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Research Report No. 190

**SORPTION OF CHLORINATED  
ORGANIC COMPOUNDS  
BY  
SEDIMENTARY ROCKS**

By

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1994

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**Sorption of Chlorinated Organic Compounds by Sedimentary Rocks**

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December, 1994

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## **Abstract**

The sorption of dichlorobenzene and trichlorobenzene on carbonate and shale rocks collected in Kentucky demonstrate that rock organic matter content is a good indicator of sorptive reactivity in rock systems. Although this is similar to soil systems, significant differences between sorption in rock and soil systems exist. Sorption isotherms on these rocks are nonlinear and sorption can be an order of magnitude higher than predicted using correlations from soils and their organic matter content. This sorption reaction could lead to significant concentration tailing during contaminant cleanup. Experimental elution of trichloroethylene from rock filled columns verified that cleanup times might be extended due to both sorption and diffusion into rock.

## **Introduction**

Water below the ground surface can be contaminated by chemical spills, leaking storage tanks, and improper disposal. Particularly vulnerable, however, may be that water which resides within the fractures and dissolutional cavities of sedimentary rock. This water can be contaminated by pollutants admitted directly through dumping in sinkholes or below-grade waste disposal, and indirectly through water moving through thin soil layers. Because water flow rates in these systems can be large, ranging up to thousands of meters per day, contaminants may travel widely and disperse haphazardly in a relatively short amount of time. These waters are often used for drinking water, agricultural uses, and may eventually combine with surface or other groundwaters. Consequently, the dissipation of the contamination, or renovation of these waters is important.

Subsurface rock can contain mixtures of carbonate and clay, sand, and other materials reflecting both terrestrial and marine origin. Carbonate rocks may contain more than 90% calcium carbonate and arise from marine deposition of calcium-containing marine life and various cementing agents. Other rocks contain components of terrestrial origin such as clays and sands. Water flow through these rocks can be complex, ranging from karst caverns, where substantial dissolution of rock has occurred, in carbonate rock to fissures and fractured rock of mixed composition.

Reactions of contaminants with these rocks which act to retain the contaminants are collectively referred to as sorption. Contaminant appearance at some point within such a

system will then depend both on the flow rate and the extent to which it is sorbed. Whereas considerable research has been performed on the sorption interactions of relatively nonpolar organic compounds in soils, sediments and aquifer sands (Schwarzenbach and Westall, 1981; Chiou et al., 1983; Karickhoff, 1984), little is known about the interactions of organic compounds in rock systems. This report describes an investigation of the sorption of three relatively nonpolar organic compounds on a series of different sedimentary rocks of mixed composition. The results will be compared to sorption in soils.

### *Sorption Models*

Sorption is the process of chemical distribution of a compound between a dissolved form and a sorbed form. The extent to which a compound is sorbed reflects compound, solid, and solution properties, and the resulting distribution can be shown as a relationship between sorbed and solution concentrations often referred to as the sorption isotherm. A variety of models are available by which this sorption isotherm is described mathematically.

A linear sorption model depicts an amount of contaminant sorbed,  $q_e$ , as directly proportional to the solution concentration of contaminant,  $C_e$ :

$$q_e = K_D C_e \quad (1)$$

This linear sorption isotherm suggests a sorption energy which does not vary with coverage and can arise from a homogenous surface or phase where the contaminant accumulates. The distribution coefficient,  $K_D$ , can be estimated a priori for soils and sediments using the compound's organic carbon normalized partition coefficient,  $K_{OC}$ , and the fractional organic



carbon content of the soil(W/W),  $f_{OC}$ :

$$K_D = K_{OC} f_{OC} \quad (2)$$

A variety of correlations are available relating  $K_{OC}$  to physical/chemical properties of the contaminant. One correlation which has been developed from the sorption of a series of chlorinated benzenes on soils (Schwarzenbach & Westall, 1981) is:

$$\log K_{OC} = 0.49 + 0.79 * \log K_{OW} \quad (3)$$

An alternative way of presenting this apparent uniformity of sorption by soil organic matter is through normalizing the sorption on all soils by their organic carbon content:

$$\frac{q_e}{f_{OC}} = K_{OC} C_e \quad (4)$$

Although this simple model is computationally efficient and useful for parameter estimation, recent evidence suggests that there can be two problems: 1) the  $K_{OC}$  may not be the same for each soil, and, 2) there may be nonlinearity in the solid/solution phase relationship. Variations in  $K_{OC}$  have been attributed to different forms of organic matter and to mineral sorption. Isotherm nonlinearity may arise from surface adsorption phenomena and absorption where the interactions between absorbed molecules increases or decreases their affinity for those matrices (Weber et al., 1992).

Although a variety of models are available to describe nonlinear sorption isotherms,

the Freundlich isotherm model often describes experimental data quite well over a large concentration range:

$$q_e = K_F C_e^n \quad (5)$$

The  $K_F$ , the Freundlich unit capacity coefficient, and  $n$ , the Freundlich exponent, reflect different aspects of the sorption process, but to date it is not possible to predict them independently unless the  $n$  is unity, in which case the Freundlich isotherm reduces to the linear isotherm model (Equation 1). The Freundlich isotherm model can be linearized by taking the logarithm of both sides:

$$\log q_e = \log K_F + n \log C_e \quad (6)$$

where the slope of the log-linear line is the Freundlich exponent. Similar to Equation 4, the Freundlich isotherm can be normalized to the organic carbon content of the solid phase and the resulting linearization,

$$\log \frac{q_e}{f_{OC}} = \log \frac{K_F}{f_{OC}} + n \log C_e = \log K_{F_{OC}} + n \log C_e \quad (7)$$

demonstrates that the slope of the linear line would be unaffected, but that the intercept, the organic carbon normalized Freundlich constant or  $K_{F_{OC}}$ , differ from the  $K_F$  of Equation 6.

### *Contaminant Transport*

Water flow in rock systems can occur along bedding planes, fissures, fractures or in karst conduits. Flow along such natural openings in rock is frequently

referred to as preferential flow. Porosities in these systems may be very low, yet ground water velocities can be rather high (Freeze and Cherry, 1979). Realistic modeling of contaminant movement in these rocks must address reactions of the contaminant. Sorption during transport through rock may be related to the surface area which is available for reaction, but the relationship between particle surface area and reactive surface area is not straightforward. The total reactive surface area of rock may be much greater than the external surface area of a sample. In soils, the organic matter has been shown to act as a phase into which organic contaminants accumulate. In rocks, researchers have not identified the source of sorption reactivity and its relationship to available surface area. Archie(1952) defined primary porosity to be the fluid external to the rock mass which contains the flowing water, whereas secondary porosity may be fluid filled regions not directly in contact with flowing water and can be internal to the rock mass.

The partitioning of a contaminant between a solution and media has particular significance with respect to contaminant transport in ground water. Sorption will slow down, or retard, the movement of a contaminant. A simple model for transport of a compound in porous media is the one dimensional advective/dispersive equation

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial X^2} - V_x \frac{\partial C}{\partial X} - \frac{\rho_b}{\theta} \frac{\partial q}{\partial t} \quad (8)$$

where  $D_x$  is the dispersion coefficient in the x direction,  $V_x$  is the rate of advective transport in the x direction,  $\rho_b$  is the dry bulk density, and  $\theta$  is the porosity (volume of voids/volume total).

If we assume that the sorption reaction is at equilibrium, and a linear isotherm model equivalent is appropriate, after substitution and rearrangement, equation 8 can be written (Freeze & Cherry, 1979):

$$\left(1 + \frac{\rho_b K_p}{\theta}\right) \frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial X^2} - V_x \frac{\partial C}{\partial X} \quad (9)$$

Therefore, when fast reversible reactions with linear isotherms describe partitioning, the average velocity of contaminant movement relative to ground water movement is the retardation factor, R,

$$R = \frac{v_a}{v_c} = 1 + \left(\frac{\rho_b}{\theta}\right) K_p \quad (10)$$

where  $v_a$  is average linear velocity of ground water and  $v_c$  is the apparent velocity retarded species.

The retardation factor is independent of contaminant concentration for a linear isotherm model, but when sorption is described with a non-linear isotherm, retardation factors are concentration dependent. Sorption follows a non-linear isotherm, and the expression for the retardation factor will depend on concentration. For example, if the data can be described with Freundlich isotherm, the retardation factor is (van Genuchten and Wierenga, 1976):

$$R = 1 + \left(\frac{\rho_b}{\theta}\right) n K_F C^{n-1} \quad (11)$$

For a Freundlich isotherm model where the exponent is less than unity, the result is a retardation factor which increases as the solution concentration is lowered.

Equilibrium sorption conditions in soils may not be reached instantaneously and may require months or years (Ball and Roberts, 1991). This nonequilibrium behavior has been explained by mass transfer at the grain scale (Weber et al., 1991). The intra-particle diffusion model assumes that diffusion occurs in saturated pores within particles and that this diffusion is also slowed by equilibrium sorption within the pores (Grathwohl and Reinhard, 1993). The quantity of mass diffused per unit area, or the flux, will likely be proportional to the concentration gradient (Freeze and Cherry, 1979). If a porous media has a finite sorption capacity, equilibrium is approached most quickly when the concentration gradient, and therefore flux, is at a maximum. As the concentration gradient decreases, flux will correspondingly decrease. As a result, when sorption approaches equilibrium, either due to sorption or desorption, the rate of mass transfer slows. This relationship may act to slow the cleanup of contaminated systems.

## **Experimental**

The reactions of contaminants with solid phases in the subsurface may be important determinants of contaminant travel and removal times. In this report, a series of experiments which examine the sorption of hydrophobic organic compounds on natural sedimentary rocks are described.

Rock samples were collected from near-surface and at depth from different locations in Kentucky. Both mechanical coring and hand collection from outcrops were used. Properties of the rocks collected are shown in Table 1. Prior to use in the sorption experiments, the rocks were crushed with either a jaw crusher or a Soil Test Versa Tester 30 M (Evanston, IL) compression machine. Where smaller particle sizes were desired, the crushed rock was finely ground with a laboratory mill (Tekmar Analytical Mill) to reduce the particle size to pass a #60 (250 microns) sieve.

Organic carbon content of the rocks was determined after first exhaustively treating the rocks with acid. Rocks were treated with either nitric (0.5 N) or hydrochloric (0.5 N) acid and then the residue analyzed for total carbon using a TOC analyzer. Little difference in the measured organic carbon content was noted for these different treatments. Surface area determination was made with nitrogen adsorption on a AUTOSORB-6 surface area analyzer.

The organic compounds used in this research were 1,4-dichlorobenzene (DCB), 1,2,4-trichlorobenzene (TCB) and trichloroethylene (TCE). They were dissolved in reagent grade methanol to form different stock solutions ranging from 2500 to 19000 mg/l of the solution.

Table 1. Properties of the rocks used in Experiments

Rock type	Depth of Collection from surface(ft)	Surface Area (m <sup>2</sup> /g)	Organic Carbon %
Fayette	8	3.54	0.60
Martin	10	2.95	0.14
Hardin	108	7.59	0.46
Tates Creek	10	2.43	0.062
Clays Ferry	10	--	0.075
Cowbell	40	6.39	0.10

Equilibrium sorption of the compounds was determined after mixing known quantities of rock,  $M$ , with known volumes of fluid,  $V$ , in glass vials. After addition of the organic compound using a microliter syringe to attain the initial concentration,  $C_0$ , the vials were capped with Teflon faced septa, wrapped with Parafilm, and tumbled end over end for a time period sufficient to reach equilibrium. After this time period, the final solution concentration,  $C_e$ , of solute in the reactor was measured. Because of the volatility of these solutes, solid/liquid separation was through centrifugation. The supernatant was extracted with hexane to isolate the contaminant and the hexane was analyzed using gas chromatography (Hewlett Packard 5890) with electron capture detection. The apparent quantity of solute sorbed was obtained using the relationship

$$q_e' = (C_0 - C_e) * \frac{V}{M} \quad (12)$$

The time required to attain an apparent equilibrium with the rock material was determined through a rate study. Samples prepared as described above were centrifuged and analyzed for the solute concentration over a period of 14 days. The results for one rock and TCB are shown in Figure 1. It was determined that for the rock fragments examined, equilibrium was reached in 3 days for trichlorobenzene and less time was required for dichlorobenzene and trichloroethylene. During the three day equilibration period, solute losses in the reaction vials were determined to be an average of 8.5% for trichlorobenzene and 5.5% for dichlorobenzene. The impact of these losses on sorption determination could be reduced by controlling rock/solution ratios to achieve overall reductions in solution



