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**The Impact of Pore-Water Velocity on Nonequilibrium
Transport of Nonionic Organic Compounds in Soil**

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John Richard Zimmerman

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THE IMPACT OF PORE-WATER VELOCITY ON NONEQUILIBRIUM
TRANSPORT OF NONIONIC ORGANIC COMPOUNDS IN SOIL

By

John Richard Zimmerman

A THESIS

Submitted to
Michigan State University
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ABSTRACT

THE IMPACT OF PORE-WATER VELOCITY ON NONEQUILIBRIUM TRANSPORT OF NONIONIC ORGANIC COMPOUNDS IN SOIL

By

John Richard Zimmerman

Column studies were performed to investigate the impact of pore-water velocity (v_0) on transport of benzene, toluene, *p*-xylene and naphthalene in three nonaggregated media: soils with organic carbon content (f_{oc}) = 0.30 and 1.0% and aquifer material with f_{oc} = 0.05%. To understand the effect of velocity variation on mass transfer rate coefficient (k), pore-water velocities ranging over almost two orders of magnitude (1.7 - 93.2 cm/hr) were evaluated. Consistent with the results of past investigators, v_0 and k were positively correlated. To determine if the effect was related to contaminant residence time in the column, $\log(k)$ was plotted against $\log(LR/v_0)$, where L is column length and R is retardation coefficient. On the higher organic carbon content soil, $\log(k)$ vs. $\log(LR/v_0)$ relationships for individual compounds were linear ($R^2 = 0.89$ to 0.97). Regression line slopes plotted against $\log(K_{ow})$ values revealed strong positive linear correlation ($R^2 = 0.99$), indicating that k is increasingly dependent upon contaminant residence time (and therefore v_0) as compound hydrophobicity decreases. This study indicates that there may be a quantifiable relationship between k and v_0 which has a mechanistic basis.

To my parents, Ken and Carol Zimmerman, and to my sisters and brothers, Kim,
Cindy, Dave, Pat and Adam.

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INTRODUCTION

This thesis is comprised of four main sections: Chapter 1, which is essentially a research paper to be submitted for publication; Appendix A, a more extensive literature review than that found in Chapter 1; Appendix B, which describes in greater detail the materials and methods used in the experimental work; and Appendix C, which includes data tables which are too long to be included in the body of the paper to be published.

CHAPTER 1

THE IMPACT OF PORE-WATER VELOCITY ON NONEQUILIBRIUM TRANSPORT OF NONIONIC ORGANIC COMPOUNDS IN SOIL

Abstract

Column studies were performed to investigate the impact of pore-water velocity (v_0) on transport of benzene, toluene, *p*-xylene and naphthalene in three nonaggregated media: soils with organic carbon content (f_{oc}) = 0.30 and 1.0% and aquifer material with f_{oc} = 0.05%. To understand the effect of velocity variation on the mass-transfer rate coefficient (k), pore-water velocities ranging over almost two orders of magnitude (1.7 - 93.2 cm/hr) were evaluated. Consistent with the results of past investigators, v_0 and k were positively correlated. To determine if the effect was related to contaminant residence time in the column, $\log(k)$ was plotted against $\log(LR/v_0)$, where L is column length and R is retardation coefficient. On the higher organic carbon content soil, $\log(k)$ vs. $\log(LR/v_0)$ relationships for individual compounds were linear ($R^2 = 0.89$ to 0.97). Regression line slopes plotted against $\log(K_{ow})$ values revealed strong positive linear correlation ($R^2 = 0.99$), indicating that k is increasingly dependent upon contaminant residence time (and therefore v_0) as compound hydrophobicity decreases. This study indicates that there may be a quantifiable relationship between k and v_0 which has a mechanistic basis.

Background

Public concern over extensive soil and aquifer contamination has led researchers to investigate methods of modeling transport of hydrophobic organic compounds in these environments. An essential part of any such model is the description of contaminant distribution between solid and aqueous phases. As a first approximation, it was assumed that the sorption to and from soil solids occurs immediately and could be described an equilibrium process. However, experimental results often showed a slow approach to equilibrium or a dual sorption pattern wherein a period of fast (equilibrium) sorption was followed by a slow period which could be described using a kinetic model. Lapidus and Amundson (1952) are generally attributed with first describing the slow approach to equilibrium using a first-order rate equation. Cameron and Klute (1977) later described sorption as a two-site process, with part of the sites participating in rate-limited (slow) sorption and the other part in instantaneous sorption. For an extensive review of non-ideal processes in general, including two-site sorption, the reader is referred to Brusseau and Rao (1989a).

The main purpose in developing the models has been to predict contaminant fate (e.g., concentration profile with depth) for a particular situation. In order to accomplish this, model parameters must be determined independently and entered into the model. Several investigators have attempted to provide methods for independently predicting k values without using fitting techniques. Brusseau and others have noticed an inverse relationship between k and partition coefficient, K_p , (Brusseau et al., 1991; Brusseau, 1992; Brusseau and Reid, 1991; Karickhoff, 1980) and some have stated that this may be

a method of predicting k for use in other soil/sorbate situations (Brusseau and Rao, 1989b).

One challenge, however, is understanding the effect of pore-water velocity (v_0) on that relationship between k and K_p . Brusseau (1992) noted that values of k for a high velocity were over one order of magnitude higher than values at a lower velocity. Other authors have noted an effect of v_0 on BTCs and degree of nonequilibrium exhibited (Bouchard, et al., 1988; Brusseau et al., 1991). Maraqa (1995) reported that k increased with v_0 for benzene and dimethylphthalate in soil column studies. This then casts doubt on our ability to predict k from a corresponding K_p without considering pore-water velocity effects. What is needed is a relationship between v_0 and k and an explanation for that observed relationship. This work is an attempt to define such a relationship.

Materials and Methods

Column experiments were designed to study chemical desorption from soil solids. First soil columns were flushed with a solution containing all target compounds at a high flow rate until effluent concentrations were near influent values. At this point, solution flow was stopped for approximately one day before flushing the column again at a low flow rate. This allowed diffusion of chemicals into less accessible sorption sites. Matrix solution was then flushed through the columns and desorption phase breakthrough curves were obtained. The compounds were mixed in one solution and co-eluted; it has been shown in previous studies that competition effects are minimal at low contaminant concentrations (Maraqa, 1995). The target pore-water velocities were 2.0, 5.3, 14.1, 37.5 and 100 cm/hr.

The solution matrix consisted of a 0.01 N solution of CaCl_2 buffered with a 10 mM solution of KH_2PO_4 which was sterilized in an autoclave to inhibit biological growth. Benzene, toluene, *p*-xylene and naphthalene were used in the study. Table 1 shows properties of the compounds.

Table 1. Properties of chemicals at 25°C. (Schwarzenbach et al., 1993)

Compound	Mol. wt. (g/mol)	$-\log P^0$ (atm)	$-\log C_w^{\text{sat}}$ (mol·L ⁻¹)	C_w^{sat} (mg·L ⁻¹)	$\log K_{\text{ow}}$ [(mol·L ⁻¹ octanol)· (mol·L ⁻¹ water) ⁻¹]
Benzene	78	0.9	1.64	1787	2.13
Toluene	92	1.42	2.25	517	2.69
<i>p</i> -xylene	106	1.93	2.77	180	3.15
Naphthalene	128	3.43 ^a	3.61	31	3.36

a. Value shown is $-\log P^0(\text{L})$ for solid phase

Two soils, Metea and SPCF, with $f_{\text{oc}} = 0.30$ and 1.0%, respectively, and one aquifer material, Wurtsmith, with $f_{\text{oc}} = 0.05$, were used in the study. Table 2 shows the size distribution of the soils and sand. These were sterilized by ≈ 2 Mrad of gamma radiation, which has been shown to be an effective method of sterilization which does not significantly alter the soil characteristics.

Table 2. Soil sieve analysis

Soil or Sand Type	Organic Carbon, %	Grain size			
		(250-425 μm)	(150-250 μm)	(53-150 μm)	(0-53 μm)
SPCF	1.0	10.6%	22.8%	55.2%	11.4%
Metea	0.30	10.6%	22.8%	55.2%	11.4%
Wurtsmith	0.05	15%	70%	15%	0%

An example of the experimental setup for one column is shown in Figure 1. Columns were 15.2 to 15.4 cm long and 1.1 cm inside diameter (i.d.), and tubing was 1.27 mm i.d.. The columns, diffusion disks, tubing and tee fitting shown in Figure 1

were all stainless steel. The syringe shown in Figure 1 was glass, and the syringe plunger head and three-way valve were all made of Teflon.

In order to prevent or inhibit microbial growth, the tubing, columns, tee fittings, and three-way valves were sterilized in an autoclave. The bottle was vented by placing a needle in the rubber septum of the effluent bottle, with a 0.22 μm filter placed at the head of the needle. In between the syringe and the soil column, the stainless steel tubing was threaded through a small hole in a heating block which was maintained at $\approx 60^\circ\text{C}$.

Samples were collected by depressing an air-filled syringe at A in Figure 1, causing the solution in the sample loop to be ejected into a 22 mL headspace vial held at B. Vials were then capped quickly in order to prevent sample volatilization. Compound concentrations were measured using headspace gas chromatography.

Prior to saturating the columns with solution, CO_2 was injected into the media-filled columns in order to displace air in the void spaces. This prevented formation of pockets of relatively water-insoluble air in these spaces. See Appendix B for further details about experimental methods.

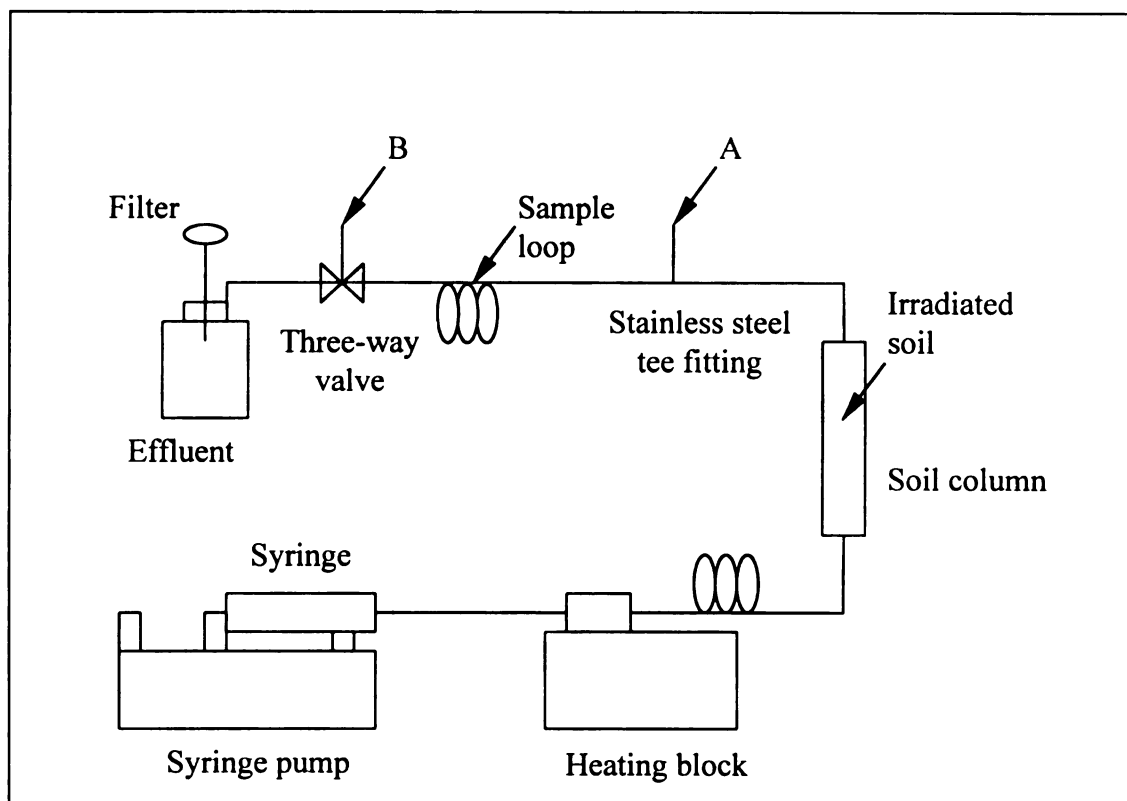


Figure 1. Experimental setup

Parameter Estimation

The desorption breakthrough curves were analyzed using the nonlinear least squares inversion program CXTFIT (Parker and van Genuchten, 1984) to determine nonequilibrium parameters. The advective-dispersion equations (including nondimensional equations) describing 1-D transport of sorbing solutes through a homogeneous soil column under steady state conditions are found in the literature (Brusseau, 1991).

Required model input parameters included pore water velocity (v_0), dispersion coefficient (D), retardation coefficient (R), column length (L), and relative influent concentration (C^*). The model then used least squares fitting to determine nonequilibrium parameters β (fraction of instantaneous retardation) and ω . From the model outputs of β and ω , the fraction of instantaneous sorption sites, F , and the dimensional mass-transfer rate coefficient, k , were calculated. Parameters such as F , R and β , which should be considered along with mass-transfer coefficients in order to be meaningful, are tabulated in Appendix C.

Results

The program was run in either equilibrium or two-site mode, depending on which fit the data better. In the equilibrium mode, it was assumed that sorption at all sites occurred instantaneously and obeyed a linear sorption isotherm. The two-site model described sorption as instantaneous at a portion of the sites and rate-limited at the other sites. See Appendix C for data tables containing results.

Several trends were observed from the results. First, as expected, the equilibrium model was used slightly more often at the lowest velocity (≈ 2.0 cm/hr) than at any other. This occurs because the characteristic sorption time is near the compound residence time at that low pore-water velocity, leading to the equilibrium model more accurately describing sorption.

