumed to sorb only on the surface of minerals. The uptake of nonionic organic com-

pounds, however, cannot always be explained solely by soil organic matter (Garbarini and Lion, 1986), and significant sorption by clay minerals may occur even in aqueous solutions (MacIntyre and Smith, 1984; Mingelgrin and Gerstl, 1983). Estes *et al.* (1988) recently observed that slow sorption of TCE by a suspension of montmorillonite continued over a 28-day period. In dry soils and in soils containing small amounts of organic matter, sorption of organic pollutants likely occurs on mineral surfaces (Chiou and Shoup, 1985; Chiou, 1989). Although reactions of both polar and nonpolar aromatic hydrocarbons with clay minerals have been studied by a number of investigators and have been reviewed by Pinnavaia (1983), Mortland (1986), and Raussell-Colom and Serratosa (1987), reactions involving nonpolar aliphatic halocarbons have received little attention.

Steinberg *et al.* (1987) observed that small concentrations of the volatile, nonpolar aliphatic halocarbon, 1,2-dibromoethane (EDB), used as a soil fumigant, have persisted in soils for as long as two decades following application. This persistence was attributed to the entrapment of EDB molecules in intraaggregate micropores in soils. Because of slow diffusion of these molecules through the "immobile aqueous phase" in the interior pores of soil aggregates, they remained out of equilibrium with the bulk soil solution. Consequently, they were removed only slowly. Similar nonequilibrium conditions during the sorption-desorption in the aqueous phase of polynuclear aromatic hydrocarbons by soils and sediments have been observed by others

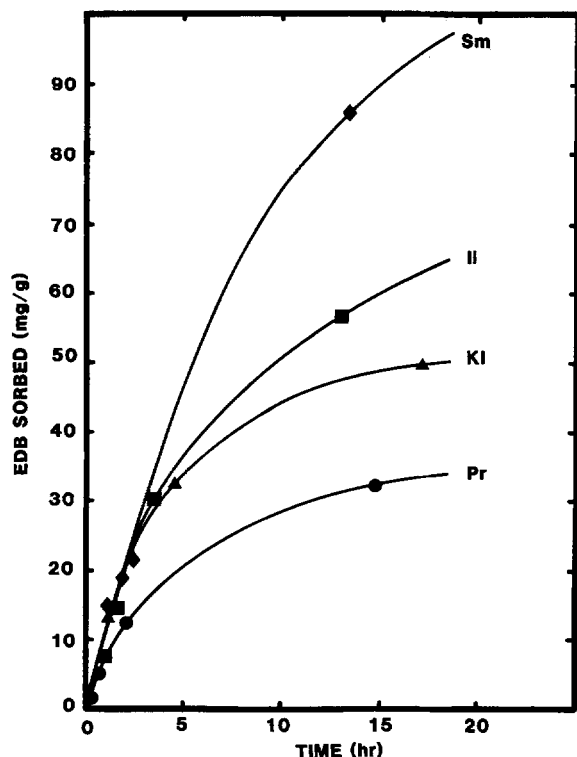


Figure 1. Vapor phase sorption of 1,2-dibromoethane by clay minerals, pyrophyllite (Pr), kaolinite (KI), illite (II) and smectite (Sm).

(e.g., Karickhoff, 1984; Wu and Gschwend, 1986). The objective of the present investigation was to determine the role of clay minerals in the sorption and retention of nonpolar volatile halocarbons in soils. Because the vapor phase is an important means of transport for these chemicals, the vapor state was used to study their reactions with mineral surfaces.

MATERIALS AND METHODS

The clay minerals pyrophyllite (API No. 49, Robbins, North Carolina), kaolinite (No. 4, Oneal Pit, Macon, Georgia), illite (Fithian, Illinois), and smectite (montomorillonite No. 26, Clay Spur, Wyoming) were obtained from Ward's Natural Science Establishment, Rochester, New York. These clay minerals were chosen to include 2:1 phyllosilicates having zero charge (pyrophyllite), low layer charge (smectite), and high layer charge (illite) and a 1:1 phyllosilicate (kaolinite). The minerals were ground in an agate pestle and mortar and screened through a 45- μ m sieve. The halocarbons EDB and TCE were obtained from Aldrich Chemical Co., Milwaukee, Wisconsin and were of 99% purity and spectrophotometric grade.