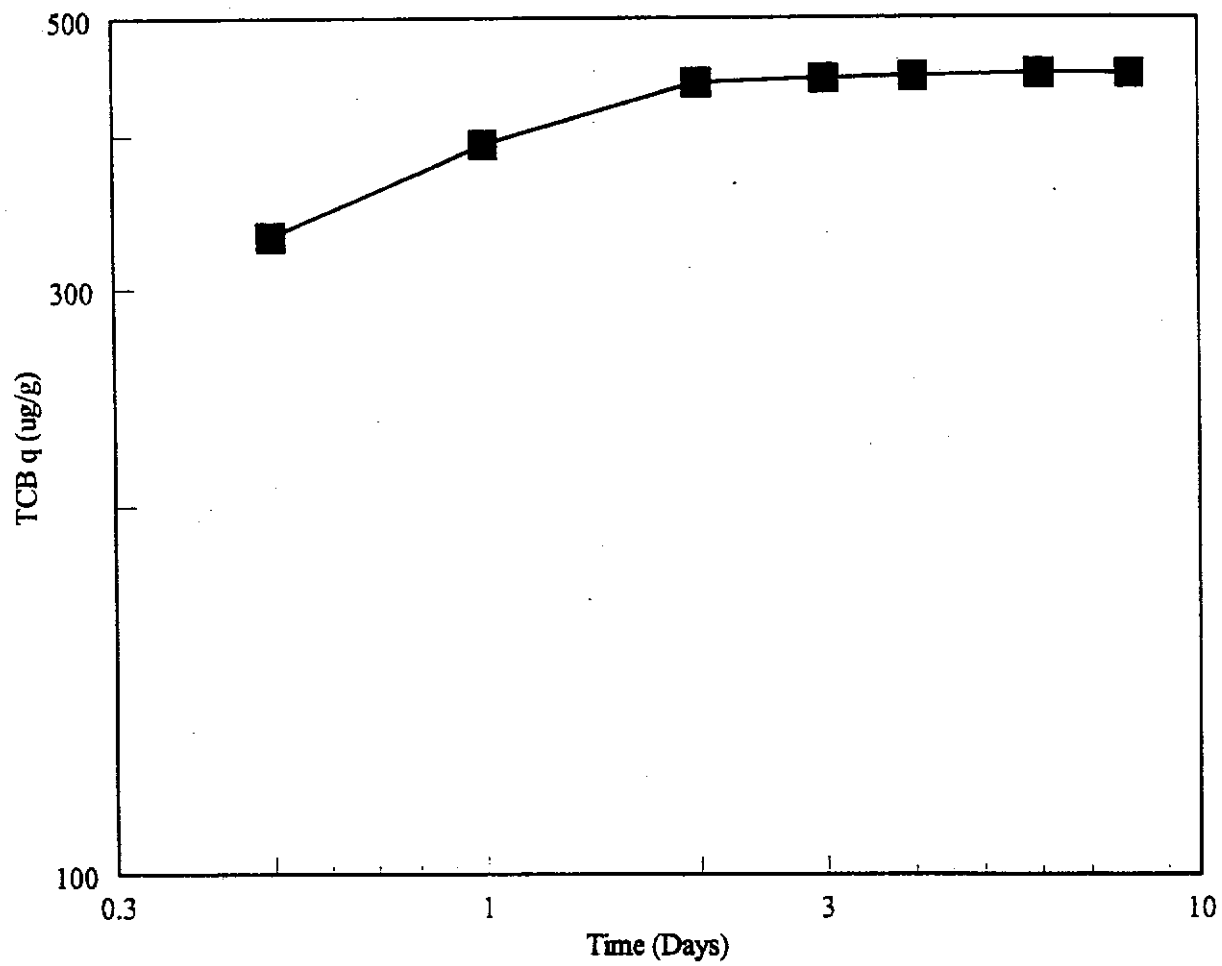


Figure 1. Results of a TCB sorption rate study on Fayette rock.

concentration which exceeded 50%. These losses may be due to volatilization and or sorption onto the reactor components. Extraction of vials with hexane indicated that at least 60% of the lost solute could be recovered. Consequently, the sorption data is corrected by using the method used by Lion et al., 1990, where the lost solute was assumed to be reversibly sorbed to reactor components and the corrected sorbed phase concentration calculated from:

$$q_e = [(C_0 - C_e) - K_L * C_e] * \frac{M}{V} \quad (13)$$

Where the equilibrium constant,  $K_L$ , in the above expression is found from the loss analysis and assuming that losses in the reactor follow a linear isotherm dependent on the final concentration of solute in the vial. The magnitude of the correction can be seen in the data in the Appendix and for the rocks examined it ranges from 1% to 9% of the apparent sorbed phase concentration.

Standard solutions of the organic compounds were prepared and analyzed during all experiments. The standards are made by injecting the organic compound into the extraction vial containing hexane and water in a 1:1 ratio. Losses in preparing the standards could be minimized by injecting solute directly into water with hexane on top and capping the vial immediately after injection.

Rock material divided into a large (#20 - #30, 600 - 850  $\mu\text{m}$ ) and small (#40 - #60, 200 - 450  $\mu\text{m}$ ) size fractions was used in column experiments. All particles were extensively rinsed before use to minimize the presence of fines. Ground water solution was

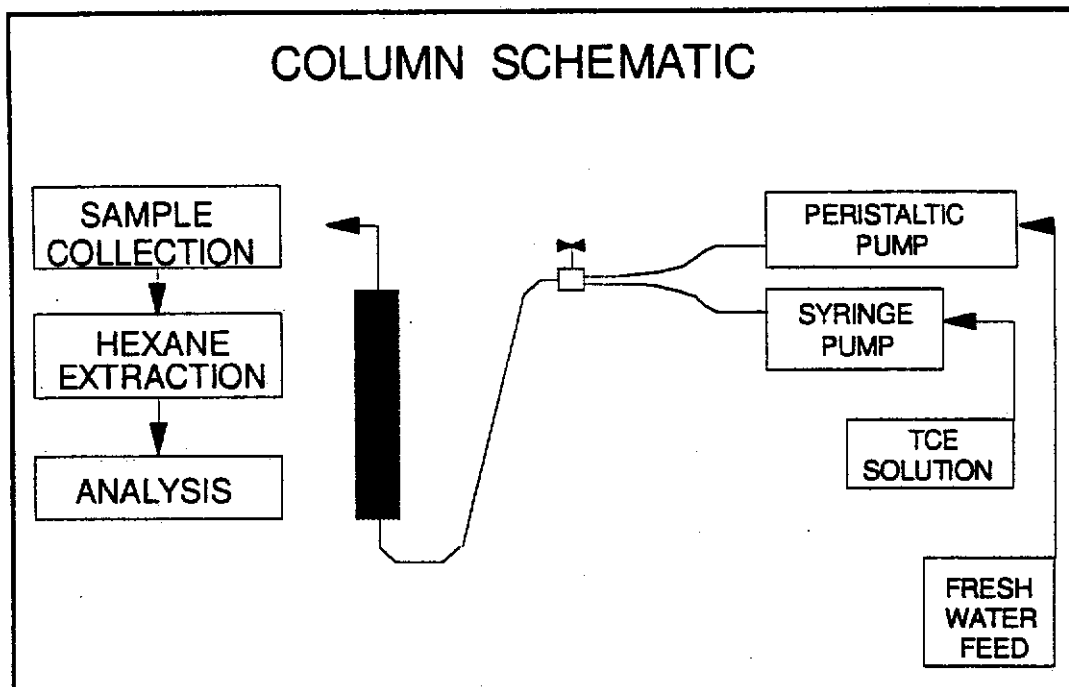


Figure 2. Schematic of column apparatus used in flow through experiments.

prepared to simulate the natural systems where large scale contaminant transport takes place, and to minimize any dissolution of samples. This was solution of distilled, deionized water with 48.80 meq/L of  $\text{NaHCO}_3$  and 0.94 meq/L of  $\text{Na}_2\text{CO}_3$ . The pH was 8.13. Although this mixture was undersaturated with respect to calcite, even at equilibrium it would permit only minor dissolution. The column system is shown in Figure 2.

In column experiments, flow was driven through a 25 cm long, 1 cm diameter HPLC column (Supelco Inc. Bellefonte, PA) with a peristaltic pump (Masterflex, Cole-Parmer, Chicago, IL) for the simulated groundwater and a syringe pump (Harvard Apparatus, South Natick, MA) for the contaminant. The syringe pump was variable speed, and adjusted to match the flow in the peristaltic pump. A mixing tee (Alltech, Deerfield, IL) connected the stainless steel tubing output line (Supelco Inc., Bellefonte, PA) of each pump to a single column feed line. This tee had separate on/off valves for each input line, allowing a rapid switch between lines. The contaminant contacts only glass and stainless steel during the entire process and should minimize the sorption of organic contaminant to reactor components (Lion et al., 1990).

Rock media was placed into the column in 1 cm lifts. The column was tapped on a hard surface to promote settling between each lift. The weight of the column was used to determine the mass of media. The column was operated in an upflow mode. After column filling, de-aired ground water solution was pumped through the column at the rate of approximately 7 pore volumes per hour. After 30 pore volumes of water had passed through the column, the top frit was removed and rinsed with distilled, deionized water to remove any minor accumulation of rock material at the column exit. This was done with

the column remaining in its vertical position to minimize water loss. The flow of deaired ground water solution was resumed once the frit was replaced. A minimum of ten additional pore volumes of ground water solution were passed through the system after frit cleaning. At the appropriate time, flow was switched from the peristaltic pump/ground water supply to the syringe pump/contaminant supply. There was virtually no flow interruption during the switching process. The syringe consistently contained 15 ml of contaminant, approximately 2 pore volumes, which was delivered to the column at the same rate as the ground water solution.

Samples of the column effluent were taken from tubing at the end of the column in 7 ml, chloride-free vials containing known amounts of hexane and ion chromatograph eluant. Sampling began before any contaminant had passed through the column and continued at regularly spaced intervals for varying amounts of time. Sampling continued for a minimum of 25 pore volumes.

Sample vials were weighed to determine the volume of captured liquid. They were agitated for several minutes and contacted for an additional 30 minutes to ensure TCE separation into hexane. The hexane portion of samples were analyzed for TCE in the gas chromatograph. The aqueous portion of the samples were analyzed for chloride in a Dionex LCM-3 ion chromatograph with conductivity detector.

## Results and Discussion

### *Sorption Equilibria in Rock Systems*

In Figure 3, the TCB sorption isotherms on the rocks are shown as the sorbed phase concentration,  $q_e$ , as a function of the equilibrium solution concentration,  $C_e$ . It is apparent from the Figure that when normalized for the mass of the original rock, a wide range of sorption intensity is exhibited for the different rock samples. The isotherms are distinctly nonlinear and Freundlich isotherm parameters were calculated from logarithmic transformed data. Log transformed data is preferred in this case because of the error is proportional to concentration and this transformation almost normalizes the residuals. The Freundlich isotherm model parameters are shown in Table 2. Confidence limits on the Freundlich exponent,  $n$ , confirm that in all cases it is less than unity.

The sorption of DCB was always lower than the sorption of TCB on a rock sample. This suggests a hydrophobic motivation for the sorption reaction and is consistent with the sorption of these compounds onto soils and sediments reported by previous investigators. In Figure 4, the sorption of DCB and TCB is compared on three of the rock materials. The degree of nonlinearity for both compounds is similar on each rock, and, as can be seen in the confidence limits of Table 2, on many rocks it is not possible to statistically distinguish differences between the exponents for the two compounds. Although similar Freundlich  $n$  values suggest similar distributions of association energies across the concentration range examined for the two solutes, it is probably more accurate to compare these isotherms at similar sorbed phase concentrations. It was found that normalizing the solution phase

Table 2. The Freundlich isotherm model parameters for sedimentary rock.

Rock Type	TCB		DCB	
	n (95% C.I.)	$K_F$ ( $\mu\text{g/g}(\text{l/mg})^n$ )	n (95% C.I.)	$K_F$ ( $\mu\text{g/g}(\text{l/mg})^n$ )
Fayette	0.65 (+/- 0.08)	196.75	0.57 (+/- 0.06)	71.4
Martin	0.64 (+/- 0.04)	23.44	0.55 (+/- 0.13)	11.8
Hardin	0.62 (+/- 0.05)	106.6	0.71 (+/- 0.10)	40.4
Tates Creek	0.67 (+/- 0.09)	10.86	0.90 (+/- 0.06)	5.63
Clays Ferry	0.81 (+/- 0.04)	17.64	0.90 (+/- 0.05)	10.8
Cowbell	0.76 (+/- 0.05)	27.6	0.87 (+/- 0.1)	19.6

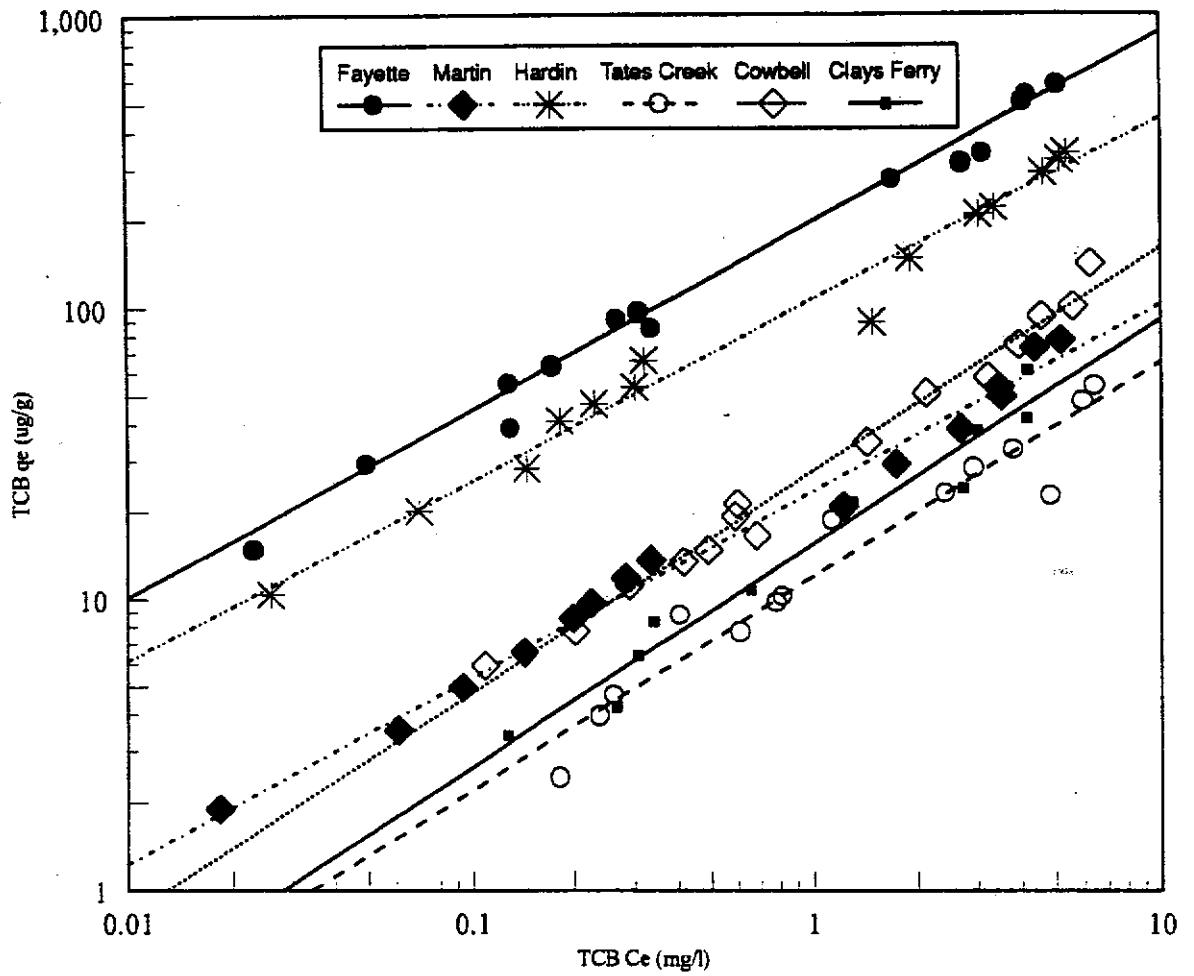


Figure 3. Experimental data and linearized Freundlich isotherm model fits for TCB sorption by six rocks.