Second, the equilibrium mode was also used more often for the Wurtsmith aquifer material than the Metea and SPCF soils. This was probably due to the much lower organic carbon content of the aquifer material. At this low level the partition coefficients were relatively low. Also the average Wurtsmith grain size was larger than the other soils, and the 0-53 μm grain size was essentially absent in that sand. Ball and Roberts (1991) state that the length scale for intraparticle diffusion is the particle grain size, so we can conclude that either 1) intramineral diffusion was probably not a rate-limiting factor in this case, or 2) columns were not given enough time for chemicals to diffuse deeply into intraparticle sorption sites.

Third, the retardation factors for the SPCF soil are consistent until the highest flow rate, when R drops significantly. The drop in R at higher flow rates was noticed by

van Genuchten et al. (1974) who explained that it occurred because of the decreased time available for compounds to contact soil solids. This is important because one explanation for increased k values at higher v_0 is the decreased K_p . Therefore, the effect of K_p on k in this case is not significant.

Discussion

k vs. K_p Relationship

The objective of this study was to move toward obtaining a quantitative relationship between k and K_p or v_0 or both. In order to determine whether there was such a relationship, plots of $\log(k)$ vs. $\log(K_p)$ were made of all compounds and soils for each individual velocity. In all but one case, these plots showed no significant correlation. Therefore, at this point we cannot assume that there is a $\log(k)$ vs. $\log(K_p)$ relationship for this study. However, it should be noted that K_p values used here only covered a range of approximately 2 orders of magnitude. Performing a similar study with compounds covering a larger range of K_p may have led to a significant relationship.

k vs. v_0 Relationship

Plots of the data for Wurtsmith aquifer material experiments showed a slight trend of increasing k with increasing v_0 . However, there were too few points for this soil because most of the data was fit using an equilibrium model. The plot showing all compounds in Metea soil columns showed a weakly positive correlation.

Values of $\log(k)$ were plotted against $\log(v_0)$ for all compounds on the SPCF soil as shown in Figure 2. The figure shows that k and v_0 are positively correlated, as has been found in past studies (Maraqa, 1995). One possible explanation for the observed relationship is that k is dependent upon contaminant residence time in the column. This

would be evident from a plot of k vs. v_0 because contaminant residence time is inversely proportional to v_0 . In order to test whether the trend is related more to residence time or to pore-water velocity alone, $\log(k)$ was plotted against $\log(LR/v_0)$ (where LR/v_0 is contaminant residence time) for all compounds on SPCF soil as shown in Figure 3.

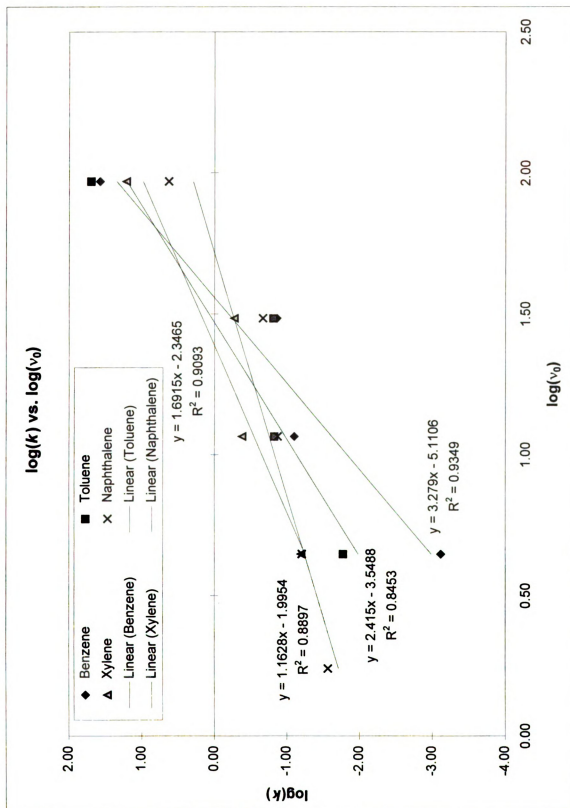


Figure 2. log(k) vs. log(v₀) for all compounds on SPCF soil.

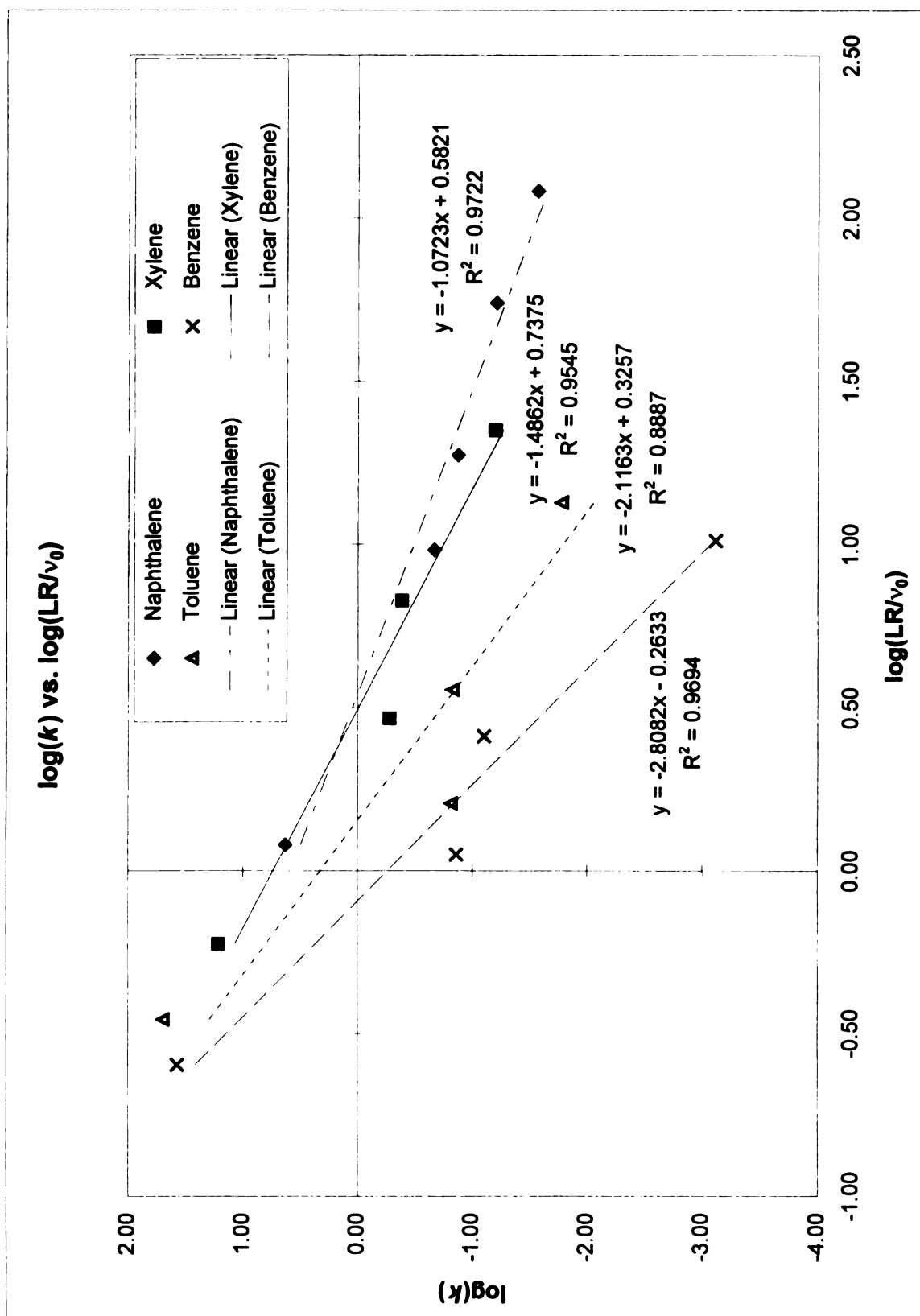


Figure 3. $\log(k)$ vs. $\log(LR/v_0)$ for all compounds on SPCF soil.

Comparison of regression lines from Figure 2 and Figure 3 reveals slightly better correlation for plots of $\log(k)$ vs. $\log(LR/v_0)$, which appears to indicate that the observed trend of positive correlation between k and v_0 is more related to contaminant residence time than to pore-water velocity alone. Observation of Figures 2 and 3 revealed a trend of increasing slope with decreasing hydrophobicity. To determine if there was a quantifiable relationship, slopes from Figure 3 (slope = $d\log(k)/d\log(LR/v_0)$) were plotted against $\log(K_{ow})$. Figure 4 clearly shows that the slope becomes more negative for less hydrophobic compounds. In other words, k is a stronger function of contaminant residence time for less hydrophobic compounds.

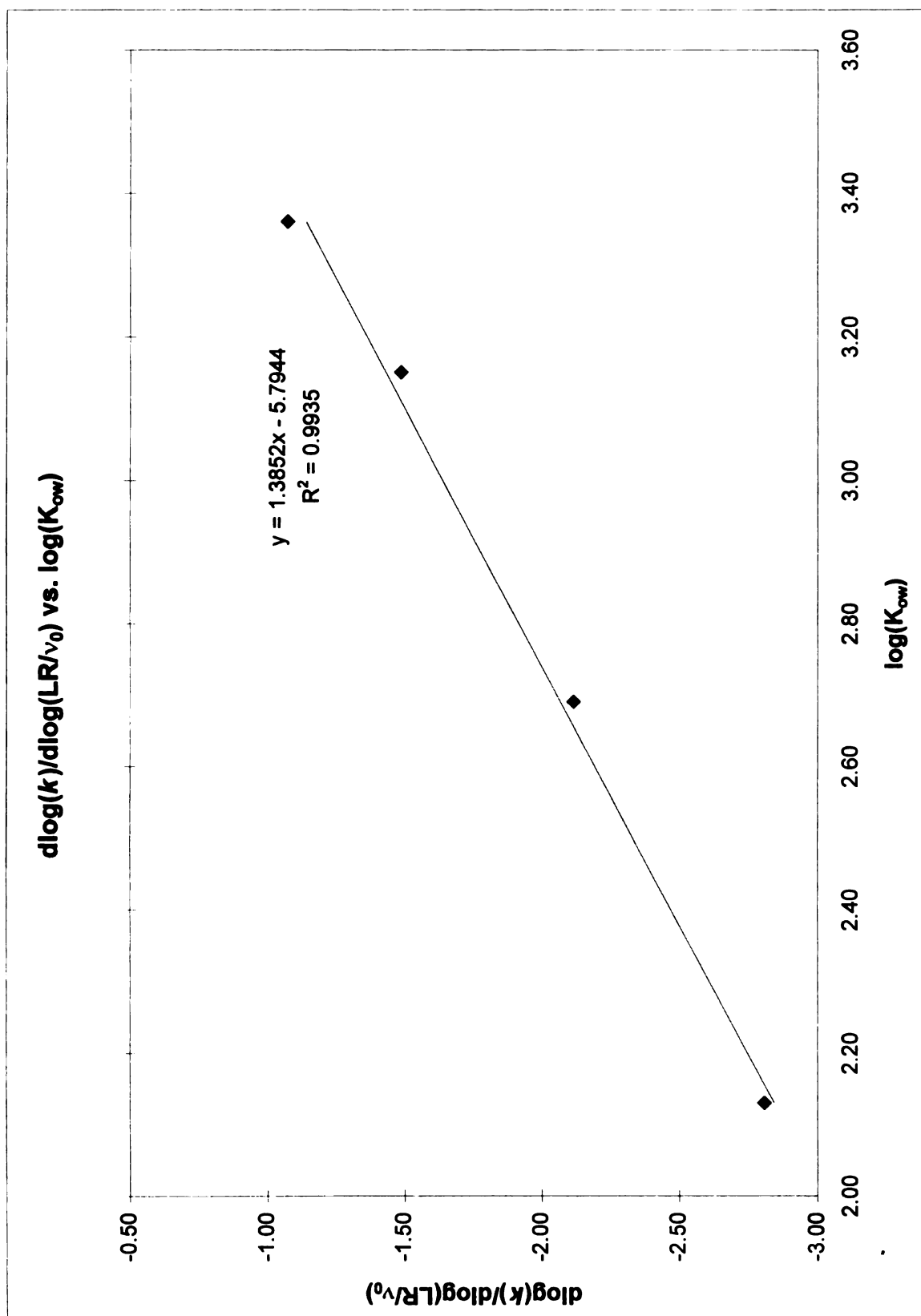


Figure 4. $\frac{d\log(k)}{d\log(LR/v_0)}$ vs. $\log(K_{ow})$ for all chemicals on SPCF soil.

The linear relationship observed in Figure 4 may be used with confidence as a predictive tool in the future only if it can be explained mechanistically. The following discussion is an attempt to explain the trends observed. First we must acknowledge that the mass-transfer coefficient obtained is a lumped parameter, encompassing all sources of slow desorption from soil solids. The three primary explanations for rate-limited sorption are (Brusseau, 1989a): 1) chemical nonequilibrium, which would not apply because the sorbates are nonpolar and essentially chemically nonreactive in this situation; 2) physical nonequilibrium, which is not evident, as indicated by the symmetric, sigmoidal breakthrough curves observed in nonsorbing tracer studies; and 3) intrasorbent diffusion, which is the most likely cause. Intrasorbent diffusion is slow movement of sorbing compounds in one or a combination of three different domains: 1) in intraparticle pore water, 2) along mineral surfaces of pores, or intraparticle diffusion (IMD) and 3) within the organic matter located on pore walls or grain surfaces, or intra-organic matter diffusion (IOMD).

Film diffusion, which some consider as contributing to physical nonequilibrium, was determined to not be a factor in this study. This was determined by calculating film mass-transfer coefficients for all compounds at each velocity using the method outlined by Merk (1980) for chemical sorption in fixed bed activated carbon adsorbers. Aqueous diffusivities were estimated using the Wilke-Chang relationship as outlined in Weber and DiGiano (1996). The differences between the mass-transfer rate coefficients for the highest and lowest velocities varied by less than 0.01% for the largest diameter particles (worst case).