Portions of the clay (~ 0.5 g) were placed in 5×1.5 cm glass columns, prepared from disposable pipets, and held in place with glass wool inserted into both

ends of the column. The clay in the column was dried overnight at 110°C to remove any sorbed moisture. For sorption, dry nitrogen gas (N_2) was passed through the liquid EDB or TCE contained in a U-tube (Sawhney, 1985) at 1-ml/min rate, and the N_2 stream saturated with vapors was passed through the clay for different periods of time. Glass tubing was used for all connections. After each sorption the column was flushed with N_2 for 2 min to remove excess free chemical in the column. To determine the amount sorbed, the clay was extracted with methanol at 75°C in a glass screw-cap vial with a Teflon-lined silicone rubber septum. The methanol extract was then diluted with water, extracted with hexane, and analyzed by gas chromatography (GC) as described by Sawhney *et al.* (1988).

Desorption was carried out by passing N_2 through the treated column at the same rate as used in the sorption experiment. EDB or TCE desorbed in the N_2 stream was collected in two hexane traps placed in series, each containing 10 ml of hexane in a 14-ml glass vial with screw-cap Teflon septa, and analyzed by GC.

Surface areas of clays were measured using the Quantasorb Sorption System (Quantachrome Corp., Syosset, New York) and the Brunauer, Emmett, and Teller (BET) equation. Two-point BET surface areas were obtained at relative N_2 pressures of 0.1 and 0.3. X-ray powder diffraction (XRD) analyses of clays were carried out using powder samples and Scintag diffraction equipment.

RESULTS AND DISCUSSION

Sorption and desorption of 1,2-dibromoethane

The data in Figure 1 show that the clay minerals pyrophyllite, kaolinite, illite, and smectite continued to sorb EDB from the vapor phase for several hours. The rate of sorption was initially rapid but decreased with time. Further, the clay minerals sorbed large quantities of EDB; in about 16 hr, the smectite sample sorbed as much as 9% EDB by weight, the illite sample 6%, the kaolinite sample 5% and the pyrophyllite sample 3%.

Sorption of EDB by the nonexpanding phyllosilicates (pyrophyllite, kaolinite, illite) must have occurred on the external surfaces of the mineral particles. The XRD patterns of the expanding mineral smectite after sorption of as much as 10% EDB by weight showed no change in its d-values or intensities of peaks (Figure 2). Thus, the sorption of EDB probably did not occur in the interlayer spaces of smectite and was therefore confined to the external mineral surfaces of smectite also. Early experiments by Jurinak (1957) also indicated that the sorption of EDB occurred on the external surfaces of smectite clays.

The amounts of EDB sorbed, however, were not well correlated with the external (BET) surface areas of the clay minerals (Table 1). Whereas, sorption by the py-

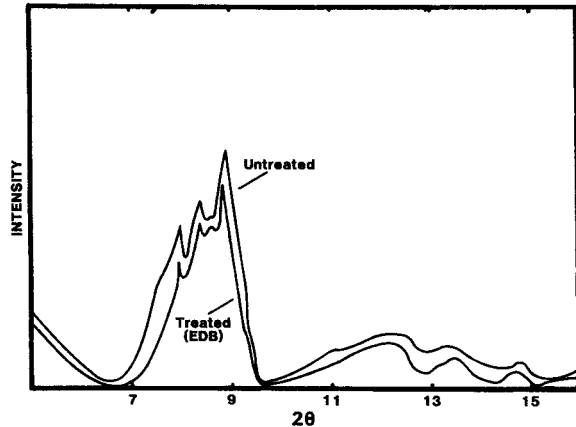


Figure 2. X-ray powder diffraction pattern of clay mineral smectite before and after 1,2-dibromoethane (EDB) sorption. $\text{CuK}\alpha$ radiation.

rophyllite, kaolinite, and illite increased with increasing BET area, the amount sorbed per unit surface area decreased as the surface area increased. Smectite, having surface area less than that of the kaolinite and illite, sorbed much more relative to its surface area. Calculations based on the amounts of EDB sorbed by the minerals in 16 hr, their surface areas, and the cross-sectional molecular area of EDB (29.6 \AA^2) show that the apparent average layer thicknesses of EDB sorbed ranged from two layers in the illite to four layers in the smectite. As will be discussed below, the differences in sorption of EDB relative to surface areas of these minerals are likely due to differences in the structure of the sorption surfaces of the porous clay aggregates composed of primary particles.