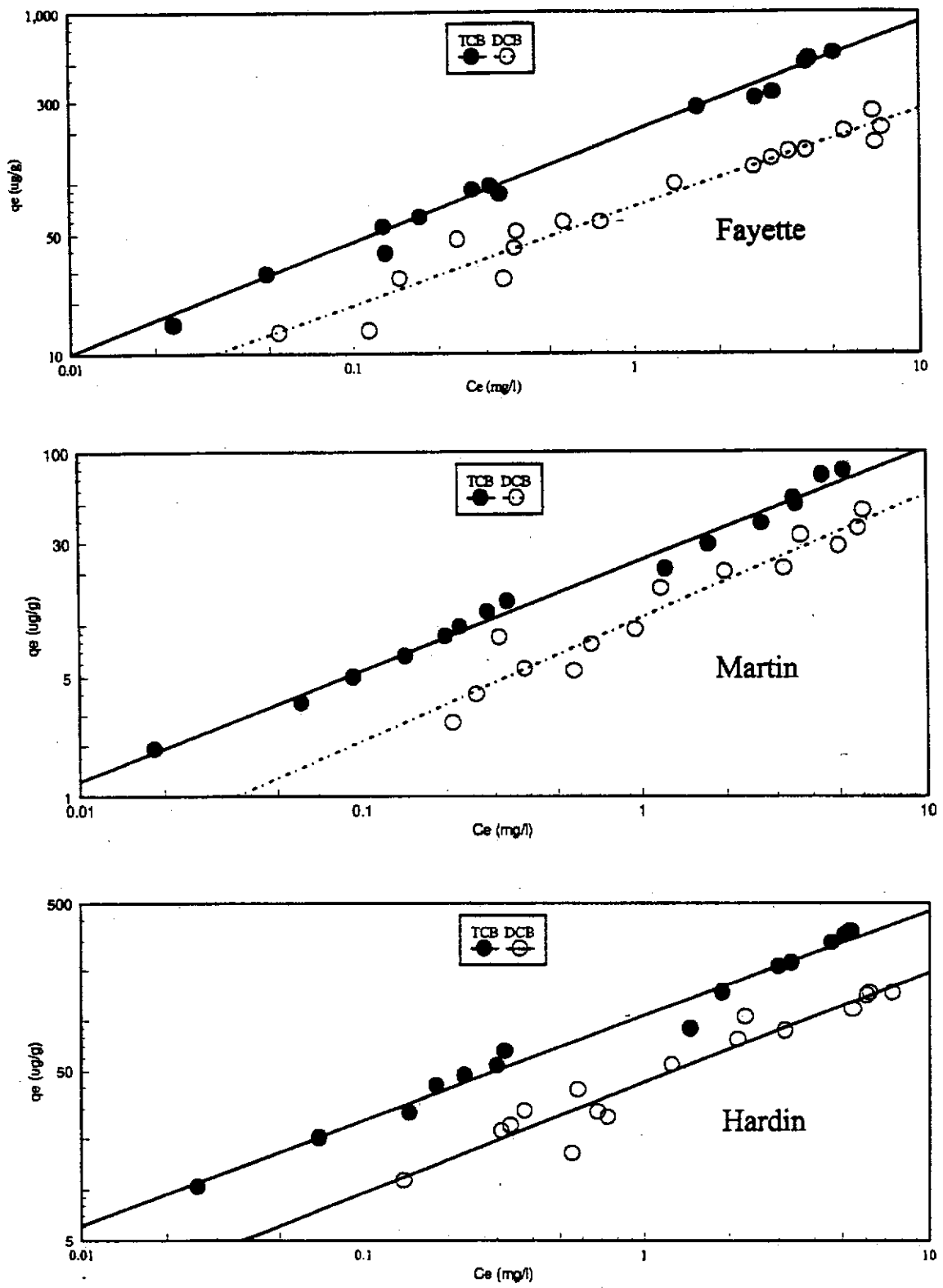


Figure 4. Experimental data and Freundlich isotherm model fits for TCB and DCB sorption on Fayette, Martin and Hardin respectively.

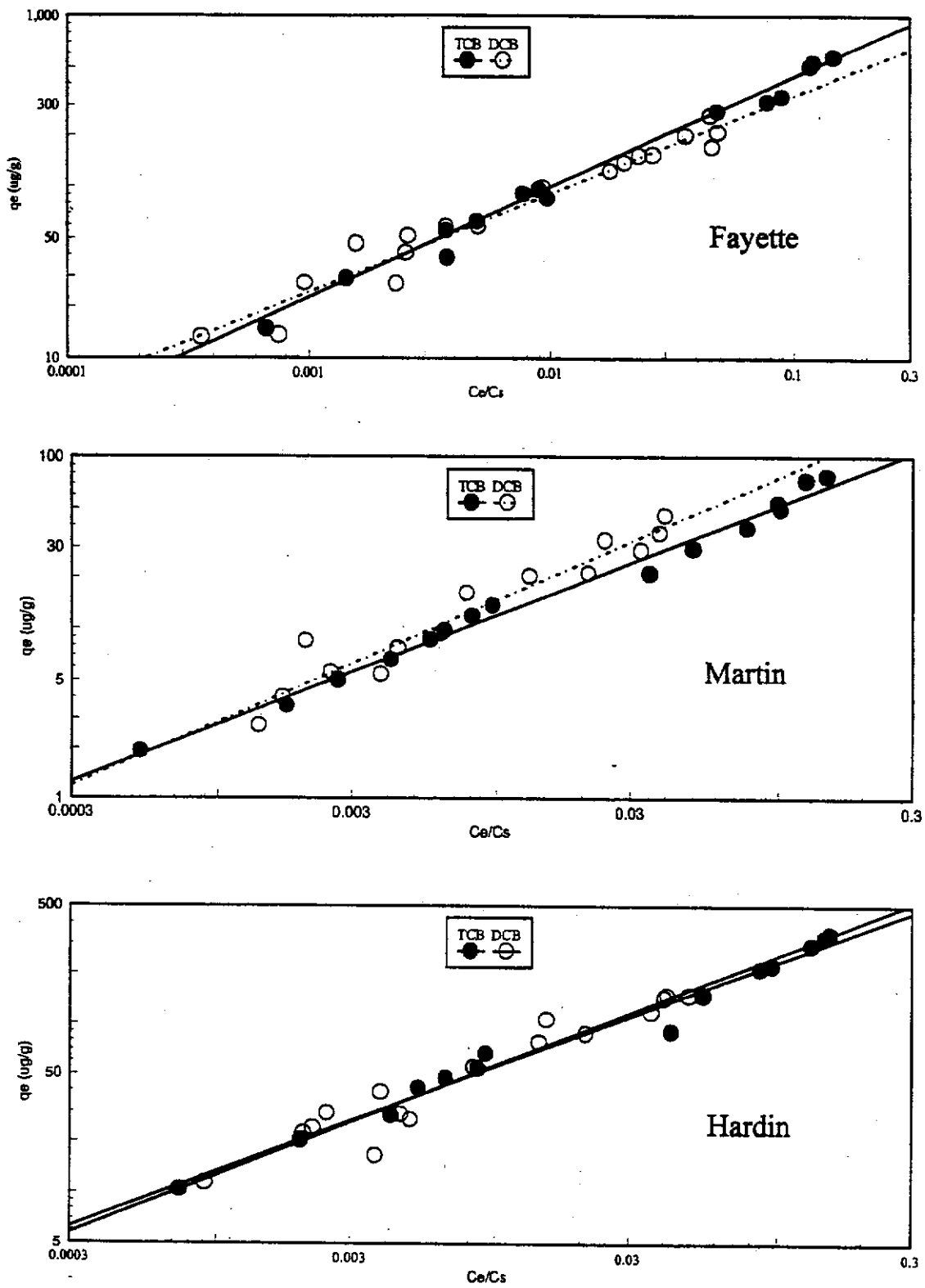


Figure 5. Experimental data and isotherms for TCB and DCB sorption at similar sorbed phase concentration by Fayette, Martin and Hardin. The solution phase concentration is normalized to solubility of the compound.

concentration for the solubility (liquid or subcooled liquid) of the contaminant as shown in Figure 5, led to isotherms which are identical. This equalization of sorption after normalization for solubility of the solute is also consistent with a sorption motivated by hydrophobicity of the solute.

The extent of isotherm nonlinearity on these rock materials leads to Freundlich exponents which range from 0.6 to 0.9. This suggests regions on these rocks which are heterogeneous with respect to the energy of association for organic compounds. As such, the presence of multiple solutes would be expected to lead to competition during sorption. Indeed, the sorption of DCB on the Fayette rock material was measured in the presence and absence of TCB and the sorption of DCB was reduced as shown in Figure 6.

The nonlinear sorption isotherms do not permit calculation of  $K_{OC}$  values for the rock samples, because it is based on a linear isotherm model, but the effect of organic content on the sorption of DCB and TCB can be seen in Figure 7 where the sorption has been normalized for the organic carbon content of the rock. It is significant that the organic carbon normalized isotherms are coincident and when compared to the sorption which would be expected from soil organic matter, the sorption by these rocks is greater than that anticipated from a soil  $K_{OC}$ . The disparity between organic carbon normalized sorption and that predicted for a soil increases as the concentration is reduced. The BET surface area may also be linked to sorption capacity of the rock, but as shown in Figure 8, the sorption surface area does not provide the same degree of agreement as organic carbon normalization, although those rocks with the highest organic carbon content show the highest sorption on a surface area basis.