In light of the discussion of diffusion mechanisms mentioned above, the trends seen in Figures 2-4 may be explained as follows. Brusseau et al (1991) presented an interpretation of the first-order mass-transfer model by defining k in terms of a diffusion coefficient and a length scale, based on the assumption that intra-organic matter diffusion was the rate-limiting mechanism. They stated that $k = cD_{py}/(l^2(1-F))$, where c is a shape factor, D_{py} is the diffusion coefficient for the specific sorbate/sorbent pair (L^2/T), l is the characteristic diffusion length (L), and F is the fraction of instantaneous sites. They also cited the work of Ball (1991) who interpreted k in terms of retarded intraparticle diffusion: $k = [15D_p/(R_{im}a^2)]$, where D_p is the pore diffusion coefficient (L^2/T), R_{im} is the retardation factor for sorption occurring inside the particle, and a is the particle radius (L).

Based on these two interpretations, we may state that $k \propto D/l^2$, where D is a diffusion coefficient (L^2/T) and l is a characteristic diffusion length. Though one diffusion mechanism may dominate, experimental techniques used in this study do not allow us to make definitive conclusions regarding the absolute dominance of either IOMD or IPD. Indeed, the former appears to be more important, but we cannot exclude the latter as a contributor. Based on the proportionality shown, the mass-transfer rate coefficient, k , must be dependent upon two factors, D and l , and the inverse correlation observed between k and v_0 must be related to one of these two variables, or both.

The first possibility is that contaminant residence time has an effect on D . Cussler (1984) noted that diffusion coefficients may change with changing concentration gradients. The concentration gradients for this system change with velocity as follows.

When the soil column is flushed with clean solution, the portion of contaminant-saturated solution in larger pores is flushed out immediately. However, in less accessible locations, contaminant must first diffuse into larger pores where it can be flushed out of the column. With high pore-water velocity the concentration gradient which drives the diffusion is increased rapidly as clean water is flushed through pores faster, filling the larger pores with clean solution and driving the gradient up. At lower velocities the gradient is lower because the ratio of the rate at which clean solution is replacing contaminated solution is smaller. The smaller ratio occurs because diffusion of contaminants from smaller pores occurs as clean water fills the larger pores. The additional contaminant in the large pores lessens the effect of flushing with clean solution.

This effect would be more evident for less hydrophobic compounds which are preferentially partitioned to the aqueous phase. Diffusion coefficients of compounds strongly sorbed to organic matter on particle walls would be less affected by the changing concentration gradient because their diffusion coefficients are strongly affected by diffusion within organic matter. Organic compound diffusion in organic matter has been compared by some authors to that in polymers, where diffusivities are 2-8 orders of magnitude lower than in the aqueous phase (Pignatello, 1989). Therefore, diffusion is controlled by organic matter diffusion more for more strongly sorbed (more hydrophobic, high K_{ow}) compounds and less in less hydrophobic compounds (low K_{ow}). This would explain the different slopes for each compound as shown in Figure 3, and the relationship between $d\log(k)/d\log(LR/v_0)$ and $\log(K_{ow})$ shown in Figure 4.

The second explanation relates to a change in the characteristic diffusion length, l . In order to understand the possible effect, one must understand that CXTFIT describes the diffusion process as movement between two bulk phases of solution in pores. One phase is the contaminated solution, and the other is clean solution. The concentration gradient is the difference between the bulk concentrations of the clean solution and the contaminated solution. As v_0 increases, the clean solution is forced through some pores which are not accessed at lower velocities. As solution reaches these less accessible locations, the distance between the bulk clean phase and the contaminated phase decreases, and subsequently the diffusion path length decreases. This effect would be more evident, again, for compounds which are partitioned more to the aqueous phase. The effect on k would be less pronounced for compounds preferentially sorbed to organic matter because diffusion within the organic matter into the aqueous phase would dominate, as described above.

Summary and Conclusions

Column studies were performed with four nonionic organic compounds on three different nonaggregated porous media at five velocities from ≈ 2 to 100 cm/hr. Desorption breakthrough curves were modeled using CXTFIT in order to obtain mass-transfer rate coefficients, k . Breakthrough curves for the Wurtsmith aquifer material were best modeled in the equilibrium mode, indicating that nonequilibrium was minimal for this very low organic carbon content medium.

Results from the SPCF soil columns indicated that k increased with increasing velocity, which is consistent with the results of past investigators. The effect was more

pronounced for less hydrophobic compounds. A plot of $d\log(k)/d\log(LR/v_0)$ vs. $\log(K_{ow})$ revealed a strong linear correlation. Two possible explanations of the observed trends were presented. The first explanation is that diffusion coefficients, which are proportional to k , were affected by the change in velocity. The second explanation is that clean solution reached smaller pores as pore-water velocity increased, thus decreasing the diffusion path length, which is inversely proportional to $k^{1/2}$.

These results indicate that we may have a predictive tool for determining k for the range of velocities and compounds studied. Further studies would include compounds covering a larger range of K_{ow} and more soils with a wider range of organic carbon contents. In addition, a study which allowed increased equilibration time would provide insight into the validity of the explanation for the slope vs. $\log(K_{ow})$ relationship.

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APPENDICES

APPENDIX A

APPENDIX A

Literature Review

Introduction

Extensive petroleum contamination of soils and groundwater has led researchers to investigate fate and transport of organic contaminants in these media. This has led to the development of models which attempt to describe mathematically the fundamental processes occurring in such systems. These models use a mass balance approach with such removal terms as biodegradation, volatilization and leaching. Sorption of contaminants to soil solids affects each of those processes either directly or indirectly. For example, studies have suggested that compounds entrapped in soil micropores are not available for biodegradation (Alexander and Scow, 1989). Also, the amount of contaminant leached from the soil with percolating rainwater depends upon the solution phase concentration, which is directly related to sorbed concentration. Therefore, a thorough understanding of sorption processes is essential to accurate modeling of fate and transport of contaminants in soils and groundwater.

As a first approximation, it was assumed that sorption of organic compounds to soil or aquifer solids occurred instantaneously and could therefore be described by an equilibrium distribution between phases. However, observations such as breakthrough curves with extensive tailing, indicated slow sorption was occurring. Lapidus and Amundson (1952) are generally credited with first describing the slow approach to

equilibrium using a first-order rate equation. An extensive review of nonideal processes, including those related to sorption, is given in Brusseau and Rao (1989a).

In soil columns, three basic mechanisms could be responsible for the slow sorptive uptake or release (Brusseau and Rao, 1989b). The first possibility is chemical nonequilibrium (CNE), which is caused by a slow reaction at specific sites on the sorbent surface. This generally does not occur with nonionic organic compounds, but may occur with ionic or polar organic compounds.

The second potential cause of sorption nonequilibrium is slow diffusion between immobile and mobile pore water. The immobile water may be in one of several locations such as internal porosity of soil aggregates, thin liquid films surrounding soil particles or at contact points between individual soil particles. This is called physical nonequilibrium (PNE) and affects both sorbing and nonsorbing solutes. Symmetric sigmoidal breakthrough curves of nonsorbing tracers such as tritiated water are evidence that PNE does not contribute to nonequilibrium.

The final potential cause of nonequilibrium is slow diffusion within the sorbent matrix, which may be referred to as intrasorbent diffusion. Two basic mechanisms have been proposed. These are intraorganic matter diffusion (IOMD) and intramineral diffusion (IMD). Intraorganic diffusion (IOMD) is the movement of nonionic organic compound (NOC) molecules through a natural organic matter (NOM) matrix, which may be flexible or rigid (Brusseau and Rao 1989a; Brusseau et al. 1991). For example, an NOC molecule moves from the exterior to the interior of the NOM matrix under the influence of a concentration gradient. On its way, it is detained at various spots by weak bonding forces, such as van der Waals forces, with hydroxyl or other organic functional

groups on the NOM. It may also be subject to steric hindrance as it moves. The sorbate would be hindered more in the more rigid portion of the NOM, where its shape and size would affect movement. High concentrations of a cosolvent such as methanol would lead to the rigid portions becoming more flexible, thus increasing the rate of diffusion (Brusseau et al., 1991).

Intramineral diffusion is movement of NOC molecules through a solid inorganic aggregate (Ball and Roberts, 1991; Farrell and Reinhard, 1994a; Harmon and Roberts, 1994). The aggregate is formed by the cohesion of individual particles, leaving fissures where the particles come together, providing medium-size pores (mesopores).

Intraparticle micropores are also present within the primary particles. As an NOC molecule moves toward the interior of the particle under the influence of a concentration gradient, its movement is hindered as it adsorbs to surfaces along its path. Movement is most restricted as it moves through the micropores, due to the enhanced adsorption as it interacts with more than one surface. The tortuosity of pores increases resistance to movement. Brusseau and Rao (1989b) cite several studies which indicate that IMD is not likely to be important for NOCs. However, other investigators contend that for low organic carbon porous media intramineral diffusion is the reason for slow sorption. Pignatello and Xing (1996) summarize evidence supporting each theory.

Intraorganic Matter Diffusion:

1. Nonequilibrium behavior increases with increasing organic matter content.
2. Diffusion rates increase with presence of cosolvents.
3. Sorption is noncompetitive in most cases.

4. Diffusion rates decrease for those compounds capable of forming hydrogen bonds with reactive surface sites found in organic matter.

Intramineral Diffusion:

1. Diffusion rates are almost always inversely dependent upon grain size.
2. Diffusion rates generally increase following acidification of inorganic particles, leading to dissolution of mineral oxides which cement the clays together. This opens up pores and increases freedom of movement within the particle.

These different descriptions have been used by researchers in attempting to model sorption of chemicals on porous materials. For example, Ball and Roberts (1991) performed batch experiments to study adsorption rates of two chlorinated organic compounds on aquifer sand and used a pore or radial diffusion model to fit the data. They concluded that the particle size may be an appropriate length scale for diffusion based largely on their observation that uptake rates increased significantly with pulverization of particles. However, the pore diffusion model greatly overpredicted the effect of decreasing the particle radius. A significant difficulty in the modeling was independent determination of the apparent diffusivity. This occurs due to the inability to describe tortuosity and steric hindrance sufficiently. In addition, diffusion may occur through organic matter sorbed to grain surfaces, and coefficients of diffusion through organic matter (as approximated by diffusion through polymers) can vary by 2-3 orders of magnitude.

Farrell and Reinhard (1994a, 1994b) improved on the work of Ball and Roberts (1991) by measuring desorption rates covering seven orders of magnitude for chlorinated

compounds on aquifer sand at 100% relative humidity. They noted that the pore diffusion model could not fit both the fast and slow desorbing portions of the data. They proposed that sorption in intra-aggregate micropores may be responsible for the slow release of contaminants.

Cameron and Klute (1977) described sorption as a two-site process, with part of the sites participating in equilibrium distribution between solid and aqueous phases. At the second type of sites, sorption is considered to be rate-limited (i.e., equilibrium is not reached instantaneously, but is approached slowly). This description has been shown to accurately model contaminant movement in many situations.

Previous Determination of Mass-transfer Coefficient

One current limitation is our inability to accurately determine the mass-transfer coefficient associated with the rate-limited sites. One method of determining the mass-transfer coefficient is to perform laboratory soil column tests and use a computer program to perform least squares regression to fit the breakthrough curve data. The coefficient is an output of the model. The major difficulty associated with this method is our inability to directly apply coefficients obtained in laboratory studies to field situations. Perhaps the greatest difference is that soil column studies are often performed at much higher flow rates than would be found in an actual field situation.

Inverse relationship $\log(k)$ vs. $\log(K_p)$

Several investigators have noticed the inverse relationship between mass-transfer coefficient and soil-water partition coefficient (Karickhoff, 1980; Brusseau and Rao, 1989b, Brusseau and Reid, 1991; Brusseau, 1992). Brusseau and Rao (1989b) offer the following explanation for the observed relationship. The mass-transfer coefficient, k , is a

function of three parameters: 1) the diffusivity of the diffusing species, 2) the resistance to diffusion associated with the sorbent matrix and 3) the diffusion path length. The partition coefficient, K_p , is equal to $K_{oc}f_{oc}$, and K_{oc} is a function of chemical structure and size, and for intraorganic matter diffusion, f_{oc} is related to diffusion path length. The authors performed a linear regression of the data in an attempt to develop a predictive tool for determining mass-transfer coefficient. They compiled data from several studies for both hydrophobic organic compounds (HOCs) and nonhydrophobic organic compounds (NHOCs) and found that a line could be fit through each data set. Data was obtained from batch, column and gas-purge experiments. The correlation was good for both, but higher for the HOCs.

However, the applicability of the equation describing the linear fit is questionable in light of later work performed, wherein various flow rates were used in determining mass-transfer and partition coefficients. Brusseau (1992) showed that for low organic carbon aquifer materials, an inverse relationship between the two coefficients was present for both high and low pore-water velocities (low velocity ≈ 5 cm/hr and high velocity between 45 and 90 cm/hr), but the line describing the relationship at high pore-water velocity was shifted above that for the low velocity by about 2 orders of magnitude. The correlation was poor for both lines. This indicates that the relationship found in the previous study (Brusseau and Rao, 1989b) determined using data from all three measurement techniques (batch, gas-purge and column studies) may have been somewhat coincidental because variations in velocity for the experiments would have resulted in increased scattering of data.

Pore-water velocity variation

Data presented by Bouchard et al. (1988) showed an increase in retardation with decreasing pore-water velocity, and nonequilibrium was observed to increase with increasing velocity. They attributed the sorption nonequilibrium to solute diffusion within the organic matter matrix. Maraqa (1995) showed that mass-transfer coefficient increased with increasing pore-water velocity, noting that the dependence indicates that mass-transfer coefficient is a time-averaged parameter. As stated above, Brusseau (1992) investigated the impact of pore-water velocity on nonequilibrium transport of nonionic organic compounds in low organic carbon content aquifer materials. He found that increasing velocity shifted the regression line of $\log(k)$ vs. $\log(v_0)$ significantly upward.