The data in Figure 3 show the fractions of EDB retained by the clay minerals following desorption for different periods of time. Before the desorption was begun, these samples had undergone EDB sorption for 1 hr at the same flow rate as used for desorption. The results show that only a fraction of the EDB sorbed in 1 hr desorbed in the same time period. Following desorption for 1 hr, the pyrophyllite, kaolinite, smectite, and illite still retained 57%, 92%, 75%, and 94%, respectively, of the amounts sorbed. Even after desorption for 24 hr, the pyrophyllite retained 6%, the kaolinite 34%, the smectite 19%, and the illite 56% of

Table 1. Calculated layer thickness of 1,2-dibromoethane (EDB) sorbed on mineral surfaces after 16 hr.

Mineral	BET	EDB Sorbed		Number of layers
	Surface area (m^2/g)	(mg/g)	(mg/m^2)	
Pyrophyllite	12.3	34	2.8	3
Kaolinite	26.8	52	1.9	2
Illite	43.4	62	1.4	<2
Smectite	24.9	94	3.7	4

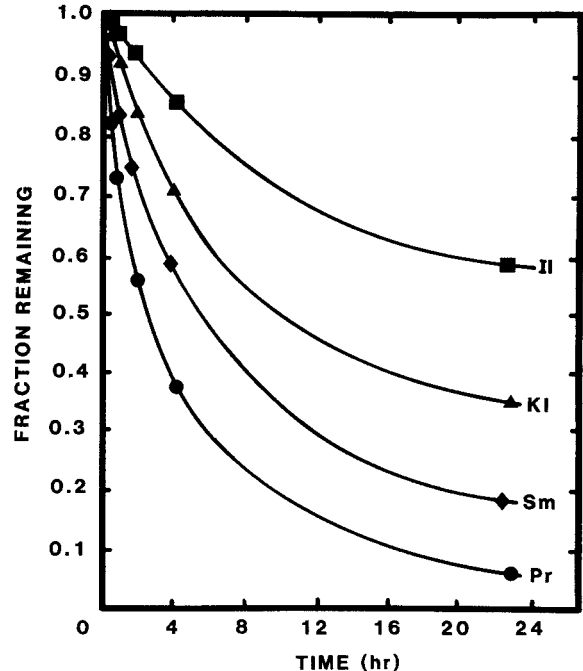


Figure 3. Desorption of 1,2-dibromoethane from clay minerals pyrophyllite (Pr), kaolinite (Kl), illite (Il), and smectite (Sm) following sorption for 1 hr, plotted as fractions of the initially sorbed chemical remaining at different time periods.

the amounts sorbed in 1 hr. Whereas the initial desorption, generally constituting a substantial portion of the sorbed chemical, was rapid, subsequent desorption was slow. The rapidly desorbing component was likely sorbed on external surfaces of the aggregates of clay particles and the slowly desorbing component on mineral surfaces forming the intraaggregate micropores (Figure 4). The slow desorption observed here is analogous to hysteresis attributed to capillary condensation of vapors in porous media (Gregg, 1951; Iler, 1979).

The amounts of EDB sorbed and retained by the different minerals are given in Table 2. Whereas the

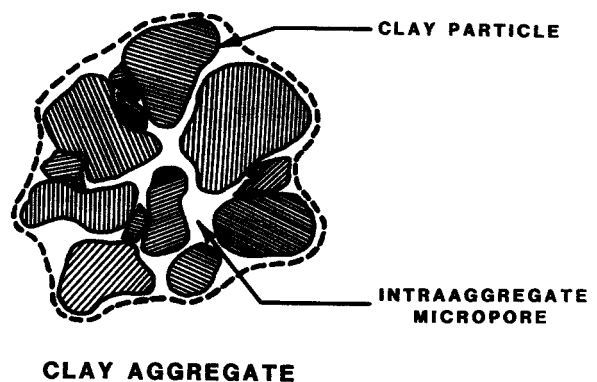


Figure 4. Cross section of an aggregate of clay particles, showing intraaggregate micropores.

