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UNIVERSITY OF ALBERTA

DIFFUSION OF ORGANIC CHEMICALS IN WEATHERED SHALE AND MONTMORILLONITE CLAY: MEASUREMENT AND COMPARISON TO RATES OF SORPTION

BY

NORMAN SAWATSKY ©

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ABSTRACT

Diffusion is usually invoked as being fundamental to the rate of sorption and desorption of organic contaminants in soil materials. There is still, however, much debate as to the nature and level of resolution at which diffusion is important in determining rates of solute movement. One of the major problems in this area has been the inability to define the geometry of the porous medium which is available for diffusion. This has lead to the introduction of diverse fitting parameters which can be used to fit any data set to the appropriate model. The fact that a particular model can be used to fit a given data set cannot be used as direct proof of a given mechanism, unless the fitting parameters within that model can be confirmed outside the original data set. This project was designed to investigate whether diffusion was controlling measured rates of sorption for 1-naphthol, naphthalene, and anthracene. The specific objective was to confirm parameters used for fitting the diffusion model to specific observations. In this way, the validity of the diffusion model could be directly tested rather than allowing this model to become an empirical equation. This was accomplished through use of soil material for direct measurement of diffusion coefficients, measurement of microaggregate distribution, and measurement of rates of sorption.

Diffusion coefficients for 1-naphthol and naphthalene were measured in a weathered shale based on the breakthrough time and on the steady state flux of solute through the shale. Steady state solute flux through the clay barrier was 9 to 35 times lower than that predicted based on breakthrough diffusion coefficient within the clay barrier. Naphthalene concentration in the pore solution of a nonsorbing clay material was only 40% of that in the free solution suggesting that the clay textured material restricted the entry of the solute into the clay pore

space. Based on this work, and results from previous measurements reported in the literature, it is suggested that the restricted entry is due to a change in activity of the solute as it enters the narrow clay pores.

The rate of sorption of 1-naphthol, naphthalene and anthracene were measured in a weathered shale material. Sorption rates were compared against diffusion coefficients and measured microaggregate size distribution in the deposit to determine if microaggregation was controlling the measured rate of sorption in the deposit. Sorption of organic contaminants tested was dominantly controlled by the organic material within the shale. Micromorphological features of the weathered shale suggested that organic matter was unevenly distributed throughout the shale. Correalation between the rate of diffusion and the rate of sorptive uptake was observed for naphthalene and anthracene. The rate of sorption for 1-naphthol, however, was 100 to 1000 times lower than predicted by microaggregate diffusion. The proposed model for solute diffusion within aggregates, where organic matter was controlling the rate of uptake could therefore explain observed rates of sorption for naphthalene and anthracene but not for 1-naphthol.

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GLOSSARY OF SYMBOLS

A	surface area
C	solute concentration
C_0	solute concentration in the source reservoir
C_p	solute concentration in the pore solution
C_r	solute concentration in the collection reservoir
C_t	total solute concentration in the soil (concentration of solute sorbed by the soil + solute concentration in the pore solution)
D_0	diffusion coefficient in free water
D_a	apparent diffusion coefficient
D_{diff}	diffusion coefficient
D_{disp}	dispersivity
D_e	effective diffusion coefficient, defined as $D_0\tau_a$
D_{meas}	measured diffusion coefficient
D_p	diffusion coefficient as measured by the two cell method
D_s	diffusion coefficient as measured by the steady state method
D_{su}	surface diffusion coefficient
D_t	diffusion coefficient measured by the time lag method
J_s	solute flux
K_a	apparent sorption coefficient

K_d	sorption coefficient
K_m	mineral referenced sorption coefficient
K_{om}	organic matter referenced sorption coefficient
L	path length
L_e	tortuous path length due to the geometry of a porous medium
M_t	mass of solute uptake from solution at time t for batch reaction of limited volume
M_∞	mass of solute uptake at infinite time for batch reaction of limited volume
P	pressure potential
Q	cumulative solute flux per unit area of surface
R_a	apparent retardation coefficient
R_d	retardation coefficient due to sorption
R_{md}	measured retardation coefficient
R_{om}	organic matter referenced retardation coefficient
S	concentration of solute sorbed by the soil
Se	solubility of organic solute in electrolyte solution
So	solubility of organic solute in free water containing no electrolyte
T	temperature in degrees K
U	energy required to initiate diffusion (for activated diffusion)
V	volume
X_1	fraction of solute sorbed by fast phase sorption sites in the two site sorption model
a	activity coefficient of the solute in solution

f	partitioning factor giving the fraction reduction in solute concentration between the soil pore space and the external saturating solution
$f_u(t)$	fraction of solute taken up from a batch equilibrium reaction at time, t
g	gravitational constant
k_2	rate coefficient for solute uptake by the slow sites in the two site sorption model
k_s	salting out or Setchenow coefficient
n	porosity
n_e	effective porosity or porosity available for diffusion
r	radius
t	time
x_p	volume fraction of pore space in the soil
x_s	volume fraction of solid phase in the soil
t_e	solute breakthrough time, as measured by the intercept of the steady state solute flux as $Q \to 0$.
v	flow velocity
κ	Boltzmann's constant
λ	ratio of the critical molecular diameter to the pore volume
η	solution viscosity
ρ	bulk density
ρ_s	particle density
ρ_w	solution density
σ	surface tension

τ_a	apparent tortuosity value

Chapter 1

INTRODUCTION

Diffusion is a fundamental process controlling transport of contaminants in soil materials. Diffusion rates can affect rates of movement of contaminants in soils, rates of sorption and desorption, biodegredetion rates and groundwater leaching rates in the soil.

In most cases, solute transport under macroscale conditions has been described by the convection dispersion equation. In the absence of sorption and potential gradients other than solute concentration and under constant water movement, the convection dispersion equation can be written as (e.g. Freeze and Cherry, 1979),

$$\frac{\partial C}{\partial t} = (D_{disp} + D_{diff})\nabla^2 C - v\nabla C \qquad 1.1$$

where C is the concentration of solute, t is the time, D_{disp} is the dispersivity, D_{diff} is the diffusion coefficient and v is the flow velocity. Dispersivity describes solute dispersion due to differences in path length and flow velocity within various pore spaces in the porous medium. Thus, as flow velocity decreases, dispersivity will become less important. Therefore, by this equation, as flow velocity becomes small, both v and D_{disp} become less important and diffusion becomes the dominant form of solute transport. The solute transport equation will then be reduced to Fick's second law of diffusion. For soil systems, there are two major conditions where this will happen:

1. Conditions of low hydraulic conductivity. In general, for materials with hydraulic conductivities less than 10^{-8} m s^{-1}, diffusion will become the dominant form of solute transport (e.g. Gillham et al, 1984; Rowe, 1987).

2. For aggregated and fractured systems, most of the water movement will be in the macropore region around aggregated materials. Within soil aggregates, transport becomes dominantly diffusion limited. Thus, flow in these systems can often be described by some form of a dual porosity model (e.g. Brusseau et al., 1994; Brusseau and Rao, 1989b) where interaggregate flow is dominated by convective flux and intraaggregate transport is dominated by diffusive flux.

In order to understand where problems in measurement of diffusion occur, it is useful to first categorize the types of diffusion coefficients and levels of resolution at which diffusion occurs. Four types of diffusion mechanisms have been identified in the literature(e.g. Li and Gregory, 1974; Robinson and Stokes, 1959; Shackelford and Daniel, 1991). Under differing circumstances, different mechanisms may become dominant in controlling diffusion in the deposit.

In a self diffusion system the species of interest is diffusing purely against its own concentration gradient. All other species in solution are maintained at the same concentration across the column. Self diffusion is generally the diffusion mechanism which is studied in most experimental designs. Because organic contaminants generally exist in low concentrations in water solution and most organic contaminants exist in a nonionic form, this is likely the most important diffusion process for the transport of organic contaminants in soil systems.

Tracer diffusion has also been described but seems to be a special case of self diffusion. In this type of design, a small amount of the diffusing substance is replaced with a measurable isotope of a different element (e.g., the replacement of NaCl in solution with a small amount of ^{42}KCl, Shackelford and Daniel, 1991) so the diffusion process can be monitored for the system. The tracer diffusion coefficient will be equal to that of the self diffusion coefficient provided the tracer behaves similarly in solution to the species of interest.

For diffusion of ionic species solute diffusion can take place as a result of both a concentration gradient and an electrical potential gradient. Thus, the diffusion rate of opposite charged ions in solution are often influenced by each other. This has been termed salt diffusion. If both ionic species have similar diffusion rates, the net rate of diffusion will be the same as that of the self diffusion coefficient. However, if the two solvated ions have different rates of diffusion, salt diffusion for the faster ion will tend to be slower than that of the self diffusion and the slower ion will tend to be faster than the self diffusion. Salt diffusion is common in disposal sites containing ionizable solutes, salt spills, and in experimental designs where the measured species is introduced as a soluble salt.

Counter-ion diffusion is similar to salt diffusion. In this case, however, the entire solution is electrically neutral but two like charged species are introduced at the opposite end of the column. Because of the development of an electrical potential across the column, the diffusion rate of each species will be controlled by the net diffusion of the other species in the opposite direction.

In some instances, diffusion may also be dependent on coupled flow processes. In this instance, diffusion may be influenced by the presence of electrical, thermal, or hydraulic gradients within the deposit. Coupled flow processes can counteract diffusion of a solute species in fine textured deposits with low porosity and high solute activity (e.g.

Olsen, 1969). In theory, this may occur because the formation of a concentration or electrical gradient in solution will create a potential gradient for both the solvent and the solute. If the potential for solvent flux is near to or greater than that of the solute, a net solvent flux may occur which will influence the rate of solute flux. Under extreme conditions, the solvent flux is highly favored and the potential gradient will be entirely offset by the movement of solvent rather than the movement of solute. Under these conditions, the porous material through which diffusion is occurring will form an impervious barrier to solute movement. In practice, coupled flow processes are generally insignificant in soils except for fine textured deposits with high concentration gradients. For bentonite clays, coupled flow processes may become important for movement of dominant cations from a saline deposit or saline disposal site (e.g. Greenberg et al., 1973). Cation diffusion may become affected by drag coupling as solution concentrations approach 10^3 mg L^{-1} for deposits composed dominantly of montmorillonite (calculated from Greenberg et al., 1973) or values near 10^6 mg L^{-1} for deposits composed dominantly of kaolinite (calculated from Olsen, 1969). For most ions, therefore, the required concentration is much higher than is found in any natural deposit or disposal systems and coupled flow will not be a dominant mechanism controlling solute transport.

There are 3 main levels of resolution at which diffusion can occur in a natural materials. The rate of diffusion in the deposit, and the influence of environmental parameters on the diffusion rate will depend on the level of resolution. In the following discussion and subsequent chapters, saturated conditions will be assumed within the soil. It is recognized that as conditions become increasingly unsaturated, diffusion within the larger pore space will become increasingly less important and diffusion processes within smaller pore regions and within the near clay surface region will become increasingly important. In addition, for organic moities, diffusion in air filled porosity will also become increasingly dominant as the soil dries.

Bulk diffusion is used here to define diffusion in pore spaces where the mean free path of the diffusive species is much smaller than the pore diameter. Under these conditions, the pore wall will have little influence on the diffusion coefficient. With the exception of macromolecules, most contaminant molecules in natural systems will be nanometers or smaller in size. The dominant pore spacing in natural soils (μm or larger) will therefore have little impact on the rate of diffusion of the molecule. The pore size distribution of the soil will tend to influence the apparent tortuosity value. Apparent tortuosity values have been reported to vary from about 0.5 to 0.01 over a wide range of geological deposits (Freeze and Cherry, 1979). Large amounts of soil compaction are required decrease the apparent tortuosity. (e.g., Oscarson and Hume, 1993). Thus, to a first order approximation, diffusion coefficients will remain relatively constant over a wide range of soil types and soil conditions if bulk diffusion is the dominant mechanism of solute transport.

Micropore diffusion (Knudsen's diffusion for gaseous systems) occurs when pore diameters are sufficiently small that pore wall interactions play a significant role in controlling overall diffusion. For gaseous systems, slower diffusion rates result from interactions of the solute with the pore wall directly. In theory, when the solute molecule contacts a pore wall, there is a brief period of sorption, after which time the solute is equally likely to reverse directions as continue on the same path. For liquid-solid media, the interaction of the solvent with the pore walls must also be considered. Pore solvent interactions could increase the fluid viscosity near the pore wall surface which would reduce diffusion rates near the surface of the pore wall (Nye, 1979). Electrostatic interactions between the diffusing species and a charged porous medium can also affect diffusion in the near surface region (Nye, 1979). This has also been termed restrictive diffusion (e.g. Chantog and Massoth, 1983; Prasher and Ma, 1977; Satterfield et al. 1973). Although the various parameters which can influence restrictive diffusion are not quantitatively defined, several empirical models have been developed which allow for some analysis of pore size range over which restrictive diffusion will be important. For micropore diffusion, the effective tortuosity tends to increase as the critical diameter of the solute approaches that of the pore size. Satterfield et al. found that the pore diffusion coefficient ranged from 4 to 30% of the bulk aqueous diffusion coefficient. The apparent tortuosity value could be estimated by following empirical relation:

$$\mathrm{Log}\frac{1}{\tau_a} = 0.37 + 2.0\lambda \qquad 1.2$$

where τ_a is the apparent tortuosity value and λ is the ratio of the critical molecular diameter to the pore diameter (ranged from 0.09 to 0.5 in the study). In a similar study, Chantong and Massoth (1983) found that the regression for the tortuosity value was described by the equation,

$$\mathrm{Log}\frac{1}{\tau_a} = 0.625 + 1.95\lambda \qquad 1.3$$

Although micropore diffusion will be slower than the bulk diffusion, both of the above relations suggest that the value will remain within a factor of 100 for the range of pore sizes analyzed. According to the above relations, micropore diffusion seems to become insignificant as the pore size approaches 20 to 30 times the diameter of the solute molecule. Thus except for macromolecular compounds, micropore diffusion will generally be important only for nanomenter and subnanometer size pore spaces. Micropore diffusion may be significant for the interlayer spacing of clay materials, within small cracks in mineral particles and diffusion of solute within organic materials.

Activated diffusion may occur as the pore size is near that of the solute molecule. Under these conditions, there can be a large repulsive energy between the solute molecule and the pore wall. To facilitate diffusion, a large activation energy may first have to be overcome. At this point, the use of diffusion to describe solute movement may not be completely valid since diffusion assumes a continuum of pores which may not be present in the material. This has been mentioned by Prasher and Ma (1977) for diffusion in zeolite material.

To a first order approximation, bulk diffusion can be assumed to follow Stokes' law for diffusion (Robinson and Stokes, 1959). This formula cannot be strictly applied since Stokes' law assumes that particle size is much greater than that of the solvent species. Alternatively, the application of Stokes' law does suggest some relationships, namely that the rate of solute diffusion will tend to be inversely proportional to solution viscosity and directly proportional to absolute temperature. For an activated diffusion process, however, diffusion must occur between potential holes in the medium which are approximately the same size as the molecule. Under these conditions, the solute molecule must overcome both the energy barrier required to move from one potential hole to another and an energy of disorder which describes the energy required to create a hole for the solute molecule within the diffusing medium (Nye, 1979). Both of these systems can, however be described by some form of the equation,

$$\mathbf{D}_{\mathbf{meas}} = \mathbf{const.}\ \mathbf{e}^{-U/\kappa T} \qquad 1.4$$

where D_{meas} is the measured diffusion coefficient, U is the energy required for diffusion, κ is Boltzmann's constant and T is the temperature in degrees Kelvin. Thus, whereas to a first approximation temperature has little influence on the rate of bulk diffusion, activated diffusion may be strongly influenced by temperature changes.

For diffusion in soil organic matter, it has been suggested that a polymer diffusion model may be more appropriate. The main difference between this model and those described previously is the a priori assumption of a fixed pore system in the previous models. For a constant solvent system with a dilute solute concentration, it is possible that solute-polymer interactions will be minimal. Under these conditions the polymer diffusion model may be described by Fickian diffusion. Much of the diffusion in polymers, however, may proceed by non-Fickian diffusion and may be influenced by such factors as swelling stress or strain on the polymer during solute movement, orientation of molecules within the polymer, and swelling or dissolution kinetics of the polymer itself within the solution medium (Frisch, 1980). Diffusivity of the penetrant will be a function of polymer density, rigidity of the polymer and cross-linking structure of the polymer (Rogers, 1965). Under these circumstances, it is likely that no one diffusion model will apply to all possible diffusion scenarios.

The interpretation of diffusion coefficients in the literature may also be confounded by the use of lumped parameters in the diffusion measurement. Shackelford (1991) summarizes some of the different measured diffusion coefficients reported in the literature and their physical interpretation.

Diffusion coefficients in pore systems are generally compared to the free water diffusion coefficient. In order to describe the difference in diffusive paths between the pore system and free water, a tortuosity factor, τ, is included. The measured diffusion coefficient is therefore defined as,

$$\mathbf{D}_{\mathbf{meas}} = \mathbf{D}_0\tau \qquad 1.5$$

By definition, the tortuosity factor only describes the difference in path lengths between a free water and a structured pore system, or, (Freeze and Cherry, 1979; Porter et al., 1960)

$$\tau = \left(\frac{\mathbf{L}}{\mathbf{L}_e}\right)^2 \qquad 1.6$$

where L is the path the molecule follows in free water and L_e is the path of the molecule in the porous medium. In all experimental designs, however, the actual value of τ cannot be quantified and the tortuosity value becomes a lumped parameter describing all differences between measured diffusion coefficients and those observed in free water. Some researchers use the more generic term, "impedance factor," to acknowledge the influence of factors other than tortuosity in the rate of diffusion through a porous medium. In general, tortuosities between 0.01 and 0.5 have been reported (Freeze and Cherry, 1979).

When sorption occurs in the soil, measurement of the diffusion coefficient independent of sorption can often be time consuming and in some instances, impossible due to the degradation or volatilization of the solute with time. In order to measure diffusion independent of sorption in the soil, equilibrium conditions must first be established between the solution phase and the sorbed phase within the soil pore solution. Thus diffusion measurements must either be conducted using long term experimental designs or the measured diffusion coefficient also includes a term accounting for solute sorption in the soil matrix. Due to the difficulty in experimental design required for the former approach the latter approach is usually accepted. For most experimental designs, the sorption coefficient is simplified by using a linear approximation of the sorption isotherm. Under these conditions, retardation due to sorption is given by,

$$\mathbf{R_d} = 1 + \frac{\rho}{\mathbf{n}}\mathbf{K_d} \tag{1.7}$$

where ρ is the bulk density of the soil, n is the porosity, and K_d is the linear distribution coefficient for the sorbed phase in the soil (ml g^{-1}). The measured diffusion coefficient then becomes,

$$\mathbf{D_{meas}} = \frac{\mathbf{D_0}\tau}{\mathbf{R_d}} \tag{1.8}$$

In the above equation, a second fitting parameter is introduced into the equation. In several instances, this has led to differences between estimates of K_d made from the diffusion experiment and those made from direct measurement of sorption. (e.g. Berry and Bond, 1992; Cheung, 1990; Jensen and Radke, 1988; Kim et al., 1993; Muurinen et al.

1985, 87; Myrand, 1992; Satterfield et al., 1973; Staunton, 1986; Staunton and Nye, 1983). It must be recognized, however, that within the above equation, the value of K_d is a fitting parameter which is only reliable if assumptions made on other values within the equation and assumed boundary conditions are correct for the given porous medium.

Surface diffusion is also invoked as a possible mechanism for diffusion in the soil. In many instances where retardation coefficients measured in separate experiments do not agree with that calculated based on equation 1.5, this fitting parameter is invoked to explain the difference in the two diffusion coefficients (Berry and Bond, 1992; Cheung, 1990; Jensen and Radke, 1988; Kim et al., 1993; Muurinen et al. 1985, 87; Satterfield et al., 1973; Staunton and Nye, 1983; Staunton, 1986). In theory, sorbed solute can diffuse along the surface of the sorbent if the solute molecule has sufficient energy to overcome the energy of sorption. Because the solute molecule is diffusing across the surface of the medium, diffusion in this phase would require a continuous surface sorbed phase throughout the path length to facilitate diffusion. If surface diffusion is present, the measured diffusion coefficient is a function of both sorbed phase and pore diffusion, or (Nye, 1979),

$$D_{meas} = \left(\frac{1}{1+\frac{\rho}{n}K_d}\right)\left(D_0\tau + \frac{\rho}{n}K_d D_{su}\right) \qquad 1.9$$

where D_{su} is the theoretical surface diffusion coefficient. In practice, D_{su} is usually determined as a fitting parameter in the above equation rather than being measured directly in the experiment.