Therefore it has been shown that mass-transfer coefficient is related to both partition coefficient and pore-water velocity. What is needed, then, is a relationship describing the dependence upon pore-water velocity and partition coefficient. And in order for the relationship to be widely applicable, the mechanisms which control contaminant sorption behavior must be understood. This study, which uses soils of varying organic carbon content with pore-water velocities ranging over nearly two orders of magnitude, provides additional data which may be interpreted in order to elucidate rate-limiting processes occurring in transport of sorbing NOCs in soil columns.

The objective of this study is to elucidate the relationship between pore-water velocity and mass-transfer coefficient for soils with a range of organic matter contents. Part of that objective is to discuss the processes which control rate-limited sorption, with

the eventual goal of developing a quantitative relationship among partition coefficient, pore-water velocity and mass-transfer coefficient.

APPENDIX B

APPENDIX B

Materials and Methods

Solution Matrix

The solution matrix consisted of a 0.01 N solution of CaCl_2 which is buffered using a 10 mM solution of KH_2PO_4 . The pH of the resulting solution was ≈ 4.5 . This is necessary to prevent dissolution of mineral grains and also to provide a solution which is similar in ionic strength to what would be encountered in a field situation. All solution used in the columns was sterilized in an autoclave for at least 15 minutes. Autoclave tape was used to verify complete sterilization in each batch autoclaved.

Chemical Compounds

The following compounds are used in this study: benzene, toluene, p-xylene and naphthalene. These were chosen based on the following criteria: prevalence in contaminated soil, potential for leaching into groundwater (i.e., water solubility and volatility) and measurement detection limits. Table 3 shows properties of the compounds.

Table 3. Chemical properties of compounds at 25°C. (Schwarzenbach et al., 1993)

Compound	Mol. Wt.	$-\log P^0$ (atm)	$-\log C_w^{\text{sat}}$ ($\text{mol}\cdot\text{L}^{-1}$)	C_w^{sat} ($\text{mg}\cdot\text{L}^{-1}$) ^b	$\log K_{\text{ow}}$ [($\text{mol}\cdot\text{L}^{-1}$ octanol)· ($\text{mol}\cdot\text{L}^{-1}$ water) ⁻¹]
benzene	78	0.9	1.64	1787	2.13
toluene	92	1.42	2.25	517	2.69
p-xylene	106	1.93	2.77	180	3.15
naphthalene	128	3.43 ^a	3.61	31	3.36

a. Value shown is $-\log P^0(\text{L})$ for solid phase

b. Values were calculated from compound molecular weight and aqueous solubility in $\text{mol}\cdot\text{L}^{-1}$.

Porous media

Because the main purpose of the study was to move toward obtaining a widely applicable relationship among mass-transfer coefficient and pore-water velocity or partition coefficient, or both, one aquifer material and two soils with organic matter contents of 0.05, 0.3 and 1.0%, respectively, were used. Media with varying organic carbon were chosen because previous studies have indicated that the primary variable affecting organic chemical sorption behavior is organic carbon (Voice, 1983).

The two soils were analyzed by the Department of Crop and Soil Science to determine percent organic carbon. Percent organic carbon of the aquifer material was measured using a Perkin Elmer CHN analyzer.

Ball and Roberts (1991) and Farrell and Reinhard (1994b) noted the dependence of sorption rate parameters on grain size, so efforts were made to obtain soils with similar grain size distributions. Table 4 shows the size distribution of each soil. Similar grain size distributions were obtained by performing a sieve analysis on the SPCF soil, calculating the particle size distribution and then separating other soils by size and recombining fractions to obtain a similar distribution. The finest sieve used was No. 270, which has an opening of 53 μm . Therefore, the fraction collected by the bottom pan contained grains up to 53 μm in diameter. This is noted because the finest fraction of the Metea soil appeared finer (i.e., it was more cohesive and poured less easily) than the finest fraction of the SPCF soil. So though the same size is reported, the Metea soil contains more fine particles. It should also be noted that the Wurtsmith aquifer sand is

typical of low organic content material in that it lacks the fines usually present in surface soil. Therefore, its grain size distribution varies from the Metea and SPCF soils.

Soils were sterilized by ≈ 2 Mrad of gamma radiation for approximately 0.9 hour at the Nuclear Reactor Laboratory at University of Michigan in Ann Arbor. Gamma radiation is an effective method of sterilization which does not significantly alter the soil characteristics.

Table 4. Soil sieve analysis

Soil or Sand Type	Organic Carbon, %	Grain size			
		(250-425 μm)	(150-250 μm)	(53-150 μm)	(0-53 μm)
SPCF	1.0	10.6%	22.8%	55.2%	11.4%
Metea	0.3	10.6%	22.8%	55.2%	11.4%
Wurtsmith	0.05	15%	70%	15%	0%

Plate counts

Plate counts were performed in order to test for the presence of microorganisms in the soil-filled column. The method is as follows. First, 18.4 g of powdered general purpose nutrient agar was mixed with 800 mL of deionized water in an Erlenmeyer flask, and the solution was brought. Foil was placed loosely over the mouth of the flask, which was then sterilized in an autoclave for 30 minutes. The solution was taken from the autoclave and allowed to cool to about 60°C. It was then poured into commercially sterilized petri dishes in the laminar flow hood work area. The solution was cooled overnight, allowing the solution to solidify.

As stated above, the purpose of the plate counts was to test for the presence of microorganisms in the soil columns, but not necessarily the sample loops. Therefore, the sample loops were removed and sterilized in an autoclave for 15 minutes to kill any

microorganisms which may be present. The loops were then re-attached to the columns, and matrix solution was injected into the system with a syringe pump in order to fill the sample loop. Samples were collected by first removing the effluent spout from the collection bottle, then connecting an air-filled plastic syringe to the tee at the beginning of the sample loop, which was then depressed in order to force the solution out of the sample loop. One mL samples were collected in commercially sterilized polystyrene sample tubes, which were capped immediately.

These samples were taken to the laminar flow hood where three 100 μL aliquots from each sample were spread on the cooled agar plates. The plates were sealed with paraffin wax paper and placed in an incubator at 30°C, where they remained for four days, at which time the samples were inspected for microbial growth.

Experimental Setup

The proposed experimental setup is shown in Figure 5. Because this study is focused on sorption processes alone, it is essential to account for all potential losses and eliminate the sources when possible. Any losses which are not accounted for lead to overestimation of contaminant sorbed by soil solids. The most probable losses are volatilization, microbial degradation and sorption to equipment. In order to reduce sorption to equipment, stainless is used wherever possible. The soil column, tubing and tee fitting shown in Figure 5 are all stainless steel. The syringe is made of glass. The syringe plunger head and three-way valve are all made of Teflon, which has been shown to absorb organic chemicals. Its use in these two cases was unavoidable.

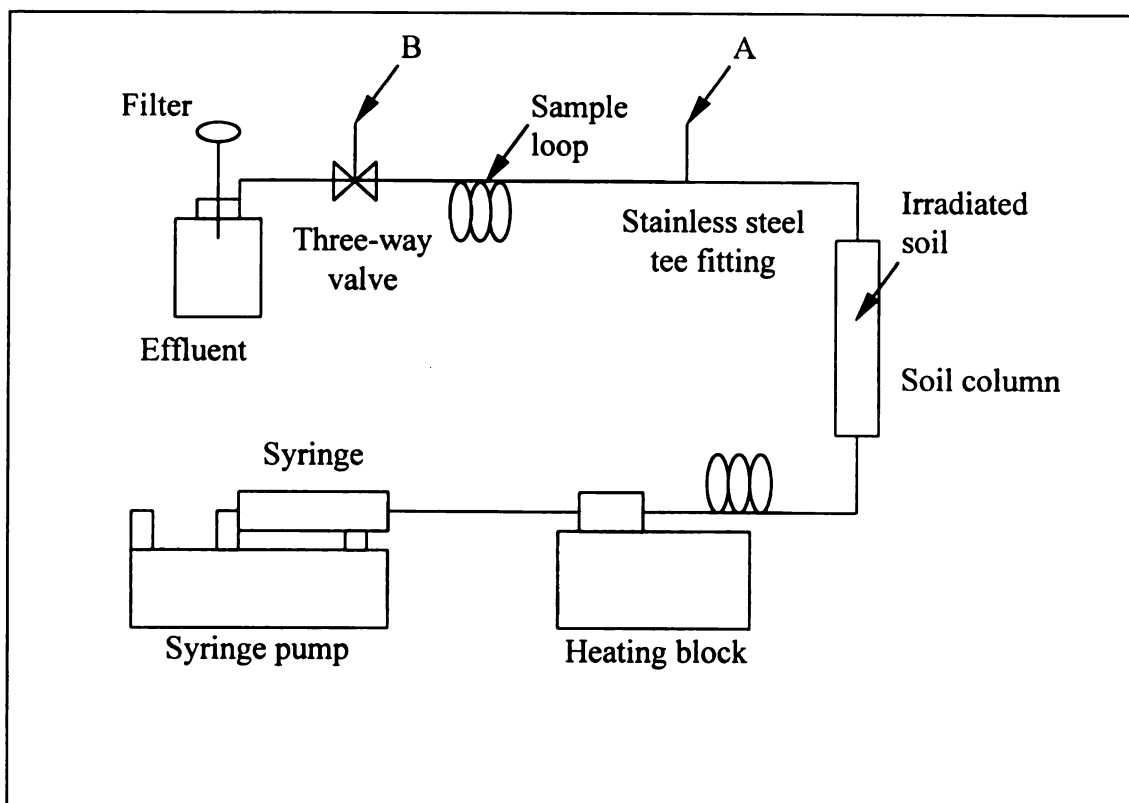


Figure 5. Experimental setup

Prevention of contaminant biodegradation

Extensive measures were required to ensure that microbial degradation of compounds did not occur within the system. First, as much of the equipment as possible (tubing, column, tee fitting, three-way valve) and the matrix solution were sterilized in an autoclave for at least 15 minutes. Second, when the system was set up, none of the entrances to the system (e.g., tubing ends) were touched. Third, because it has been observed that microorganisms can diffuse against the direction of solution flow, measures were taken to prevent them from entering the effluent bottle and moving into the system. The bottle needed be vented in order to prevent pressure buildup. Therefore, a needle was placed in the rubber septum, and a 0.22 μm filter was placed at the head of the needle in order to prevent invasion by microorganisms. The filter and needle were used directly after opening from commercially sterilized packages. Fourth, microorganisms in the soil are killed by treating the soil with gamma radiation. Finally, between the syringe and the soil column, the stainless steel tubing was threaded through a small hole in a heating block which was maintained at $\approx 60^\circ\text{C}$. This is an added measure to prevent microbial growth in the system.

Prevention of volatilization

Volatilization of compounds is only possible where the solution comes in contact with air. Therefore, the system must be checked to ensure that leaks are not present and that volatilization of compounds from the effluent front are minimal. This was done by performing a test of the system without the soil column. First, a solution was prepared with target compounds at the proposed influent concentrations. The syringe was filled

with the solution, and then it was depressed until solution was seen emptying into the effluent bottle. The syringe pump was then turned on in order to provide positive pressure to the system. Next the three-way valve was rotated so that a sample could be taken. The stainless steel cap on the tee at “A” in Figure 5 was removed, and an air-filled syringe was connected to the tee via a stainless steel fitting. Air was forced through the sample loop, and a solution sample was collected at point “B” in Figure 5.

The volume was determined by weighing the sample vial and cap before and after the sample was added. A sample was collected after the loop was refilled by the syringe pump at the set volumetric flow rate. This occurs after approximately one to two hours. Another sample was taken at approximately three to four hours after the pump was turned on. A final sample was taken after the system had been flushed for approximately one day.

The compound concentrations were determined by headspace gas chromatography. If the concentrations dropped from the initial sample to the second or third, then there may be a leak in the system or a problem with volatilization at the front of the solution flow. If the concentration in the final sample was much smaller than the first three, then chemical absorption by the Teflon plunger head or three-way valve may have been present.

Porosity and bulk density determination

Two of the necessary input parameters for the CXTFIT program are porosity and bulk density. Porosity (θ) was determined as follows. First, a dry, empty steel column with end fittings and caps was weighed. Second, one cap was removed, the column was

filled with water, the cap was replaced, and the column weighed. The column was then emptied and dried in an oven at 100°C. After the column was removed from the oven and cooled, the end fittings and caps were replaced and covered with foil. The columns were then heated in an autoclave for 30 minutes. Following this the columns were removed and cooled, and the foil was removed. Dry soil was then added to each column, and the end caps replaced. The columns were then weighed. Following this, the end caps were removed, and the columns connected to the system. A 50 mL plastic syringe was filled with CO₂, which was then injected slowly into the soil column to displace air in the pores. The use of CO₂ enables complete saturation of the column by replacing relatively insoluble pore air with the very water-soluble CO₂. Solution matrix was then flushed through the system for at least one day in order to fully saturate the column. The saturated column was then removed from the system, end caps again replaced, and the column weighed.

The porosity is equal to pore volume divided by the total volume. The column volume (in mL) is simply equal to the difference between the water-filled column weight and the empty, dry column weight in grams (1 mL of water weighs 1.00 g at 20°C). The pore volume (in mL) is equal to the weight of the saturated soil column in grams minus the weight of the dry soil-filled column. The porosity is then simply equal to the pore volume divided by the total volume. In previous studies using the same columns, the dead volume (volume in end fittings and caps) is less than 1% of the total volume, and therefore is negligible. Table 5 shows soil column properties.