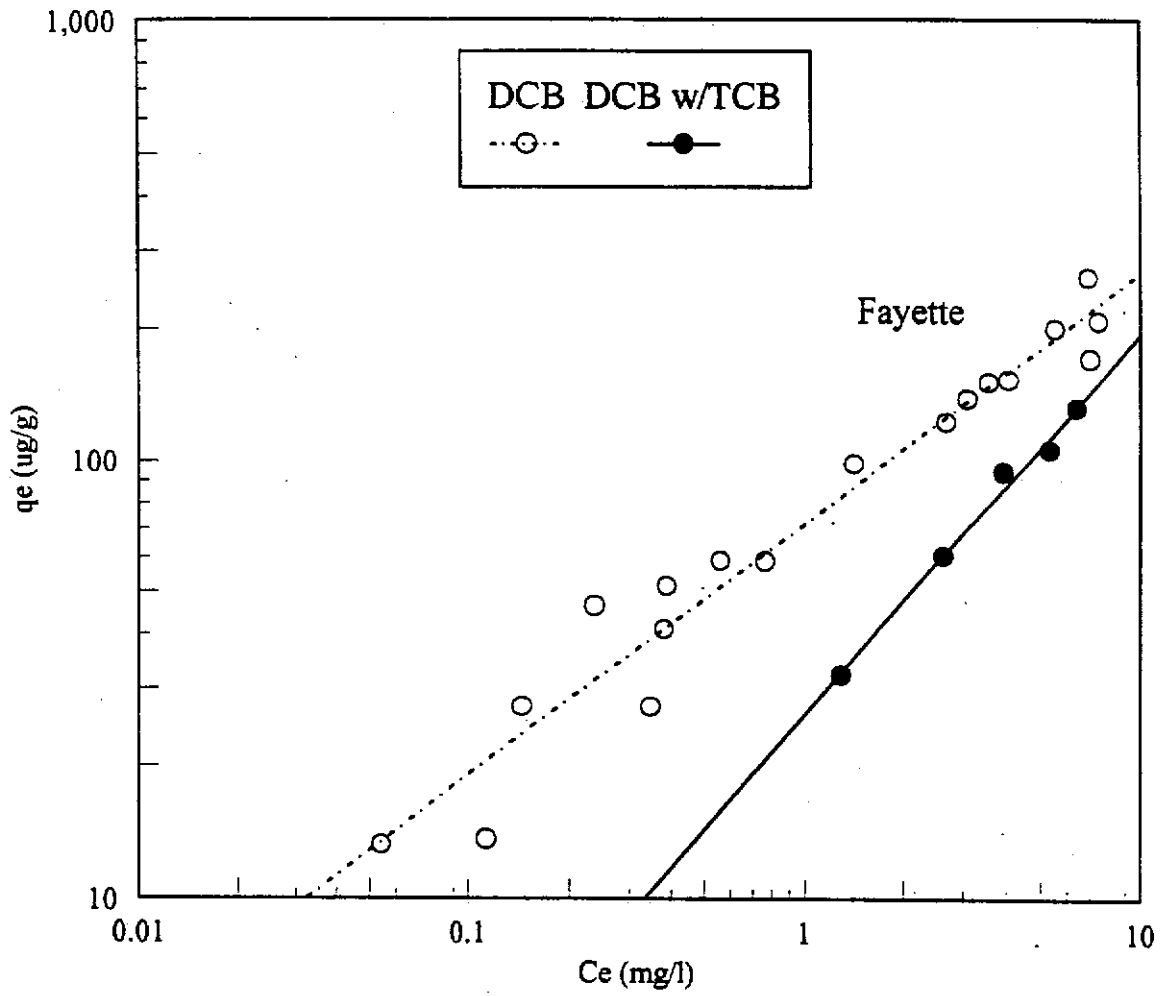
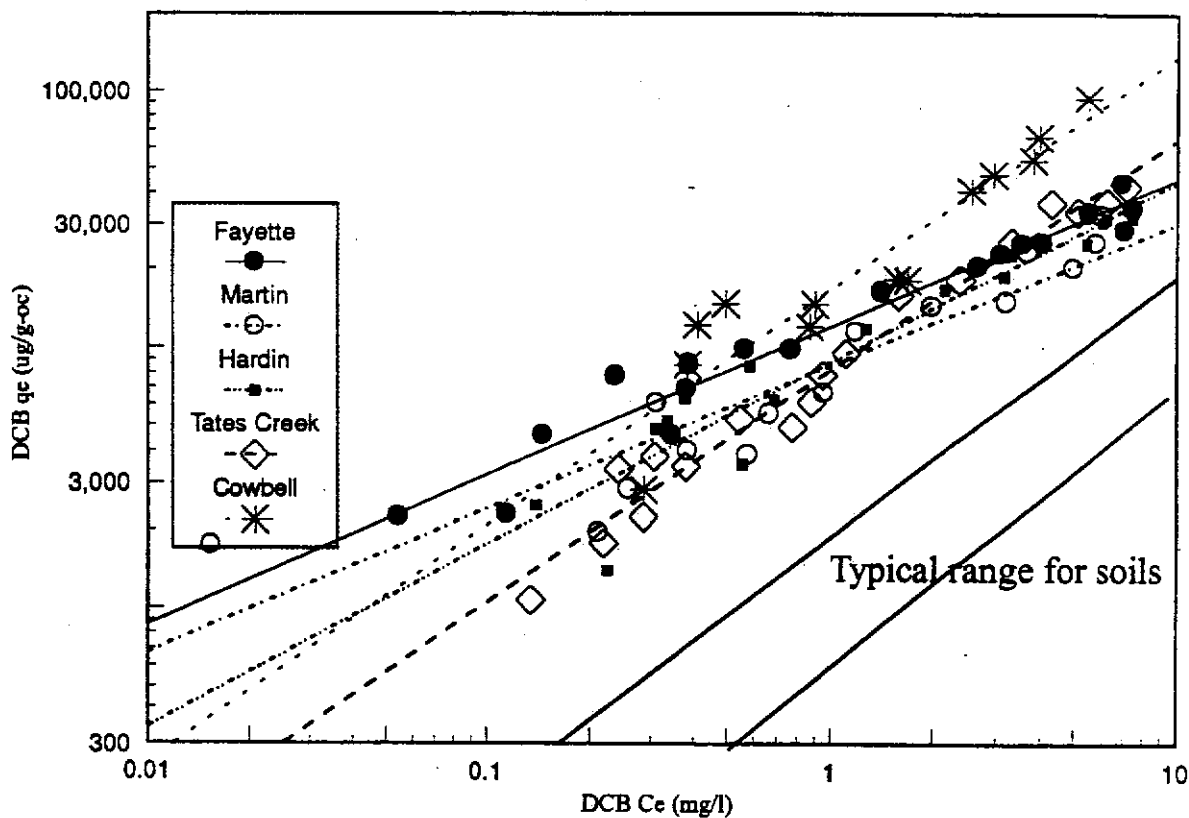
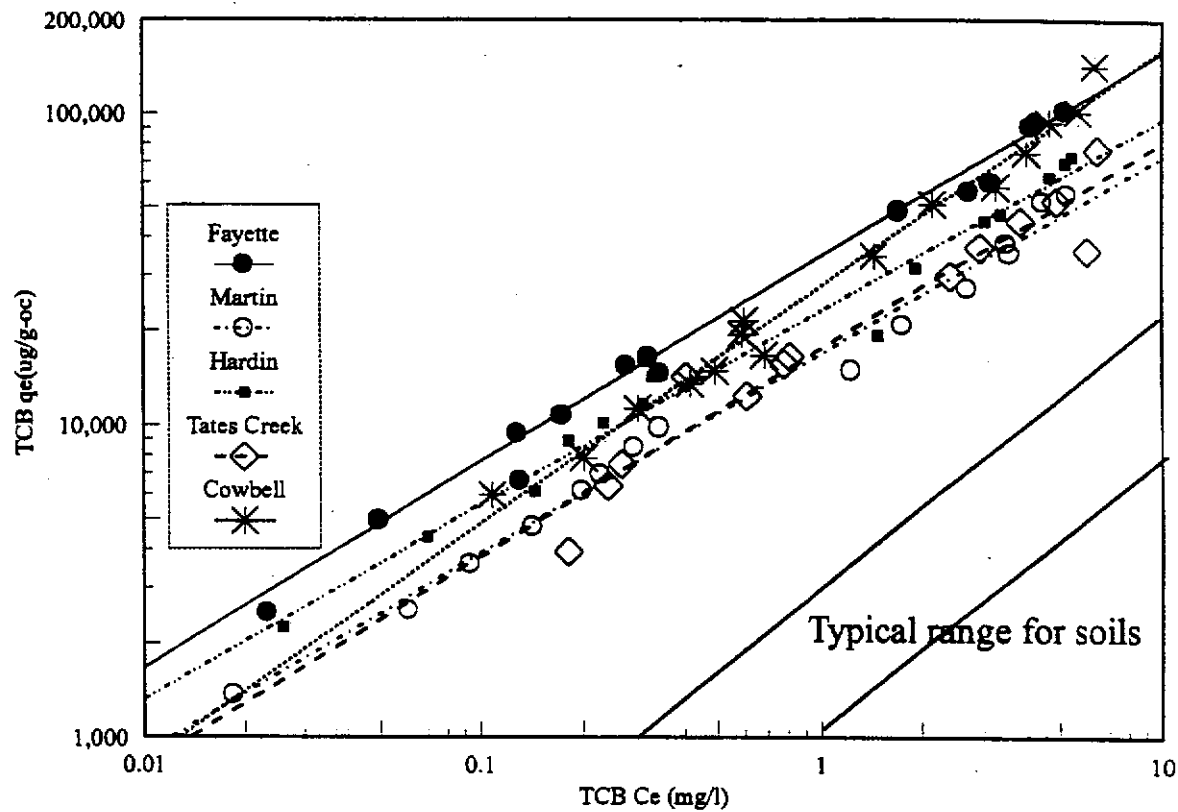
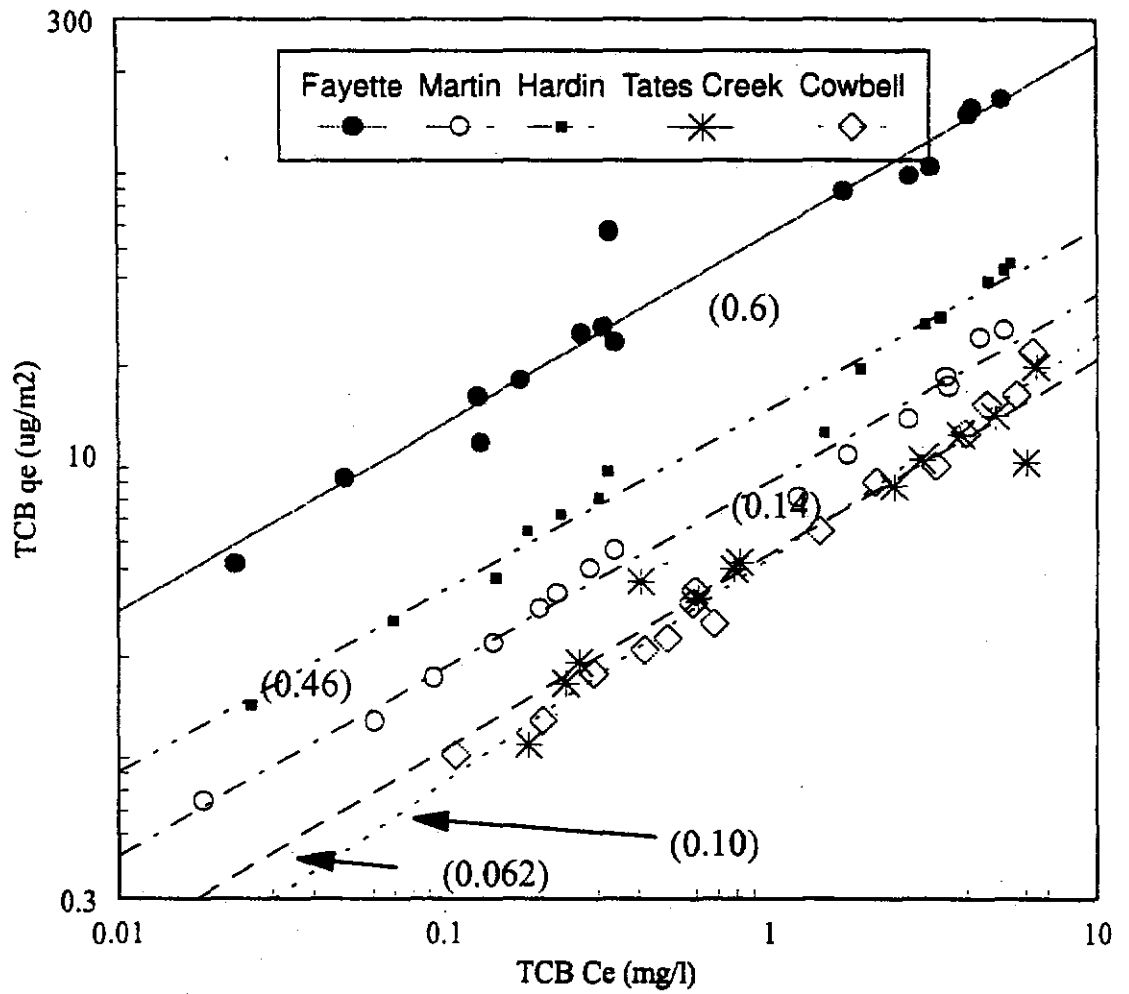


Figure 6. Comparison of DCB sorption on Fayette rock material with and without the presence of TCB and also the TCB sorption on Fayette.



**Figure 7.** Experimental data and Freundlich isotherm models for sorption of (a) TCB (b) DCB by five rocks normalized to the organic carbon fractions of the rocks compared to range reported on soils.

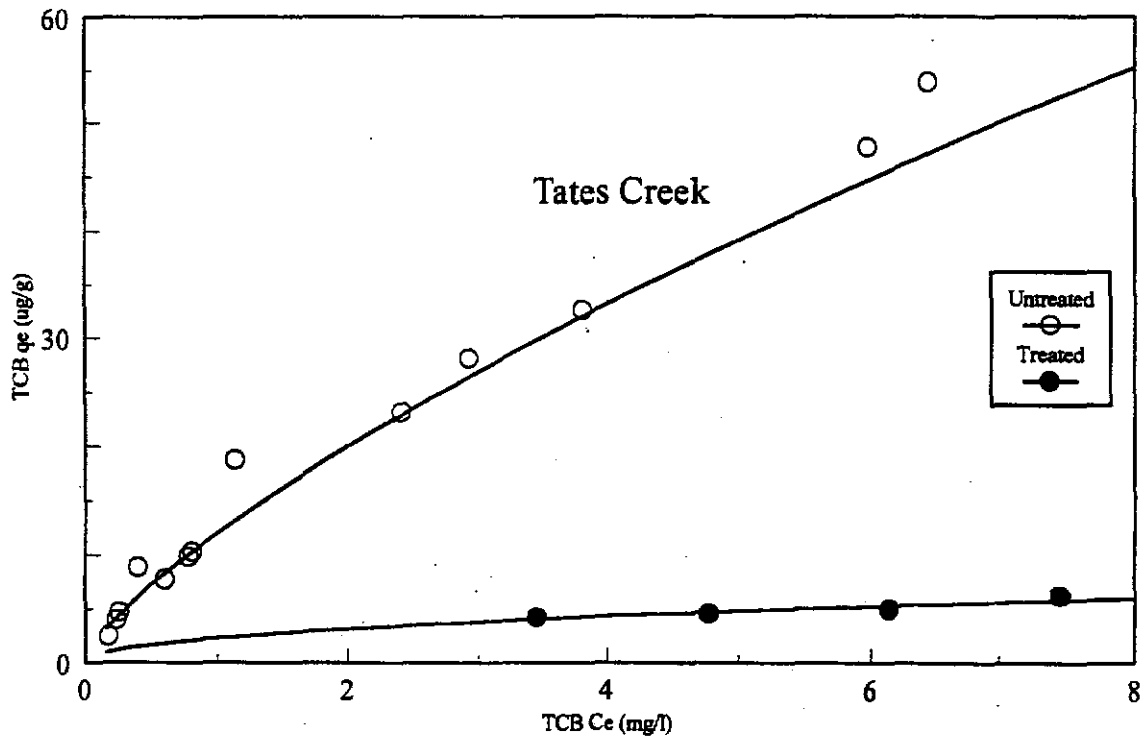
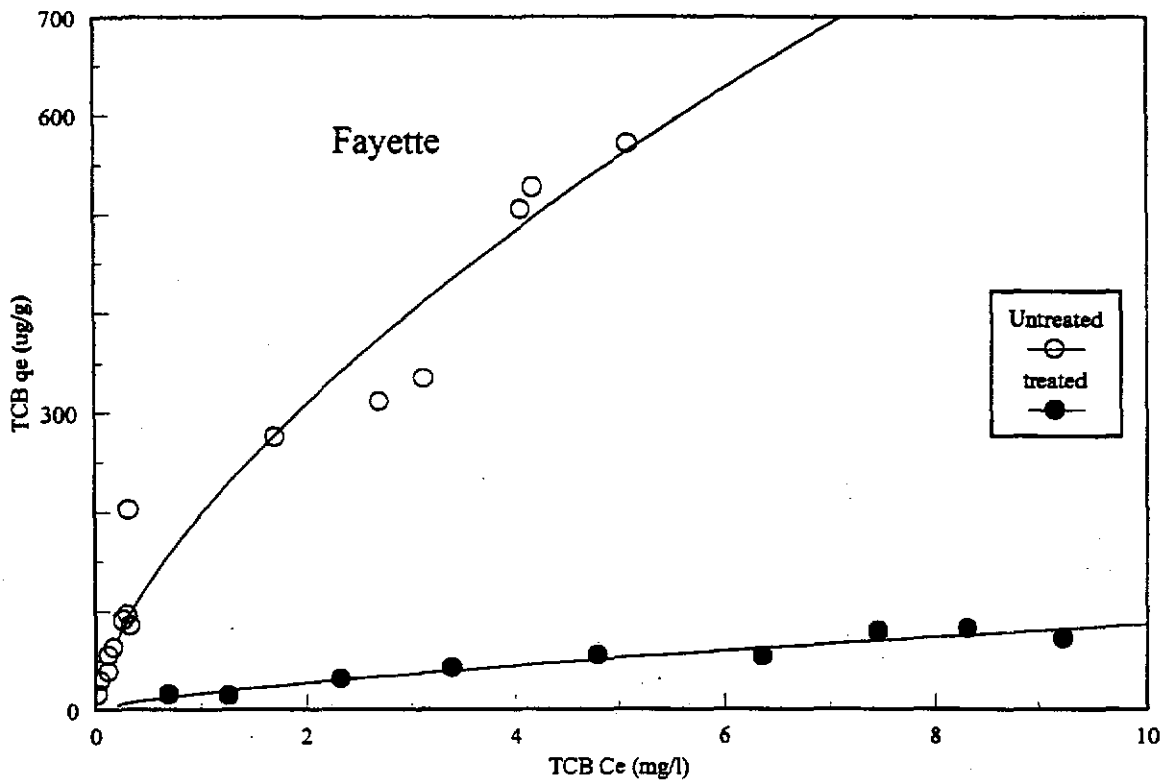


**Figure 8.** Experimental data and Freundlich isotherm models for sorption of TCB by five rocks, normalized to the surface areas of the rocks. Rock foc shown in parenthesis.