In some instances, particularly for diffusion in charged clay materials, it is recognized that the total pore space within the clay system may not be available for diffusion of the solute molecule due to the interaction of the clay double layer with that of the solute. In this case, an effective porosity term, n_e is usually introduced. The introduction of this term divides the pore space into two distinct regions, one solution region near the surface of the clay in which the solute species is completely excluded from the water solution, and a second region away from the clay surface where solute concentration is the same as that in the bulk solution outside the clay pore space. Although some attempts have been made to quantify resistance factors near the clay surface (Nye, 1979), most reports which have used the effective porosity model use this value as a fitting parameter to explain either decreases in measured pore solution concentration with compaction of the clay (e.g. Cho et al., 1993; Oscarson and Hume, 1994; Oscarson et al., 1992) or changes in impedance factor for diffusion of solutes through clay materials (Kim et al. 1993). Thus, this term is often employed as a fitting parameter to account for discrepancies between observed results and calculated diffusion coefficients, or discrepancies between source reservoir concentrations and those measured within the clay pore space without any a priori knowledge that this factor is in fact controlling diffusion within the clay barrier.

For all diffusion models within either small scale (aggregate) or larger scale (impermeable barrier) research, most measurements of diffusion coefficients require some use of fitting parameters that presumably reflect the complex geometry of the medium. This is often done because several parameters, particularly apparent tortuosity in relation to diffusion through porous media (all scale), retardation coefficients (particularly in micro-scale research but occasionally in large scale research) and path length for diffusion (micro-scale research) are often difficult to quantify independent of the test data. Thus, these parameters often become fitting parameters for the particular diffusion model employed in interpreting the test data (Shackelford, 1991). Although these fitting parameters can be used to make a diffusion model describe the system, this cannot be used as proof that the particular value of these fitting parameters accurately describe the physical characteristics of the system.

For micro-scale (aggregate or particle) research, the concept of diffusion is often used to describe the movement of contaminants since uptake rate curves often have the appearance of diffusive rate curves given similar experimental boundary conditions and there is no direct evidence of other chemical or physical parameters which may be causing the observed rates (e.g. Brusseau and Rao, 1989b). The problem with this approach is that since no direct evidence is available for the assumptions used, the fit of the model cannot be used as direct proof of the mechanism.

Because of the use of various fitting parameters within the diffusion model, there still is much uncertainty as to what is actually controlling diffusive flux in the soil. In many instances, quantification of values is not directly possible so determination of mechanism must be conducted by process of elimination using concurrent results from different methods of diffusion measurement. In his 1990 thesis, Ball presents a discussion on the implications of the use of different assumptions to explain rates of sorption and how different models can be used to explain the same set of results. It is apparent that most of the assumptions cannot be directly eliminated based on a single data set, so many of the experimental results can be made to fit different models which may or may not have valid physical meaning. Thus, some sort of verification process must be conducted to simplify some of the assumptions which are being proposed about the nature of diffusion within the soil matrix.

The present research has attempted to rely on the generation of parameters outside of the experimental data set to obtain evidence that the proposed mechanism is a valid one for the material investigated. Thus, direct comparisons are possible between predicted and observed patterns of solute transport which can be used to verify the predictive equation.

In this dissertation the more generic term, apparent tortuosity is applied to the tortuosity parameter. This value represents a fitting parameter since not all the quantities which potentially can comprise this term can be quantified for the system. However, this value still does have some physical meaning within a given material. Thus, an estimate of the apparent tortuosity value for the given deposit should still be possible.

This thesis contains 5 chapters investigating the influence of diffusion on the transport of solutes in a clay textured matrix. The second chapter investigates the diffusion of naphthol and naphthalene in a weathered shale and montmorillonite clay. Experimental conditions were chosen which would allow for independent verification of the fitting parameters. Thus, checks could be employed which would test assumptions based on different diffusion theories.

Chapter 3 investigates the distribution of shale aggregates under batch equilibrium conditions. In this chapter, the intent was to determine a natural diffusion path length which may be present in sediment sorption studies. Where these studies have been conducted in the past, either relatively large aggregates were employed or aggregates were created from ground and homogenized soil material (e.g. Brusseau et al., 1994; Scow and Hutson, 1992; Scow et al., 1986,). These studies tend to hide inherent heterogeneity which may exist in the soil. Most of the water stable aggregates may be present in the sample due to heterogeneous distribution of materials in the deposit (e.g. Edwards and Bremner, 1967) which may become important in determining rates of solute uptake as aggregate size becomes smaller.

The fourth chapter combines the diffusional and aggregation data and attempts to investigate how diffusion may be controlling uptake of the contaminant in the material. In this chapter, some qualitative attempts were also made to characterize distribution of sorptive material. Because sorption of organic contaminants is dominantly associated with organic matter, the diffusional rate becomes very dependent on the placement of organic materials within the soil matrix. For a homogeneous system, values determined on the basis of macroscale analysis or average values determined for the whole material will also be accurate for microscale samples within the matrix. As the material becomes more heterogeneous, macroscale properties will become invalid when applied to the microsites. In this chapter, an attempt was made to assess what would happen to microsite diffusion as the deposit becomes increasingly heterogeneous, and how this compared to observed sorption rates in the material.

The final chapter offers a synthesis of work conducted for the thesis and how this work might fit into a general model describing solute uptake and desorption by the soil.

This chapter also contains some material related to discussions in chapter 1 and 3. Some of this material was thought to be too speculative in nature to be contained in the body of the thesis and thus was reserved for the discussion. However, as most literature information did tend to agree with the theories proposed, it was thought necessary to include some of this information in the final discussion. It is thought that this discussion should set possible investigations which could be used to test the theories developed.

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Chapter 2

Diffusion of 1-naphthol and naphthalene through clay materials: apparent exclusion of solute from the pore space of montmorillonite clay.

2.1 Introduction

Diffusion is the dominant process controlling migration of contaminants in fine grained deposits where hydraulic conductivity is low (e.g. Crooks and Quigley 1984; Desaulniers et al. 1981; Goodall and Quigley 1977; Johnson et al. 1989; Quigley et al. 1984). Diffusion processes will become the dominant form of mass dispersion at seepage velocities of about 10^{-7} cm s^{-1} and the dominant form of mass transport at seepage velocities of 10^{-8} cm s^{-1} (e.g. Gillham et al 1984; Rowe 1987). Since this situation is likely for clay barriers, fine grained natural deposits and soil aggregates, diffusion is an important transport process in pollutant migration.

Diffusion results in the transport of the contaminant plume along the concentration gradient due to random motion of the contaminant molecules. In the absence of advective flow, self diffusion of a molecule will be described by Fick's first and second laws i.e.,

$$\mathbf{J_s} = \mathbf{D_e} \nabla \mathbf{C} \tag{2.1}$$

and

$$\frac{\partial C}{\partial t} = \nabla \mathbf{J_s} = \mathbf{D_e} \nabla^2 \mathbf{C} \tag{2.2}$$

where,

$\mathbf{J_s}$=the flux of solute per unit area per unit time

$\mathbf{D_e}$=the solute diffusion coefficient

C=concentration in soil pore solution

Methods of diffusion measurement have been reviewed previously (Shackelford, 1991). Because of the difficulty in defining the nature of the diffusing medium, most experimental setups are designed to measure an effective diffusion coefficient,

$$D_e = D_0 \tau_a \qquad 2.3$$

where,

D_0=free water diffusion coefficient

τ_a=the apparent tortuosity value

For solute molecules which sorb on the medium, it is often difficult to design an experiment that can independently measure the diffusion and sorption coefficients, so the measured diffusion coefficient often includes a term describing retardation due to sorption.

Ideally, tortuosity is a geometric factor which accounts for the travel path of a solute molecule in the soil pores. For diffusion measurements, however, the tortuosity factor cannot be directly measured. Therefore, this factor is used to account for all differences between the measured effective diffusion coefficient and the free water diffusion coefficient. Thus, the more generic, "apparent tortuosity" term is applied here. Because the apparent tortuosity value is difficult to measure in a complex medium such as soil, no attempts have been made to justify the estimated parameter with that present in the actual medium. Some authors have attempted to use free water diffusion coefficients to estimate apparent tortuosities of the clay medium (e.g. Miyahara 1991; Oscarson et al 1994). These results indicate an apparent tortuosity of around 0.1 for low molecular weight solutes. This value seems to compare reasonably with the difference between clay and free water diffusion coefficients for several species (e.g. Oscarson et al. 1992; Sawatsky and Oscarson, 1991a). Depending on bulk density, apparent tortuosity between 0.05 and 0.2 seem reasonable for clay materials (Oscarson and Hume 1994).

Measurements of the diffusion rate of organic moities through clay barriers have been conducted only within the last few years (e.g. Barone et al. 1992; Myrand et al, 1992). Because direct soil analysis of organic contaminants is difficult, measurements have been made using a form of the source reservoir technique proposed by Rowe et al. (1988). For this method, boundary conditions must be established linking the source reservoir with the clay cell. This generally requires the assumption that the solution matrix within the clay pores at the boundary is the same as that of the exterior solution and that solute flux within the clay cell is given by the change in solute concentration in the external solution. Since steady state conditions are not established across the clay cell, retardation due to sorption must also be accounted for in the method. The original method called for analysis of both the rate of change of solute concentration in the source reservoir with time and the concentration profile within the clay cell at the end of the experiment. This method allowed for direct verification of the effective diffusion coefficent, D_e, the retardation coefficient due to sorption, and validity of the boundary conditions. For organic contaminants, solute concentration within the cell has not been analyzed due to the difficulty in measuring the pore solution concentration. Thus, these model parameters have not been directly verified. In some instances, this has led to large discrepencies between diffusion coefficients measured experimentally and those estimated based on free water diffusion, tortuosity and sorption in the soil material (e.g. Myrand et al. 1992). The discrepency could be due to three possible factors; an incorrect analysis of tortuosity within the deposit, a change in sorption due to compaction of the clay cell (suggested by Myrand et al. 1992), or a restricted entry of solute molecules into the clay pore space from the free solution.

There is growing evidence to suggest that clay size materials can restrict entry of some ionic species into the pore space (Oscarson 1994; Oscarson and Hume 1994; Oscarson et al. 1992). This may also be true for the entry of organic moieties into the pore space of a clay barrier. If solute exclusion does occur, this could explain much of the difference between observed and calculated results for both inorganic and organic moities. To examine this question, an experiment was conducted to independently measure the diffusion coefficient and the sorption of 1-naphthol and naphthalene in a weathered shale.

2.2 Materials and Methods.

To investigate diffusion of 1-naphthol and naphthalene, the diffusion coefficient of the compound was measured with and without the influence of retardation due to sorption in the clay. To compare the two values, retardation coefficients were estimated based on sorption coefficients determined by batch equilibrium. Discrepencies between diffusion coefficient measurements were investigated based on the inherent assumptions in each calculation and the pore solution concentration of naphthalene in a structured non-sorbing (montmorillonite clay) medium.

2.2.1 Diffusion Experiments

Samples of a weathered shale material, deposited during the Cretaceous era were used for the study. Shale was collected along the North Saskatchewan river near Devon, Alberta.

The clay sized fraction in the shale was dominantly montmorillonite clay The shale had a neutral pH and contained 1.6% recalcitrant organic carbon which was dominantly responsible for the sorption of the organic compounds tested. Other physical and chemical properties of the shale material have been listed previously (Qualizza, 1994). Reference Montmorillonite clay (STx-1) was obtained from the Clay Minerals Society Source Clay Repository in Columbia, Missouri. Prior to use, exchangeable cations were replaced with Ca^{2+}, samples were air dried and ground to <106 μm.

All stock solutions were prepared in a 0.01M $CaCl_2$ solution containing 10^{-5} M $HgCl_2$ to suppress biological activity during the experiment. Prior to introduction into the diffusion cell, pH of the solution was adjusted to pH 7.0 (near that of the clay samples) using $Ca(OH)_2$. For the source reservoir, 1-naphthol and naphthalene were dissolved into the stock solution to obtain a final solution concentration of 1.4 mM and 0.15 mM respectively. Solutions were sealed in a glass storage bottle (fig 2.1a) and connected to the diffusion cell. To avoid vacumn buildup in the solution reservoir, bottles were vented daily. Although some loss of naphthalene and 1-naphthol did occur from stock solution reservoirs during the experiment, replacement of the stock solution every 4 days for 1-naphthol and every 2 days for naphthalene was found to be adequate to maintain the solution concentration within 95% of the starting solution concentration.

Diffusion cells used were based on a design described by Sawatsky and Oscarson, 1991 with some modifications (fig 2.1b). Clay cells consisted of a stainless steel ring (i.d.=4.7 cm, length=0.4 cm) which was sandwiched between two porous stainless steel frits (mean pore diameter=40 μm) and sealed into the diffusion cells using Teflon® O-rings. Frits were in direct

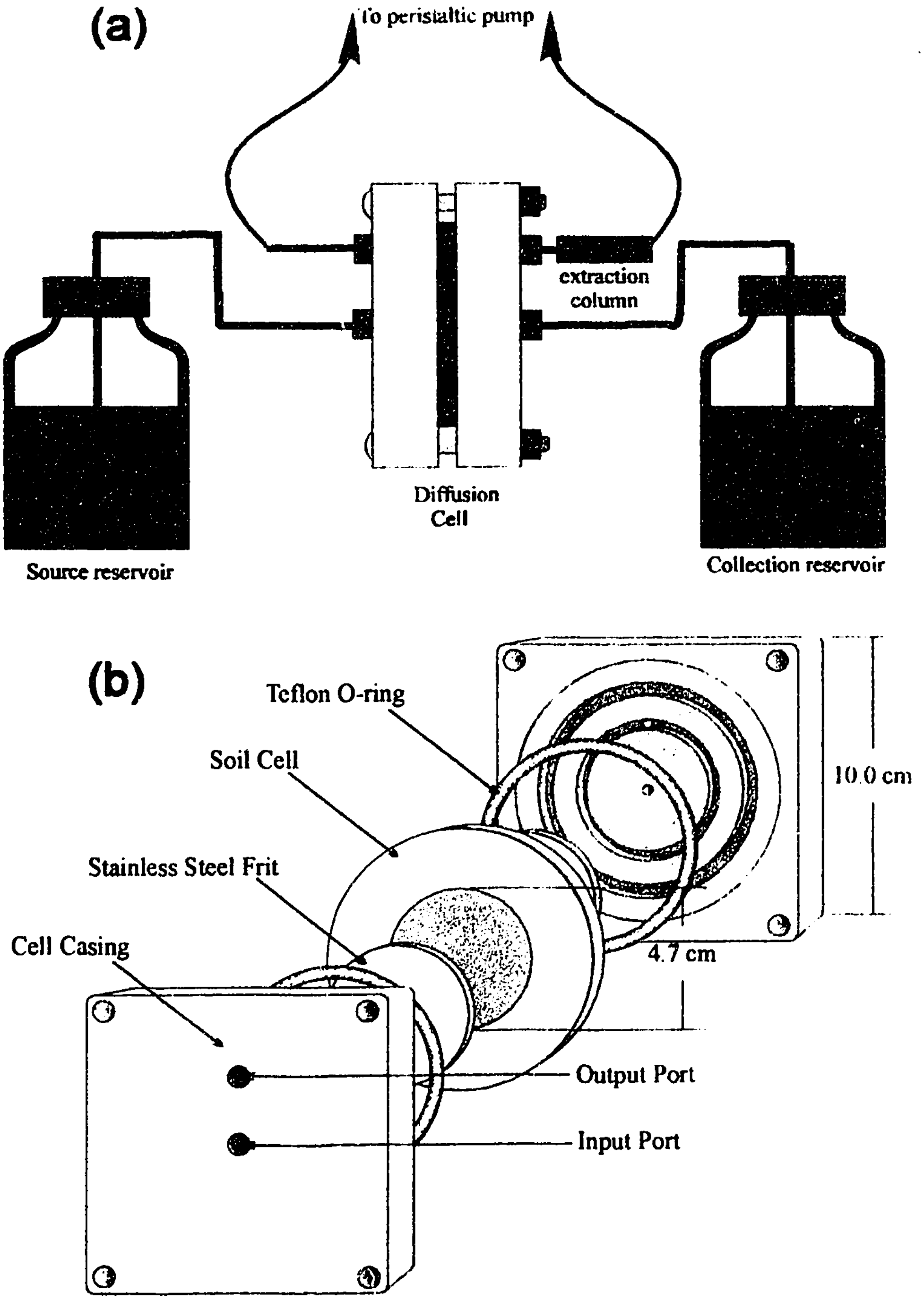

Figure 2.1 a,b Diffusion cell diagram showing the operating cell (a) and the cell components (b)

contact with the input port, at the center of the cell and the output port, on the outer periphery. A flow channel was grooved along the outer circumference of the cell to distribute flow evenly across the sample surface (fig 2.1b).

Prior to compaction, $CaCl_2$ solution was added to the sample to bring the moisture content to 95% calculated saturated moisture content at the compacted bulk density. The sample was then equilibrated for 24 hrs. The sample was compacted in the stainless steel rings to the desired bulk density using a hydraulic press. After compaction, diffusion cells were assembled and soils were placed in contact with stock $CaCl_2$ solution for 1 week prior to use. Nowak (1984) reported that saturation occurred in less than a week for non-wetted bentonite samples at ρ_b=2 Mg m^{-3}.

After saturation, 1-naphthol or naphthalene was introduced into the source reservoir. Source solution was passed over one surface of the diffusion cell at an average rate of 150 ml day^{-1}. At the opposite end of the cell, the $CaCl_2$ stock solution was passed over the surface of the diffusion cell at a rate of 20 ml day^{-1}. Stainless steel tubing was used from the reservoir to the input port and from the output port to 2 cm past the output port. A Piper model PC-14T peristaltic pump connected to the output port of the diffusion cell was used to maintain constant solution flow.

After the experiment, soil samples were removed from the diffusion cell, dried at 110°C and weighed to determine moisture content and bulk density of the cell.

2.2.2. Solution Analysis

After passing through the diffusion cell, solution from the collection reservoir was passed through 2 Alltech Maxi-clean disposable extraction columns which were placed together in series. Each column contained 900 mg of C18 stationary phase. Preliminary analysis with naphthalene and 1-naphthol indicated that the breakthrough volume was not reached for the maximum solute concentration of the present experiment. Columns were removed daily and sorbed solute was extracted from the column by back washing with Dichloromethane. Solute concentration in the extracting solution was determined using gas chromatography.

Solute concentration in the source reservoir was determined at the time of stock solution preparation and again just before stock solution replacement (4 days for 1-naphthol and 2 days for naphthalene). At the time of preparation, solute concentration was determined directly on the bulk solution. Prior to replacement of the source reservoir a 1 to 2 ml solution aliquot was collected from the output port of the diffusion cell. Solute was extracted with Dichloromethane and the concentration of solute in the reservoir was determined using gas chromatography.

2.2.3 Solute extraction from clay pores

For montmorillonite clay, naphthalene concentration in the clay pore space was determined immediately after the diffusion experiment. A 2.5 cm diameter core was extracted from the center of the clay plug (adjacent to the input port). The core was placed in a stainless steel ring fitted with a screw press containing a Teflon® plunger. The clay was then sectioned into 0.5 mm slices. Each slice was placed in a glass vial and mixed with 5 ml of distilled H_2O.

Samples were sealed with aluminum lined screw caps, shaken for 24 hrs at 300 rpm and 25±1°C and centrifuged at 2000 g for 30 min. Concentration of naphthalene in the extraction solution was determined using purge and trap G.C. analysis. For the calculation of pore solution concentration, it was assumed that naphthalene was only present in the clay pore solution (i.e. that no sorbed naphthalene was extracted during analysis). Previous analysis had indicated that sorption of naphthalene on montmorrillonite clay was less than 0.3 ml g^{-1}. Control 5 ml. solutions containing known concentrations of naphthalene were subject to the same procedure to ensure that no loss of naphthalene occurred during extraction.

2.2.4. Calculation of Diffusion Coefficients

The advantage of the steady state method used here is that it allows for the separate calculation of two diffusion coefficients from the same data set. These coefficients are calculated based on different assumptions and react differently to erroneous boundary conditions, thus allowing for direct analysis of the validity of established boundary values. If constant source and collection reservoirs are maintained throughout the experiment, solute flux per unit cross-sectional area will approach a steady state as $t \rightarrow \infty$. The solute flux across the clay barrier is then given by the equation (Crank, 1975),

$$Q = \frac{D_s C_0}{L}\left(t - \frac{L^2}{6D_t}\right) \qquad 2.4$$

where,

Q=cumulative flux of solute per unit area

C_0=concentration of solute in the source reservoir

L=path length

D_s=diffusion coefficient estimated on the steady state flux of solute through the soil

D_t=diffusion coefficient estimated by the time lag method

The slope of the line of cumulative solute flux per unit area with time will give a steady state diffusion coefficient independant of sorption, or,

$$D_s = D_e n_e = -\frac{\Delta Q}{\Delta t}\frac{L}{C_0} \qquad 2.5$$

where,

n_e=effective porosity or porosity available for diffusion (generally assumed to be equal to total porosity)

In addition, an x intercept time, t_e, can be defined at Q=0. The value of D_t is then,

$$D_t = \frac{D_e}{R_d} = \frac{L^2}{6t_e} \qquad 2.6$$

where R_d describes the retardation due to sorption. If sorption is fast relative to solute flux and linear with concentration, the retardation coefficient, R_d, can be defined as,

$$R_d = 1 + \frac{\rho}{n}K_d \qquad 2.7$$

where,

ρ=bulk density

n=porosity

K_d=ratio of the concentration of solute in the sorbed phase to that of the solution phase.