Table 5. Soil column properties summary

Wurtsmith Aquifer Sand				
Column target velocity (cm/hr)	Length (cm)	Pore volume (mL)	ρ (g/cm ³)	θ
2.0	15.4	5.50	1.52	0.365
5.3	15.4	5.40	1.53	0.352
14.1	15.3	5.50	1.53	0.364
37.5	15.2	5.30	1.55	0.355
100.0	15.2	5.50	1.53	0.366
Metea Soil				
Column target velocity (cm/hr)	Length (cm)	Pore volume (mL)	ρ (g/cm ³)	θ
2.0	15.3	5.61	1.64	0.38
5.3	15.4	5.67	1.59	0.38
14.1	15.3	5.58	1.60	0.38
37.5	15.2	5.40	1.60	0.37
100.0	15.4	5.77	1.54	0.39
SPCF Soil				
Column target velocity (cm/hr)	Length (cm)	Pore volume (mL)	ρ (g/cm ³)	θ
2.0	15.2	7.61	1.35	0.50
5.3	15.2	6.02	1.43	0.41
14.1	15.2	6.93	1.36	0.47
37.5	15.2	6.31	1.38	0.42
100.0	15.2	6.98	1.30	0.46

Pore-water velocity

Because the primary variable of interest is the desorption rate (as opposed to adsorption rate), only the desorption phase breakthrough curves were examined. In addition, it is important that distribution of the compounds between soil and solution be at or near equilibrium at the beginning of the desorption phase. As noted earlier in the introduction, sorptive uptake usually consists of a fast period (from a few minutes to a few hours) wherein roughly 50% of the solid sorptive capacity is reached, followed by slow uptake of contaminant until equilibrium is reached. Due to this slow uptake, it was decided that adsorption should be approached using a fast flow rate until the breakthrough front showed effluent concentrations very near influent concentrations, followed by a period of waiting and another period of flushing at a lower flow rate.

The high/low flow rate is necessary for the following reasons. 1) The possibility of biodegradation is always present, despite extreme care in preparation of system setup, and therefore, the duration of the experiment should be limited as much as possible. This is accomplished by rapidly approaching adsorption equilibrium 2) Intrisorbent diffusion is commonly seen as the limiting factor causing nonequilibrium, in order to accurately determine the mass-transfer rate must mimic the natural diffusive system (e.g., the desorption rate from the inner layers of organic matter would be much lower than the rate from the outer layers to the surrounding water layer).

The study used pore-water velocities of 2.0, 5.3, 14.1, 37.5 and 100 cm/hr. The highest flow rate, 100 cm/hr, was chosen because it is the maximum flow rate at which the column soil will not be pushed upward by the force of the water. For a sandy soil the maximum infiltration rate is just over 2 cm/hr. This sets the lower limit. The

intermediate velocities were chosen so as to be logarithmically evenly spaced between the two extremes.

General

The compounds were placed in one solution and co-eluted. It has been shown in previous studies that competition effects are minimal at low contaminant concentrations (Maraqa, 1995). The soil columns were run at saturated conditions in order to mimic the worst case scenario in a field situation.

APPENDIX C

APPENDIX C

Data Tables

Table 6. Model output parameters for Wurtsmith aquifer sand.

Target ν_0	Compound	R	K_p	β	ω	SSE	R^2	k	F	Model ν_0	D	Mode
2	Benzene	1.10	0.024	x	x	0.071	0.964	x	x	2.29	0.243	Equilibrium
2	Toluene	1.12	0.029	x	x	0.073	0.963	x	x	2.29	0.243	Equilibrium
2	Xylene	1.15	0.036	x	x	0.131	0.928	x	x	2.29	0.243	Equilibrium
2	Naphthalene	1.30	0.072	0.833	1.025	0.048	0.975	0.703	0.272	2.29	0.243	Two-site
5.3	Benzene	1.15	0.035	x	x	0.007	0.997	x	x	5.28	0.728	Equilibrium
5.3	Toluene	1.25	0.058	0.955	0.003	0.013	0.995	0.016	0.776	5.28	0.728	Two-site
5.3	Xylene	1.34	0.078	0.941	0.011	0.015	0.995	0.049	0.766	5.28	0.728	Two-site
5.3	Naphthalene	1.74	0.172	0.775	0.068	0.023	0.993	0.060	0.473	5.28	0.728	Two-site
14.1	Benzene	1.41	0.098	0.880	0.016	0.001	0.977	0.0714	0.589	11.8	0.714	Two-site
14.1	Toluene	1.47	0.111	0.858	0.004	0.104	0.973	0.0159	0.553	11.8	0.714	Two-site
14.1	Xylene	1.61	0.146	0.818	0.016	0.180	0.956	0.0410	0.521	11.8	0.714	Two-site
14.1	Naphthalene	1.94	0.224	0.730	0.059	0.356	0.921	0.0874	0.443	11.8	0.714	Two-site
37.5	Benzene	1.03	0.007	x	x	0.106	0.944	x	x	31.7	1.67	Equilibrium
37.5	Toluene	1.05	0.011	x	x	0.089	0.958	x	x	31.7	1.67	Equilibrium
37.5	Xylene	1.09	0.021	x	x	0.094	0.955	x	x	31.7	1.67	Equilibrium
37.5	Naphthalene	1.38	0.086	0.898	0.0716	0.053	0.982	1.064	0.627	31.7	1.67	Two-site
100	Benzene	1.06	0.013	x	x	0.003	0.99	x	x	82.4	4.55	Equilibrium
100	Toluene	1.08	0.019	x	x	0.014	0.99	x	x	82.4	4.55	Equilibrium
100	Xylene	1.22	0.053	0.921	0.368	0.004	0.998	20.7	0.569	82.4	4.55	Two-site
100	Naphthalene	1.43	0.103	0.911	0.065	0.004	0.999	2.74	0.704	82.4	4.55	Two-site

a. When the equilibrium model was used the nonequilibrium parameters were not obtained, as indicated by an x.

Table 7. Model output parameters for Metea soil.

Target v_0	Compound	R	K_p	β	ω	SSE	R^2	k	F	Model v_0	D	Mode
2	Benzene	1.15	0.035	x	x	0.0218	0.991	x	x	1.89	0.398	Equilibrium
2	Toluene	1.17	0.039	x	x	0.2505	0.850	x	x	1.89	0.398	Equilibrium
2	Xylene	1.05	0.012	0.952	0.129	0.6238	0.524	0.32	0.0 ^a	1.89	0.398	Two-site
2	Naphthalene	3.50	0.580	0.286	1.16	0.0531	0.979	0.057	0.000	1.89	0.398	Two-site
5.3	Benzene	1.33	0.079	0.798	1.92	0.0179	0.996	2.25	0.186	4.84	0.359	Two-site
5.3	Toluene	1.32	0.077	0.758	2.18	0.1322	0.960	2.14	0.002	4.84	0.359	Two-site
5.3	Xylene	1.29	0.069	0.775	0.693	0.5563	0.739	0.75	0.00	4.84	0.359	Two-site
5.3	Naphthalene	4.10	0.742	0.272	0.986	0.1211	0.974	0.10	0.037	4.84	0.359	Two-site
14.1	Benzene	1.15	0.035	0.870	0.657	0.0746	0.976	3.30	0.003	11.5	3.19	Two-site
14.1	Toluene	1.43	0.101	0.699	0.973	0.2848	0.882	1.70	0.00	11.5	3.19	Two-site
14.1	Xylene	1.21	0.049	0.826	0.665	0.1740	0.933	2.37	0.00	11.5	3.19	Two-site
14.1	Naphthalene	4.35	0.789	0.297	0.618	0.2102	0.945	0.15	0.087	11.5	3.19	Two-site
37.5	Benzene	1.27	0.062	0.787	1.93	0.0482	0.986	12.72	0.00	27.1	7.97	Two-site
37.5	Toluene	1.33	0.076	0.752	1.57	0.1199	0.962	8.49	0.000	27.1	7.97	Two-site
37.5	Xylene	1.88	0.204	0.532	1.2	0.0621	0.983	2.43	0.000	27.1	7.97	Two-site
37.5	Naphthalene	5.72	1.092	0.403	0.463	0.1836	0.972	0.24	0.277	27.1	7.97	Two-site
100	Benzene	2.31	0.333	0.913	0.0528	0.0309	0.995	1.40	0.847	81.9	24.4	Two-site
100	Toluene	2.58	0.401	0.868	0.141	0.0302	0.996	2.20	0.784	81.9	24.4	Two-site
100	Xylene	3.60	0.660	0.744	0.325	0.0578	0.993	1.88	0.646	81.9	24.4	Two-site
100	Naphthalene	7.48	1.645	0.394	0.563	0.1103	0.986	0.66	0.300	81.9	24.4	Two-site

a. Note that in some cases, the actual F value was some very low negative value, but is shown as 0.0 in the table.

Table 8. Model output parameters for SPCF soil.

Target v_0	Compound	R	K_p	β	ω	SSE	R^2	k	F	Model v_0	D	Mode
2	Benzene	1.65	0.243	x	x	0.042	0.988	x	x	1.7	1.28	Equil
2	Toluene	2.51	0.564	x	x	0.112	0.977	x	x	1.7	1.28	Equil
2	Xylene	4.46	1.293	x	x	0.067	0.978	x	x	1.7	1.28	Equil
2	Naphthalene	13.84	4.797	0.072	3.000	0.292	0.944	0.031	0.000	1.7	1.28	Two-site
5.3	Benzene	2.99	0.566	0.824	0.00138	0.143	0.979	0.00076	0.736	4.44	0.664	Two-site
5.3	Toluene	3.91	0.825	0.766	0.0523	0.104	0.977	0.01670	0.686	4.44	0.664	Two-site
5.3	Xylene	6.53	1.567	0.876	0.175	0.0513	0.99	0.063	0.854	4.44	0.664	Two-site
5.3	Naphthalene	16.03	4.264	0.080	3.13	0.1788	0.967	0.062	0.019	4.44	0.664	Two-site
14.1	Benzene	1.97	0.333	0.896	0.021	0.0251	0.994	0.096	0.789	11.6	1.64	Two-site
14.1	Toluene	2.74	0.597	0.891	0.058	0.0387	0.99	0.149	0.828	11.6	1.64	Two-site
14.1	Xylene	5.14	1.420	0.769	0.640	0.1574	0.976	0.411	0.713	11.6	1.64	Two-site
14.1	Naphthalene	14.28	4.556	0.139	2.150	0.1840	0.973	0.133	0.074	11.6	1.64	Two-site
37.5	Benzene	2.25	0.382	0.823	0.0272	0.0706	0.985	0.1372	0.681	30.5	3.48	Two-site
37.5	Toluene	3.22	0.679	0.829	0.0421	0.0774	0.987	0.154	0.752	30.5	3.48	Two-site
37.5	Xylene	5.89	1.500	0.769	0.359	0.0960	0.99	0.529	0.722	30.5	3.48	Two-site
37.5	Naphthalene	19.28	5.603	0.207	1.630	0.2723	0.974	0.214	0.164	30.5	3.48	Two-site
100	Benzene	1.54	0.193	0.681	3.020	0.0039	0.998	37.58	0.095	93.2	11.8	Two-site
100	Toluene	2.14	0.401	0.467	9.250	0.0163	0.99	49.82	0.00	93.2	11.8	Two-site
100	Xylene	3.66	0.940	0.273	7.090	0.0563	0.983	16.34	0.000	93.2	11.8	Two-site
100	Naphthalene	7.36	2.247	0.136	4.430	0.0965	0.98	4.00	0.000	93.2	11.8	Two-site

Table 9. Column data for Wurtsmith aquifer material with target $v_0 = 2$ cm/hr.

Pore volumes	C/C_0			
	Benzene	Toluene	Xylene	Naphthalene
0.00	0.74	0.74	0.70	0.86
0.30	0.94	0.93	0.86	0.89
0.71	1.01	0.98	0.90	0.88
1.03	0.72	0.77	0.78	0.83
1.39	0.0209	0.0406	0.1437	0.3105
1.77	0.00415	0.00807	0.0234	0.0853
2.12	0.00307	0.00532	0.0131	0.0494
2.64	0.00212	0.00326	0.00867	0.0285
3.04	0.00169	0.00299	0.00705	0.0229
3.61	0.00143	0.00238	0.00512	0.0204
4.02	0.000887	0.00217	0.00485	0.0172
4.90	0.000817	0.00137	0.00371	0.0141
6.06	0.000505	0.000971	0.00255	0.0120
7.46	0.000396	0.000817	0.00196	0.0114

Table 10. Column data for Wurtsmith aquifer material with target $v_0 = 5.3$ cm/hr.

Pore volumes	C/C_0			
	Benzene	Toluene	Xylene	Naphthalene
0.00	0.977	1.012	0.975	1.046
0.32	0.946	0.972	0.914	0.978
0.75	1.064	1.101	1.059	1.103
1.11	0.612	0.729	0.866	0.999
1.42	0.0247	0.0512	0.156	0.363
1.89	0.00428	0.00914	0.0299	0.122
2.27	0.00280	0.00623	0.0163	0.0723
2.55	0.00199	0.00447	0.0112	0.0500
2.92	0.00160	0.00356	0.00856	0.0345
3.32	0.00125	0.00277	0.00748	0.0305
3.84	0.00115	0.00227	0.00576	0.0234
4.28	0.000951	0.00212	0.00518	0.0207
5.02	0.000835	0.00176	0.00423	0.0165
5.94	0.000760	0.00168	0.00346	0.0140
6.34	0.000607	0.00150	0.00328	0.0133
7.70	0.000766	0.00182	0.00342	0.0171
8.70	0.000537	0.00135	0.00269	0.0123
9.62	0.000350	0.00119	0.00262	0.0114
10.49	0.000307	0.00102	0.00217	0.00839
11.62	0.000496	0.00109	0.00228	0.01010
13.59	0.000372	0.000883	0.00185	0.00788
16.55	0.000279	0.000748	0.00166	0.00783
20.20	0.000228	0.000691	0.00149	0.00601

Table 11. Column data for Wurtsmith aquifer material with target $v_0 = 14.1$ cm/hr.