The increasing sorption on the rock material with increasing solute hydrophobicity and increasing rock organic carbon content suggest that organic matter within the rock is a source of sorption reactivity. To further confirm this, two samples were combusted in a muffle furnace at 450 degrees centigrade for 24 hours, a process which should remove most of the organic carbon. The loss of material upon ignition was 3.5% and 0.4% for Fayette and Tates Creek respectively. Sorption isotherms performed on the residue remaining and adjusted for the loss of mass through ignition are shown in Figure 9. It can be seen that the sorption on ignited rock is very weak when compared to the untreated rock. This minimum sorption might be attributed to sorption on mineral fragments or losses from the reactor.

It may not be surprising that the results on rocks differ from that found in soils. The organic matter in sedimentary rock is quite different from the organic matter in soils. During rock-forming processes, Diagenesis of organic matter leads to a reduction in its oxygen content relative to soil organic matter (Durand et. al, 1980). Such changes might be expected to reduce the solubility of the organic matter and lead to formation of a more hydrophobic organic matrix. With respect to sorption of organic contaminants, these changes may form surfaces in the rock material which act to adsorb organic contaminants, rather than a matrix within which they partition.

One sedimentary rock which contains large quantities of organic matter is coal. To further study the effect of sedimentary rock organic matter on sorption, the sorption of TCB was determined on four coal samples. The results, shown in Table 3 and Figure 11, demonstrate that sorption isotherm nonlinearity is also observed in these systems. When the solid phase concentration is normalized to the fraction of organic carbon and the isotherms



**Figure 9.** Comparison of TCB sorption on heat treated and untreated samples (a) Fayette , (b) Tates Creek. The losses due to treatment were 3.5% and 0.4% for Fayette and Tates Creek respectively.



Table 3. Freundlich isotherm model parameters and organic carbon contents for coal samples.

Rock Type	TCB n	$K_F$	OC %
Canada Coal	0.59	3592.0	72.6
Sub Bituminous	0.66	5490.4	54.38
Anthracite	0.39	5258.3	79.6
Lignite	0.68	3146.0	40.06

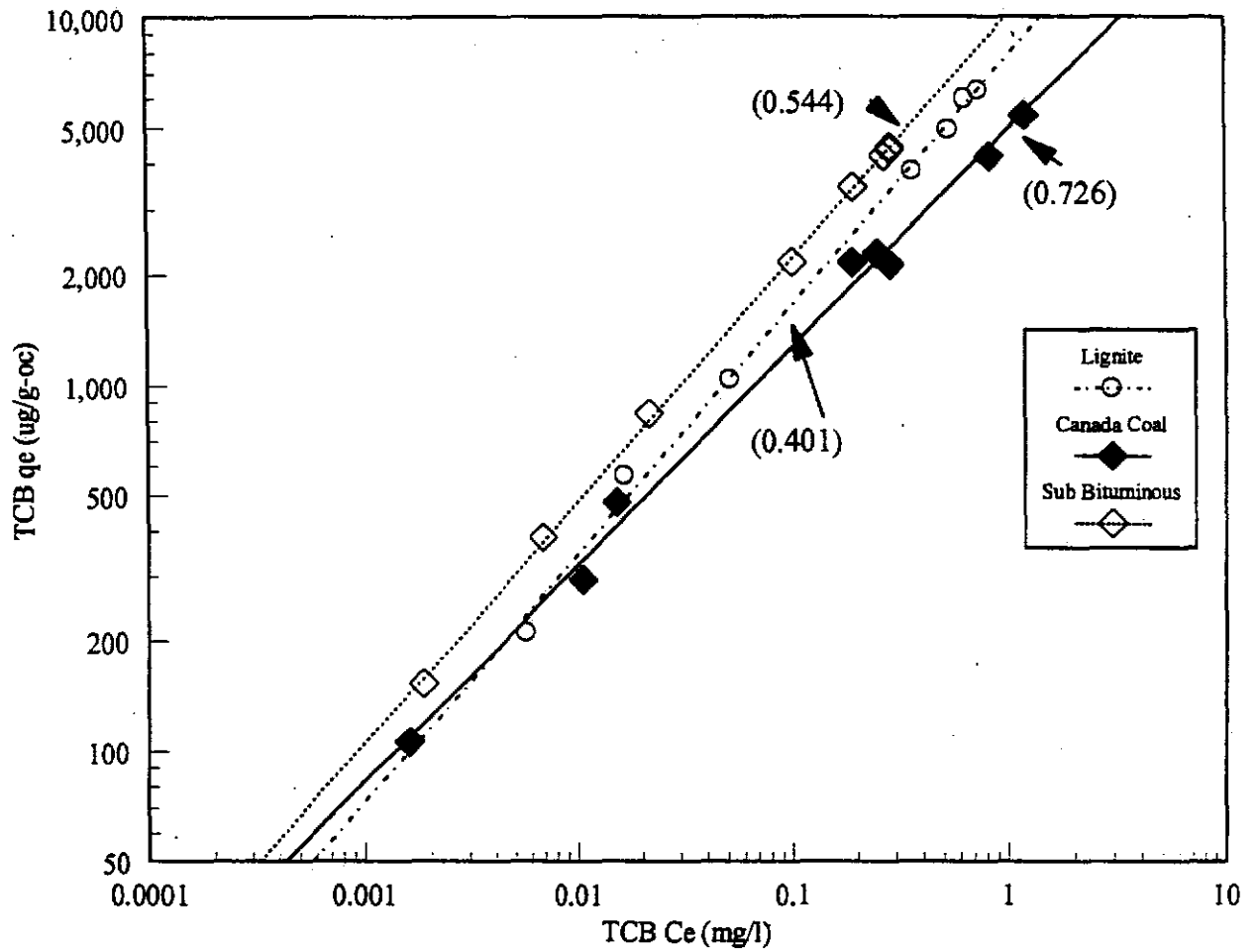


Figure 11. TCB sorption on three coals. The solid phase concentration is normalized to organic carbon. Coal  $f_{oc}$  shown in parenthesis.

are plotted, the isotherms coincide, much like the sedimentary rocks, although here the organic carbon is 40-73% of rock mass compared to 0.01-0.1% with shales and limestones.

In Figure 12, the organic carbon normalized coals and shales/limestones are compared to those of soils. Although the ranges for coal are slightly below those of the shales/lime stone, they are all considerably above that of the soils. Considering the wide range of organic matter contents (0.01-73%), the agreement is quite close. Although it is not possible at this time to make conclusions regarding the differences in sorption between the different limestones, shales, and coals, the organic matter in coals may be less accessible to sorbing organic molecules.

To determine the extent to which the organic matter in rocks might be obscured by mineral components, several rock samples were extracted with acid. The two samples, Fayette and Limestone, had acid extractable fractions of 20 and 90%, respectively. Sorption isotherms performed on the residue remaining and adjusted for the loss of mass through acid treatment are shown in Figure 10. That its removal did not increase sorption also indicates that the sorptive regions on the rocks were not obscured by carbonate.

#### *Sorption on Rocks in Flow through Systems*

A series of column experiments which sent two pore volumes of TCE contaminated fluid into columns containing rock material indicated that sorption non-equilibrium was observed during breakthrough and elution in the column. As shown in Figure 13, the effluent concentration failed to reach the influent concentration and the breakthrough was very close to that of the tracer, much faster than that predicted with the sorption isotherm.

Flow interruption studies, which halted flow shortly after the column contaminant

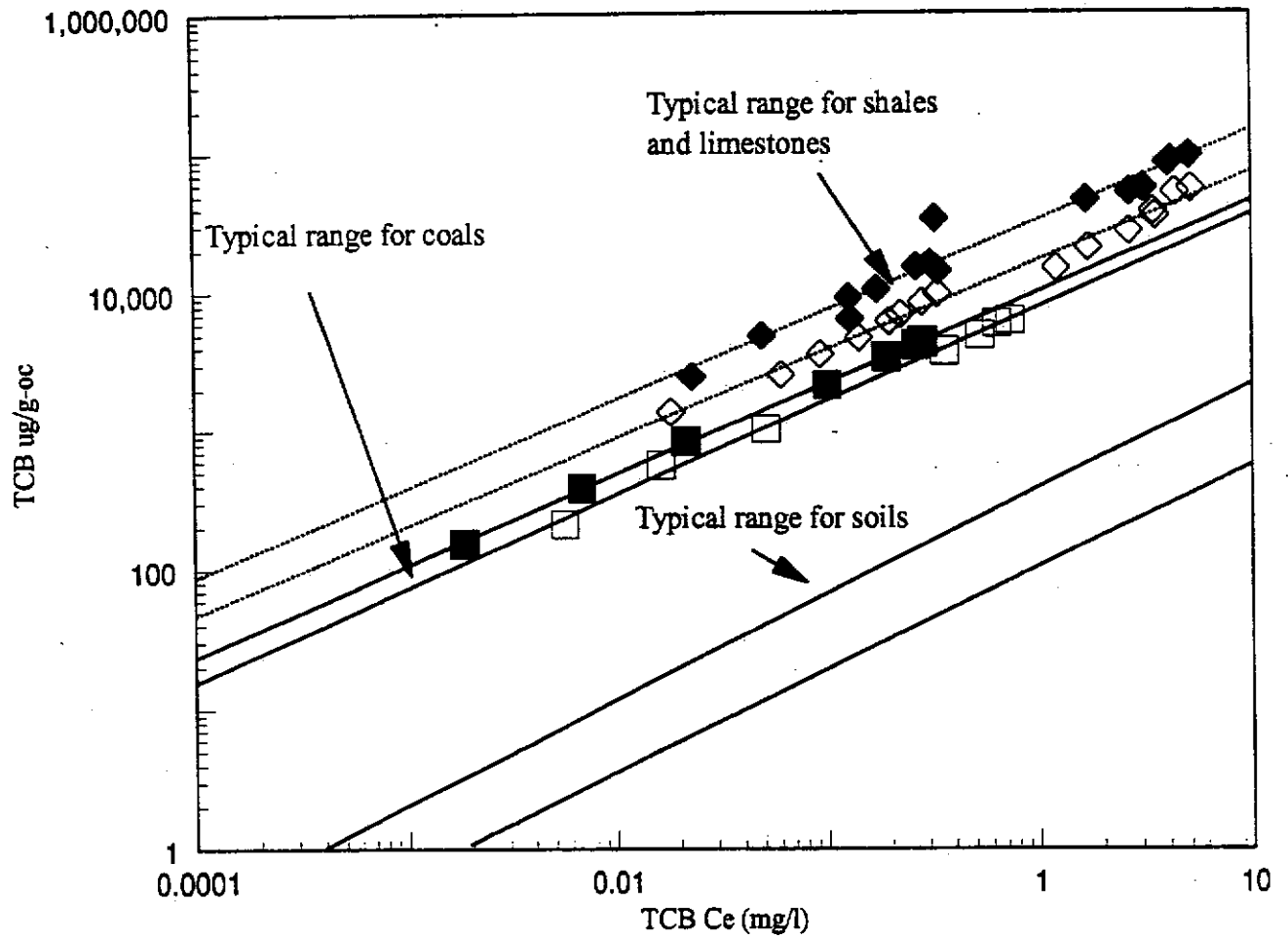
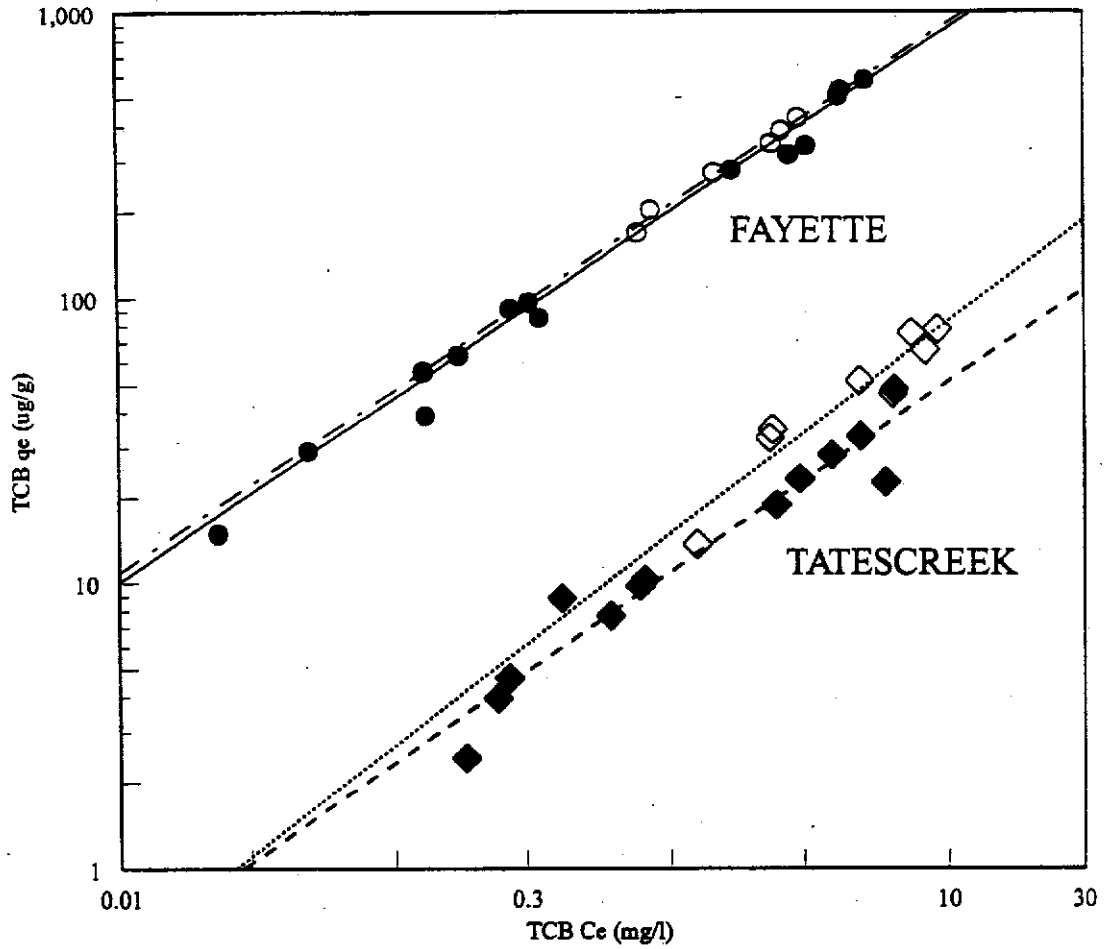