Equation 2.4 is subject to the following initial and boundary conditions:

$$C_p(0 < x \le L, 0) = 0,$$

$$C_p(0, t) = C_0$$

$$C_p(L, t) = C_r \cong 0$$

where,

C_p=solute concentration in the pore solution of the cell

C_r=solute concentration in the collection reservoir.

In the above equations, D_s is independent of sorption. Therefore if the batch measured sorption coefficient is different from that of the compacted material, only the predicted value of D_t should be affected. Alternatively the effective porosity term, n_e, only affects the measurement of D_s. Thus if effective porosity is lower than the total clay porosity, measured values of D_s will be lower than that predicted by D_e but the value of D_t should not be affected. Although the calculation of D_s and D_t are subject to the same boundary conditions, the effect of an incorrect boundary condition will be different for the two estimates. If solute is partially excluded from the clay pore space, $C_p(0,t)<C_0$, and the measured value of D_s (equation 2.5) will be lower than predicted based on equation 2.3. However, D_t will not be directly affected. If the external solution concentration is used to predict sorption in the clay cell, the retardation coefficient will be overestimated and the measured value of D_t will appear larger than the actual value.

2.2.5 Determination of K_d

Sorption and desorption isotherms were determined using batch equilibrium techniques in a solution similar to that used in the diffusion trials. Solution:solid ratio for shale material (22:1) was chosen to ensure that final solution concentration remained in the range of 20 to 80% of the starting concentration (Bowman and Sans, 1985). Labelled solutions were prepared by adding about 100 Bq ml^{-1} of the ^{14}C labelled compound to stock 1-naphthol (100 to 750 ug ml^{-1}) or naphthalene (5 to 22 ug ml^{-1}) solutions. Triplicate soil samples were weighed into individual glass centrifuge tubes which were then filled with the stock solution. Tubes were sealed with minimal headspace using Teflon® lined screw caps and placed into a LAB-line Orbit Environ-shaker. Samples were oscillated at 300 rpm and $25 \pm 1^{\circ}$ C for periods of between 2 and 140 hr (naphthalene) or 2 hrs to 2 weeks (1-naphthol). After the equilibration period, samples were centrifuged at 2000 g for 30 min and a 1ml aliquot of the solution was removed, mixed with 15 ml. of Optiphase Hisafe 3 scintillation cocktail and the concentration of ^{14}C in the sample was determined by liquid scintillation counting. Longer time periods were used to determine the rate of sorption in the soil matrix. The sorption coefficient was calculated based on the difference between initial and final concentrations of solute in the supernatant. Preliminary tests revealed no measurable uptake of the solute by the glass centrifuge tubes.

2.2.6 Long-term solute stability

After 2 weeks sorption for 1-naphthol, 4 random samples were selected to check for compound purity. Concentration of solute in the solution was measured using Gas Chromatography and compared with that predicted by ^{14}C scintillation counting.

To measure the ^{14}C mass balance of the sample, 4 random samples were selected after a two week and 140 hr. sorption period for 1-naphthol and napthalene respectively. After centrifuging and decanting excess water, approximately 100 mg of wet soil was removed from the cell and combusted in an OX300 Biological Oxidizer. Labelled carbon in the gas stream was collected and measured using liquid scintillation counting. Moisture content was determined on the remaining soil by oven drying at 110^0 C. The amount of ^{14}C collected in the biological oxidizer was then compared against the calculated amount based on the amount of ^{14}C lost from solution during the sorption period.

To measure long-term stability of sorbed 1-naphthol, soil subsamples from 3 of the sorption cells were placed as a slurry on a stainless steel frit with (average pore diameter=0.5mm) and sealed into an HPLC filter column. Water solution was passed through the clay slurry using a Waters, 501 HPLC pump for 14 days. Effluent was collected and 1-naphthol concentration in the effluent was determined by extraction with dichloromethane and analysis by Gas Chromatography.

2.3 Results

2.3.1 Concentration of napthalene in the pore space

Because of the difficulty in accurately sectioning the clay plug into 0.5 mm slices, there was considerable error associated with the determination of the concentration profile of naphthalene in the montmorillonite clay (fig 2.2). Slices taken immediately adjacent to either reservoir were influenced by free solution on the surface of the clay cell and were not included in the analysis. Although there was considerable scatter in the pore solution concentration, the concentration profile within the clay was described reasonably well by a straight line plot. Thus the use of a linear pore solute concentration gradient across the clay cell (equation 2.5) seems reasonable. Based on the best fit straight line plot, C/C_0 within the clay pore space ranged from 0 immediately adjacent to the collection reservoir to 0.4 adjacent to the source reservoir. A value of $C/C_0 < 1$ at the source reservoir interface was predicted for all three cells, suggesting some form of solute exclusion was occurring. Since 1-naphthol was found to sorb onto montmorillonite clay, no similar profile could be obtained for the concentration of naphthol in the clay pore pace.

2.3.2 Measurement of D_s and D_t

For naphthalene and naphthol in the shale material, t_e ranged from 11 to 29 days (fig 2.3a,b). The cumulative flux profile for naphthalene in montmorillonite clay was similar to that in the weathered shale except the breakthrough time of naphthalene in montmorillonite clay was between 2 and 3 days. For diffusion in montmorillonite, the proximity of t_e to the x,y intercept meant that small variations in measurements would result in large variations in the estimated value of t_e. Therefore, the calculated D_t value in montmorillonite clay was not considered to be reliable.

Representative cumulative flux curves for naphthalene and 1-naphthol are shown on figures 2.3a,b. For both naphthalene and 1-naphthol, approximately 500 hrs was needed before steady state conditions were obtained.

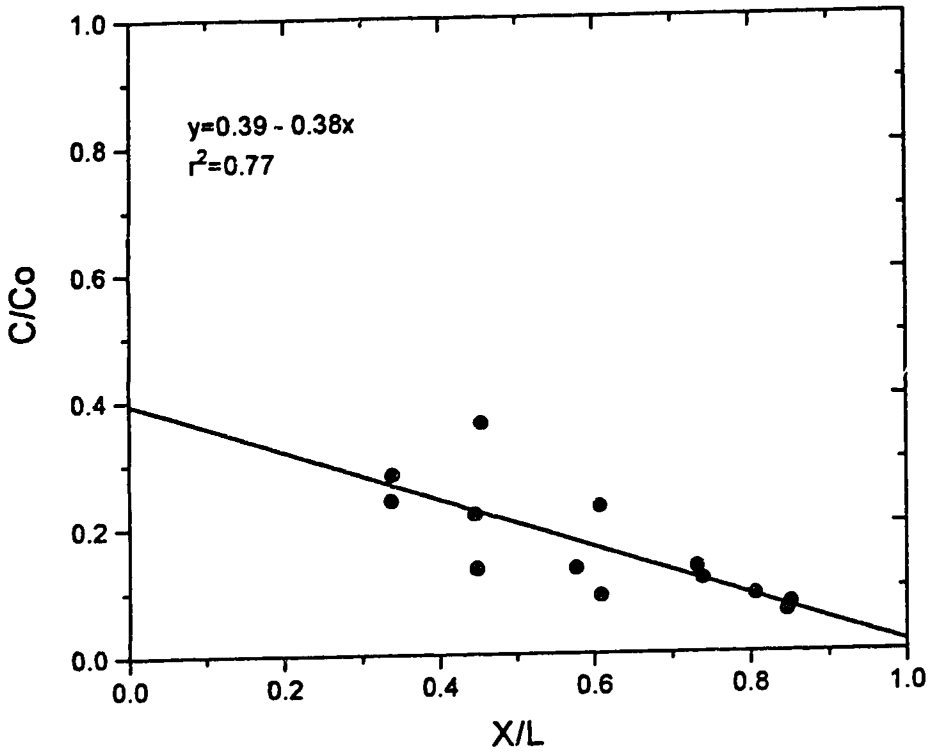

Figure 2.2 Concentration profile for naphthalene in montmorillonite clay at the end of the experiment. Results of three diffusion cells.

Calculated values of D_s and D_t are listed in table 2.1. Calculated diffusion coefficients generally varied within a factor of 2. This type of variation has been reported previously for the steady state method (e.g. Cho et al, 1993b). For the diffusion of 1-naphthol in the shale material, the values of both D_s and D_t did not vary significantly over the soil density range of 1.2 to 1.6 Mg m^{-3}. The value for t_e in compacted clay might be expected to vary over a factor of 2 for the given density range (Oscarson and Hume, 1994). This, however, is less than the variation in measured diffusion coefficients.

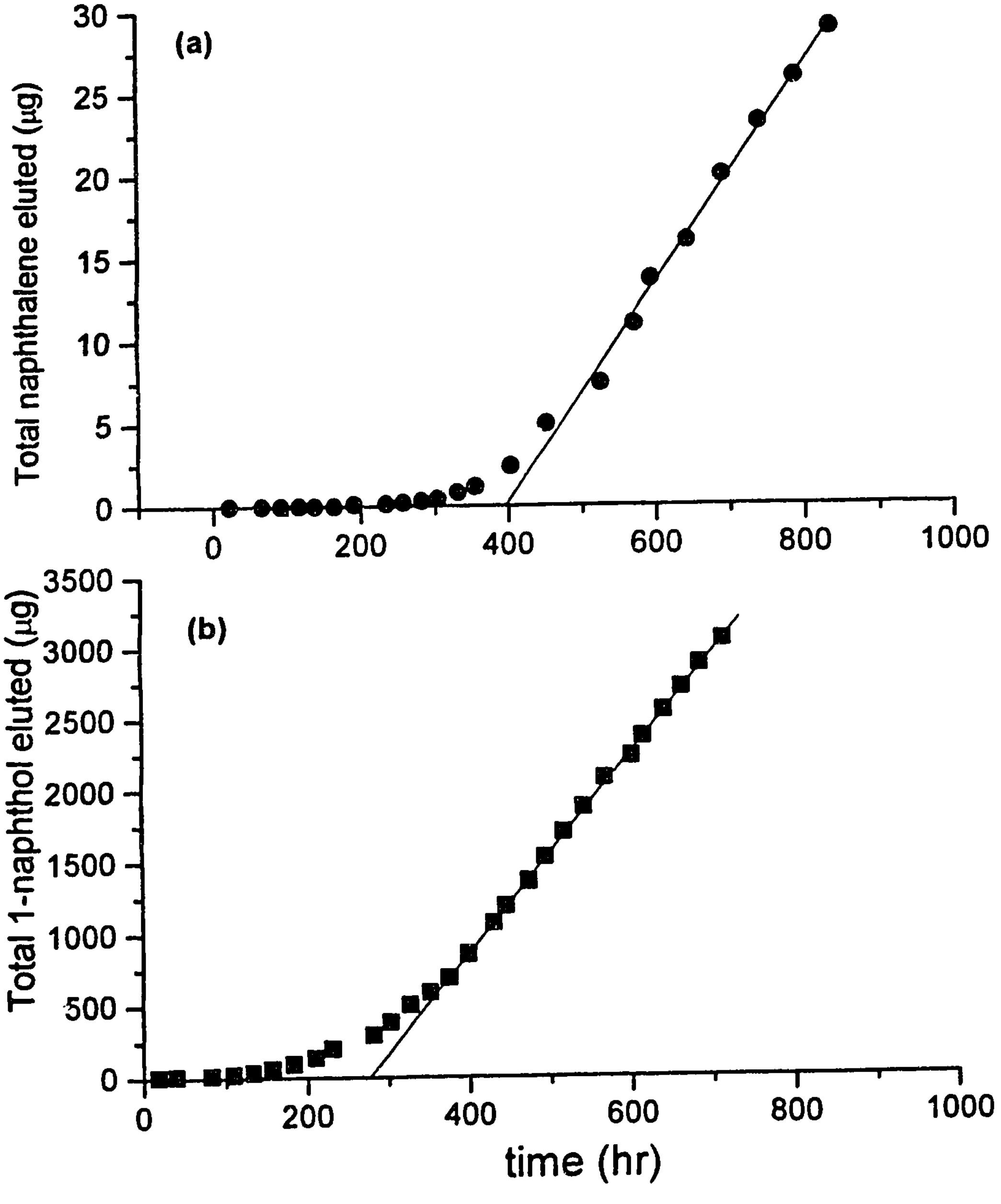

Figure 2.3 Cumulative flux for (a) naphthalene and (b) 1-naphthol through the compacted shale cell as a function of time.

Values of D_s were greater than D_t except for diffusion on napthalene in montomorillonite clay (table 2.1). For the shale material, measured values of D_s were on average 8 and 1.4 times greater than that of D_t for 1-naphthol and naphthalene respectively. From equations 2.5 and 2.6, the relationship between D_s and D_t is given by;

$$\mathbf{D_s = D_t R_d n_e} \qquad 2.8$$

If all other assumed parameters in equations 2.5 and 2.6 are correct, this would yield an average predicted R_d of 17 and 3 for 1-naphthol and naphthalene respectively (table 2.1).

2.3.3 Determination of K_d

For naphthalene, sorption on the shale seemed to reach equilibrium after approximately 24 hrs. No significant difference in measured sorption coefficients was observed for periods between 24 and 140 hours thus only 24 hour data are presented here. The predicted K_d for naphthalene in the shale after 24 hr. was 38 ml/g (fig 2.4). Previous sorption equilibrium tests conducted on the same soil had predicted an average equilibrium sorption coefficient of 27 ml g^{-1} for the same concentration range (Qualizza, 1994) (fig 2.4). Batch equilibrium experiments conducted in the present study and previous measurements (Qualizza, 1994) indicated little or no sorption of napthalene in montmorillonite clay.

Table 2.1 Measured diffusion coefficients for 1-naphthol and napthalene in weathered shale and Ca^{++} saturated montmorillinite clay.

1. 1-naphthol diffusion in weathered shale

Density Mg m^{-3}	D_s $\mu m^2 s^{-1}$ (a)	D_t $\mu m^2 s^{-1}$ (b)	R_d predicted (c)	R_d measured (d)	f (e)	D_e from D_s $\mu m^2 s^{-1}$ (e)	D_e from D_t $\mu m^2 s^{-1}$ (f)
1.23	30.2	1.81	31.1	90	0.40	142	66
1.25	13.4	1.64	15.5	93	0.40	64	62
1.3	8.94	1.56	11.2	100	0.40	44	63
1.38	22.8	2.74	17.4	113	0.40	120	125
1.39	20.4	2.96	14.5	115	0.40	108	137
1.42	16.3	2.47	14.2	120	0.40	88	119
1.56	6.33	1.13	13.6	149	0.40	38	67
1.57	7.52	1.22	15.1	151	0.40	46	74
1.58	6.35	1.05	15.0	153	0.40	39	65

2. naphthalene diffusion in montmorillonite clay

1.41	7.01	11.5	1.3	1	0.40	37	11
1.47	5.99	13.1	1.0	1	0.40	33	13
1.48	7.72	9.7	1.8	1	0.40	44	10

3. naphthalene diffusion in weathered shale

1.48	2.15	1.92	2.5	92	0.40	12	80
1.49	2.65	1.61	3.8	93	0.40	15	68
1.51	2.48	1.80	3.2	96	0.40	14	79

[a] calculated by equation 2.5.

[b] calculated by equation 2.6.

[c] calculated by equation 2.8

[d] calculated by equation 2.7: K_d values are given in the text, n is estimated based on soil density, assuming average particle density=2.65 Mg m^{-3}.

[e] estimated from naphthalene concentration extracted from the pore solution of montmorillonite clay

[f] calculated from equation 2.14

[g] calculated from equation 2.17 substituted into equation 2.6

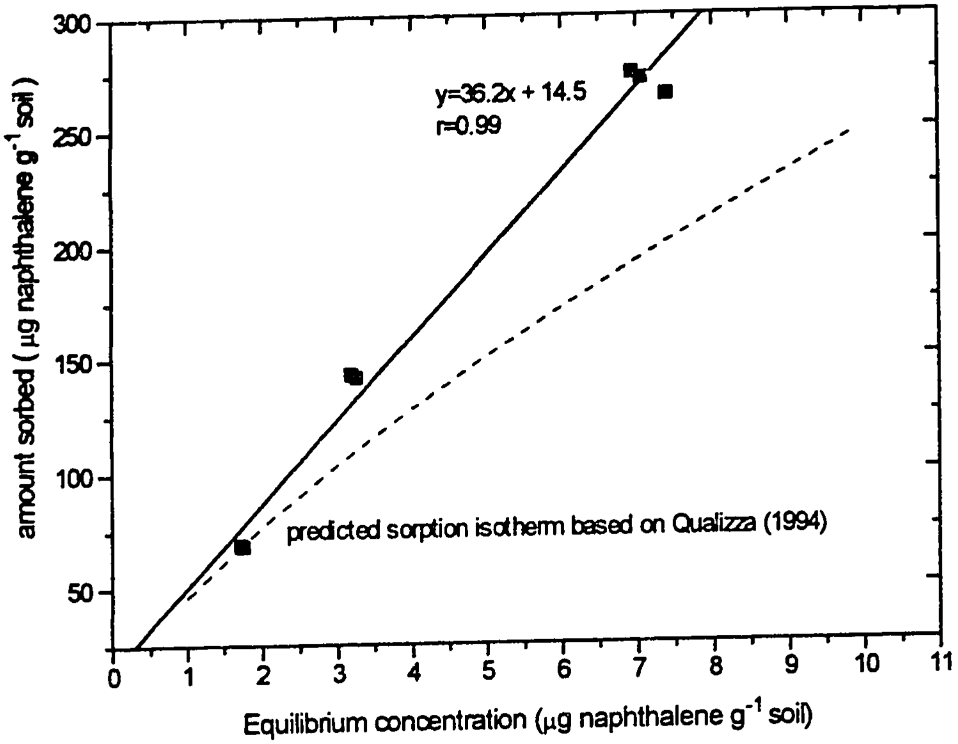

Figure 2.4 Equilibrium sorption isotherm for naphthalene on the weathered shale material. Sorption time = 24 hr.

For 1-naphthol, uptake of solute by the clay in batch equilibrium experiments continued for at least two weeks after addition (fig 2.5). Because of equilibrium sorption isotherms could not be established during the test period and diffusion experiments were conducted over a period of approximately 6 weeks, some estimate in the change in sorption between 2 and 6 weeks was desired. A two-site sorption model proposed by Karickhoff (1980) was used to analyze the sorption results. This model can be used to predict rates of sorption for reversible chemical and diffusion controlled reactions (Brusseau and Rao, 1989). Model predictions suggested that the sorption at 2 weeks accounted for over 90% of the total sorbed concentration at 900 hrs or the maximum time period in which clay was in contact with solute during the diffusion experiment. When the model was used to predict the a 2 week sorption isotherm based on a twenty four hour sorption isotherm generated for the same soil (Qualizza, 1994) model prediction was found to agree reasonably well with present results (fig. 2.6).

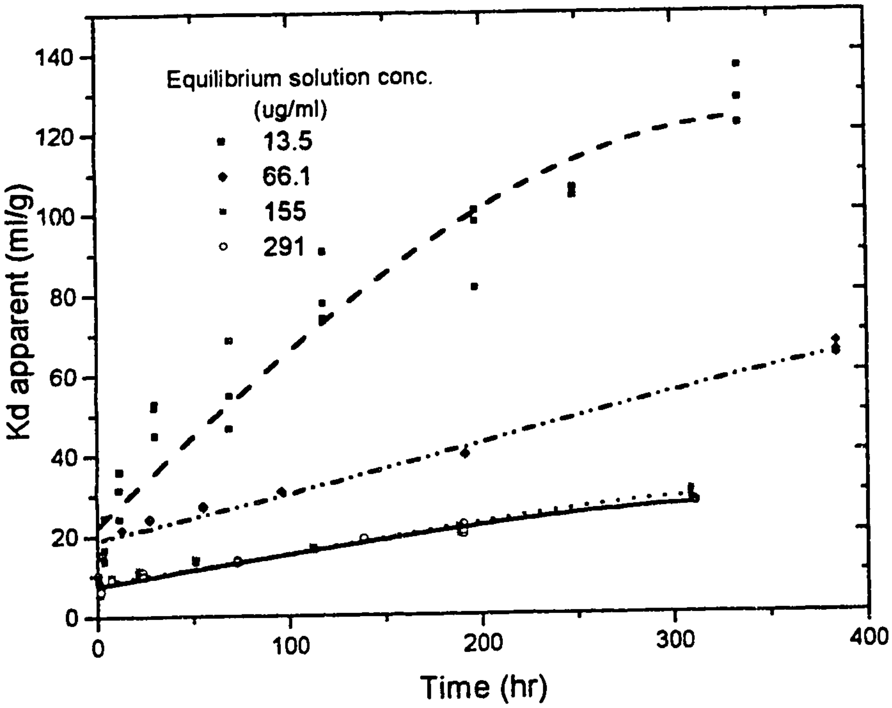

Figure 2.5 Apparent distribution coefficient for the sorption of 1-naphthol in the weathered shale as a function of equilibration time and starting solution concentration.