Pore volumes	C/C_0			
	Benzene	Toluene	Xylene	Naphthalene
0.00	1.175	1.171	1.232	1.279
0.30	1.154	1.184	1.212	1.279
0.67	1.155	1.158	1.221	1.307
1.03	1.067	1.120	1.185	1.311
1.39	0.0843	0.124	0.277	0.601
1.76	0.0150	0.0221	0.0454	0.126
2.12	0.00517	0.0101	0.0263	0.0721
2.48	0.00229	0.00532	0.0152	0.0476
2.85	0.00189	0.00398	0.0109	0.0383
3.21	0.00157	0.00327	0.00800	0.0358
3.58	0.00129	0.00279	0.00703	0.0260
3.94	0.00108	0.00249	0.00620	0.0226
4.30	0.00098	0.00189	0.00508	0.0189
4.67	0.00085	0.00189	0.00499	0.0173
5.03	0.00095	0.00157	0.00406	0.0187

Table 12. Column data for Wurtsmith aquifer material with target $v_0 = 37.5$ cm/hr.

Pore volumes	C/C_0			
	Benzene	Toluene	Xylene	Naphthalene
0.00	0.943	0.988	0.978	1.100
0.31	1.027	1.074	1.061	1.173
0.69	0.680	0.707	0.705	0.876
1.06	0.363	0.448	0.621	0.971
1.82	0.00406	0.00684	0.0165	0.0590
2.20	0.00285	0.00471	0.0108	0.0415
2.61	0.00199	0.00351	0.00770	0.0284
3.02	0.00163	0.00276	0.00635	0.0260
3.35	0.00146	0.00252	0.00554	0.0238
3.71	0.00142	0.00218	0.00483	0.0191
4.10	0.00106	0.00191	0.00416	0.0184
4.46	0.00105	0.00188	0.00381	0.0156
4.84	0.000869	0.00170	0.00335	0.0149
5.61	0.000674	0.00128	0.00273	0.0124

Table 13. Column data for Wurtsmith aquifer material with target $v_0 = 100$ cm/hr.

Pore volumes	C/C_0			
	Benzene	Toluene	Xylene	Naphthalene
0.00	0.930	0.946	0.951	1.004
0.28	0.911	0.942	0.977	1.032
0.64	0.914	0.943	0.974	1.015
1.00	0.763	0.820	0.924	1.050
1.37	0.0472	0.0695	0.1507	0.3155
1.73	0.00674	0.0110	0.0281	0.0639
2.09	0.00388	0.00610	0.0150	0.0371
2.46	0.00294	0.00397	0.00979	0.0265
2.82	0.00212	0.00335	0.00741	0.0215
3.19	0.00181	0.00285	0.00643	0.0196
3.73	0.00153	0.00243	0.00537	0.0171
4.28	0.00099	0.00177	0.00374	0.0131
4.82	0.000854	0.00161	0.00356	0.0132
5.37	0.000789	0.00135	0.00298	0.0114
5.91	0.001601	0.00213	0.00338	0.0111

Table 14. Column data for Metea soil with target $v_0 = 2$ cm/hr.

Pore volumes	C/C_0			
	Benzene	Toluene	Xylene	Naphthalene
0.00	1.065	0.837	0.646	1.032
0.29	0.921	0.741	0.619	0.917
0.65	0.908	0.648	0.580	0.868
1.06	0.733	0.616	0.448	0.775
1.36	0.105	0.314	0.362	0.555
1.72	0.0205	0.0893	0.28	0.640
2.08	0.00731	0.0236	0.20	0.590
2.43	0.00071	0.00135	0.0136	0.300
2.79	0.00288	0.00532	0.0650	0.437
3.14	0.00233	0.00390	0.0443	0.410
3.50	0.00162	0.00252	0.0247	0.320
3.81	0.00148	0.00224	0.0190	0.333
4.23	0.00119	0.00170	0.0123	0.304
4.92	0.000191	0.00029	0.00153	0.173
5.28	0.000912	0.00115	0.00629	0.220
5.64	0.000784	0.00100	0.00488	0.174
6.23	0.000686	0.000838	0.00377	0.147
6.48	0.000738	0.000799	0.00362	0.139
7.21	0.000603	0.000650	0.00281	0.114
7.58	0.000599	0.000628	0.00264	0.100
7.94	0.000985	0.000645	0.00249	0.118
8.35	0.000556	0.000536	0.00219	0.0866
8.65	0.000554	0.000505	0.00204	0.0793
8.79	0.000526	0.000506	0.00186	0.0709
9.33	0.000543	0.000467	0.00185	0.0744
9.77	0.000555	0.000474	0.00168	0.0982
10.31	0.000470	0.000447	0.00140	0.0743
10.86	0.000466	0.000400	0.00141	0.0792
11.38	0.000279	0.000325	0.00103	0.0516
11.63	0.000312	0.000381	0.00117	0.0639
11.93	0.000288	0.000383	0.00119	0.0584
12.43	0.000302	0.000334	0.00112	0.0538
12.89	0.000297	0.000327	0.00102	0.0495
13.39	0.000263	0.000301	0.00095	0.0459
14.10	0.000234	0.000251	0.000847	0.0428
15.00	0.000263	0.000269	0.000819	0.0351
15.66	0.000292	0.000269	0.000749	0.0335
15.94	0.000221	0.000265	0.000749	0.0295
16.80	0.000184	0.000222	0.000723	0.0270

Table 14 (cont'd)

17.83	0.000091	0.000126	0.000333	0.0073
18.42	0.000224	0.000216	0.000657	0.0259
19.17	0.000227	0.000188	0.000591	0.0194
20.18	0.000215	0.000208	0.000632	0.0233
21.09	0.000193	0.000204	0.000600	0.0202

Table 15. Column data for Metea soil with target $v_0 = 5.3$ cm/hr.

Pore Volume	C/C_0			
	Benzene	Toluene	Xylene	Naphthalene
0.00	1.109	0.908	0.674	0.977
0.30	1.028	0.834	0.648	0.903
0.56	1.010	0.865	0.670	1.003
0.82	0.955	0.849	0.666	0.902
1.10	0.748	0.714	0.530	0.781
1.37	0.357	0.550	0.454	0.754
1.62	0.118	0.300	0.358	0.667
1.88	0.0317	0.1203	0.2548	0.549
2.14	0.0134	0.0545	0.1883	0.486
2.41	0.00712	0.0258	0.1316	0.416
2.67	0.00483	0.0151	0.0965	0.399
2.98	0.00353	0.00950	0.0712	0.401
3.24	0.00287	0.00719	0.0540	0.401
3.53	0.00221	0.00495	0.0365	0.312
3.78	0.00205	0.00432	0.0312	0.338
4.04	0.00175	0.00359	0.0235	0.271
4.31	0.00153	0.00286	0.0183	0.252
4.58	0.00146	0.00271	0.0159	0.247
4.91	0.00127	0.00229	0.0122	0.206
5.27	0.00115	0.00192	0.00992	0.222
5.62	0.00104	0.00170	0.00810	0.189
6.64	0.000821	0.00123	0.00525	0.149
6.94	0.000764	0.00118	0.00477	0.122
7.42	0.000712	0.00109	0.00415	0.114
7.67	0.000655	0.00097	0.00359	0.108
8.00	0.000658	0.00096	0.00353	0.106
8.32	0.000643	0.00095	0.00324	0.134
8.59	0.000642	0.000879	0.00297	0.127
8.85	0.000616	0.000900	0.00296	0.122
9.19	0.000658	0.000923	0.00294	0.120
9.46	0.000584	0.000847	0.00280	0.108
9.87	0.000490	0.000767	0.00238	0.0900
10.31	0.000435	0.000695	0.00221	0.0940
10.56	0.000404	0.000649	0.00208	0.0832
10.89	0.000401	0.000668	0.00205	0.0824
11.40	0.000385	0.000587	0.00188	0.0749
12.52	0.000511	0.000568	0.00163	0.0615
14.74	0.000281	0.000395	0.00117	0.0419
15.02	0.000316	0.000426	0.00123	0.0386

Table 15 (cont'd)

15.37	0.000304	0.000381	0.00115	0.0391
15.81	0.000279	0.000343	0.00108	0.0372
16.80	0.000401	0.000384	0.00108	0.0306
17.74	0.000254	0.000296	0.00093	0.0270
18.48	0.000204	0.000285	0.00096	0.0293
20.33	0.000166	0.000281	0.000777	0.0209
21.17	0.000157	0.000250	0.000735	0.0175
22.60	0.000176	0.000257	0.000704	0.0164
24.12	0.000131	0.000237	0.000648	0.0160
25.44	0.000168	0.000217	0.000616	0.0162
26.10	0.000158	0.000229	0.000483	0.0123
26.92	0.000127	0.000275	0.000658	0.0124
28.23	0.000149	0.000200	0.000529	0.0139
29.46	0.000141	0.000221	0.000586	0.0126
30.77	0.000133	0.000198	0.000491	0.0103
32.66	0.000144	0.000243	0.000481	0.0102
33.87	0.000116	0.000229	0.000470	0.0087
35.11	0.000119	0.000148	0.000373	0.0098
36.84	0.000370	0.000216	0.000342	0.0103
37.58	0.000067	0.000166	0.000355	0.00699
39.22	0.000142	0.000157	0.000439	0.00678
40.42	0.000111	0.000150	0.000356	0.00674
44.14	0.000091	0.000141	0.000359	0.00502
45.27	0.000055	0.000129	0.000284	0.00538
46.08	0.000130	0.000160	0.000370	0.00615
47.91	0.000045	0.000137	0.000329	0.00357
48.69	0.000075	0.000141	0.000251	0.00513
49.98	0.000062	0.000113	0.000302	0.00405

Table 16. Column data for Metea soil with target $v_0 = 14.1$ cm/hr.

Pore volumes	C/C_0			
	Benzene	Toluene	Xylene	Naphthalene
0.00	1.018	0.753	0.903	0.922
0.30	0.955	0.739	0.862	0.879
0.63	0.816	0.737	0.769	0.917
0.87	0.691	0.628	0.629	0.740
1.15	0.523	0.547	0.541	0.696
1.42	0.281	0.457	0.399	0.681
1.66	0.113	0.341	0.239	0.578
1.93	0.0379	0.2515	0.1170	0.521
2.22	0.0151	0.1772	0.0531	0.437
2.49	0.00797	0.1266	0.0278	0.390
2.74	0.00556	0.1030	0.0183	0.400
2.99	0.00395	0.0745	0.0117	0.342
3.35	0.00280	0.0518	0.007410	0.301
3.61	0.00236	0.0416	0.005866	0.300
3.85	0.00206	0.0328	0.004723	0.265
4.11	0.00182	0.0280	0.004143	0.284
4.35	0.00163	0.0229	0.003507	0.238
4.60	0.00158	0.0202	0.003265	0.239
4.96	0.00130	0.0153	0.002595	0.209
5.32	0.00113	0.0120	0.002170	0.199
5.68	0.00103	0.0100	0.001937	0.171
6.03	0.000895	0.00799	0.001618	0.153
6.41	0.000793	0.00712	0.001484	0.144
7.23	0.000645	0.00550	0.001193	0.1297
7.49	0.000610	0.00520	0.001175	0.1314
7.75	0.000579	0.00460	0.001052	0.1180
8.11	0.000912	0.00625	0.001922	0.1302
8.38	0.000830	0.00618	0.001942	0.1218
8.65	0.000997	0.00574	0.001686	0.1210
9.03	0.000926	0.00560	0.001579	0.1284
9.53	0.000874	0.00487	0.001582	0.1128
9.90	0.000771	0.00472	0.001452	0.0950
10.16	0.000714	0.00425	0.001334	0.0892
10.44	0.000702	0.00411	0.001261	0.0966
10.82	0.000664	0.00406	0.001354	0.0891
11.76	0.000708	0.00347	0.001214	0.0651
12.65	0.000586	0.00334	0.001202	0.0538
13.51	0.000454	0.00324	0.001168	0.0456
14.47	0.000390	0.00304	0.001059	0.0437

Table 16 (cont'd)

15.28	0.000416	0.00282	0.001011	0.0640
17.79	0.000392	0.00208	0.000709	0.0387
18.31	0.000312	0.00206	0.000603	0.0323
18.60	0.000244	0.00210	0.000814	0.0347
19.81	0.000394	0.00201	0.000712	0.0331
20.66	0.000330	0.00178	0.000581	0.0436
21.50	0.000298	0.00212	0.000834	0.0388
22.34	0.000419	0.00211	0.000900	0.0361
23.20	0.000220	0.00194	0.000781	0.0250
23.99	0.000202	0.00168	0.000729	0.0568
24.58	0.000286	0.00171	0.000723	0.0392
25.41	0.000168	0.00155	0.000709	0.0408
26.46	0.000207	0.00158	0.000653	0.0268
27.54	0.000178	0.00142	0.000610	0.0236
28.18	0.000181	0.00137	0.000591	0.0257
28.78	0.000218	0.00137	0.000598	0.0287
29.67	0.000215	0.00142	0.000614	0.0222
30.51	0.000173	0.00140	0.000659	0.0254
31.55	0.000203	0.00102	0.000569	0.0243
32.36	0.000138	0.00105	0.000381	0.0218
33.20	0.000287	0.00149	0.000633	0.0201
34.21	0.000181	0.00122	0.000681	0.0122
39.31	0.000152	0.00102	0.000515	0.0217
39.67	0.000119	0.00126	0.000554	0.0181
40.01	0.000104	0.00119	0.000665	0.0093
40.53	0.000256	0.00103	0.000617	0.0185
40.94	0.000228	0.00111	0.000584	0.0174
41.73	0.000091	0.00111	0.000546	0.0197
42.04	0.000112	0.00114	0.000560	0.0256
43.04	0.000121	0.00111	0.000516	0.0324
44.26	0.000336	0.00098	0.000483	0.0239
47.31	0.000105	0.00106	0.000468	0.0165

Table 17. Column data for Metea soil with target $v_0 = 37.5$ cm/hr.