Figure 12. Typical ranges of organic carbon normalized TCB sorption on sedimentary rocks and soils.



**Figure 10.** Comparison of TCB sorption before (solid symbol) and after (empty symbol) acid treatment of samples. Loss of rock mass due to the acid treatment was 20% and 90% for Fayette and Tates Creek respectively.

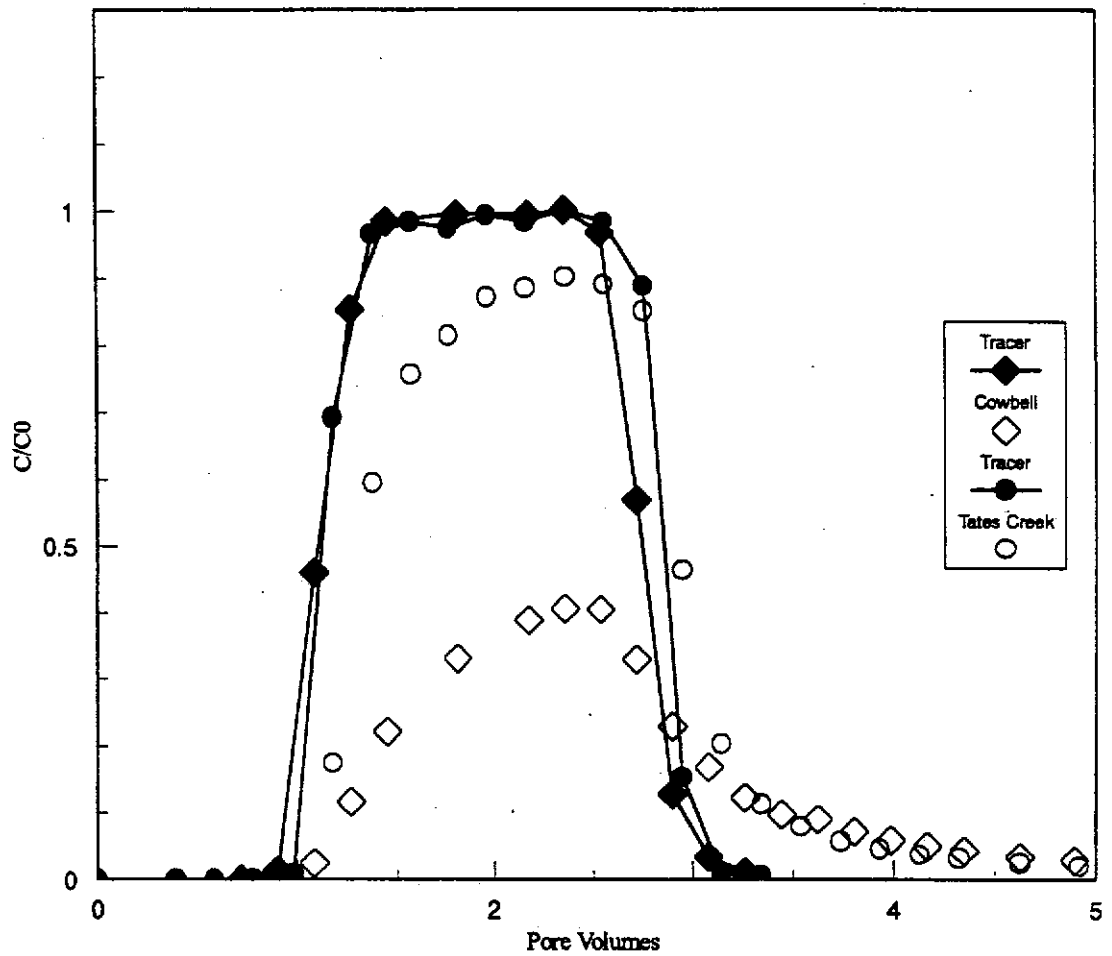


Figure 13. The results of column runs for TCE on both carbonate and a carbonate/shale rock.

concentration had peaked, were used to provide additional contact time for the rock to proceed towards equilibrium. A drop in effluent concentration during interruption verified that additional sorption was taking place and could also be used to quantify the extent of the reaction. The results of an interrupt study with larger limestone media are shown in Figure 14. The distinct drop in solution concentration after the flow interruption confirms that the continuous run was not at equilibrium. The tracer did not show the same reduction in concentration after extended contact, suggesting that a sorptive-diffusive rate limitation was operative. Further extending the contact time to three days led to a further drop in solution concentration

It was not possible to determine if equilibrium was attained after the three day contact time from column data alone. However, comparing column sorption to the limestone isotherm presented in Figure 15, shows that the three day interrupt point reached 80% of the equilibrium sorption and the one day attained slightly less than 40% of equilibrium sorption.

It is significant that column flow interruption achieved sorbed quantities near those predicted by the isotherm because the isotherm was obtained with limestone with diameters less than 75 microns, while the column data was obtained with limestone from 600 to 850 microns in diameter. Sorption capacity in the grain interior may not be available for sorption/diffusion, but in this research, although surface area had an effect on the rate of sorption, the ultimate sorptive capacity was not strongly impacted. While that is consistent with the minor effect of the carbonate removal on sorption capacity shown earlier, it is not clear at this time how the organic matter accessibility occurs. The distribution of organic

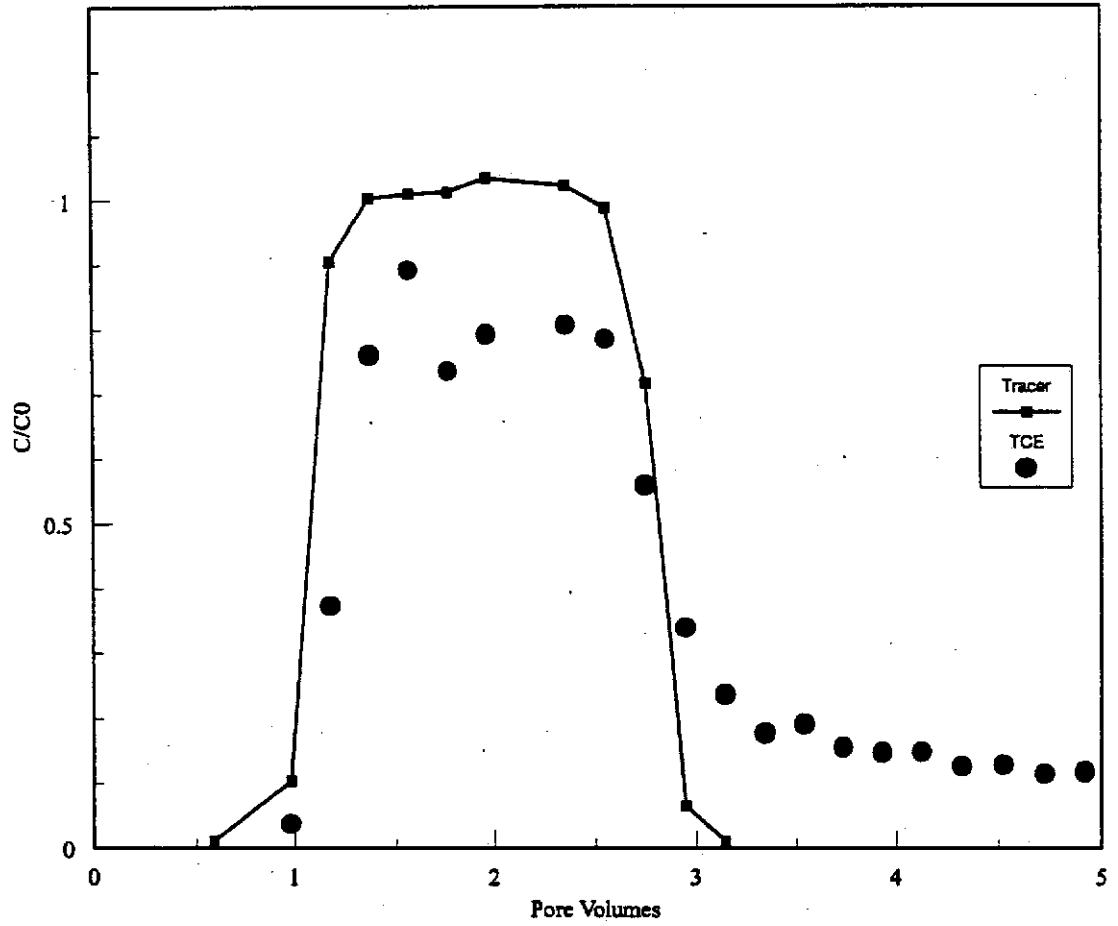


Figure 14. One day flow interrupt with larger Tates Creek rock media.



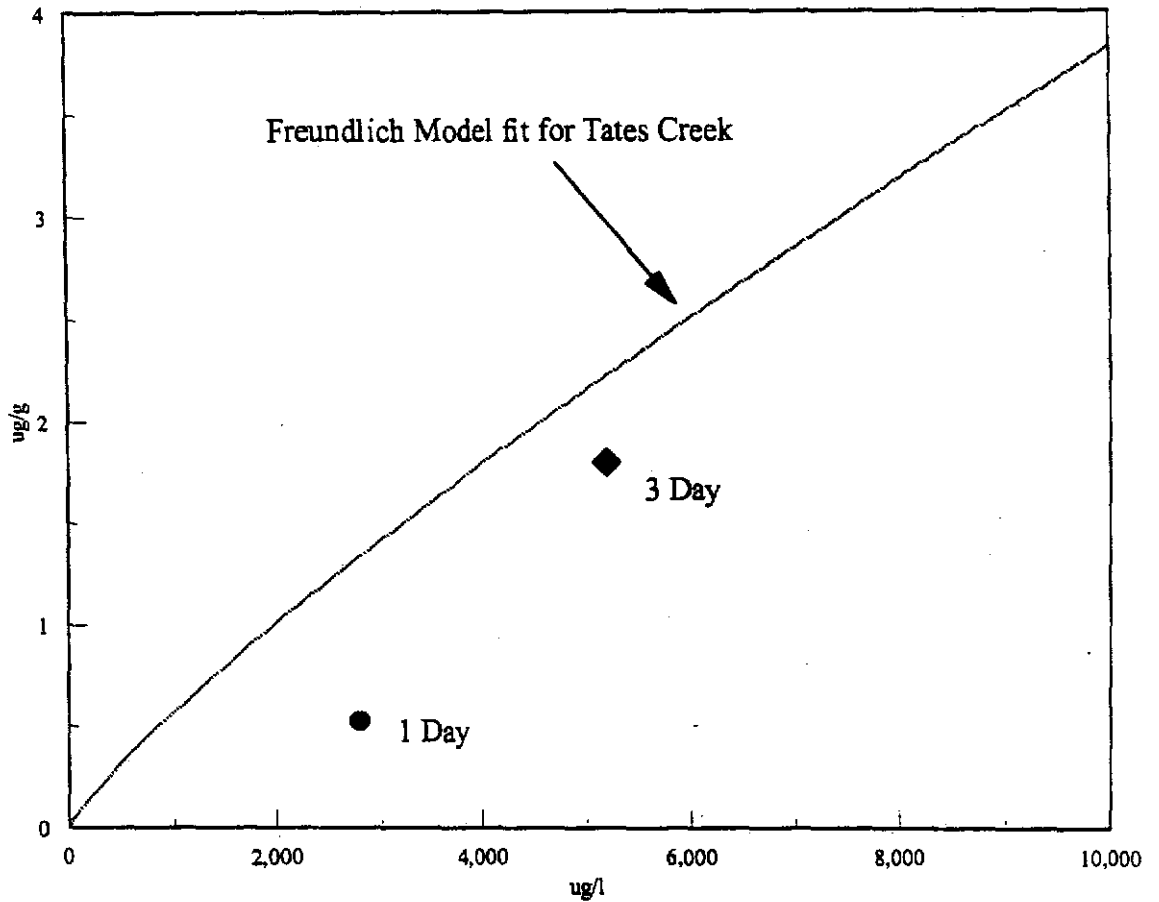


Figure 15. Comparison of quantity of TCE sorbed in flow interrupt studies to the TCE sorption isotherm from completely mixed systems.

matter over the external surface area and throughout these intra-particle spaces cannot be determined at this time.