Table 2. Sorption and retention of 1,2-dibromoethane (EDB) by clay minerals.

Mineral	Amount sorbed ($\mu\text{g/g}$)		Amount retained ($\mu\text{g/g}$)	
	1 hr	1 hr ¹	1 hr ¹	24 hr ¹
Pyrophyllite	1735	988	104	
Kaolinite	2460	2263	836	
Illite	3865	3633	2164	
Smectite	7232	5424	1374	

¹ Desorption time following 1-hr and 24-hr sorption.

amounts sorbed by the minerals and retained after 1 hr desorption were in the order smectite > illite > kaolinite > pyrophyllite, the amounts retained following an exhaustive 24-hr desorption treatment were in the order illite > smectite > kaolinite > pyrophyllite. Differences in retention of the organic molecules by the different clay minerals after 24 hr, corresponding to the slowly desorbing component, were probably due to the relative abundance, size, and configuration of the intraaggregate micropores. In the dehydrated states of the minerals used here, individual particles of the pyrophyllite with no layer charge should have been the least aggregated, whereas the illite and the smectite having layer charge, should have occurred as aggregates containing substantial microporosity. Although the low sorption and retention by the pyrophyllite may be explained on this basis, quantitative estimates of sorption and retention in relation to aggregation and porosity of the clays are difficult to establish from these data.

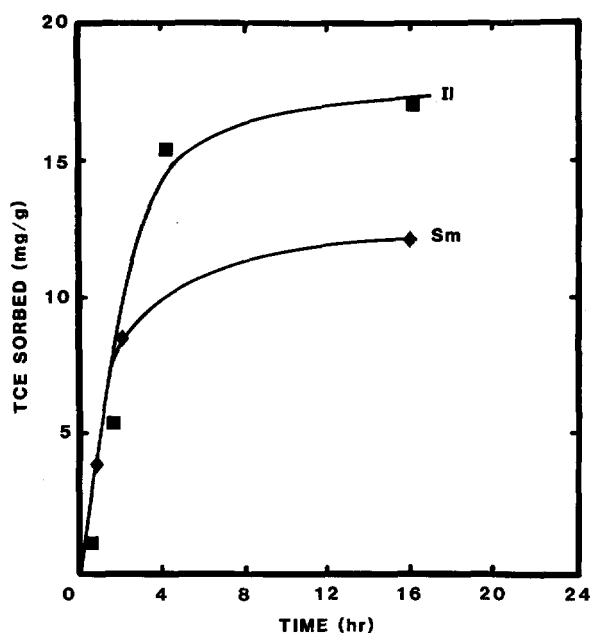


Figure 5. Vapor phase sorption of trichloroethene by illite (II) and smectite (Sm).

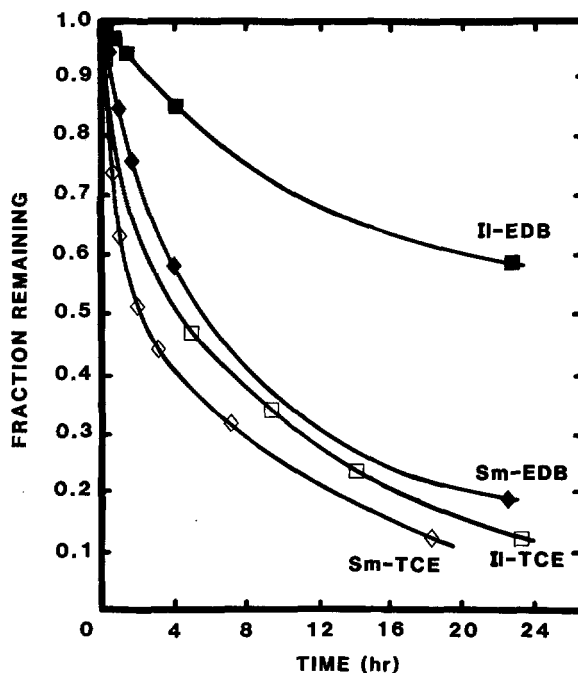


Figure 6. Desorption of trichloroethene (TCE) and 1,2-dibromoethane (EDB) by clay minerals illite (II) and smectite (Sm) following sorption for 2 hr and 1 hr respectively, plotted as fractions of the initially sorbed chemical remaining at different time periods.