For both naphthalene and 1-naphthol, some non-linearity of sorption isotherms was observed. Sorption of 1-naphthol in the weathered shale could not be described accurately by a linear sorption isotherm (fig. 2.6). For naphthalene, sorption was somewhat higher than that predicted by Qualizza (1994) (fig. 2.4). Since a comparison between estimates of D_s and D_t

suggested little sorption in the clay cell, conservative sorption estimates were accepted for naphthalene and 1-naphthol. Thus distribution coefficients of 27 and 39 ml g^{-1} were accepted for naphthalene and 1-naphthol respectively (eq. 2.7). It is believed that this will tend to underestimate actual sorption over part of the clay cell.

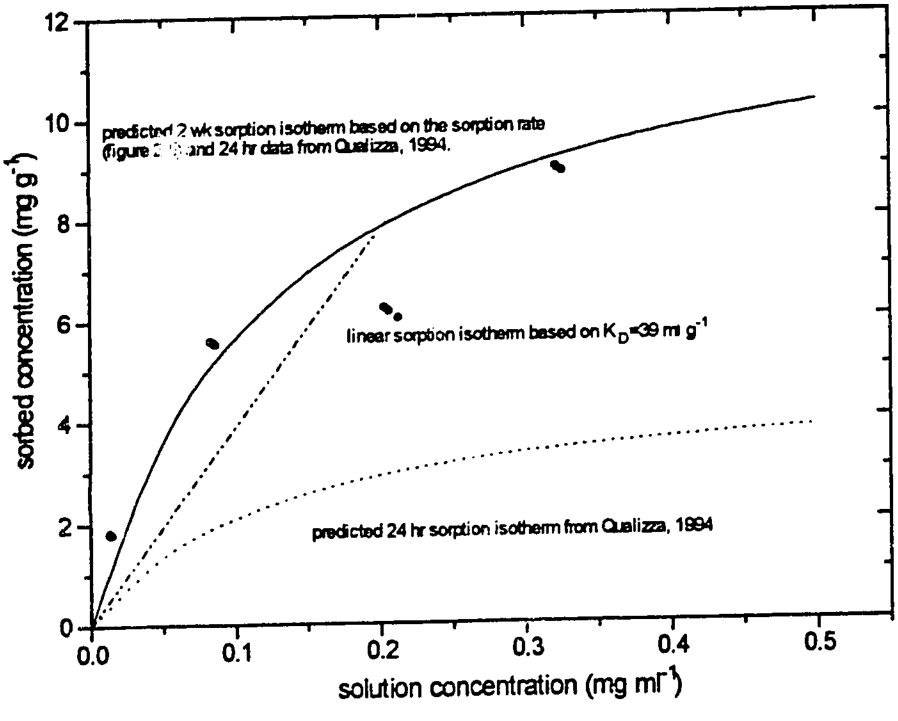

Figure 2.6 Measured sorption coefficient for 1-naphthol on weathered shale after 2 weeks sorption as compared with results of Qualizza (1994).

2.3.4 Solute stability

Gas chromatography analysis of 1-naphthol solution after 2 weeks and naphthalene after 24 hrs was not significantly different from that measured by liquid scintillation counting (pr = 0.05). Measured solute concentrations by G.C. were all within 5% of the predicted concentration using scintillation counting.

Solute extraction of 1-naphthol during the two week period after sorption accounted for 70 to 90% of the total estimated contaminant sorbed on the clay (range of triplicate analysis). Although not all 1-naphthol was recovered, detectable amounts of solute were still being leached from the cell after 2 weeks. Most of the solute sorbed in the clay, therefore, was believed to remain in the original form during the experimental period.

For soil samples subjected to combustion at the end of the sorption experiment (140 and 300 hr. for naphthalene and naphthol respectively), total ^{14}C collected from the shale accounted for at least 95% of the predicted ^{14}C concentration from batch equilibrium results. Since the organic moiety sorbed onto the shale remains relatively stable over long periods of time, and average molecular residence time in the pore space will be relatively short (less than 24 hr) for the 0.4 cm cell length, diffusion results were believed to be relatively reliable.

2.4 Discussion

2.4.1. Assumption of linear sorption isotherms

Where sorption has been mesured, sorption isotherms have been modelled by assuming sorption by the clay was directly proportional to solution concentration. It is recognized from figures 2.4 and 2.6 that neither sorption isotherm was linear with solution concentration. The assumption of linearity in this case will lead to two errors. If the sorption isotherm is linear, solute breakthrough fronts through the column will be symetrical wheras the isotherms depicted in figures 2.4 and 2.6 will result in a steeper initial breakthrough front tailing as steady state is approached. Additionally, the predicted linear sorption isotherm for both naphthalene and 1-naphthol was based on the predicted sorption coefficient at the maximum solute concentration within the diffusion cell. Where the solute concentration is below this value, sorption will tend to be greater than predicted by the linear isotherm. When nonlinear isotherms were used, it was found that the precision was not greatly improved. Additionally, diffusion the inclusion of a non-linear term resulted in a greater difference between observed and predicted results rather than a smaller difference. Although it is recognized that sorption isotherms were not linear, the inclusion of a non-linear term did not seem to add to the disscussion but did add confusion to the presentation of results. Thus only analysis using the assumption of linear sorption isotherms is presented here.

2.4.2 Variation in estimates of D_s and D_t

Results of the diffusion analysis suggested that some form of solute exclusion was taking place in the clay cell for both 1-naphthol and naphthalene. The concentration of naphthalene in the pore water of the non-sorbing (montmorillonite clay) medium suggested that solute movement in the pore water was being restricted by the clay material. In addition, although values of D_s in the weathered shale material were greater than D_t, the difference in the two values was not great enough to account for the sorption coefficients measured in batch equilibrium experiments. When values of D_s and D_t were compared directly using equations 2.5 and 2.6, the predicted retardation coefficient was 8 and 30 times lower than that estimated by batch equilibration experiments for 1-naphthol and naphthalene respectively (table 2.1).

Measured values of D_s (table 2.1) suggested very low apparent tortuosity coefficients. For non-hydrated molecules, free water diffusion coefficients can be estimated based on the molecular volume (Wilkes and Chang, 1955). If the diffusion coefficient of benzene is assumed to be 1020 $\mu m^2 s^{-1}$ (Bonali and Witherspoon, 1968), the free water diffusion coefficient for naphthalene and 1-naphthol is about 690 $\mu m^2 s^{-1}$. Based on equation 2.3 and the measured value of D_s, the average value for τ_a was 0.02 and 0.003 for diffusion of 1-naphthol and naphthalene in the weathered shale respectively. This is at least a factor of 5 lower than estimated apparent tortuosities for similar clay textured materials (e.g. Oscarson 1994; Miyahara et al. 1991; Myrand 1992). For the measured values of D_t, retardation coefficients would have to be much greater than those predicted based on the diffusion coefficients and within a factor of 3 of those predicted by batch equilibrium experiments if a tortuosity value of between 0.1 and 0.3 is accepted (Miyahara et al. 1991; Myrand 1992; Oscarson 1994) (table 2.1). The low measured values of D_s, coupled with the clay slice data for naphthalene, suggest that the difference between measured and predicted retardation coefficients is due to some form of solute exclusion.

Three mechanisms can be proposed to explain partial exclusion of the solute from the clay pore space: exclusion of solute from soil micropores, reduction of solute concentration over a large portion of the clay size pore space, or reduction of solute concentration within the near surface region of the pore.

Solute exclusion, due to the inability of the diffusing species to enter smaller pores within the structured material has been used to explain similar differences between measured and estimated coefficients (Oscarson, 1994). The mechanism implies that there are accessible pores, containing the same concentration of solute as the outside solution and non-accessible pores. For this mechanism to be valid, the structured soil would contain innacessible pore space which was not present in the mechanically mixed batch soil sample. Small micropores, such as those found interlayer spacing between clay layers would be present before and after mechanical mixing. Thus, according to this mechanism, the critical pore size would have to be larger than that found in the clay interlayer spacing. Alternatively, it can be proposed that the reduction in effective porosity in the structured soil is due to a large volume of dead end pore space. This hypothesis assumes that the pore space is still accessible to the diffusing species, but diffusion is not possible through part of the pore space.

If solute is excluded from the pore space, D_e will remain constant. The effective porosity, n_e, however will be lower than the total porosity of the deposit (equation 2.5). Thus, the value of D_s will seem to decrease if it is assumed that $n_e = n$. The measurement of D_t will not be directly affected. However, if the critical pore size hypothesis is accepted, then exclusion will tend to decrease the observed sorption coefficient since some of the solid phase will be inaccessible to the diffusing solute. Alternatively, according to the dead end pore hypothesis, all pore sizes equal to or greater than those present in the batch equilibrium experiment will still be accessible for solute sorption but some space is not available for diffusion. Thus K_d should remain constant.

Prediction of the change in sorption due to the critical pore size hypothesis is difficult due to the lack of direct data on the distribution of the sorbed phase in the soil material. It is, however, reasonable to assume that:

1. the amount of sorption will be approximately related to the proportion of available surface area.
2. if solute exclusion does occur, it will occur dominantly in the smaller clay pores where pore wall interactions are strongest.

Thus, to a first approximation, the effect of exclusion on sorption should be related to the amount of surface area excluded. For most pore shapes, the change in surface area can be related to volume as:

$$\mathbf{dA} = \frac{\mathbf{3}}{\mathbf{r}}\mathbf{dV} \qquad 2.9$$

where A is the surface area, V is the volume and r is the pore radius. Yates et al (1992) present a numerical model with calculated fitting parameters which can be used to relate the change in soil water content with water potential. This will be approximately related to the surface area change as:

$$\mathbf{dA} = \frac{\mathbf{3P}}{\mathbf{2\sigma}}\mathbf{dV} \qquad 2.10$$

where σ is the surface tension and P is the pressure potential. If an effective porosity of 0.4 is used, the calculated surface area of the larger pores represents less than 2% of the total expected surface area of the clay (1 to 2 m g^{-1}). This requires a much greater reduction in the observed retardation coefficient than is given by the results of the present study. In the present results, an apparent reduction in K_d is observed. However, the reduction in K_d suggests that pore accessibility is much greater than the 2% predicted by the above model. Thus, neither the dead end pore hypothesis nor the pore exclusion hypothesis seem to be controlling solute flux into the clay barrier.

Diffusion from the bulk solution is driven by a potential gradient between the bulk solution and solution in the clay pore space. This potential gradient could be altered however if the clay pore structure influences solute potential within the pore space. If a change in solute or solution potential exists within the compacted clay matrix, the clay could act to reduce the concentration of the solute of interest from the clay pore space. Thus, the average solute concentration in the clay pore space would be lower than that in the free solution. The magnitude of the concentration reduction would depend both on the size and ionic potential of the diffusing species. Sorption on the soil should be similar to that observed in dilute phase experiments. A lower "apparent sorption coefficient," however, will be observed if the change in the boundary condition at the clay surface is not accounted for.

Solute can also be excluded from only the near surface water interface of the pore space due to the existence of the diffuse double layer near the clay surface. For anions, it is expected that the near surface concentration is lower than that at the pore center. For hydrophobic organic compounds, a similar phenomenon may be expected since the increased ionic potential near the clay surface would tend to decrease hydrophobic solute activity. This mechanism would suggest that most of the pores are available for solute transport but the total porosity available for diffusion is less than the total soil porosity. Thus, although the effective porosity will be less than the total porosity, the sorption coefficient in the deposit should remain relatively constant. In addition, if diffusion can occur in the diffuse double layer, the effect should be reversed for cationic species. For cationic species, average solute concentration in the pore space would be expected to be higher than that of the surrounding solution due an increase in cation concentration near the clay surface. Thus for cationic species, solute diffusion in the diffuse double layer would have to be lower than that of the central pore, or calculated effective porosities should be equal to or greater than the total clay porosity. Additionally, the work by Zhang and coworkers (Zhang et al. 1990a,b,c) suggests that the concentration of hydrophobic organic contaminants may increase within the interfacial water. If they are correct, effective porosities should also seem to increase for hydrophobic organic contaminants or the interfacial solute should be associated with high energies of sorption which would restrict movement of solute within the interfacial region. In the above studies, Zhang et al. stated that solute partitioning was responsible for the increase in solute concentration at the interface, suggesting actual energies of sorption were low.

Experimental results suggest that one of the latter two hypotheses (here referred to as concentration reduction and interface exclusion) was acting on the given solutes in the clay cell. Thus results from this experiment and some literature data were analyzed with respect to expected results based on the second and third proposed mechanisms.

2.4.3 Relationship between solute concentration reduction and the measured diffusion coefficient

If the clay is partitioning solute out of the pore space, we can define a partitioning factor, f, as:

$$f = \frac{C_p}{C_0} \qquad 2.11$$

The value of f can be determined directly from an extrapolation of the concentration profile of the diffusing species within the clay pores to the clay:source reservoir interface. If solute is sorbed by the clay, total measured concentration in the clay material will be

$$C_t = x_p C_p + x_s S \qquad 2.12$$

where C_t is the total solute concentration in the clay, S is the sorbed concentration, C_p is the concentration within the clay pores $x_p$and x_s are the volume fraction of pore space and soil respectively. Then,

$$f = \frac{C_t}{C_0(n + \rho K_d)} \qquad 2.13$$

With the change in boundary conditions, equation 2.5 must be rewritten as,

$$D_s = -\frac{\Delta Q}{\Delta t}\frac{L}{fC_0} \qquad 2.14$$

Partitioning of solute out of the clay pore space will not directly affect the breakthrough time, t_e. However, the amount of solute sorbed by the clay will be dependent on the pore solution concentration. For a linear sorption isotherm,

$$\frac{S}{f} = C_0 K_d \qquad 2.15$$

Thus, if the boundary condition is defined as $C_s(0,t)=C_0$, sorption in the deposit will be overestimated by a value of 1/f. Thus, actual sorption in the cell is given by,

$$K_d = \frac{S}{C_p} = \frac{S}{C_0 f} \qquad 2.16$$

If batch equilibrium experiments are used in the calculation of K_d, this value must be substituted into equation 2.7 to account for the change in boundary conditons, and equation 2.7 becomes,

$$R_d = 1 + \frac{\rho}{n} f K_d \qquad 2.17$$

For naphthalene, a value of $f=0.4$ was observed in montmorillonite clay (table 2.1). Since the shale material is clay textured and the dominant clay mineral in the shale deposit is montmorillonite, a similar value of f is likely for the compacted shale. No similar value can be directly obtained for 1-naphthol but it is was assumed that the factor f is similar to that of naphthalene. Thus a value of $f=0.4$ has been accepted for all clay materials. Using this value, the ratio of the calculated values of D_e from the time lag and steady state methods were 1.3 and 5.0 for 1-naphthol and naphthalene respectively (table 2.1). This was in contrast to ratios of 8 and 30 respectively if concentration reduction is not assumed.

The inclusion of a correction factor for the change in the naphthalene concentration profile within the shale could account for most of the variation between D_t, and D_s. Predictions of D_e also fell within the expected range for the clay. If the free water diffusion coefficient for naphthalene and 1-naphthol is about 690 $\mu m^2 s^{-1}$, the average apparent tortuosity was about 0.1 for all data sets except for the calculation of D_e based on the steady state method for naphthalene in the shale ($\tau_a=0.02$). Apparent tortuosity values for H_2O in similar clay materials in the density range of 1.2 to 1.6 Mg m^{-3} ranged between 0.09 and 0.14 (e.g. Oscarson 1994; Miyahara et al. 1991).

Some errors may have been introduced into this calculation due to the assumptions that no naphthalene sorbed on the montmorillonite clay and that the value for f was the same for 1-naphthol and naphthalene. For 1-naphthol, the value of f would be nearly the same if it is proposed that concentration reduction does occur and that reduction is due purely to some steric hindrances within the pore space. If the electrical potential of the solute is important in determining concentration reduction, as is proposed here, the f factor would likely be larger for 1-naphthol than for naphthalene due to its more polar charge distribution.

For diffusion of naphthalene through montmorillonite, it was assumed that no naphthalene was sorbed on the clay. This value was based on batch equilibrium tests using a soil:solution ratio of 1:10 (Qualizza, 1994). If the clay was able to sorb naphthalene, the value of f would have been overestimated. A sorption coefficient of 0.3 ml g^{-1} is sufficient to explain the deviation between predicted values of D_e based on the two diffusion coefficient measurements. Sorption coefficients of less than 0.4 ml g^{-1} could not be detected in the present experiment (pr=0.05).

Several other researchers have reported differences between observed and measured experimental parameters. This has been particularily true for large anions or cations such as Cs^+ (Cho et al., 1993a,b); $CO_3^=$ (Oscarson and Hume, 1994); I^- (Oscarson et al, 1992); TcO_4^- (Sawatsky and Oscarson, 1991a,b); and for relatively hydrophobic organic contaminants (Myrand, 1992). Table 2.2 lists calculated values for Cs^+ in bentonite clay (from Cho et al, 1993a,b). In the original data, discrepancies were observed between effective diffusion coefficients based on the steady state and time lag methods (table 2.2). This corresponded to a difference between the measured and predicted concentration at the clay surface based on batch equilibrium tests. If it is assumed that there is a concentration drop at the clay surface, then an f value of 0.32 can be estimated.

For Cs^+, diffusion experiments have also been conducted which do not employ estimates based on external solution concentration. Using the 2 cell method, Cho et al (1993b) have independently verified diffusion coefficient measurements for Cs^+(table 2.2,

D_p). In the two cell method, the contaminant is initially mixed into the clay matrix of part of the diffusion cell. Solute is then allowed to diffuse through the cell for a period of time and the diffusion coefficient is determined based on the solute flux into the uncontaminated portion of the cell. For a complete discussion on the cell design, see Shackelford (1991) or Hume (1993). The measured value of D_p will be given by D_e/R_d but unlike D_t, the boundary condition is based on in-clay pore solution concentration. Thus, if partitioning is occurring, the value of R_d should be predicted reasonably well by the estimated sorption coefficient (100 ml g^{-1}, Cho et al, 1993a). Based on the values of D_p, an average D_e for Cs^+ in bentonite of 275 um^2 s^{-1} is calculated (table 2.2). Given that the free water diffusion coefficient isa about 2000 um^2 s^{-1} (Li and Gregory, 1974) τ_a falls well within the expected range. If no partitioning term is included in the estimate of D_e based on the steady state and time lag methods, then the value of De_s is a factor of 13 smaller and De_t is a factor of 2 larger than De_p. Although measurements of De_t and De_p are within experimental error, De_s is not. If partitioning is assumed, all estimates of the diffusion coefficient agree within a factor of 2. In an estimation of the Cs^+ sorption coefficient in compacted clays, Oscarson et al (1994) found that the apparent K_d value for Cs^+ in compacted bentonite dropped to 37% of that measured in a mixed clay/water suspension for clay densities between 0.9 and 1.5 Mg m^{-3}. The measurement of K_d in the compacted clay relied on the boundary condition $C_p(0,t)=C_0$. Therefore, the drop in the measured K_d could also correspond to a change in the boundary condition. This corresponds well to the average value of f=0.32 for the diffusion experiments.

Exclusion of the organic chemical from the soil pore volume is also suggested in the data reported by Myrand et al (1992) (table 2.3). The experimental design is a modified version of that used by Rowe et al (1988). In this experimental design, diffusion is allowed into a clay cell from a source reservoir of known volume and solute concentration. The diffusion coefficient is then estimated by fitting the drop in solution concentration in the source reservoir with time to a semianalytical solution of the advection-dispersion transport equation using the POLLUTE computer model developed by Rowe and coworkers (For a discussion on the methodology, see Rowe and Booker, 1984, 1985). For the data presented by Myrand et al. (1992), the measured diffusion coefficient was assumed to be given by equation 1.8. The values for D_0 and τ were then estimated for the deposit and the value for K_d was calculated by substitution of equation 1.7 into equation 1.8. However, if solute exclusion occurred, then the concentration of solute within the pore space was less than that of the source reservoir and the actual value for R_d would have been underestimated by this method. Since the drop in solution concentration is a function of D^2, the actual value for R_d would be given by,

$$\mathbf{R_{md} = f^2 R_d} \qquad 2.18$$

where R_{md} was the measured retardation coefficient obtained by assuming the pore concentration was the same as the surrounding solution concentration. Based on the estimate of R_d from batch equilibrium, then f is between 0.5 and 0.3 for benzene, trichloroethylene and toluene in the clay (table 2.3). The actual value of f cannot be confirmed since there was no clay concentration profile in this experiment. These results do, however, correspond to the value of f for naphthalene and 1-naphthol used in the present experiment.