Pore volumes	C/C_0			
	Benzene	Toluene	Xylene	Naphthalene
0.00	1.049	1.047	1.055	1.198
0.32	0.922	0.892	0.954	1.165
0.60	0.846	0.768	0.830	1.089
0.86	0.819	0.722	0.760	1.053
1.14	0.658	0.627	0.665	0.939
1.42	0.387	0.467	0.564	0.909
1.69	0.154	0.269	0.439	0.792
2.34	0.0221	0.0606	0.240	0.582
2.60	0.0135	0.0390	0.194	0.581
2.86	0.00798	0.0230	0.136	0.438
3.12	0.00593	0.0171	0.115	0.441
3.38	0.00438	0.0121	0.0863	0.393
3.67	0.00352	0.00924	0.0689	0.373
3.93	0.00320	0.00799	0.0590	0.371
4.20	0.00270	0.00642	0.0472	0.325
4.49	0.00239	0.00545	0.0385	0.321
4.75	0.00201	0.00441	0.0298	0.253
5.12	0.00177	0.00375	0.0244	0.263
5.49	0.00152	0.00324	0.0199	0.224
5.86	0.00138	0.00277	0.0161	0.242
6.23	0.00122	0.00247	0.0136	0.191
6.45	0.00115	0.00231	0.0124	0.202
6.97	0.00103	0.00208	0.0105	0.177
7.34	0.00095	0.00183	0.0088	0.160
7.71	0.00094	0.00181	0.0085	0.159
8.19	0.00147	0.00307	0.0135	0.196
8.56	0.00124	0.00297	0.0126	0.163
8.93	0.00116	0.00271	0.0150	0.151
9.30	0.00106	0.00267	0.0105	0.142
9.69	0.00106	0.00214	0.00952	0.150
10.06	0.00116	0.00231	0.00926	0.128
10.42	0.00106	0.00237	0.00885	0.115
10.79	0.00120	0.00218	0.00871	0.114
11.16	0.00116	0.00223	0.00869	0.105
12.08	0.00108	0.00230	0.00759	0.0971
13.08	0.00130	0.00192	0.00673	0.0837
13.93	0.00134	0.00216	0.00618	0.0789
14.88	0.00123	0.00376	0.00877	0.0971
15.79	0.000802	0.00173	0.00554	0.0593

Table 17 (cont'd)

16.71	0.000788	0.00151	0.00508	0.0983
17.64	0.000401	0.00135	0.00500	0.0548
19.67	0.000429	0.00119	0.00413	0.0224
20.09	0.000349	0.00109	0.00390	0.0443
20.42	0.000332	0.00113	0.00451	0.0204
21.34	0.000366	0.00112	0.00382	0.0215
22.30	0.000375	0.00120	0.00354	0.0383
23.25	0.000349	0.00114	0.00389	0.0353
24.12	0.000400	0.000939	0.00314	0.0330
25.06	0.000291	0.000992	0.00288	0.0308
26.03	0.000179	0.000880	0.00289	0.0297
26.90	0.000215	0.000804	0.00317	0.0280
27.82	0.000187	0.000824	0.00325	0.0287
28.77	0.000238	0.000790	0.00312	0.0275
29.73	0.000256	0.000807	0.00319	0.0281
30.62	0.000156	0.000799	0.00315	0.0278
31.66	0.000184	0.000823	0.00325	0.0287
32.62	0.000127	0.000813	0.00321	0.0283
33.43	0.000171	0.000799	0.00315	0.0278
34.86	0.000144	0.000821	0.00324	0.0286
35.36	0.000141	0.000827	0.00326	0.0288
36.23	0.000188	0.000833	0.00329	0.0290
37.08	0.000182	0.000804	0.00317	0.0280
38.14	0.000116	0.000798	0.00315	0.0278
38.93	0.000106	0.000848	0.00335	0.0295
39.90	0.000126	0.000807	0.00319	0.0281
40.88	0.000137	0.000815	0.00322	0.0284
41.67	0.000113	0.000772	0.00305	0.0269
47.79	0.000139	0.000770	0.00304	0.0268
48.99	0.000100	0.000807	0.00318	0.0281
49.69	0.000115	0.000812	0.00320	0.0282

Table 18. Column data for Metea soil with target $v_0 = 100$ cm/hr.

Pore Volumes	C/C_0			
	Benzene	Toluene	Xylene	Naphthalene
0.000	0.88	0.88	0.87	1.03
0.28	1.03	1.01	1.01	1.00
0.54	1.05	1.04	1.05	0.99
0.80	1.01	1.01	1.02	1.12
1.06	1.0275	1.0300	1.0438	1.08
1.32	1.0642	1.0620	1.0789	0.954
1.58	0.9767	0.9979	1.0463	0.962
1.84	0.7619	0.8397	0.9720	0.990
2.10	0.4960	0.6265	0.8429	0.838
2.36	0.2963	0.4470	0.7480	0.821
2.62	0.1810	0.3062	0.6363	0.776
2.88	0.1062	0.1909	0.4841	0.682
3.14	0.0756	0.1403	0.4169	0.654
3.40	0.0521	0.0975	0.3232	0.592
3.66	0.0410	0.0765	0.2698	0.544
3.92	0.0244	0.0554	0.2056	0.464
4.18	0.0184	0.0445	0.1671	0.419
4.44	0.0160	0.0401	0.1541	0.455
5.13	0.0085	0.0184	0.0995	0.352
5.48	0.0067	0.0151	0.0863	0.364
5.83	0.0042	0.0093	0.0591	0.245
6.17	0.0045	0.0104	0.0666	0.318
6.52	0.0037	0.0089	0.0593	0.286
6.87	0.0029	0.0068	0.0492	0.277
7.21	0.0026	0.0059	0.0440	0.243
7.56	0.0023	0.0053	0.0410	0.262
7.91	0.0021	0.0048	0.0378	0.221
8.25	0.0020	0.0043	0.0355	0.215
8.60	0.0017	0.0039	0.0200	0.212
8.95	0.00279	0.00632	0.03234	0.297
9.29	0.00254	0.00563	0.02817	0.251
9.64	0.00232	0.00511	0.02641	0.250
9.99	0.00214	0.00459	0.02397	0.226
10.33	0.00154	0.00367	0.01829	0.176
11.20	0.00139	0.00338	0.01725	0.188
12.07	0.00098	0.00276	0.01444	0.160
12.93	0.00107	0.00224	0.01192	0.137
13.80	0.00072	0.00190	0.01015	0.126
14.67	0.000890	0.00207	0.00956	0.110

Table 18 (cont'd)

15.53	0.000646	0.00192	0.00865	0.114
16.40	0.000677	0.00206	0.00815	0.101
17.27	0.000778	0.00181	0.00778	0.106
18.13	0.000742	0.00171	0.00709	0.103
19.00	0.000466	0.00170	0.00656	0.0893
19.87	0.000496	0.00159	0.00627	0.0775
20.73	0.000470	0.00141	0.00545	0.0693
21.60	0.000482	0.00147	0.00539	0.0624
22.47	0.000410	0.00127	0.00460	0.0588
23.33	0.000378	0.00122	0.00479	0.0556
24.20	0.000493	0.00114	0.00444	0.0636
25.06	0.000432	0.00111	0.00391	0.0463
25.93	0.000346	0.00130	0.00372	0.0447
26.80	0.000265	0.00123	0.00388	0.0358
27.66	0.000276	0.00120	0.00396	0.0462
28.53	0.000287	0.00119	0.00367	0.0474
29.40	0.000298	0.000969	0.00302	0.0370
30.26	0.000260	0.000882	0.00289	0.0336
31.13	0.000207	0.000972	0.00308	0.0299
32.00	0.000496	0.000820	0.00289	0.0313
32.86	0.000266	0.000818	0.00282	0.0302
33.73	0.000307	0.000989	0.00287	0.0346
34.60	0.000395	0.000930	0.00310	0.0311
35.46	0.000220	0.001016	0.00316	0.0297
36.33	0.000364	0.000976	0.00264	0.0263
37.20	0.000343	0.000801	0.00269	0.0359
38.06	0.000518	0.001276	0.00396	0.0299
38.93	0.000540	0.001316	0.00394	0.0270
40.66	0.000248	0.000892	0.00298	0.0239
42.40	0.000174	0.000682	0.00266	0.0204
44.13	0.000180	0.000788	0.00267	0.0235
45.86	0.000139	0.000873	0.00292	0.0168
47.60	0.000123	0.000575	0.00187	0.0148
49.33	0.000153	0.000585	0.00206	0.0180
51.06	0.000135	0.000645	0.00228	0.0187
52.79	0.000207	0.000862	0.00264	0.0109
54.53	0.000339	0.000978	0.00291	0.0188
56.26	0.000165	0.001025	0.00296	0.0187
57.99	0.000119	0.000832	0.00252	0.0180
59.73	0.0000947	0.000665	0.00208	0.0120

Table 19. Column data for SPCF soil with target $v_0 = 2$ cm/hr.

Pore Volume	C/C_0			
	Benzene	Toluene	Xylene	Naphthalene
0.00	1.016	1.012	0.961	0.933
0.17	0.966	0.957	0.888	0.973
0.70	1.083	1.076	1.003	0.932
1.22	0.994	0.988	0.947	0.858
1.90	0.289	1.02	1.04	0.938
2.29	0.042	0.750	0.978	0.919
2.89	0.014	0.157	0.937	0.837
3.34	0.00821	0.0387	0.900	0.811
3.93	0.00595	0.0177	0.822	0.881
4.43	0.00447	0.0105	0.551	0.798
4.82	0.00356	0.00790	0.362	0.726
5.43	0.00320	0.00626	0.188	0.646
5.77	0.00239	0.00471	0.133	0.604
6.04	0.00279	0.00503	0.099	0.701
6.36	0.00282	0.00487	0.0790	0.702
6.65	0.00486	0.00410	0.0576	0.609
7.58	0.00246	0.00380	0.0320	0.686
8.49	0.00902	0.00254	0.0139	0.441
9.32	0.00202	0.00309	0.0138	0.692
9.94	0.00181	0.00283	0.0115	0.676
12.31	0.00177	0.00236	0.00696	0.606
13.27	0.00175	0.00228	0.00654	0.574
13.92	0.00137	0.00197	0.00504	0.510
14.83	0.00085	0.00119	0.00392	0.400
15.78	0.00100	0.00142	0.00386	0.325
15.69	0.000579	0.000726	0.00234	0.176
19.90	0.000831	0.001139	0.00282	0.147
20.45	0.000709	0.001016	0.00264	0.138
21.24	0.000121	0.000421	0.00098	0.0230
22.88	0.000102	0.000333	0.00075	0.0822
27.09	0.000871	0.000888	0.00271	0.0976
29.21	0.007732	0.000770	0.00213	0.0705
34.19	0.000352	0.000542	0.00153	0.0440
35.05	0.000717	0.001225	0.00259	0.0446
38.21	0.000755	0.001089	0.00255	0.0468
39.46	0.000565	0.000996	0.00234	0.0426
40.32	0.000489	0.000954	0.00228	0.0412
41.44	0.000497	0.000875	0.00228	0.0395
43.61	0.002999	0.000118	0.00043	0.0180

Table 19 (cont'd)

46.19	0.000538	0.001032	0.00225	0.0302
47.55	0.000152	0.000268	0.00076	0.0175
48.64	0.000777	0.001514	0.00298	0.0357
51.34	0.000401	0.000719	0.00167	0.0212

Table 20. Column data for SPCF soil with target $v_0 = 5.3$ cm/hr.

Pore volumes	C/C_0			
	Benzene	Toluene	Xylene	Naphthalene
0.00	1.00	0.98	0.927	0.861
0.38	1.04	1.03	0.972	0.906
0.72	1.13	1.11	1.051	0.906
1.05	1.06	1.04	0.975	1.014
1.38	1.10	1.09	1.035	0.937
1.72	1.20	1.18	1.134	0.971
2.05	1.00	1.01	0.970	0.919
2.38	0.720	1.05	1.033	1.003
2.72	0.036	0.672	1.014	0.855
3.72	0.016	0.252	0.925	0.809
4.22	0.012	0.093	1.027	0.797
4.80	0.00766	0.029	0.853	0.940
5.47	0.00556	0.0149	0.627	0.793
6.13	0.00409	0.0096	0.429	0.780
6.68	0.00307	0.00642	0.251	0.667
7.35	0.00290	0.00553	0.158	0.628
8.05	0.00224	0.00394	0.0906	0.566
9.39	0.00183	0.00304	0.0413	0.596
10.44	0.00143	0.00242	0.0230	0.624
11.18	0.00139	0.00243	0.0184	0.628
12.04	0.00125	0.00203	0.0133	0.641
12.92	0.00118	0.00180	0.0102	0.617
13.66	0.00111	0.00170	0.00872	0.577
14.52	0.00106	0.00164	0.00759	0.555
15.24	0.00099	0.00153	0.00641	0.487
17.63	0.00101	0.00140	0.00482	0.372
20.04	0.000893	0.00129	0.00390	0.251
22.24	0.000771	0.00109	0.00314	0.177
23.86	0.000693	0.00100	0.00287	0.140
26.59	0.000670	0.00096	0.00256	0.097
26.89	0.071233	0.02456	0.03569	0.0788
29.41	0.001076	0.001570	0.00364	0.0922
31.15	0.000564	0.001051	0.00263	0.0661
33.56	0.000488	0.000799	0.00220	0.0543
36.08	0.000395	0.000559	0.00165	0.0421
47.06	0.000272	0.000399	0.00104	0.0231
48.57	0.000352	0.000638	0.00164	0.0217
50.44	0.000918	0.000954	0.00232	0.0370
54.80	0.001004	0.001072	0.00212	0.0347

Table 20 (cont'd)

65.92	0.000535	0.000391	0.00086	0.0222
67.53	0.000346	0.000391	0.00083	0.0194
71.49	0.000405	0.000440	0.00094	0.0177
76.30	0.000407	0.000602	0.00114	0.0126
82.77	0.000484	0.000684	0.00106	0.0105
91.14	0.000798	0.000882	0.00138	0.0118
98.63	0.003348	0.002868	0.00284	0.0097
103.87	0.000205	0.000379	0.00055	0.0104
105.44	0.000266	0.000385	0.00071	0.0082
112.50	0.000266	0.000435	0.00088	0.0121
119.35	0.000030	0.000027	0.00008	0.0009
122.96	0.000070	0.000132	0.00024	0.0023
132.98	0.000110	0.000616	0.00218	0.0026

Table 21. Column data for SPCF soil with target $v_0 = 14.1$ cm/hr.