Sorption and desorption of trichloroethene

The sorption of TCE by the clay minerals was similar to that of EDB in that the rate of sorption was initially rapid and decreased with time. The amounts of TCE sorbed by clays, however, were less than those of EDB. For example, the amounts of TCE sorbed by the illite and the smectite in 16 hr were 17 and 12 mg/g, respectively (Figure 5), whereas the amounts of EDB sorbed by the two minerals during the same time period were 57 and 85 mg/g (Figure 1). The smaller sorption of TCE vs. EDB was probably due to its greater volatility; the vapor pressure of TCE is 60 mm at 20°C, compared with 11 mm of EDB.

Desorption of TCE from the clay minerals was also similar to that of EDB, except that the rate of desorption was faster and the fraction retained at different times was lower. The TCE desorption from the illite and the smectite following sorption for 2 hr is shown in Figure 6. Desorption was initially rapid but decreased with time; however, 75% of the TCE sorbed by the illite and 50% of that sorbed by the smectite in 2 hr remained sorbed following desorption for 2 hr. Even after desorption for 20 hr, the illite retained about 20% and the smectite >10% of the amounts sorbed in 2 hr. Clearly, sorption of TCE by the clays, just as sorption of EDB, was only slowly reversible. The desorption of EDB from the illite and the smectite is compared in Figure 6 with desorption of TCE. The

desorption of EDB, which is less volatile than TCE, is much slower. For example, following desorption for 20 hr, the illite retained >60% of the sorbed EDB as compared to only about 20% of TCE. Desorption of EDB from smectite also was slower than desorption of TCE from this mineral. Desorption for >100 hr did not completely remove the two chemicals from the clays. After 100 hr desorption, the illite retained 4% of the sorbed EDB and about 1% of TCE. The faster desorption and less retention of TCE vs. EDB was likely due to the higher volatility of TCE. The role of other factors, however, such as hydrophobicity and size of the sorbate molecule in relation to the porous clay structure, in sorption-desorption is not clear at present.

Rapid and slow desorption

The observed desorption of EDB and TCE was described by a two parallel-compartment model of efflux given by:

$$S_1 = C = S_2, \quad (1)$$

$$\begin{matrix} k_1 & k_{-2} \\ k_{-1} & k_2 \end{matrix}$$

where C is the amount of the chemical in the gas volume, S_1 and S_2 are the amounts sorbed by the clays in the rapidly and slowly desorbing compartments, and k_1 and k_2 are the first-order rate constants for desorption for the rapid and slow desorbing fractions, respectively. The total amount sorbed, S , equals the sum of S_1 and S_2 . Earlier investigations to obtain rate constants for a two-compartment system involved several transformations and extrapolations of the data from semilog plots vs. time (Karickhoff and Morris, 1985a). In the present study the untransformed data were used in a manner similar to that used by McCall and Agin (1985). The two compartments were assumed to be independent, containing different initial amounts of the sorbed chemical and having first-order rate constants for desorption. Under continuous flow of N_2 used in the present experiments, k_{-1} and k_{-2} can be neglected. Thus, the total amounts of the chemical remaining in the two compartments at time N are given by the following finite difference equations:

$$S_{1,N} = S_{1,N-1} - k_1(t_N - t_{N-1}) \left(\frac{S_{1,N} + S_{1,N-1}}{2} \right) \quad (2)$$

and

$$S_{2,N} = S_{2,N-1} - k_2(t_N - t_{N-1}) \left(\frac{S_{2,N} + S_{2,N-1}}{2} \right), \quad (3)$$

where $S_{1,N}$ and $S_{2,N}$ are the amounts remaining in the two compartments at time t_N , and k_1 and k_2 are the rate constants for the rapid and slow desorption. These equations were programmed into a LOTUS-123 spreadsheet. The parameters, $S_{1,0}$ and $S_{2,0}$, the amounts sorbed initially before desorption was begun, and k_1