Table 2.2 Measured diffusion coefficients for Cs^+ in bentomite clay

1. Diffusion coefficient for Cs^+ as measured by through-diffusion cell design

density Mg m^{-3}	D_s(a) $\mu m^2/s$	D_t(b) $\mu m^2/s$	R_d (c)	f (d)	D_e from D_s (e) $\mu m^2/s$	D_e from D_t (f) $\mu m^2/s$
1.37	21	1.9	285	0.19	233	102
1.33	32	2	268	0.42	153	227
1.38	11	1.9	289	0.36	64	199
average				0.32	150	176

2. Diffusion coefficient for Cs^+ as measured by in-diffusion cell design

density Mg m^{-3}	D_p (g) $\mu m^2/s$	R_d (c)	D_e from D_p (h) $\mu m^2/s$
1.20	0.8	220	181
1.24	1.6	234	374
1.25	1.1	238	261
1.25	1.2	238	285
average			275

[a]from Cho et al 1993a.
[b]from Cho et al 1993b.
[c]calculated from equation 2.7, K_d is assumed to be 100 ml g^{-1} (Cho et al, 1993a).
[d]calculated from equation 2.12, input variables estimated from Cho et al, 1993a.
[e]calculated from equation 2.13.
[f]calculated from equation 2.16 substituted into equation 2.6.
[g]from Cho et al 1993b.
[h]$D_e=D_pR_d$

Table 2.3 Values of f as estimated by measured and calculated retardation coefficients for benzene, trichloroethylene and toluene.

Solute	R_d measured[1]	R_d calculated[2]	f[3]
Benzene	32.3	117	0.52
Trichloroethylene	58.4	492	0.34
Toluene	74.0	734	0.32

[1]estimated based on measured diffusion coefficient (Myrand et al, 1992).
[2]calculated from batch equilibrium data (Myrand et al, 1992).
[3]estimated from equation 2.18.

It is apparent that any effect the clay will exert on pore solute concentration is dependent on the size and nature of the diffusing species. In a similar test to that conducted by Myrand, Barone et al (1992) found good agreement between predicted and measured diffusion coefficients for the more water soluble organic compounds acetone, 1,4-dioxane, and aniline. Although diffusion of chloroform and toluene was also measured, the potential error term was too large for direct comparison due to sorption of the organic constituent on the diffusion cell.

Because the diffusion data sets are limited, it is difficult to either prove or disprove any given theory regarding solute exclusion from the clay pore space. Several alternative proposals still exist which cannot be completely eliminated with the use of the present data set

There are still alternative explanations which cannot be completely eliminated by the present results. Although the proposed hypothesis seems to conform to results if it is assumed that sorption is slowly reversible, the assumption of an irreversible sorptive phase could still be used to explain some of the anomalies observed. There are several reasons however why this was discounted. It was observed for naphthol that although sorption was slow compared to the time frame of the experiment, most or all of the sorbed phase seemed to desorb at the same rate. Only a small fraction of the total sorbed phase was potentially irreversibly or very slow reversibly sorbed in the shale. Additionally, the use of an irreversible sorptive term did not explain the drop in napththalene solution concentration in the pore space of montmorrillonite clay.

If reversible sorption is assumed, data sets are still too limited and experimental errors too large to differentiate between solute exclusion from the surface of clay material and actual reduction in solute concentration within the clay pore space. However some anomalies between predicted and observed results have been suggested in several reports and for a very diverse array of compounds, including inorganic cations, anions, and hydrophobic contaminants. Presently, it seems that some form of solute exclusion, rather than a reduction in sorption coefficients is responsible for this observation.

The activity of species in small clay pores is quite distinct from that expected in more dilute solution. Although both electrical potential and ionic concentration near the clay surface will dissipate rapidly to that in the bulk solution (within tens of nanometres, depending on bulk ionic concentration and ionic species), the effect of the high electrical and ionic potential near the clay surface on molecules within two to three hundred nanometres of that surface is unknown. Given the nature of the species being investigated, it would take a small change in activity to result in the observed change in the solution composition. Setchenow coefficients, or salting coefficients have been reported extensively to describe the change in activity of nonelectrolytes in aqueous solutions. Generally, for dilute solutes in electrolyte solutions with concentrations of less than 1 to 2 molal, a relationship has been found between the nonelectrolyte solubility and the ionic concentration given by,

$$\log a = \log\left(\frac{So}{Se}\right) = k_s C \qquad 2.19$$

where a denotes the activity coefficient of the solute, So and Se are the solubilities of the solute in free water and electrolyte solution respectively, k_s is the salting coefficient and C is the concentration of the electrolyte. This relationship has also been found to hold reasonably well for seawater, where the ionic strength is determined by a series of electrolytes (Hashimoto et al, 1984). Setchenow coefficients for benzene, toluene, naphthalene, and 1-naphthol in NaCl have been listed between 0.19 and 0.21(based on molar concentrations) (Almeida et al. 1983; Perez-Tejeda et al. 1990). This means that in a pure electrolyte solution a solution concentration change of 1.1 to 2 M would be sufficient to account for the expulsion observed in the present experiment. Although no data could be found for $CaCl_2$, the indication from $MgCl_2$, $SrCl_2$ and $BaCl_2$ is that the Setchenow coefficient would be higher in this solution (Xie, 1990). Concentration changes near the surfaces of clay pores will be much higher than needed for the proposed salting out coefficient. At present, how these concentration changes within the near surface region will influence a slightly soluble solute within the pore space is undetermined.

The same treatment was not possible for the prediction of Cs^+ activity in solution concentrations at or greater than the 0.2 M solution used. The Davies equation, however, does predict that Cs^+ activity will tend to increase at solution concentrations greater than 0.2M.

It is presently impossible to estimate the effect for the center of larger pores within the clay. The theory, however, does suggest several testable hypotheses:

1. High salt concentrations within the bulk solution concentration may depress differences in activity between the bulk solution and the clay poreand suppress the salting out effect. This will be particularily true if the salting out is influenced by the surface charge on the clay. In this instance, the increase in salt concentration will suppress the activity difference between the clay pore space and the bulk solution.
2. Since activity changes will result in actual changes in free solution concentration in the pore space, apparent drops in the sorption coefficient should also be observed.
3. Diffusion measurements shoud be a function of the method of measurement and the average pore solution concentration within the cell. Measured diffusion coefficients will be a function of f^2 for the dropping concetration reservoir method, f for the steady state method, and independant of pore solution concentration in the two cell method.

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Chapter 3

Microaggregate size distribution in a weathered shale material treated with $CaCl_2$ solution.

3.1 Introduction

For measurement of sorption equilibrium and rates of sorption, most experiments are conducted on aggregated soil materials. Except where highly dispersive conditions are employed, a certain amount of soil aggregation is present in all batch and flow through cell experiments. Aggregation can affect the homogeneity of the distribution of mineral and organic components. In some cases, the aggregate size distribution may be important in determining sorption and transport within the soil and in determining the differences in the extent and rate of reaction. This is particularly important in fine textured deposits, where much of the finer silt and clay material can remain aggregated, even under strong dispersive energy inputs (e.g. Edwards and Bremner, 1967). In some cases, microaggregation will remain intact, regardless of the dispersive properties of the electrolyte solution (e.g. Levy et al, 1993). In this case, diffusive transport within the aggregate may be strongly influenced both by aggregate stability and the nature of the materials which are stabilizing the soil aggregate.

Aggregate shape and density depends upon the rate of aggregate formation (Raper et al, 1993). When aggregate formation is allowed to occur naturally over long periods, smaller, more compact aggregates will tend to form. Looser aggregates tend to form under flocculation experiments where aggregate formation occurs over relatively short time periods. Batch equilibrium and column methods used in most sorption experiments do not utilize mechanical dispersive methods generally employed to break down microaggregate structure (Edwards and Bremner, 1967) and, therefore, will tend to favor more dense, tightly packed aggregates.

Methods of aggregate size measurements have been reasonably well established, both for wet and dry aggregates (e.g., Tollner and Hayes, 1986). Dry aggregate densities can be measured by a variety of techniques, although the bulk density method (Chepil, 1950) seems to be as accurate as any other method for less cost and time.

Measurement of aggregate density for water stable aggregates have posed a larger problem due to both the need to maintain the aggregates in the experimental state prior to measurement and the observation that aggregate density tends to increase with decreasing aggregate size (Chepil, 1950; Rieu and Sposito, 1991; Sur et al, 1979, Wittmus and Marzurak, 1958). In most of these instances, estimated aggregate density is the average of primary particles with the same size as the aggregates and the aggregates themselves. If no attempt is made to separate aggregated soil material from particles, variation in aggregate density will reflect particle/aggregate composition of the given size fraction as well as aggregate density. Thus density would be expected to increase as the aggregate size begins to approach the particle size of the finer material in the deposit. This has been observed for aggregated material within the fine sand and silt sized regions (Sur et al, 1979). Aggregate density, however, can be influenced by primary particle size distribution within the aggregate. Thus finer textured materials will tend to have lower aggregate densities than coarser textured materials at the same microaggregate size (e.g. Young, 1980). When particle composition is primarily silt and clay sized material aggregate densities seem to show less variation with aggregate size (Rieu and Sposito, 1991). An average aggregate density of about 2.15 g cm^{-3} has been reported previously for silt sized aggregates (e.g. Young, 1980). This value, however, again combines the density of silt and aggregated clay material collected within the silt sized fraction sampled.

To determine if microaggregate diffusion is controlling the rate of solute uptake, the size, porosity of soil microaggregates and percent distribution of aggregated and particulate material must be known. This will allow a diffusion model to be used to directly fit solute uptake data without assumptions about the nature of water stable aggregates in solution. If a microaggregate diffusion model is used, then it is assumed within the model that little sorption occurs within the primary particles and only the amount, size and porosity of the microaggregates will be important in determining solute uptake. Under this constraint, the important parameters for the model will be the density of the aggregated fine textured material, the average size and amount of the aggregates.

In the present study, a method was developed to measure the aggregate size distribution and density of the water stable aggregated materials. Measurements were conducted under conditions similar to those used in soil batch reactions conducted previously (Qualizza, 1994, Xing, 1994) as well as those reported in the present thesis (Chapter 4).

3.2 Materials and Methods

3.2.1 Soil

The weathered shale material used for this study has been described previously in chapter 2. Prior to use, soil was Ca^{2+} saturated, air dried and ground to <106 µm.

3.2.2 Particle size analysis

Particle size analysis was conducted by a standard hydrometer method (Gee and Bauder, 1986) using forty grams of air dried soil (3.9% moisture). Dispersion of particles prior to analysis was accomplished by ultrasonic dispersion suing a Braun-sonic 1510 sonifier operated at 400 watts for 6 minutes. No pretreatment of samples was applied prior to dispersion.

3.2.3 Measurement of aggregate size distribution

In the present experiment, both aggregate size distribution and aggregate bulk density are unknown. Thus some method had to be developed to estimate both the size distribution within the shale deposit as well as the density of the aggregated material. This was accomplished by a combination of separation by settling velocity in water as well as size separation by sieving.

Because batch equilibrium experiments were being used to determine sorption rate and sorption isotherms, aggregate size distribution was determined under similar conditions. Forty grams of soil at a solution:soil ratio of 20:1 with a 24 hr equilibration period was chosen for the present study. Solutions were prepared at 20:1 solution:soil ratio and 0.01 M $CaCl_2$ and mechanically shaken at 22^0C for 24 hours. Solutions were then placed in the settling flask, diluted to 1 litre, and allowed to settle at rates of 60,45, 30, 15, 10, 5, 3, 2, 1, 0.75, 0.5, and 0.4 cm min^{-1} respectively. Volume and size of the settling flask was determined so that approximately 50% of the total volume could be removed in ≤2 min. Short settling times were chosen to prevent floculation after mechanical mixing had terminated. An exception was made for settling velocities of 0.75 cm min^{-1} (5 min.), and 0.5 and 0.4 cm min^{-1} (10 min.) where a two minute time period was too short to develop a sufficient settling front. After a sufficient settling time, the upper 50% of the solution was removed, replaced with $CaCl_2$ solution, and soil was resuspended. Solution separation was conducted 8 times at each settling velocity to extract smaller sized material. Remaining soil was centrifuged, washed in distilled water to remove $CaCl_2$, dried at 110^0 C, and weighed. This gave a total concentration of aggregate + particle distribution as a function of settling velocity in the soil.

For soil aggregates ≥44μm, aggregated material was also sieved using a nest of 106, 53 and 44μm sieves. Sieved material was washed free of $CaCl_2$, dried at 110^0 C and weighed. This gave an aggregate+particle distribution as a function of size.

After weighing, aggregated material was dispersed using ultrasonification and the resulting particle size analysis was conducted on the dispersed material.

3.2.4 Calculation of aggregate density

Settling velocity is a function of both the size and density of the aggregated material. If both the size and settling velocity of the aggregated material is known, density of the material can be determined by Stokes' Law (Robinson and Stokes, 1959),

$$v = \frac{2gr^2(\rho_s - \rho_w)}{9\eta} \qquad 3.1$$

where, r is the particle radius, ρ_s is the particle density, ρ_w is the solution density, g is the gravitational constant, and η equals the solution viscosity.

This equation contains two unknowns, namely the aggregate radius and the aggregate density. For sieved fractions, however, the total amount of aggregated soil material greater than 106, 53, and 44 µm can be determined. This weight of soil material can be compared to the cumulative aggregate settling velocity curve (fig 3b) to determine the settling velocity for these size fractions. These values for settling velocity and aggregate diameter can then be used in equation 3.1 to determine the aggregate density.

3.2.5 Measurement of aggregate size distribution by hydrometer

To check for aggregate breakdown during analysis, an approximate aggregate distribution was also measured by hydrometer. Forty grams of solution at 20:1 solution:soil ratio was diluted in a 1L flask, mixed, and hydrometer readings were made from 30 sec. to 1 hr.

3.2.6 Scanning electron microscopy of aggregated soil material

Because aggregate density was determined on soil aggregates greater than 44 µm in size, and most of the aggregated material was less than 44µ (table 3.1), a qualitative analysis of the finer silt sized aggregates was made using scanning electron microscopy. For aggregated material collected at a settling velocity of 0.5 cm min^{-1}, a small amount of the aggregated material was allowed to settle on a glass slide, freeze dried, and analyzed using a Cambridge 250 scanning electron microscope equipped with a Northern 5500 energy dispersive x-ray analyzer for elemental analysis. Particles were examined under the microscope to see if significant deviation from the predicted aggregate size range could be seen.

3.3 Results

Particle size for the shale material seemed to be follow a log-normal distribution with >50% of the total material being composed of clay sized particles (fig 3.1). Within the aggregated material, however, most of the clay and fine silt material settled at velocities between 2 and 0.5 cm min^{-1}. Very little fine silt and clay sized material was found at settling velocities greater than or equal to 2 cm min^{-1}. Soil material greater than 20 µm in diameter therefore, seemed to settle as either individual particulate matter or with only small coatings of fine material at the surface of the particle. For aggregated material, particle recovery at the maximum settling velocity of the separation was similar to that predicted by particle size analysis (fig 3.1). A comparison of particle recovery after aggregate separation with the particle size analysis did not reveal any significant difference, indicating that no significant loss of particulate matter occurred during the separation process.

For aggregated material, most of the clay and fine silt material was recovered at settling velocities greater than 0.4 cm min^{-1}. Only 5% of the total material settled at velocities less than 0.4 cm min^{-1} as compared to 72% of particles in the particle size analysis (fig. 3.1).

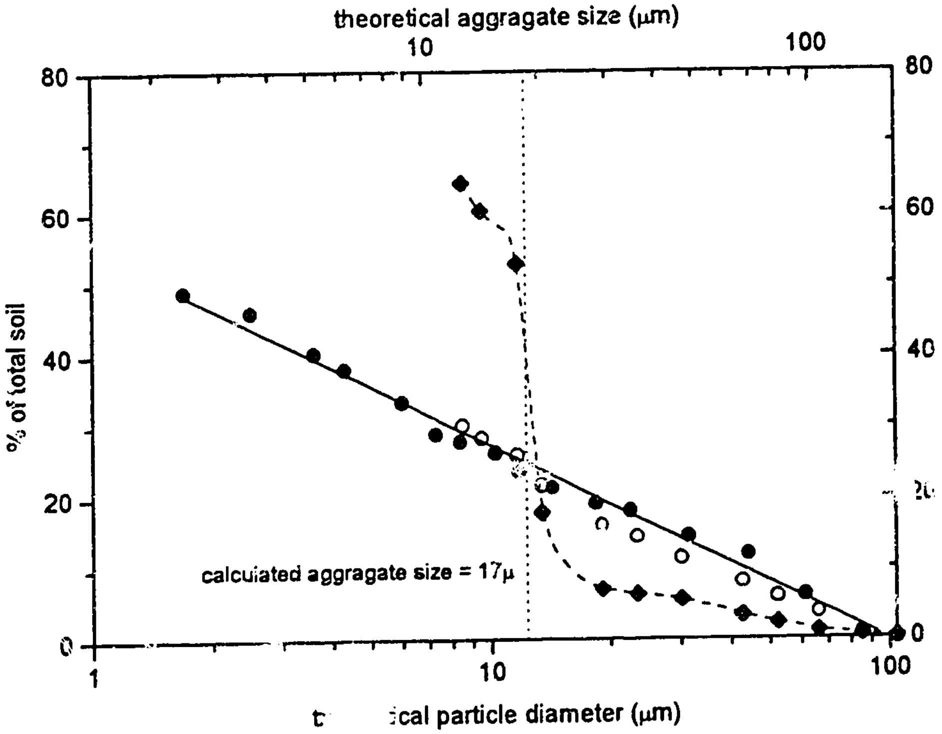

Figure 3.1 Particle size analysis of the shale deposit (●) as compared with the distribution of material in $CaCl_2$ solution. Data for the aggregated material has been divided into fine silt and clay which settled as aggregated material (♦) and coarse silt (○).

Table 3.1 lists the aggregated (total soil collected minus the particulate matter collected after soil dispersion) and particulate matter collected during wet sieving. Most of the material greater than 44 µm in diameter was collected as individual soil particles. Only 5% of the total soil material was collected as aggregated material ≥44µm in size. The amount of material collected on the 44 and 53µm sieves compared to a minimum settling velocity of 5.4 and 8 cm min^{-1} respectively (fig. 3.2). If these values are substituted into equation 3.1 for the aggregate diameter and settling velocities respectively, the calculated bulk density was 1.85 g cm^{-3} for both sieve sizes.

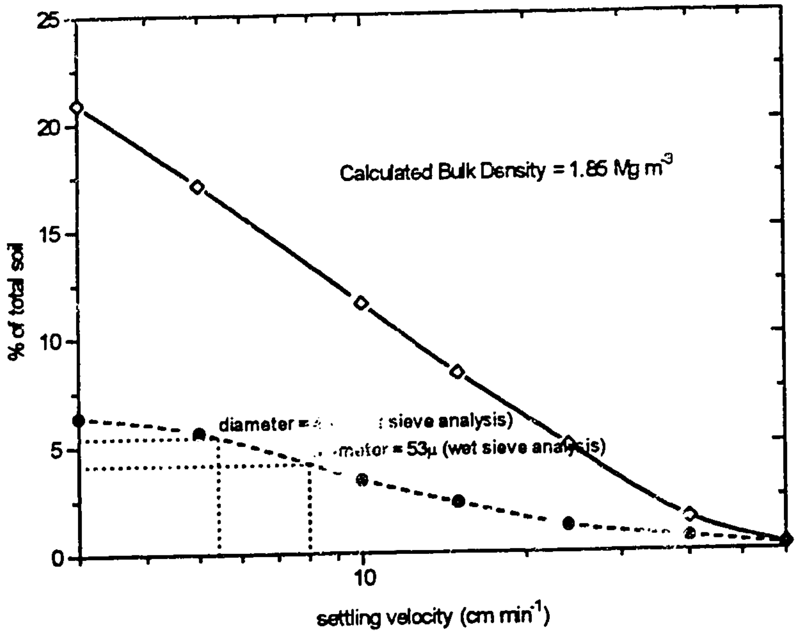

Figure 3.2 Distribution of aggregated material with settling velocity from 3 to 60 cm min^{-1}. Cumulative aggregate size distribution is given for total aggregated + particulate material within the deposit(◊) and fine silt and clay sized material collected after separation of the coarse sized fraction by dispersion of the aggregated material (●).

Table 3.1 Sieve analysis of aggregated soil (average of 4 replicates).

Sieve size (µm)	Percent of total soil		
	total soil	soil particles	soil aggregates
106	0.30 (0.18)*	0.020 (0.009)	0.28 (0.17)
53	10.0 (3.0)	5.85 (0.56)	4.1 (2.5)
44	12.3 (3.1)	6.86 (0.36)	5.4 (2.8)

*Numbers in brackets represent 95% confidence interval for the measurement.