Contaminant removal from sedimentary rock which has contacted TCE will be expected to exhibit the same nonequilibrium which occurs during loading. Because the nonequilibrium is coupled with non-linear sorption, the release of contaminants from rock may appear to slow as concentration is reduced. This important aspect of contaminant behavior in rock systems can be observed by comparing the elution portions of breakthrough curves. In Figure 16 elution of TCE from the limestone is presented with the concentration expanded on a log scale, the magnitude of concentration tailing can be seen. Although the concentrations in the column effluent are low, the long concentration-tail which results has significance for remedial work. Although contact time was only 9 minutes, or approximately 2 pore volumes at an initial concentration of 6.3 mg/l, 12 pore volumes beyond the contact time were required to reduce contaminant concentration to 2  $\mu\text{g/l}$ . Subsequent flushing of the column with hexane indicated that some TCE still remained in the rock after 30 pore volumes of fresh water had passed through the column. Because similar behavior was not observed in the tracer, suggests that a time dependent desorptive mechanism such as a sorptive/diffusive process is occurring.

Concentration tailing during elution for two different sizes of limestone media are compared in Figure 16. Both displayed concentration tailing above the detection limit for approximately 12 pore volumes beyond the contaminant plug, however, the magnitude of tailing in the small limestone is greater and is consistent with the higher sorption observed during loading. Higher surface area permits greater access to reactive regions in the rock

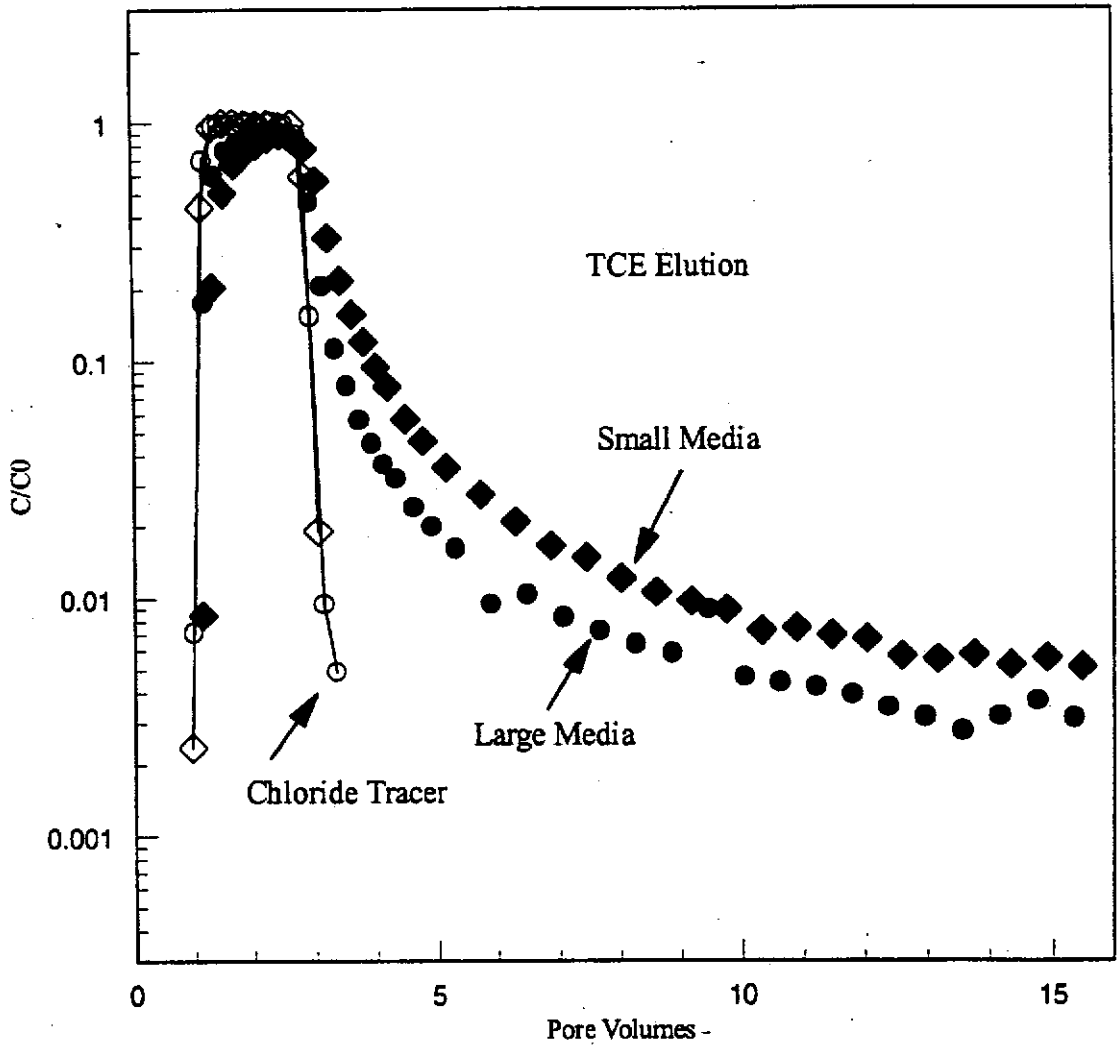


Figure 16. Comparison of concentration tailing during elution for two different sizes of Tates Creek rock.

and facilitates more sorption during identical contact periods. The resulting higher concentration after similar periods of elution would be expected from a higher mass flux from more available sorption sites. The increased surface area of the small limestone will increase the rate of sorption and desorption even if the maximum sorption capacity is not appreciably different.

The concentration tailing during elution from contaminated rocks was also dependent on flow rate. Figure 17 shows the breakthrough and elution of the 650-850  $\mu\text{m}$  limestone at fast and slow flow rates. Similar to the particle size effect, slower flow rates effected greater sorption and consequently higher effluent concentrations during elution. In Figure 18, the flow rate variation is compared during elution expressed as the contaminant flux normalized for the initial quantity sorbed. At short times, the additional length of time required for the contaminant plug to travel through the column at the slow flow rate is obvious. However, contaminant flux once the plug has passed, the contaminant flux out of the column is similar for both flow rates. This suggests that it is diffusion out of the rock controls contaminant release not fluid flow rate. This flux is consistent with a slow release of contaminant from the interior of the rock particle, as would be expected of diffusion from internal sorption sites as the rate limiting mechanism. In this case, increase in flow rate may have little or no effect on contaminant movement.

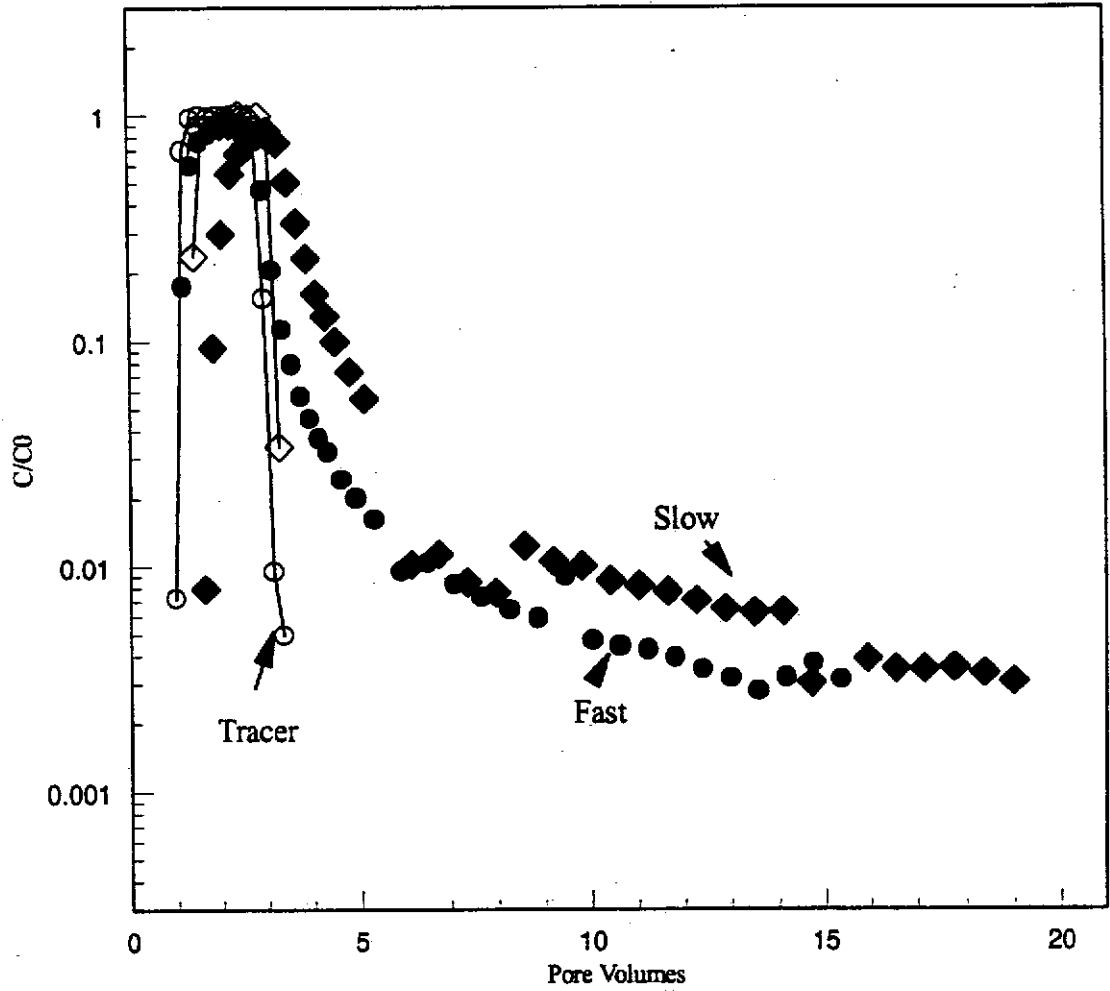


Figure 17. Breakthrough and Elution of the 650-850  $\mu\text{m}$  Tate's Creek rock at fast and slow flow rates.

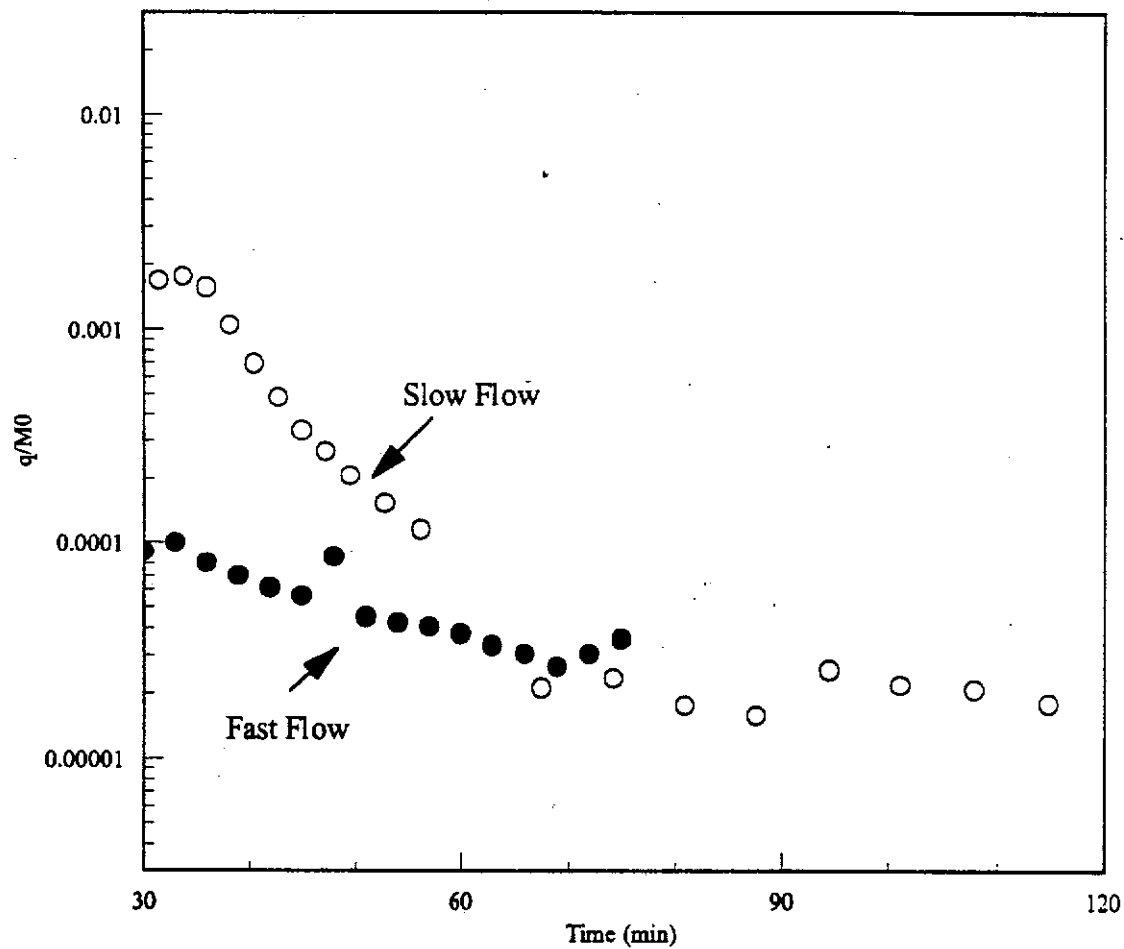


Figure 18. Effect of flow rate adjusted to show the TCE flux out of the column normalized for initial TCE solution concentration and plotted versus time.