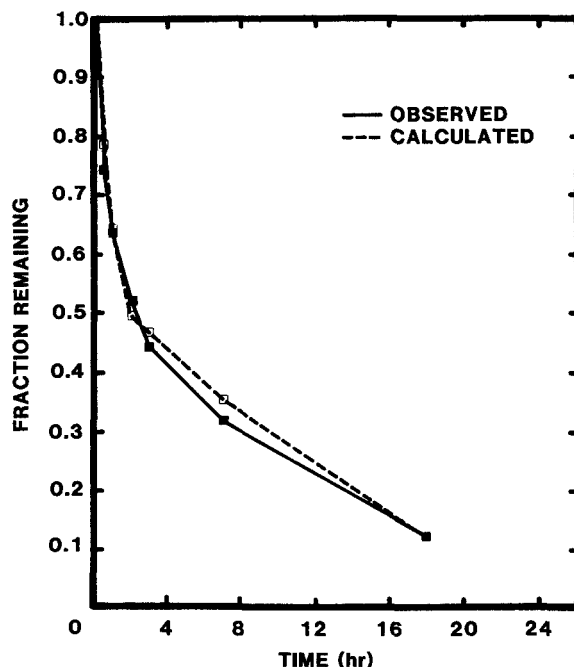


Figure 7. Desorption of trichloroethene from smectite following sorption for 2 hr. Calculated desorption isotherm was based on two-compartment model of efflux.

and k_2 were varied to obtain the best fit between the observed and the predicted fractions of the initially sorbed chemical remaining after desorption for different periods of time. The agreement between the experimental desorption isotherms and those calculated using the two compartment efflux model was excellent, as illustrated for the desorption of TCE from Sm (Figure 7).

The calculated rate constants for the rapid and slow desorptions of EDB and TCE and their proportions in each component in the different clay minerals are given in Table 3. In general, the rate constants for the initial rapid desorption were about an order of magnitude higher than for the subsequent slow desorptions. Also, the rate constants for TCE desorption were higher than for EDB; rapid desorption constants for TCE from the illite and the smectite were about three times greater than for EDB, whereas the slow desorption constant of TCE from the illite was twice as large as for EDB. Only in the smectite were the slow desorption constants of the two chemicals comparable. Inasmuch as the slow desorption likely constituted diffusion of the chemicals from pores of different sizes, the rate constants obtained by the purge technique used here represent average desorption rates from these different size pores. More than 50% of the EDB and TCE sorbed by the clay minerals appears to fall into the slow desorbing category (Table 3).

The present results, thus, demonstrate that non-polar hydrophobic organic compounds in vapor phase

Table 3. Rate constants (R) (hr^{-1}) and fractions (F) of rapid and slow desorbing fractions of 1,2-dibromoethane (EDB) and trichloroethene (TCE) obtained from desorption isotherms using curve-fitting technique.

Mineral	EDB				TCE			
	R ₁	F ₁	R ₂	F ₂	R ₁	F ₁	R ₂	F ₂
Pyrophyllite	0.66	0.47	0.09	0.53	—	—	—	—
Kaolinite	0.17	0.53	0.01	0.47	—	—	—	—
Illite	0.11	0.37	0.01	0.63	0.30	0.33	0.02	0.67
Smectite	0.38	0.43	0.05	0.57	0.78	0.48	0.60	0.52

¹ R₁ and R₂ are rate constants for the rapid and slow desorbing fractions F₁ and F₂.

were readily sorbed on dry clay mineral surfaces and diffused into intraaggregate micropores. The molecules entering the micropores likely condensed on mineral surfaces forming the pores in a manner similar to capillary condensation of vapors in micropores of the porous sorbents and were only slowly desorbed. Slow sorption and desorption of hydrophobic organic compounds observed in sediments (Karickhoff and Morris, 1985b; Wu and Gschwend, 1986) and soils (Steinberg *et al.*, 1987; Pignatello, 1989) in aqueous systems have been attributed to intraaggregate diffusion. Aggregation of small clay and silt particles in soils and sediments can occur through organic matter or oxide and hydroxide coatings or clay films (Greenland and Hayes, 1978). Slow sorption and desorption have also been attributed to diffusion into the humic substances present in soils and sediments (Karickhoff and Morris, 1985a). Thus, although in aqueous systems organic matter in soils and sediments may play a major role in slow desorption of hydrophobic organic compounds, in dry soils or in soils with low organic matter slow desorption may result from clay aggregates as observed here.

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