For the undispersed shale material, eighty three percent of the total material was collected at settling velocities between 2 and 0.5 cm min^{-1} (fig 3.1). Particle size distribution of material collected between these settling velocities was dominated by fine silt and clay sized material. Thus, most of the aggregation seemed to occur with particles less than 20µm in diameter. Based on the calculated aggregate bulk density, the majority of aggregated material was between 13 and 26µm size. To determine the aggregate size distribution curve within the sample, the cumulative aggregate size distribution curve (dashed line, fig 3.1) was differentiated with respect to aggregate size. Differentiation of the aggregate distribution curve gave a strong size peak at 17µm (fig 3.3) with little aggregated material present at sizes greater than 26µm or less than 13µm.

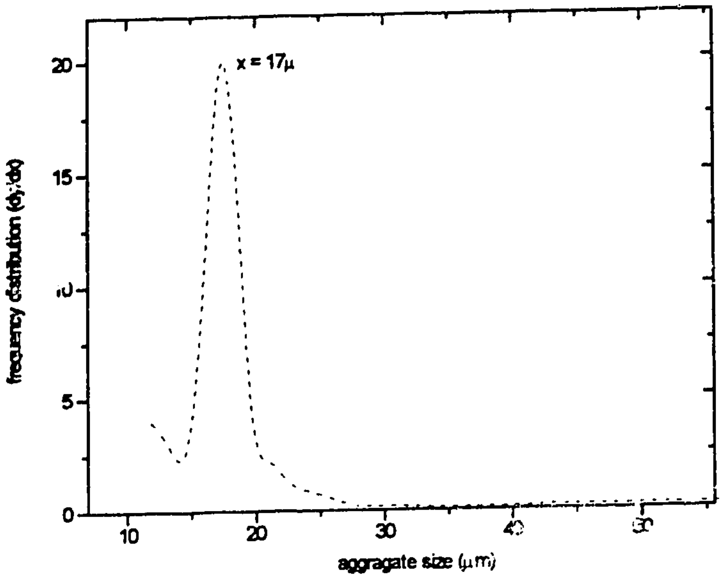

Figure 3.3 Frequency distribution of aggregate size for the fine silt and clay sized material in the shale.

Measured aggregate settling velocities were similar for both hydrometer and aggregate separation techniques. Both measurements indicated that aggregate distribution was relatively well graded, with most material settling between 0.7 and 0.3 cm min^{-1} (fig. 3.4). Hydrometer readings indicated that more material settled at slower velocities than was recorded by aggregate separation. This was likely due to hindered particle settlement as time period and particle concentration increased. Because separation analysis was conducted with shorter time periods and more dilute systems, hindered settlement would be less important in these experiments. However, no indication could be found that disintegration of aggregates was occurring during aggregate size analysis.

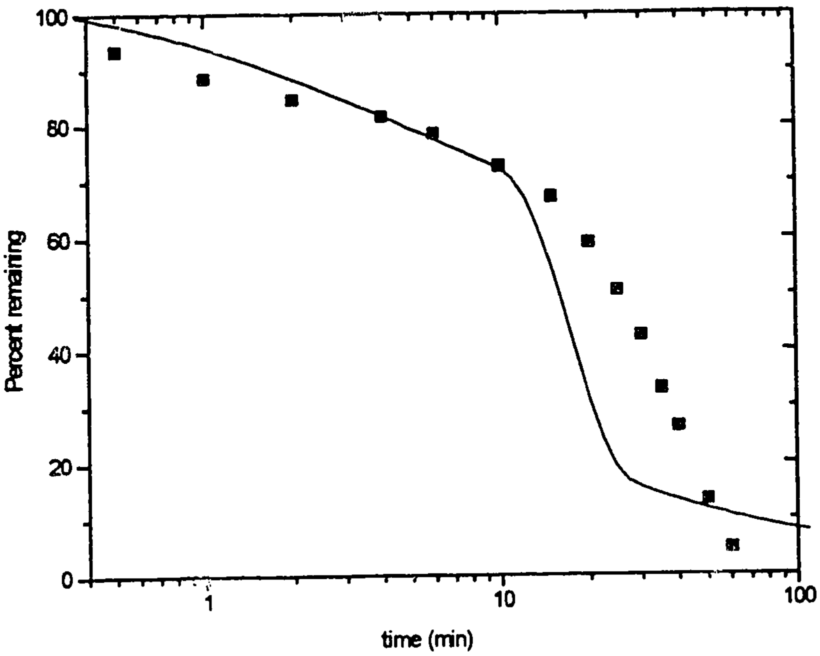

Figure 3.4 Concentration of total particle + aggregated soil material as measured by hydrometer (■) as a function of time. Curve represents calculated values based on aggregate + particle separation data (fig. 3.1) and Stokes' law.

Because aggregate size distribution was closely graded, (fig. 3.2), a visible interface was observed to develop during the experiment. Figure 3.5 shows the change in the velocity of interface settlement with time. Although insufficient data was available to analyze the hydrometer results according to the hypothesis of hindered particle settlement, it was apparent that the rate of particle settlement in the solution did decrease as solution concentration increased during hydrometer measurements. This was particularly apparent after 20 minutes settling time (fig. 3.5). Although this would have affected hydrometer readings taken after 20 minutes, the more dilute soil concentration and shorter time periods used during aggregate separation would have restricted the importance of this factor.

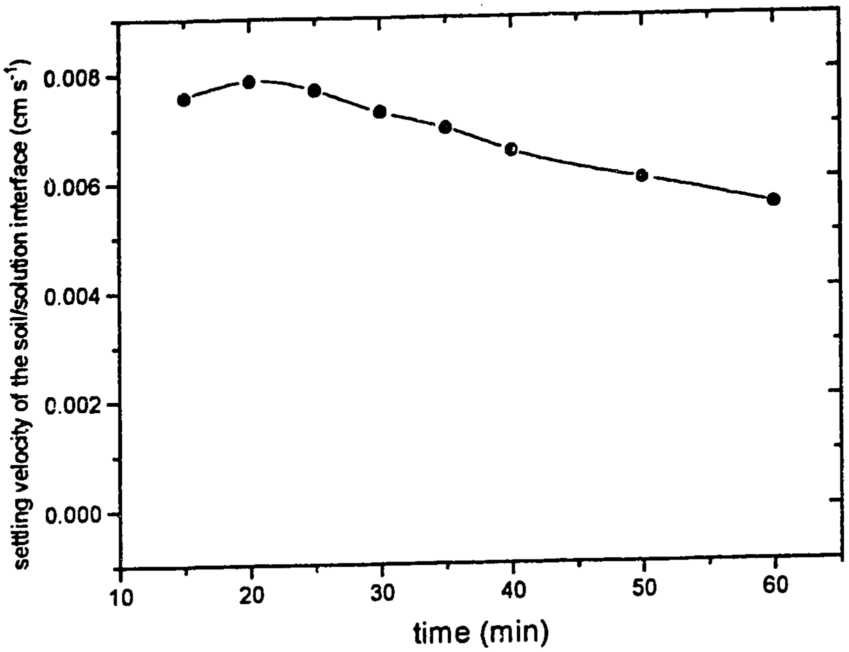

Figure 3.5 Settling velocity of the soil interface as a function of time during aggregate separation analysis.

Scanning electron microscopy of material collected at 0.5 cm min^{-1} was found to have a similar size to that predicted by calculation (fig. 3.6). Visual inspection of the precipitated aggregates indicated that the size of most of the collected material fell within a range from 8 to 25 μm, with a majority of material being about 15μm in diameter. Rare inclusions of 30 to 40μm sized particles were found (fig. 3.6(b)). X-ray analysis of these particles suggested they had lower concentrations of both silicon and aluminum than other collected particles. This was thought to be due to a higher average concentration of organic matter within these particles. The original deposit was found to contain a heterogeneous mix of inorganic and organic material. Most of the organic material tended to be located between layers of shale material (Chapter 4). Although the original deposit was mechanically mixed during soil preparation, organic material was still unevenly distributed within the sample. No attempt was made to quantify S.E.M. data.

3.4 Discussion

Considerable variability of aggregate density has been reported before, particularly in the silt sized region (e.g. Chepil, 1950; Sur et al, 1979). Alternatively, fractal analysis of the soil density has suggested that to a first approximation, the aggregate size/aggregate density relationship can be described by a log-log relationship (Rieu and Sposito, 1991). For soils where the primary particle composition favors materials smaller in size than that of the measured aggregate, aggregate density seems to be more constant with size (Rieu and Sposito, 1991; Young, 1980). Steeper slopes are observed as the aggregate size measured is closer to the dominant primary particle size (Rieu and Sposito, 1991). Young reports a relatively constant aggregate density of 2.15 g cm^{-3} within the silt sized region for 21 different soils (Young, 1980). Again, there does seem to be a correlation between decreasing aggregate density and increasing concentration of fines within the deposit. Aggregate density would be expected to tend towards 2.65 g cm^{-3} as particle size approximates aggregate size. Since the present deposit is very high in clay content, the assumption of constant aggregate density across the dominant size range (20 to 50 µm) seems reasonable.

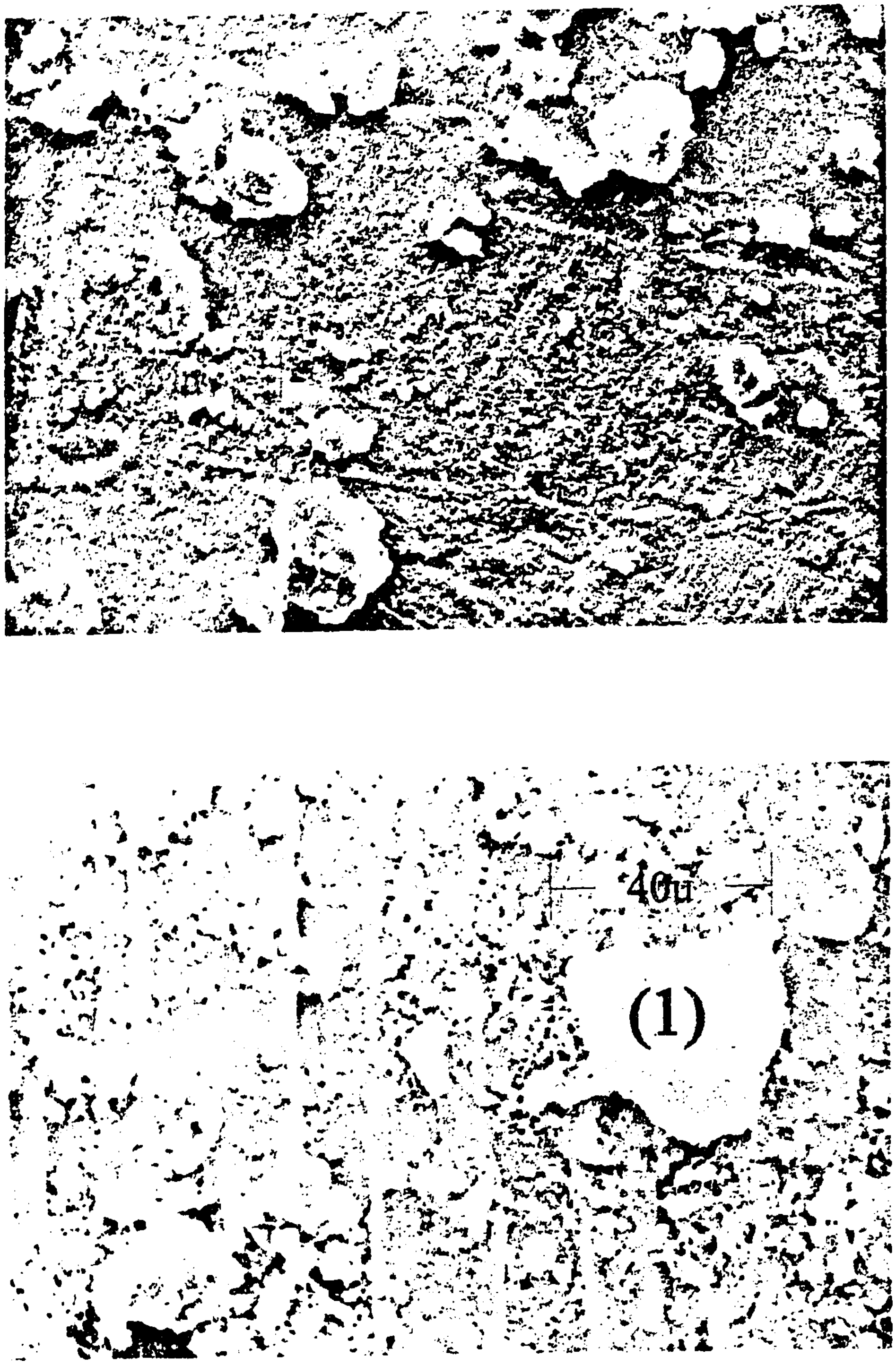

Figure 3.6 S.E.M. micrograph of particles settling between 0.5 and 0.1 cm min^{-1} (1) aggregate had a low concentration of both Si and Al relative to other particles in the micrograph.

Aggregate density (1.85 g cm^{-3}) was lower than has been reported previously. This is likely due to the fact that only the density of aggregated fine silt and clay sized material was desired in the present studies. For other studies, density is determined based on a composite of all material, including particles within the deposit which are close in size to the aggregate size range being determined. If the upper curve of figure 3.2 is used to determine the aggregate density in the present study, a value between 2.2 and 2.3 Mg m^{-3} is suggested. This is similar to that reported by Young (1980).

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Chapter 4

Comparison of diffusion and rates of sorption of 1-naphthol, naphthalene, and anthracene in a weathered shale.

4.1 Introduction

Sorption and release of organic chemicals play fundamental roles in the transport and remediation of organic contaminants in soils. Sorption kinetics of organic contaminants in soils have been an important area of research because in many instances, they can control the rate of uptake and remediation of organic contaminants (Brusseau and Rao, 1989a,b; Brusseau et al 1990,1991; Pignatello, 1990; Pignatello et al., 1993; Steinberg et al , 1988). Molecular diffusion to sites within the organic matter has been suggested as a possible controlling mechanism for sorption kinetics (Brusseau and Rao, 1989; Pignatello, 1990; Wu and Gschwend, 1986). Both intraorganic matter diffusion (Brusseau and Rao, 1989b) and intraparticle diffusion (Ball 1990) have been suggested as possible mechanisms controlling uptake of organic pollutants.

It has generally been assumed that retardation due to sorption in an aggregated medium will be the same as the average value measured for the entire soil (eg. Brusseau and Rao, 1989a,b). This approach assumes a uniform distribution of organic matter at all levels of resolution. However, micromorphological research has suggested that an aggregate hierarchy exists in soils which is strongly influenced by the presence of organic materials within aggregates (e.g. Edwards and Bremner, 1967; Oades, 1988; Oades and Waters, 1991; Tisdale and Oades, 1988). If the pore space within some stable microaggregates is dominantly coated with organic materials, retardation coefficients in these microaggregates may be several orders of magnitude greater than that of the average soil.

In previous studies (Xing, 1994, Qualizza, 1994, Present study, ch. 2,3), a weathered shale was used to investigate sorption and movement of hydrophobic organic contaminants. Examination of micromorphological features of the shale (reported here) suggested that organic material, which only accounted for 2.7% of the total mass, was concentrated in discrete zones within the shale.

Batch reaction studies and many of the column studies investigating rates of sorption are conducted on either mechanically altered soil material or soil material which has been sieved to eliminate larger size fractions. It is generally assumed that this method is sufficient to eliminate the influence of aggregation on the sorption rate (Brusseau and Rao, 1989b) Mechanical alteration of the sample will remove much of the gross variation in sample composition. However, it is likely that microscale variation still remains in the material even after mechanical disturbance. This may lead to significant effects in measured sorption rates due to the discretization of sorption zones within the material.

The present study was designed to investigate if observed rates of sorption of organic contaminants within the shale resulted from microaggregate diffusion into heterogeneously distributed organic matter sites. Sorption rates were compared against the water stable microaggregate size distribution and predicted diffusion coefficients within the microaggregates for naphthalene, anthracene and 1-naphthol.

4.2 Theory

Microscale distribution of organic material in a natural system can be very heterogeneous. Because of this, rates of diffusion into microscale regions may be very different, depending on microsite which is in contact with the sorbate. Although quantitative data on the distribution of organic material in the soil are not available, there is evidence indicating that to a first approximation, the soil can be divided into two distinct regions, one containing concentrated organic material or organo-mineral clay complexes and the other containing litlle or no organic material. In the present study, the solid portion of the shale is treated as a two domain system, either containing organic material or with no organic material present. In order to model the system, the following assumptions have been employed;

1. Soil material is divided into two distinct regions, those containing organic material or organo-mineral clay complexes and those devoid of organic matter (i.e. mineral aggregates or particles only).
2. For mineral regions, little or no sorption will occur and the and diffusion in the pore space will not be retarded by sorption.
3. For organic matter or organo-mineral regions, sorption will be equivalent to the organic matter sorption coefficient for the material. Retardation due to sorption will therefore be a function of the organic matter defined sorption coefficient (K_{om}).
4. Aggregate size distribution for organic aggregates will be similar to the average aggregate size distribution in the material, as defined in chapter 3.

For a batch equilibrium experiment, the rate of uptake should be controlled by the rate of diffusion from a solution of limited volume into the soil aggregate. If a spherical aggregate is assumed, the equation controlling uptake will be (Crank, 1975),

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{6\alpha(\alpha+1)\exp(-D_e q_n^2 t / r^2)}{9 + 9\alpha + q_n^2 \alpha^2} \qquad 4.1$$

where q_n is the nth non-zero root of

$$\tan q_n = \frac{3q_n}{3 + \alpha q_n^2} \qquad 4.2$$

and, for a linear sorption isotherm,

$$\alpha = \frac{3V}{4\pi r^3 K_d} \qquad 4.3$$

Here, M_t is the amount of solute uptake at time t, M_∞ is the equilibrium solute uptake, D_e is the effective diffusion coefficient ($D_0\tau_a$) r is the aggregate radius, V is the volume of solution, and $K_d$is the sorption coefficient for the soil. The parameter, α, therefore, is expressed as the final fractional uptake of solute for a given solution/particle volume ratio, as given by,

$$\frac{M\infty}{VC_0} = \frac{1}{1+\alpha} \qquad 4.4$$

In chapter 3, it was reported that aggregates in the mixed shale:water suspension were dominantly about 17 μm in diameter. Therefore a value of r=9 μm was assumed. Using assumptions 2 and 3, only aggregates of this diameter containing orgainic matter were considered to have slow rates of solute uptake. The sorption coefficient within these regions (K_d in equation 4.3) was assumed to be equal to$K_{\alpha m}$ (sorption coefficient for organic material). For aggregates containing little or no organic material, the sorption coefficient was assumed to be ≈ 1.

The remaining fitting parameter, D_e or the effective diffusion coefficient was then calculated from the rate of solute uptake from solution. Estimates of the effective diffusion coefficient have been made previously for 1-naphthol and naphthalene in the shale material (chapter 2). Although the diffusion coefficient of anthracene was unknown, free water diffusion coefficients of nonhydrated molecules have been shown to be proportional to their respective molecular volume (Wilkes and Chang, 1955). Based on this proportionality, and if the apparent tortuosity for naphthalene and anthracene are similar in the clay material, the effective diffusion coefficient for anthracene is expected to be about 0.56 that of naphthalene.

4.3 Materials and methods

4.3.1 Soil Material

Samples of a weathered shale material, deposited during the cretaceous era were used for the study. Shale material was from the same batch as that descirbed in chapter 2. Reference Montmorillinite clay (STx-1) was obtained from the Clay Minerals Society Source Clay Repository in Columbia, Missouri. Prior to use, all materials were Ca^{2+} saturated, air dried and ground to <106 μm.

4.3.2 Distribution of organic material

Samples of the original shale material were prepared for thin section analysis. Air-dried shale material was impregnated with 3M Scotchcast electrical resin. After impregnation, 30 μm thick sections were prepared using a Logitech polisher.

Thin section analysis was used to provide qualitative information describing the location and distribution of organic materials within the shale. After identification of the organic material, a small portion of the organic matter from the soil thin section was removed and subjected to microinfrared spectroscopy. The organic material sample was chosen to have a greater width than the minimum beam size used for microinfrared analysis (>50 μm) so no sorption bands from the resin would interfere with the I.R. spectrum.

After the diffusion experiment (ch.2, and section 4.3.6), soil cells which had been exposed to naphthalene or 1-naphthol were freeze dried. After freeze drying, the first 2 mm of the clay cell which had been in direct contact with the source solution was sliced away with a razor knife to remove any precipate which may have precipitated out from the source solution. The exposed surface was then analyzed by flourescence microscopy using a Diaplan flourescence microscope equipped with a U.V.-violet filter (355-425 nm wavelength). Both 1-naphthol and naphthalene autoflouresced when exposed to U.V. radiation. For soil samples exposed to 1-naphthol solution, autoflourescence under U.V. radiation was observed in specific regions in the shale sample. Flourescent areas were generally spherical or cylindrical in nature and less than 50 μm in size. Similar flourescence was not observed for soil cells exposed to naphthalene solution or soil samples which had been treated with $CaCl_2$ solution only.