## Summary

The sorption of hydrophobic organic contaminants occurs on rock material and may have to be considered in evaluating contaminant behavior in subsurface environments. The extent of sorption observed in a series of rocks was closely linked to the rock organic matter content, and it was greater than would be predicted for a soil of similar organic carbon content.

In the prepared samples examined in this research, accessibility of the sorptive regions was not enhanced by carbonate removal or particle size changes over a narrow size range. Because these samples may also have contained some fine material, it may be premature to generalize a facile access to all sorption regions, but there are indications that sorption regions internal to the rock are accessible.

The extent to which sorption on rock organic matter may be amenable to generalization through the use of a correlation between rock organic carbon content and sorption is made more difficult because of the nonlinear isotherm, however it was shown that rocks can adsorb about 5-10 times more contaminant than that which would be predicted from the organic matter content and correlations from soils. We were able to discern an isotherm which shows a Freundlich type affinity across a wide concentration range. The extent of isotherm nonlinearity using a Freundlich model exponent, ranged from 0.6 to 0.9.

The nonlinear sorption isotherms and internal sorption capacity apparently contributed to substantial concentration tailing during elution from a column. Whereas an

unreactive tracer behaved almost ideally, the TCE was still detectable in effluent after 10 pore volumes of clear water were passed through a column containing a relatively low organic carbon rock. It is apparent that contaminant removal under nonideal flow conditions may require long times to achieve desired concentration reductions. The rate at which contaminant is eluted in rock systems appears to be at least partially limited by the rate of diffusion out of the rock matrix.

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## **APPENDIX**

### **Data from the Sorption Experiments**

Table A1. Experimental data of TCB sorption by Fayette shale.

Sample number	Weight of water g	Weight of Rock g	Initial Concentration mg/l	Final Concentration mg/l	ug/g of TCB on rock ug/g	Corrected ug/g on rock ug/g
1	12.31	0.149	0.20	0.02	14.93	14.76
2	12.44	0.150	0.40	0.05	29.39	29.02
3	12.58	0.149	0.60	0.13	39.47	38.48
4	12.63	0.150	0.79	0.13	56.00	55.02
5	12.10	0.163	1.04	0.17	63.98	62.81
6	12.35	0.154	1.42	0.27	92.40	90.46
7	12.45	0.165	1.61	0.31	97.97	95.85
8	12.68	0.168	1.49	0.34	87.03	84.73
9	12.91	0.101	2.93	1.33	205.39	201.62
10	12.56	0.122	4.52	1.70	290.85	275.06
11	12.29	0.126	6.16	2.71	335.39	311.66
12	12.81	0.152	7.39	3.13	358.35	334.66
13	12.30	0.117	9.24	4.08	542.61	503.99
14	12.89	0.140	10.29	4.19	561.58	526.80
15	12.47	0.144	12.15	5.11	611.49	571.60

Table A2. Experimental data of TCB sorption by Martin shale.

Sample number	Weight of water g	Weight of Rock g	Initial Concentration mg/l	Final Concentration mg/l	Sorbed TCB on rock ug/g	Corrected Sorption ug/g
1	11.58	1.197	0.22	0.02	1.92	1.90
2	12.05	1.190	0.42	0.06	3.59	3.54
3	11.96	1.266	0.63	0.09	5.06	4.98
4	11.84	1.249	0.85	0.14	6.67	6.55
5	11.65	1.169	1.08	0.20	8.73	8.56
6	11.94	1.251	1.26	0.23	9.88	9.68
7	11.72	1.181	1.50	0.28	12.04	11.78
8	11.47	1.162	1.75	0.34	13.93	13.64
9	12.70	1.002	2.98	1.23	22.22	20.82
10	12.58	1.128	4.51	1.74	30.91	29.16
11	12.29	1.032	6.16	2.69	41.33	38.45
12	12.45	0.891	7.61	3.48	57.70	53.33
13	12.34	1.332	9.21	3.54	52.52	49.57
14	12.31	1.013	10.76	4.38	77.54	72.75
15	11.961	1.083	12.66	5.20	82.40	77.25

Table A3. Experimental data of TCB sorption by Hardin shale.

Sample number	Weight of water g	Weight of Rock g	Initial Concentration mg/l	Final Concentration mg/l	ug/g of TCB on rock ug/g	Corrected ug/g on rock ug/g
1	12.60	0.208	0.20	0.03	10.50	10.36
2	12.61	0.201	0.40	0.07	20.54	20.14
3	12.61	0.196	0.60	0.15	29.09	28.24
4	12.30	0.185	0.82	0.18	42.13	41.04
5	12.57	0.200	1.00	0.23	48.18	46.88
6	12.49	0.201	1.20	0.30	55.29	53.60
7	12.50	0.204	1.40	0.32	67.65	65.88
8	12.33	0.201	3.07	1.48	97.67	89.49
9	12.60	0.207	4.51	1.91	158.01	147.56
10	12.78	0.159	5.92	3.02	231.28	209.43
11	13.03	0.214	7.27	3.34	238.90	220.59
12	12.63	0.172	8.99	4.62	321.32	290.72
13	12.81	0.189	10.34	5.14	352.41	321.12
14	12.89	0.225	11.75	5.37	365.99	338.24



Table A4. Experimental data of TCB sorption by Tates Creek Limestone.

Sample number	Weight of water g	Weight of Rock g	Initial Concentration mg/l	Final Concentration mg/l	ug/g of DCB on rock ug/g	Corrected ug/g on rock ug/g
1	12.13	1.068	0.41	0.18	2.62	2.43
2	12.63	1.075	0.60	0.24	4.19	3.94
3	12.10	1.415	0.83	0.26	4.85	4.64
4	12.63	1.075	1.19	0.41	9.23	8.81
5	11.86	1.262	1.48	0.61	8.17	7.66
6	12.05	1.007	1.66	0.78	10.56	9.72
7	11.98	0.800	1.57	0.81	11.33	10.24
8	12.66	1.171	2.97	1.14	19.81	18.70
9	12.49	1.019	4.51	2.41	25.75	23.08
10	12.45	1.264	6.04	2.93	30.66	28.06
11	12.51	1.287	7.51	3.82	35.95	32.61
12	12.37	2.105	9.12	4.85	25.09	22.53
13	12.40	1.064	10.61	5.98	53.97	47.70
14	12.22	1.198	12.30	6.45	59.75	53.83

Table A5. Experimental data of TCB sorption by Cowbell shale.

Sample number	Weight of water g	Weight of Rock g	Initial Concentration mg/l	Final Concentration mg/l	Sorbed TCB on rock ug/g	Corrected Sorption ug/g
1	12.17	0.605	0.41	0.11	6.09	5.90
2	11.96	0.631	0.63	0.20	8.09	7.74
3	12.16	0.553	0.82	0.29	11.74	11.17
4	12.09	0.524	1.04	0.42	14.31	13.45
5	11.80	0.592	1.27	0.49	15.65	14.77
6	12.30	0.501	1.43	0.59	20.59	19.29
7	12.13	0.570	1.65	0.60	22.46	21.32
8	12.31	0.583	1.53	0.68	17.84	16.55
9	12.23	0.533	3.08	1.44	37.57	34.61
10	12.22	0.548	4.62	2.14	55.27	50.99
11	12.05	0.569	6.24	3.23	63.90	57.75
12	12.38	0.546	7.60	3.95	82.54	74.48
13	12.38	0.547	9.11	4.59	102.49	93.14
14	12.29	0.560	10.71	5.62	111.80	100.69
15	12.09	0.476	12.43	6.30	155.91	141.52

Table A6. Experimental data of DCB sorption by Fayette shale.

Sample number	Weight of water g	Weight of Rock g	Initial Concentration mg/l	Final Concentration mg/l	ug/g of DCB on rock ug/g	Corrected ug/g on rock ug/g
1	12.27	0.101	1.29	0.76	63.95	58.35
2	11.76	0.143	2.69	1.41	105.20	98.23
3	11.97	0.110	3.96	2.68	139.89	122.43
4	12.02	0.173	5.26	3.10	150.50	137.58
5	11.98	0.180	6.60	4.06	168.81	152.64
6	12.09	0.121	7.85	5.52	232.06	199.06
7	12.29	0.109	9.01	7.07	217.98	170.30
8	12.50	0.133	10.12	6.95	299.33	260.01
9	12.58	0.106	5.03	3.55	175.70	150.44
10	12.50	0.134	10.12	7.46	249.15	207.33
11	12.11	0.136	0.27	0.11	14.20	13.59
12	11.89	0.083	0.56	0.35	30.10	27.10
13	12.19	0.123	0.81	0.38	43.10	40.84
14	12.24	0.102	1.08	0.56	62.50	58.43
15	11.75	0.199	0.28	0.05	13.40	13.21
16	12.13	0.174	0.55	0.15	27.80	27.19
17	12.26	0.148	0.81	0.24	47.40	46.22
18	12.64	0.157	1.05	0.39	53.10	51.23

Table A7. Experimental data of DCB sorption by Martin shale.

Sample number	Weight of water g	Weight of Rock g	Initial Concentration mg/l	Final Concentration mg/l	Sorbed DCB on rock ug/g	Corrected Sorption ug/g
1	12.02	1.112	1.32	0.31	8.64	8.44
2	12.27	1.013	2.58	1.18	16.89	16.03
3	11.80	1.125	4.02	1.98	21.38	20.13
4	12.14	1.054	5.21	3.20	23.13	20.92
5	12.19	0.969	6.49	3.68	35.37	32.60
6	11.95	1.119	7.94	4.99	31.53	28.34
7	12.13	1.011	9.13	5.81	39.85	35.68
8	11.74	1.124	10.78	6.06	49.24	45.44
9	11.38	1.047	0.24	0.02	2.42	2.41
10	11.98	1.009	0.45	0.21	2.86	2.71
11	12.26	1.208	0.66	0.26	4.11	3.95
12	11.95	1.081	0.91	0.38	5.77	5.52
13	12.09	1.019	1.12	0.57	5.78	5.37
14	12.16	1.361	1.56	0.66	8.01	7.66
15	12.23	1.006	1.77	0.95	9.95	9.25

Table A8. Experimental data of DCB sorption by Hardin shale.

Sample number	Weight of water g	Weight of Rock g	Initial Concentration mg/l	Final Concentration mg/l	ug/g of DCB on rock ug/g	Corrected ug/g on rock ug/g
1	11.85	0.219	1.33	0.58	40.75	38.85
2	11.83	0.289	2.67	1.27	57.56	54.44
3	11.88	0.261	3.99	2.17	83.05	77.15
4	11.86	0.270	5.33	3.16	95.22	86.88
5	11.88	0.223	7.99	5.47	134.50	117.02
6	12.23	0.224	9.05	6.10	161.40	141.43
7	12.09	0.210	10.46	7.46	172.94	147.19
8	12.43	0.189	5.09	3.30	118.02	104.97
9	12.23	0.311	10.34	6.25	160.88	146.14
10	11.69	0.141	0.28	0.14	12.00	11.31
11	12.16	0.096	0.54	0.34	26.35	23.80
12	12.30	0.170	0.80	0.38	30.76	29.11
13	12.39	0.147	1.07	0.69	32.25	28.77
14	12.42	0.055	0.27	0.23	9.46	6.39
15	11.80	0.121	0.56	0.31	24.04	22.21
16	13.15	0.134	0.75	0.56	19.62	16.36
17	12.29	0.134	1.08	0.74	30.78	26.68

Table A9. Experimental data of DCB sorption by Tates Creek Limestone.

Sample number	Weight of water g	Weight of Rock g	Initial Concentration mg/l	Final Concentration mg/l	ug/g of DCB on rock ug/g	Corrected ug/g on rock ug/g
1	12.03	1.282	0.45	0.29	1.54	1.38
2	12.29	1.472	0.66	0.38	2.34	2.15
3	12.29	1.145	0.88	0.55	3.60	3.24
4	12.21	1.154	1.11	0.78	3.53	3.04
5	12.31	1.257	1.32	0.88	4.32	3.80
6	12.55	1.305	1.51	0.95	5.39	4.84
7	12.12	1.257	1.79	1.11	6.52	5.88
8	11.72	1.582	0.23	0.13	0.72	0.66
9	11.39	2.532	0.48	0.22	1.15	1.09
10	11.56	2.460	0.70	0.24	2.17	2.10
11	11.04	3.073	0.98	0.31	2.42	2.35
12	12.66	0.630	1.25	0.72	10.70	9.84
13	12.59	0.917	2.51	1.59	12.63	11.32
14	12.18	1.041	3.90	2.39	17.56	15.88
15	12.33	0.869	5.13	3.34	20.88	22.54
16	12.42	1.068	6.37	4.31	23.89	20.88
17	12.77	1.092	7.43	5.17	26.44	22.81
18	12.52	1.039	8.84	6.29	30.69	26.14
19	12.18	1.176	10.38	7.19	33.08	28.62

Table A10. Experimental data of DCB sorption by Cowbell shale.

Sample number	Weight of water g	Weight of Rock g	Initial Concentration mg/l	Final Concentration mg/l	Sorbed DCB on rock ug/g	Corrected Sorption ug/g
1	12.04	0.631	0.45	0.29	3.13	2.80
2	12.04	0.700	0.90	0.38	8.88	8.48
3	11.87	0.694	1.14	0.41	12.50	12.08
4	12.37	0.666	1.31	0.50	15.19	14.56
5	11.82	0.679	1.60	0.87	12.80	11.89
6	11.91	0.710	1.82	0.90	15.47	14.56
7	11.87	0.581	1.33	0.42	18.74	18.23
8	12.44	0.606	2.54	1.57	19.95	18.01
9	12.34	0.630	3.84	1.69	42.28	40.30
10	12.40	0.633	5.10	2.56	49.73	46.72
11	12.16	0.773	6.50	2.94	56.02	53.24
12	11.93	0.713	7.96	3.81	69.30	65.47
13	12.40	0.630	8.92	3.96	97.76	93.08
14	12.00	0.686	10.54	5.52	87.87	82.08