Pore Volumes	C/C_0			
	Benzene	Toluene	Xylene	Naphthalene
0.00	1.07	1.06	1.14	0.940
0.22	1.08	1.07	1.15	0.989
0.51	1.04	1.03	1.09	0.862
0.80	1.07	1.06	1.11	0.897
1.09	1.03	1.02	1.06	0.947
1.38	0.950	1.02	1.05	1.004
1.67	0.618	0.965	1.01	0.974
1.96	0.277	0.881	1.00	0.904
2.25	0.0863	0.659	0.944	0.877
2.54	0.0335	0.453	0.978	0.914
2.83	0.0167	0.240	0.887	0.851
3.12	0.0117	0.126	0.879	0.889
3.41	0.00867	0.0629	0.787	0.845
3.70	0.00725	0.0361	0.736	0.887
3.99	0.00631	0.0238	0.679	0.910
4.28	0.00558	0.0172	0.587	0.838
4.57	0.00447	0.0119	0.439	0.734
4.86	0.00456	0.0113	0.408	0.839
5.15	0.00388	0.00899	0.301	0.725
5.44	0.00368	0.00816	0.249	0.724
5.73	0.00320	0.00693	0.184	0.659
6.17	0.00286	0.00585	0.130	0.616
6.60	0.00251	0.00504	0.0925	0.595
7.03	0.00227	0.00447	0.0651	0.520
7.62	0.00219	0.00414	0.0479	0.562
8.20	0.00205	0.00372	0.0343	0.476
8.78	0.00203	0.00350	0.0271	0.521
9.36	0.00169	0.00297	0.0204	0.598
9.94	0.00148	0.00263	0.0162	0.546
10.52	0.00129	0.00228	0.0131	0.544
11.10	0.00207	0.00409	0.0194	0.594
11.91	0.00171	0.00322	0.0156	0.546
13.07	0.00170	0.00340	0.0139	0.475
14.23	0.00150	0.00255	0.0104	0.368
15.39	0.00111	0.00220	0.00862	0.318
16.55	0.00117	0.00198	0.00805	0.293
17.71	0.00113	0.00201	0.00720	0.247
19.74	0.00304	0.00414	0.00987	0.215
22.06	0.00116	0.00245	0.00684	0.156

Table 21 (cont'd)

25.53	0.00109	0.00175	0.00541	0.105
29.01	0.000987	0.00173	0.00485	0.0880
32.49	0.000979	0.00189	0.00483	0.0737
35.97	0.001008	0.00160	0.00421	0.0590
39.84	0.000338	0.000596	0.00179	0.0409
45.92	0.000284	0.000494	0.00143	0.0347
51.42	0.000527	0.000903	0.00227	0.0340
54.92	0.000385	0.000681	0.00180	0.0301
58.11	0.000588	0.001071	0.00275	0.0323
61.30	0.000483	0.000869	0.00230	0.0284
64.63	0.000586	0.001108	0.00237	0.0257
67.82	0.000510	0.000907	0.00209	0.0223
71.01	0.000510	0.001009	0.00215	0.0194
74.20	0.000480	0.000889	0.00234	0.0185
77.39	0.000280	0.000367	0.000635	0.0102
80.58	0.000230	0.000351	0.000605	0.00725
83.77	0.000220	0.000336	0.000632	0.00500
86.95	0.000194	0.000275	0.000573	0.00492
89.85	0.000168	0.000271	0.000447	0.00412
92.46	0.000174	0.000269	0.000526	0.00348
95.65	0.000179	0.000348	0.000610	0.00414
99.13	0.000281	0.000413	0.000574	0.00358
102.32	0.000281	0.000462	0.000773	0.00371
105.65	0.000217	0.000328	0.000629	0.00320
108.84	0.000177	0.000333	0.000630	0.00403
112.03	0.000144	0.000273	0.000419	0.00265
115.21	0.000042	0.000088	0.000179	0.00262
124.49	0.000170	0.000320	0.000574	0.00153
130.00	0.000060	0.000141	0.000205	0.00118
133.19	0.000231	0.000343	0.000463	0.00320
136.37	0.000088	0.000151	0.000224	0.00225
139.56	0.000000	0.000000	0.000000	0.00000
142.75	0.000022	0.000098	0.000164	0.00192
145.94	0.000025	0.000069	0.000103	0.00252
149.13	0.000045	0.000062	0.000104	0.00345
152.32	0.000549	0.000601	0.000671	0.00194

Table 22. Column data for SPCF soil with target $v_0 = 37.5$ cm/hr.

Pore volume	C/C_0			
	Benzene	Toluene	Xylene	Naphthalene
0.00	1.12	1.11	1.03	0.982
0.21	1.12	1.11	1.03	1.012
0.52	1.07	1.08	1.00	1.051
0.84	1.09	1.10	1.03	1.019
1.16	1.14	1.13	1.06	1.024
1.48	0.911	0.98	0.93	0.924
1.79	0.601	1.02	1.00	0.977
2.11	0.213	0.949	1.03	0.979
2.43	0.0798	0.716	1.03	0.987
2.75	0.0398	0.431	1.00	0.968
3.06	0.0250	0.232	0.98	0.926
3.38	0.0181	0.130	0.94	0.928
3.70	0.0134	0.0729	0.86	0.902
4.02	0.0127	0.0499	0.79	0.895
4.33	0.00972	0.0330	0.66	0.815
4.65	0.00888	0.0255	0.56	0.783
4.97	0.00820	0.0214	0.47	0.794
5.29	0.00706	0.0175	0.38	0.772
5.60	0.00620	0.0148	0.30	0.741
5.92	0.00560	0.0135	0.25	0.730
6.24	0.00503	0.0119	0.20	0.713
6.56	0.00459	0.0106	0.16	0.701
6.87	0.00428	0.00968	0.14	0.696
7.19	0.00399	0.00915	0.11	0.673
7.51	0.00375	0.00839	0.09	0.653
7.83	0.00365	0.00752	0.08	0.622
8.30	0.00325	0.00699	0.06	0.648
8.78	0.00324	0.00670	0.05	0.626
9.25	0.00374	0.00709	0.05	0.634
9.73	0.00339	0.00633	0.04	0.598
10.21	0.00386	0.00724	0.04	0.696
10.68	0.00341	0.00649	0.03	0.685
11.16	0.00287	0.00561	0.03	0.673
11.63	0.00244	0.00539	0.02	0.642
12.11	0.00236	0.00509	0.02	0.636
12.59	0.00226	0.00485	0.02	0.607
13.06	0.00248	0.00471	0.02	0.594
13.70	0.00233	0.00445	0.02	0.528
14.65	0.00208	0.00387	0.02	0.512

Table 22 (cont'd)

15.29	0.00182	0.00355	0.01	0.457
15.92	0.00156	0.00299	0.0115	0.397
16.56	0.00168	0.00343	0.0118	0.378
17.19	0.00171	0.00307	0.0107	0.346
17.83	0.00169	0.00300	0.0107	0.331
18.46	0.00154	0.00284	0.00878	0.304
19.25	0.00128	0.00253	0.00861	0.276
20.05	0.00104	0.00232	0.00824	0.257
21.16	0.00100	0.00214	0.00732	0.223
22.11	0.00118	0.00220	0.00755	0.205
23.06	0.00108	0.00187	0.00614	0.182
24.33	0.000946	0.00180	0.00587	0.175
25.60	0.000773	0.00171	0.00561	0.151
26.87	0.000841	0.00147	0.00500	0.132
28.88	0.000626	0.00120	0.00421	0.116
31.90	0.000809	0.00133	0.00401	0.0906
34.76	0.000511	0.00104	0.00336	0.0802
37.93	0.000476	0.00103	0.00297	0.0632
42.06	0.000498	0.00090	0.00285	0.0571
45.23	0.000544	0.00089	0.00255	0.0448
53.49	0.001384	0.00156	0.00327	0.0397
65.79	0.000866	0.00200	0.00410	0.0456
66.27	0.000345	0.000756	0.00237	0.0408
80.55	0.000394	0.000709	0.00168	0.0275
87.69	0.000638	0.001053	0.00270	0.0163
94.84	0.000316	0.000574	0.00138	0.0255
101.98	0.000482	0.000855	0.00181	0.0240
109.12	0.000533	0.000930	0.00198	0.0249
118.23	0.000567	0.000577	0.00133	0.0255
124.63	0.000385	0.000568	0.00150	0.00894
133.30	0.000449	0.000632	0.00116	0.00763
142.03	0.000327	0.000579	0.00130	0.00638
146.98	0.000260	0.000447	0.00151	0.00641
155.71	0.000367	0.000587	0.00147	0.01176
164.44	0.000264	0.000456	0.00102	0.01062
173.17	0.000298	0.000659	0.00145	0.00944
181.90	0.000140	0.000422	0.00086	0.00735
190.63	0.000293	0.000503	0.00112	0.00791
199.36	0.000128	0.000283	0.000653	0.00787
208.09	0.000235	0.000470	0.000927	0.00665
216.82	0.000256	0.000431	0.000860	0.00645
225.55	0.000440	0.000601	0.001135	0.01018

Table 22 (cont'd)

234.28	0.000653	0.000400	0.000718	0.00555
243.01	0.000401	0.000377	0.000738	0.00466
251.74	0.000322	0.000370	0.000767	0.00503
260.20	0.000564	0.000390	0.000711	0.00588
267.60	0.000419	0.000285	0.000538	0.00710
276.49	0.000419	0.000367	0.000750	0.00514
285.53	0.000709	0.000594	0.000945	0.00473
295.53	0.000171	0.000194	0.000471	0.00596
304.27	0.000100	0.000196	0.000514	0.00604
313.31	0.000107	0.000151	0.000361	0.00180
322.04	0.000215	0.000402	0.000744	0.00840

Table 23. Column data for SPCF soil with target $v_0 = 100$ cm/hr.

Pore Volumes	C/C_0			
	Benzene	Toluene	Xylene	Naphthalene
0.00	0.963	0.941	0.905	0.870
0.56	0.967	0.945	0.899	0.895
1.11	0.836	0.902	0.855	0.912
1.89	0.169	0.668	0.836	0.834
2.44	0.0350	0.284	0.871	0.874
3.11	0.0114	0.0734	0.645	0.767
3.67	0.00710	0.0284	0.433	0.725
4.22	0.00526	0.0158	0.285	0.666
4.89	0.00430	0.0114	0.206	0.672
5.33	0.00358	0.00856	0.139	0.657
5.78	0.00322	0.00731	0.110	0.619
6.33	0.00260	0.00624	0.0798	0.623
8.00	0.00159	0.00300	0.0205	0.260
8.56	0.00153	0.00289	0.0174	0.278
9.11	0.00138	0.00248	0.0136	0.242
9.67	0.00135	0.00239	0.0118	0.260
10.22	0.00113	0.00195	0.00859	0.216
10.78	0.00109	0.00177	0.00700	0.183
11.56	0.000896	0.00153	0.00560	0.154
12.44	0.000814	0.00137	0.00465	0.131
13.00	0.000710	0.00119	0.00376	0.111
14.33	0.000656	0.00106	0.00327	0.0892
15.56	0.000619	0.000927	0.00270	0.0633
16.44	0.000464	0.000667	0.00180	0.0398
17.78	0.000535	0.000790	0.00205	0.0433
19.11	0.000513	0.000719	0.00169	0.0339
20.78	0.000470	0.000698	0.00161	0.0274
23.00	0.000350	0.000526	0.00115	0.0188
26.33	0.000387	0.000522	0.00110	0.0147
28.00	0.000442	0.000477	0.000969	0.0127
31.33	0.000390	0.000419	0.000863	0.00908
33.00	0.000425	0.000432	0.000845	0.00714
36.33	0.000224	0.000330	0.000636	0.00536
38.00	0.000274	0.000289	0.000541	0.00434
39.67	0.000324	0.000307	0.000610	0.00462
41.33	0.000153	0.000261	0.000501	0.00339
43.00	0.000148	0.000219	0.000442	0.00296
44.67	0.000118	0.000191	0.000356	0.00230
46.33	0.000127	0.000188	0.000385	0.00236

Table 23 (cont'd)

48.00	0.000224	0.000344	0.000564	0.00596
49.67	0.000437	0.000477	0.000651	0.00419
51.33	0.000209	0.000340	0.000539	0.00318
64.67	0.000179	0.000283	0.000500	0.00298
67.56	0.000164	0.000218	0.000407	0.00240
71.33	0.000170	0.000313	0.000453	0.00229
73.89	0.000149	0.000193	0.000408	0.00184
76.33	0.000138	0.000159	0.000344	0.00155
79.67	0.000161	0.000178	0.000374	0.00161
83.00	0.000136	0.000176	0.000359	0.00138
85.78	0.000438	0.000380	0.000463	0.00105

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