For the 1-naphthol contaminated cell, a particularily large area of flourescence (approximately 70 μm in diameter) was identified and removed for further analysis. The flourescent area was chosen because the size of the area which autofloresced was larger than the minimum beam width for microingrared spectroscopy. The flourescent area was then analysed by microinfrared spectroscopic analysis. The infrared spectrum obtained from the area which autoflouresced was compared against thespectrum obtained from the organic material. Comparison was made to determine if: 1. Infrared analysis could be used to directly identify 1-naphthol in the autoflourescent region and 2. If the infrared spectrum obtained from the autoflourescent region was similar to that obtained fro organic matter form the shale material.

4.3.3 Solution

All stock solutions were prepared in a 0.01M $CaCl_2$ solution containing 10^{-5} M $HgCl_2$ to supress biological activity during the experiment. Prior to use, pH of the solution was adjusted to pH 7.0 (near that of the clay samples) using $Ca(OH)_2$.

4.3.4 Rate of sorption

Stock solution of 1-naphthol, naphthalene, and anthrracene were prepared in $CaCl_2$ solution. For each compound, four separate experiments were conducted using stock solution concentrations from 10 to 80% of the maximum solubility of the compound in water. All stock solutions contained ^{14}C labelled compound at a concentration of $\approx$200 Bq ml^{-1} except for solutions which were used for Gas Chromotography analysis. For these trials, a separate solution was prepared at the same compound concentration using unlabelled compound.

For batch experiments, soil samples were initially treated with the stock $CaCl_2$ solution for 24 hours prior to use. After 24 hours pretreatment, soil material was mixed with a stock solution of ^{14}C labelled 1-naphthol, naphthalene, or anthracene. Depending on the chemical, soil:solution ratio was adjusted so the final solution concentration of organic chemical after sorption was between 20 and 80 % of the starting solution concentration. An exception was made for sorption of anthracene in the shale material where underestimation of the final sorption coefficient resulted in only 10% of the total solution concentration remaining after 400 hours.

After mixing, soil:water solutions were sealed in a 12 ml glass vial with minimum headspace using a Teflon® lined cap. Samples were placed in a LAB-line Orbit Environ-shaker and shaken at 300 rpm and 25±1°C for periods of from 15 minutes to 140 hours (naphthalene) or 15 minutes to 400 hours (anthracene and 1-naphthol). Samples were done in triplicate for a minimum of 7 time periods spanning the range in time for each compound.

After equilibration, samples were centrifuged at 2000 g for 30 min. Approximately 1 ml of solution was removed from the centrifuged sample and mixed with 15 ml. of Ophtiphase Hisafe 3 scintillation cocktail. The concentration of ^{14}C in solution was the determined using liquid scintillation counting. Samples for each time period were done in triplicate.

For naphthlene and 1-naphthol, at least 1 sample was included at the maximum time period containing the same concentration of the organic chemical as in the labelled treatment but with no ^{14}C labelled material After equilibration and centrifugation 1 ml. of solution ws removed and the organic compound was extracted from aqueous solution using dichloromethane. The concentration of the compound in the extract was determined using gas chromotography. Concentrations of contaminants determined by G.C. were all within 95 to 105% of the estimated concentration based on scintillation counting, indicating little or no degredation of sample during the analysis period. No similar analysis was attempted for anthracene due to the low solubility of anthracene in water.

4.3.5 Desorption of 1-naphthol and anthracene

To investigate reversibility of sorption reactions, 24 hour stepwise desorption experiments were conducted for 1-naphthol and anthracene from the batch solution. Triplicate soil:solution samples were prepared as described previously for at least 5 compound concentrations ranging from 20 to 80% of the water solubility of the compound. Samples were all equilibrated for 24 hours by the batch equilibrium method. After 24 hours, samples were centrifuged, solution concentration of the compound was determined using liquid scintillation counting, and approximately 50% of the total solution volume was removed and replaced with fresh $CaCl_2$ stock solution. Soil was then resuspended in the new solution and re-equilibrated for 24 hours. Stepwise desorption experiments were continued until the solution concentration was too low to be accurately determined.

For 1-naphthol, desorption was also measured after 350 hours of sorption using a specially designed desorption cell (fig. 4.1). After equilibration and centrifugation, soil subsamples from 3 of the sorption experiments were removed, placed as a slurry on a stainless steel frit (average pore diameter=0.5 μm) and sealed into an specially designed HPLC filter column. Between 0.3 and 0.4 g of soil was placed in each soil column with a final column thickness of 1 mm. After placement in the column, the soil slurry material was compressed using a hydraulic press to ap pressure of 5000 psi and then sealed in the cell. By compressing the soil sample in the cell, solution flow was maintained through the pore space of the compacted soil material. Water solution containing no 1-naphthol was passed through the clay slurry using a Waters, 501 HPLC pump for up to 14 days. Effluent from the column was passed through an Alltech Maxiclean disposable C-18 column to remove 1-naphthol from the effluent stream. The collected 1-naphthol was then extracted from the column with dichloromethane and the amount of 1-naphthol was determined by Gas Chromatography.

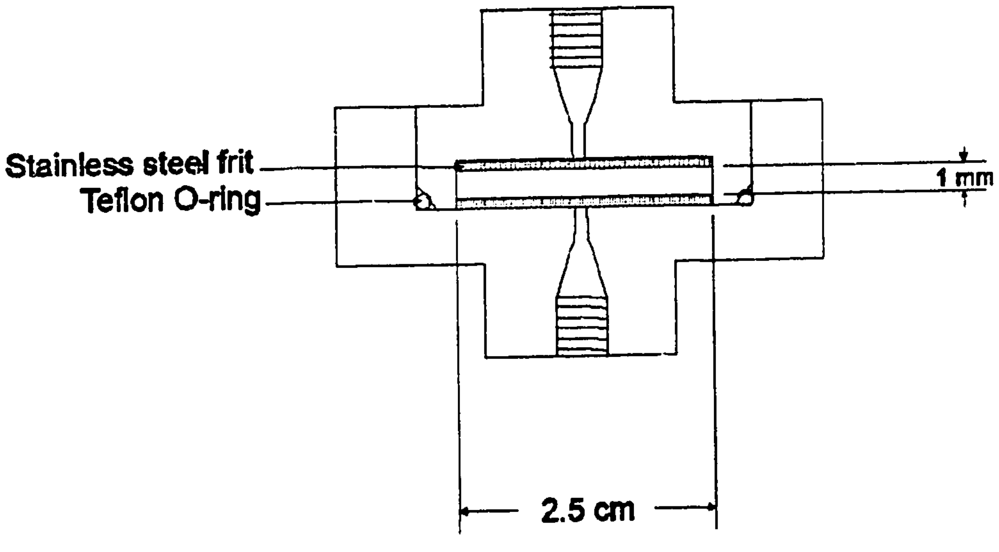

Figure 4.1. Cell design for the flow through stainless steel cell used for measurement of naphthol desorption rate.

4.3.6 Diffusion through the clay material

Method of diffusion analysis has been discussed previously in chapter 2. Diffusion measurements were used to estimate values for the effective diffusion coefficient in the clay material. These values were applied directly to estimate the expected rate of reaction in the sorption studies.

4.4 Results

4.4.1 Distribution of organic materials

Thin section analysis of the original shale showed an uneven distribution of organic matter. Under visible light microscopy organic matter in the shale was identified as zones of amorphous isotropic black material within the shale (fig. 4.2). The sample contained thin lines of organic deposit in the planar voids of the shale sample. Width of the deposits within the shale sample varied, but observed deposits were generally greater than 150 µm. in width Darker colors in the clay surrounding the organic matter deposits also suggested the presence of organo-mineral clay complexes in the shale material near the organic matter deposits.

Microinfrared analysis of the organic matter deposit removed from the shale showed strong absorbance between 2960 and 2900 cm^{-1} and again, some absorbance in the 1460 region (C-H). Evidence of substituted alcohol, aldehyde, ketone and acid groups could be observed around 3400 cm^{-1} (O-H stretch), 1730 cm^{-1} (C=O stretch), and 1240 cm^{-1} (C-O stretch, O-H deformation) Some absorbance in the regions of 1610 (aromatic

C=C) suggested the presence of aromatic material within the matrix. The absorbance peak at 825 cm^{-1} may have suggested the presence of some alunimum silicates within the analyzed region. If silicates were present, absorbance bands between 1200 and 950 cm^{-1} may also have been caused by Si-O stretch of silicate materials.

Thin section analysis was not attempted directly on the shale sample which had been ground to ≤ 106 μm. However, when the ground sample was examined using a stereomicroscope, minute regions of black material similar to the organic material in the shale could be identified. It was difficult, however, to find a region whcih was greater than 50 μm in width so identification of organic matter in the ground sample was not directly attempted.

The infrared spectrum of regions showing autoflourescence after exposure to 1-naphthol solution was similar to the spectrum obtained for organic matter in the original shale material. The absorbance band around 825 cm^{-1}, was not present in the spectrum of the sample extracted after 1-naphthol sorption (fig. 4.3). The presence of 1-naphthol could not be directly verified using spectroscopic analysis largely due to the overlap of 1-naphthol absorbance bands with those of the organic material. Due to the difficulty in extraction and accurate analysis of materials within the 20 to 30 μm range, no similar analysis was conducted on smaller centres of flourescence.

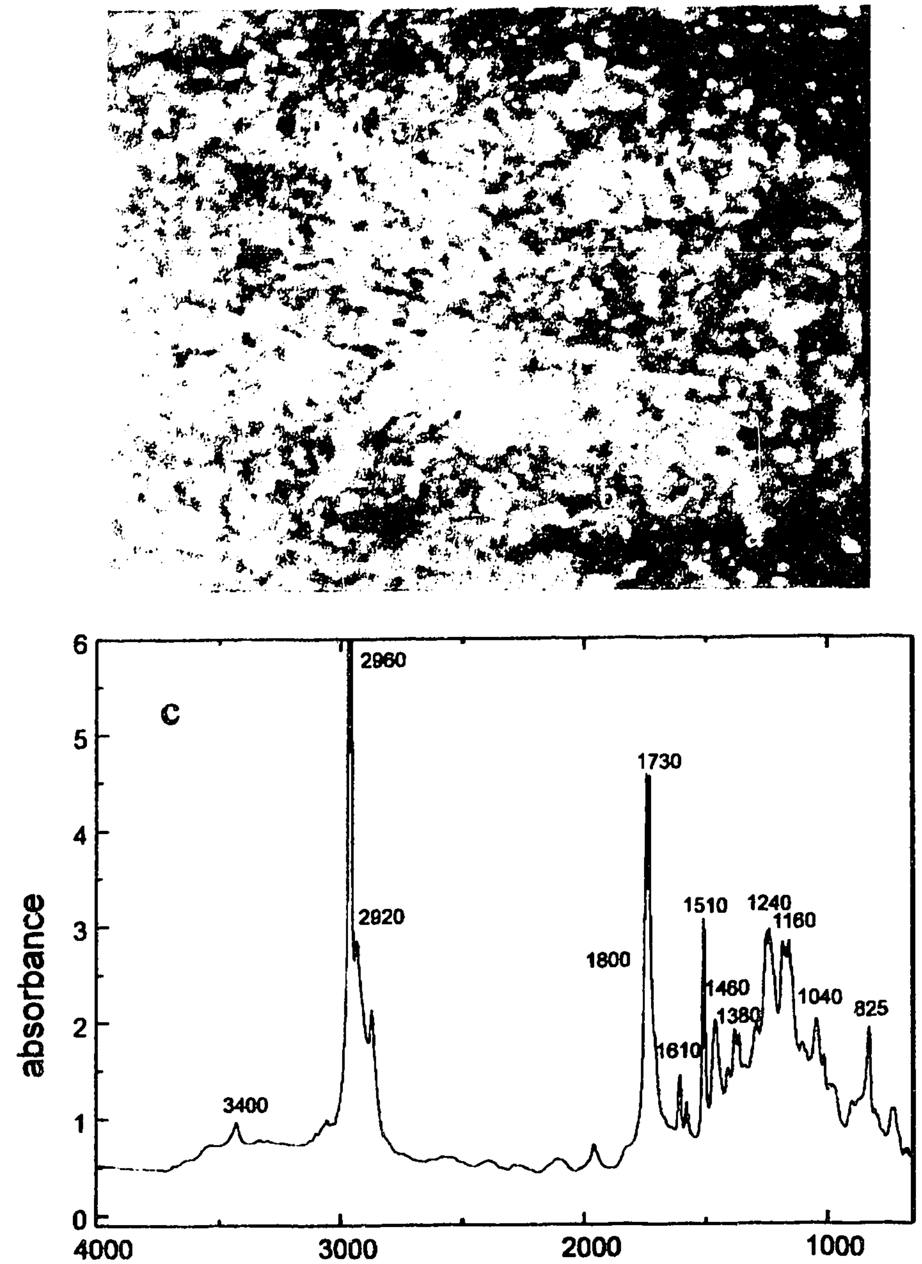

Figure 4.2 Thin section photograph of the weathered shale material under partially polarized light showing the organic matter in the deposit (a), organo-mineral clay complexes (b) and the microinfrared spectrum of a portion of the organic deposit removed from the shale sample.

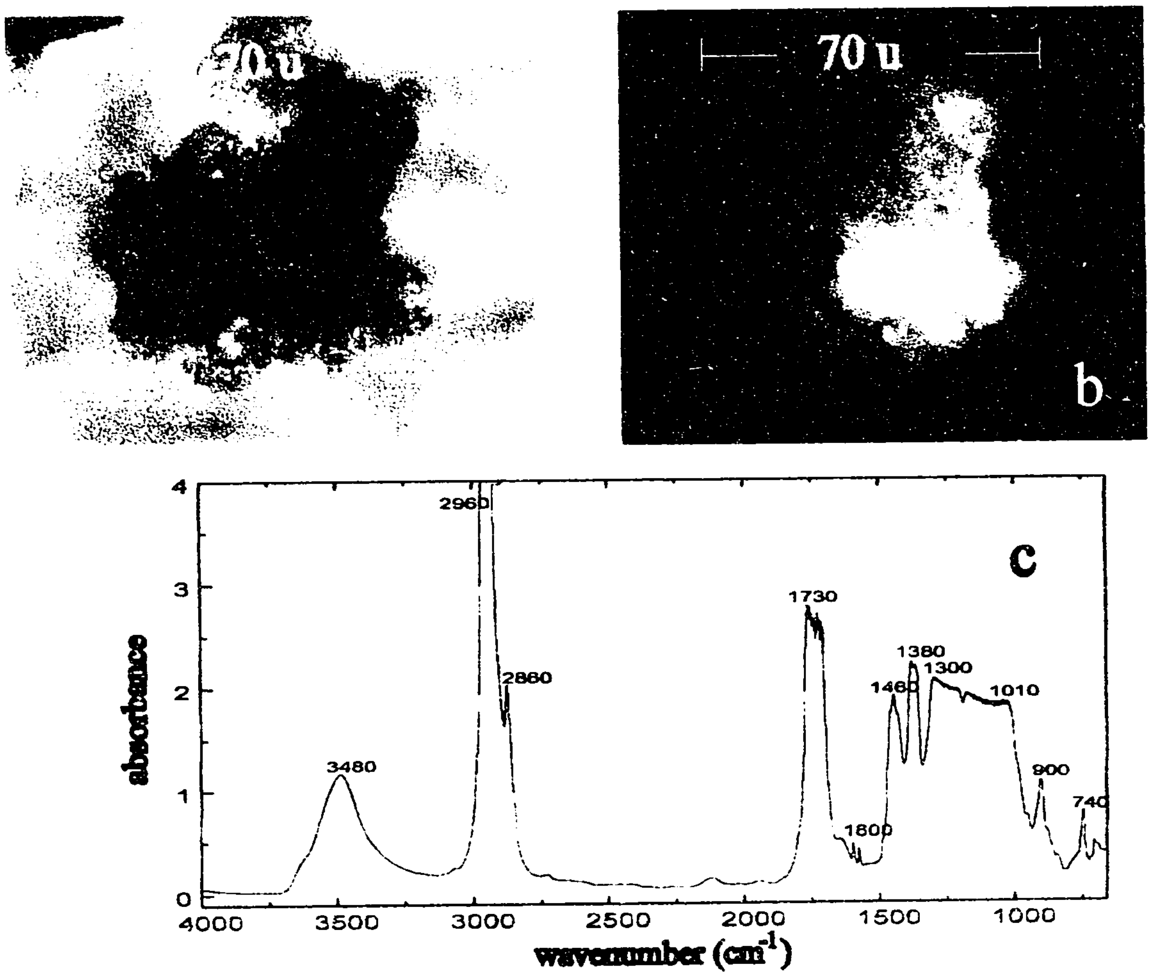

Figure 4.3 Photograph of the organic material removed from the shale material after contamination with 1-napthol (a), autoflurescence of the contaminated organic material (b) and microinfrared analysis of the extracted sample

4.4.2 Rate of Sorption on organic materials

Due to the fast rate of uptake of naphthalene in the shale material, the uptake curve was poorly measured compared to that of anthracene and 1-naphthol (fig. 4.4). Sorption equilibrium of naphthalene seemed to be reached within 12 to 24 hours of the starting time. The rate of uptake, however, seemed to be predicted well by the the diffusion equation (line, fig. 4.4).Uptake curves for 1-naphthol and anthracene were similar to those shown here for naphthalene except the curves were much better developed due to the longer time necessary to reach equilibrium Both 1-naphthol and anthracene showed slow rates of solute uptake during the 2 week sorption period. For 1-naphthol, solute concentration was still observed to be decreasing after the 400 hours.

Data collected for sorption of 1-naphthol, naphthalen and anthracene as a function of time were fit to equation 4.1 to determine an estimate for the diffusion coefficient of the contaminant in the shale sample assuming that microaggregate diffusion was controlling the rate of solute uptake. Values for K_{om} were dtermined based on the final solute uptake at the termination of the experiment. Aggregate radius was assumed to b 9 μm and aggregate density was assumed to be 1.85 g cm^{-3} (chapter 3). These values were compared with the values for the measured effective diffusion coefficients in the shale (chapter 2, D_e for anthracene was estimated based on results for naphthalene).

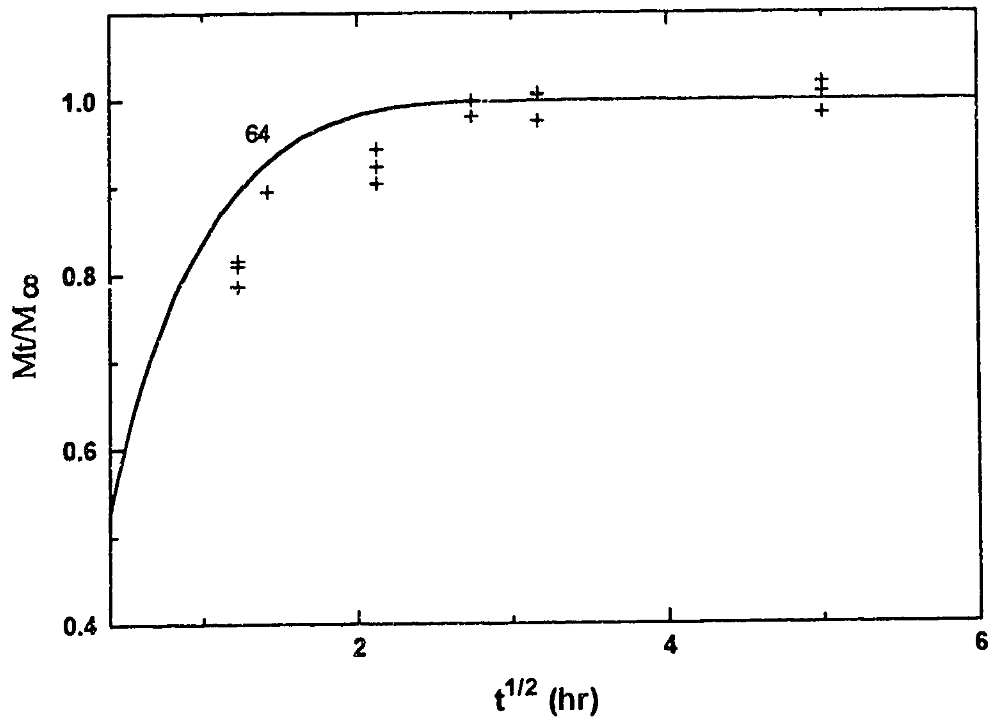

Figure 4.4 Sorption of naphthalene as a function of time (+) compared with the predicted rate of sorption (-) for an effective diffusion coefficient of 60 $\mu m^2 s^{-1}$ and log K_{om} of 3.2. Aggregate radius is assumed to be 9 μm. The value of 64 represents the final percent of solute uptake from the naphthalene solution.

The effective diffusion coefficients based on the proposed spherical model are predicted within a factor of 2 for both naphthalene and anthracene. For 1-naphthol, the rate of uptake from solution was over 100 times smaller than that predicted by the model. Thus a pore diffusion model, where pore size was sufficiently large for unhindered diffusion could not be used to explain the slow rate of solute uptake for 1-naphthol.

Table 4.1 Estimated effective diffusion coefficients for anthracene, naphthalene, and 1-naphthol based on the rate of sorption in batch equilibrium experiments compared with the effective diffusion coefficient measured for the shale sample.

Compound		estimated log Kom	D_e estimated from batch experiments[1] ($\mu m^2 s^{-1}$)	D_e estimated from diffusion in clay[2] ($\mu m^2 s^{-1}$)
Anthracene		5.2	45	7-46[3]
Naphthalene		3.2	84	12-80
1-Naphthol		3.2[4]	0.1	39-142

[1] Based on the best fit through the sorption rate data, assuming organic matter particle diameter of 20 μm and particle density of 1.85 (from Sawatsky et. al, 1995)

[2] Based on solute breakthrough times from the clay material from Sawatsky et al, 1995.

[3] estimated based on effective diffusion coefficient of Naphthalene and relationship between free water diffusion coefficients developed by Wilke and Chang (1955). Apparent tortuosity coefficient is assumed to be the same for naphthalene and anthracene.

[4] estimated on 2 week sorption data for 1-Naphthol. Value represents an underestimate of total 1-Naphthol sorption since equilibrium was not reached during the time period.

4.4.3 Desoprtion of 1-naphthol and anthracene

Stepwise anthracene desorption seemed to agree both with the reversibility of the reaction and the predicted equilibrium constant for anthracene (fig 4.5). Based on the data for sorption rates, the sorption isotherm measured after 24 hours would not have been at near equilibrium conditions. Thus, considerable hysterisis of desorption isotherms would be expected due to nonequilibrium conditions.

Anthracene was found to desorb form the soil after about the third reequilibration step. When the two week sorption isotherm was compared with the stepwise desorption isotherm (line, fig. 4.5), solution concnetration had to be decreased until it intersected with the 2 week sorption isotherm before significant desorption of anthracene took place. For rate limited desorption, it would be expected that desorption would occur only after concentration in solution was diluted below that of the predicted equilibrium isotherm (fig. 4.5). There is some suggestion that desorption slightly preceeded this value suggesting some slight overestimation of the predicted equilibrium isotherm. The actual solution concentration of anthracene at this point, however, was sufficiently low that measurement of solution concentration would have been subject to considerable error.

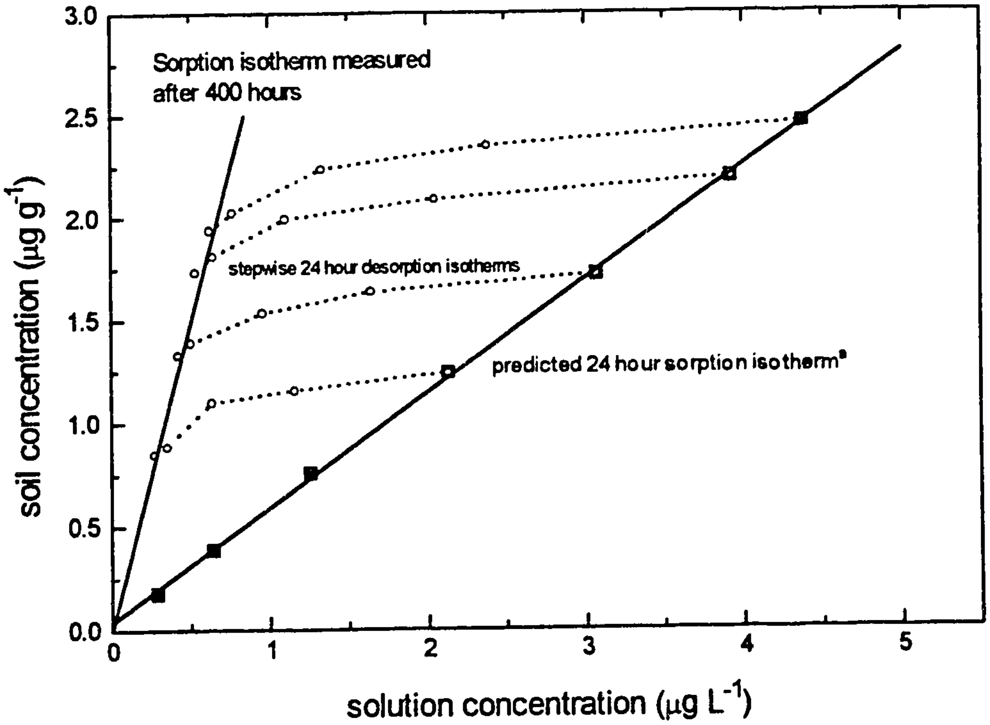

Figure 4.5. Stepwise desorption of anthracene from the weathered shale using a 24 hr. equilibration period and replacement of 50% of the total solution volume by water at each step.

For 1-naphthol, no significant desorption occured over the 5 desorption steps. (fig. 4.6) Even after solution concentrations were significantly lower than the predicted equilibrium concentration on the basis of the two week isotherm, little or no desorption occured. The stepwise desorption isotherm suggested either some form of irreversible sorption or that the actual equilibrium sorption concentration was much lower than predicted. Further analysis by stepwise desorption was not possible due to the low solution concentrations.

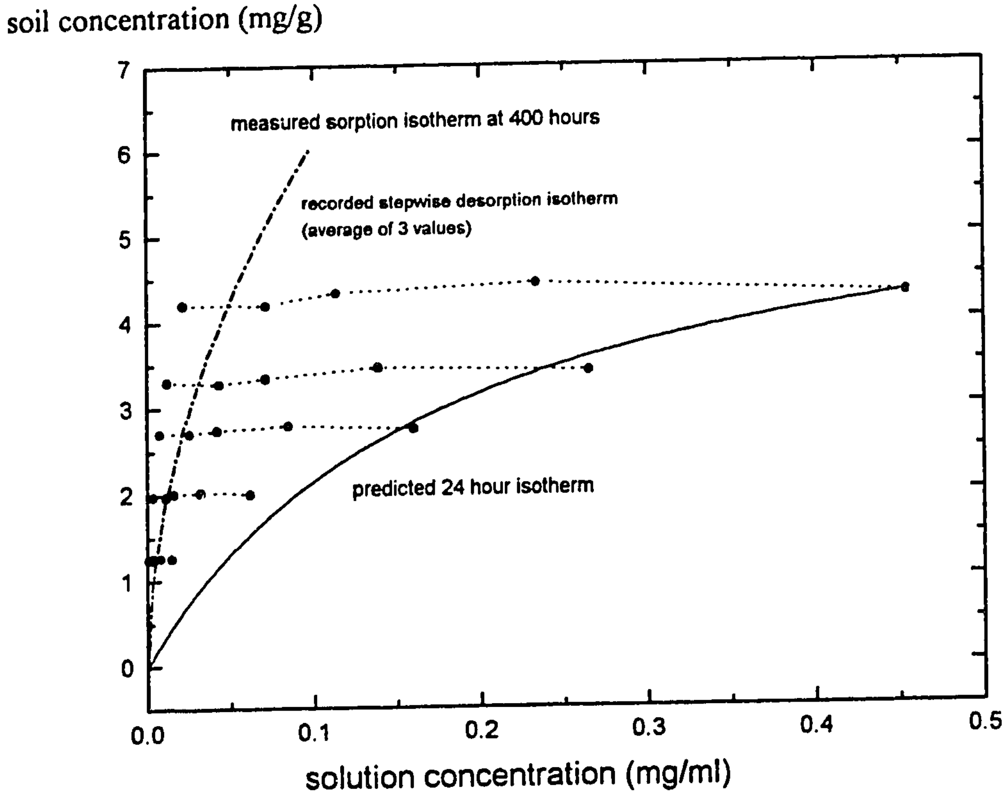

Figure 4.6. Stepwise desorption of 1-naphthol from the weathered shale using a 24 hour equilibration period and 50% solution replacement.

Since no desorption was measured during the stepwise desorption study for 1-naphthol, further analysis was conducted using the filter columns to determine if 1-naphthol was irreversibly sorbed in the shale material (fig. 4.7).

Results for sorption of naphthol from table 4.1 were used to predict a theoretical desorption isotherm assuming all material was reversibly sorbed in the shale sample. To estimate the theoretical rate of desorption the estimated value of D_e was substituted into the equation for solute diffusion into an infinant reservoir from a spherical particle containing uniform solute concentration (Crank, 1975). Results from the filter column were compared with predicted results.

When the shale material was extracted from batch solution and placed in the filter cell, approximately 0.3 ml.of solution containing 1-naphthol was also introduced in the pore space of the compacted shale material. This represented approximately 1/40 th of the total 1-naphthol introduced into the filter column. The first collection period illustrated in figure 4.7 was conducted after at least 10 pore volumes had been eluted through the collection column. It was assumed that all 1-naphthol originally present in the introduced solution was removed during the first collection period. Therefore, the amount of 1-naphthol collected during this time period represented a total of solution-naphthol + naphthol desorbed from the soil. To estimate the amount of sorbed naphthol removed for this period, the total amount of solution naphthol introduced initially present in solution was subtracted from the total amount collected. The difference between the two values was used to calculate the first data point represented in figure 4.7. For all other data points, it was assumed that all naphthol collected was desorbed from the shale sample.

For desorption of 1-naphthol using the filter columns, 3 replicates were attempted, but results from only 2 are reported here (fig 4.7). In the third replicate, there was evidence that by-pass solution flow occured around the clay cell, so this cell was rejected from the test data set. For the two replicates analyzed, Most of the 1-naphthol seemed to be reversibly sorbed in the shale material. Desorption seemed to follow predicted D_e calculated from the rate of sorption of 1-naphthol in the batch equilibrium experiments. The desorption rate, however, was at least a factor of 100 lower than that which would have been predicted based on the effective diffusion coefficient measured in the diffusion cell (table 4.1). For the first data set, approximately 10% of the total sorbed material did not desorb during the analyzed period. Deviation from the desorption isotherm predicted by the rate of solute uptake occured after 48 hrs. No test was conducted to determine the concentration of solute remaining in the clay cell at the end of the experiment. Thus the difference between the observed and predicted line could also have been due to an incorrect mass balance for the cell. No apparent deviation from the predicted line was observed for the second data set.

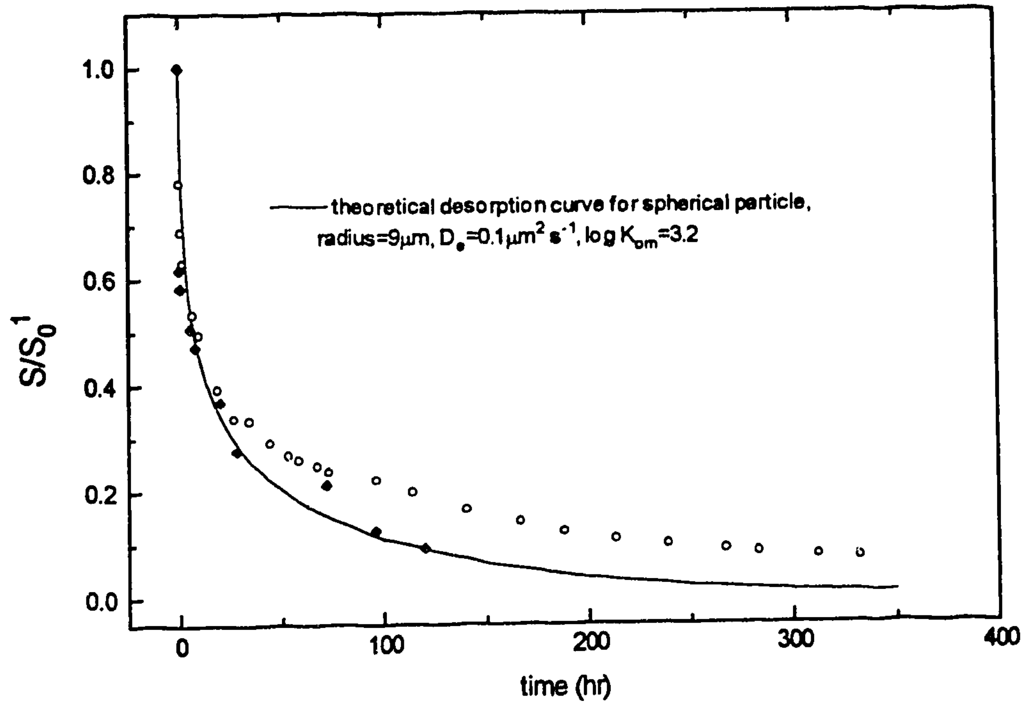

Figure 4.7. Desorption of 1-naphthol from the clay cell as a function of time. [1]The value of S_0 represents the total amount of 1-naphthol sorbed in the shale material after 2 weekds as the value of C is caluclater after subtraction of the cumulative amount of 1-naphthol collected from the C-18 column.

4.5 Discussion

Calculations have been based on the fact that organic material is located in small aggregates, 9 μm in radius. With the mechanical disturbance used in the present experiment, clay materials from the shale will tend to remain as small aggregates about 20 μm in diameter (chapter 3). Although size distribution of water stable aggregates ranged from about 100 μm to 10 μm, the assumption that all material is concentrated at an aggregate size of about 17 μm will lead to only small errors. If pore space within the aggregate tends to be coated with organic material, movement of the organic contaminant within the pore space will be controlled by D_e/R_{om} where,

$$R_{om} = 1 + \frac{\rho}{n} K_{om} \qquad 4.5$$

Alternatively, for pore regions where the mineral material is in direct contact with the surface of the pore, diffusion within the pore will be controlled by the sorption coefficient for the mineral deposit.

Twenty four hour sorption coefficients for the shale material have been estimated previously as log K_{om} = 3.1, 5.0, and 2.3 for naphthalene, anthracene and 1-naphthol respectively (Qualizza, 1994). Based on the predicted diffusion coefficient and 2 week equilibrium experiments, similar values would be predicted from the present data set for a 24 hour equilibrium period and soil:solution ratios of 1:10 (naphthalene and 1-naphthol) and 1:1100 (anthracene) (Qualizza, 1994). For the mineral material, a value of K_m can be estimated at 2.3, $\leq$0.3 and $\leq$3 ml g^{-1} for 1-naphthol, naphthalene and anthracene respectively (Qualizza, 1994) where K_m is the sorption coefficient for the clay minerals in the shale. Thus diffusion into mineral aggregates will be faster than can be observed using the present methodology. Any slow rates due to aggregate diffusion can therefore be assumed to be due to sorption within organic matter or organic coated minerals.

Because organic matter was distributed within distinct regions larger than 20 μm within the original shale, grinding would have resulted in a similar distribution of material in this fraction as that observed in the size distribution data (chapter 3). It was assumed that 2.7% of the total aggregates (by wt.) will diffuse at a rate controlled by R_{om} with an average particle radius of 9 μm and a particle density of 1.85 Mg m^{-3} (chapter 3). Since the aggregate density of material which is dominantly organic matter will tend to be somewhat lower than the average aggregate density, aggregates containing large amounts of organic matter will tend to be larger than predicted here. Therefore, the actual path length may be greater than 9 μm used here. Uptake data for naphthalene and anthracene, however, seem to conform reasonably well to that predicted by the assumed values.

For 1-naphthol, sorption and desorption from the shale was considerably slower than predicted based on simple diffusion analysis. The predicted sorption rate of 1-naphthol seems to conform to the slower sorption rate curve predicted by Brusseau and Rao (1989b) for polar organic contaminants. Alternately, the observed rate of sorption for both naphthalene and anthracene seem to be in the same range as the expected sorption rate predicted by Brusseau and Rao (1989b) for more hydrophobic organic contaminants.

1-Naphthol is a weak acid with a pKa of 9.3 (Chen, 1992). Thus, 99.9% of the naphthol in solution should have been in the uncharged form at the pH used in the present study. Sorption on pure clay minerals, alternatively, is much stronger than that observed for anthracene or naphthalene (Qualizza, 1994). Modelling studies have suggested that there is potential for 1-naphthol to form polar interactions with humic substances (Qualizza, 1994). This type of bonding structure may be stabilized by some form of ionic bridging using Ca^{2+} in solution. Although direct evidence is not available for 1-naphthol, molar heats of sorption on test organic compounds for phenol has suggested the possibility of complex sorption mechanisms (Xing, 1994). The difference in the nature of sorption may have meant that chemical sorption mechanisms or some other form of diffusion such as intra-organic matter or intra-particle diffusion may have been more important in controlling 1-naphthol uptake.

Molecular diffusion has previously been suggested as a possible controlling mechanism for sorption kinetics (Brusseau and Rao, 1989b, Pignatello, 1990, Wu and Gschwend, 1986). In general microaggregate diffusion models have been rejected because the rate of sorption tends to be slower thant the predicted rate of diffusion based on equation 4.1 if a homogeneous material is assumed (eg. Brusseau and Rao, 1989a). In the present study, an organic matter diffusion model seemed to explain rates of uptake reasonably well. The only major difference between the microaggregate diffusion model seen here and the intraorganic matter diffusion model is that restricted pore diffusion does not need to be invoked in order to explain uptake rates. Rates of uptake will be sufficiently slow if organic materials are concentrated in regions of 20 μm within the aggregate.

The varying results for 1-naphthol, however, do suggest that other rate controlling mechanisms may also be involved. This may be due either to some form of retarded diffusion or chemisorption which is controlling uptake of 1-naphthol. Several researchers have found long term sorption rates which cannot be explained without some other retarded diffusion process (Ball, 1990, Steinberg et al. 1988). Results for 1-naphthol seem to conform more closely to these results than to uptake results for anthracene and naphthalene.

It is dangerous to make generalizations based on characteristics of this particularily heterogeneous deposit. Additionally, only short term sorption (less than 6 weeks) sorption rates have been measured the present study. Extrapolation to predict values over periods of years may be subject to considerable error, particularily in cases such as 1-naphthol where it is quite clear that sorption equilibrium cannot be obtained during short term analysis. Where soils have been subject to long term contaminant events, desorption results often do not fit any pure diffusion based model. For example, Steinberg et al, (1988) studied desorption of dibromomethane from deposits which had up to 19 years of contamination history. In this deposit, rates of desorption were found to be highly temperature dependant and showed only a secondary dependance on aggregate size. For a given aggregate size, desorption rates were several orders of magnitude lower than could be predicted by any reasonable retardation coefficient. It is unlikely that a pure physical model could predict this type of desorption behaviour. There are, however, several observations which should be noted with the microaggregate diffusion model:

1. Organic matter clay complexes are fundamental to much of the microaggregate developement. Water stable microaggregates containing high amounts of organic matter occur dominantly between 2 and 250 μm in size. For water stable aggregates, smaller sized aggregates are progressively more resistant to breakdown than larger aggregates (Dexter, 1988; Edwards and Bremner, 1967; Gregorich et al, 1988; Levy et al, 1993; Oades and Waters, 1991; Tisdall and Oades, 1982).
2. For microaggregates containing high concentrations of organic material, mineral grains within the microaggregate also have been shown to be coated with organic material between 0.5 and 1 μm thick (Sullivan and Koppi, 1987). This suggests that intraorganic matter diffusion path lengths may be very short but

interorganic matter path lengths may extend over much of the range of the microaggregate.

3. When organic matter is degraded in a soil, larger water stable aggregates seem to be disrupted first. Organic matter within the smallest size fraction (2-20μm) seems particularily resistant to breakdown Small water stable microaggregates are suggested to contain highly altered, less substituted organic matter centers around which the mineral material adheres (Dexter, 1988; Oades et al, 1987; Oades and Waters, 1991; Tisdall and Oades, 1982; Weill et al, 1988). Material in this fraction would likely have a greater sorption coefficients than the bulk soil organic matter (Xing, 1994).
4. Measurements of sorption coefficients in short term rate experiments indicate a correalation between the rate of sorption and the measured distribution coefficient for the deposit (Brusseau and Rao, 1989b). Although samples were mechanically altered, procedures employed in most studies would have likely left water stable microaggregates (<250 μm in size) intact. Additionally, there is some evidence to suggest that procedures which destabilize the microaggregate can increase the rate of sorption (e.g. Ball and Roberts, 1991; Karickoff and Morris, 1985; Pignatello, 1990; Steinberg et al., 1987). Diffusional controlled sorption into a varying sized (20 to 250 μm) particles coated with organic matter will result in a range sorption rates which is inclusive for predicted rates of sorption of hydrophobic organic chemicals.

For aggregated soils, dual porosity or two domain models have been employed to describe solute flow (eg. Brusseau et al, 1994; Brusseau and Rao, 1989, 1990). These models assume mass flow occurs dominantly around the aggregate and diffusion limits uptake within the aggregate materials. Diffusion limitations have been used successfully in several previous studies to describe both solute sorption (Wu and Gschwend, 1986) and biodegradation of sorbed organic contaminants (Scow and Alexander, 1992, Chung et al, 1993). In all cases, a homogeneous aggregate is assumed. In the present study, a one-dimensional 4 mm path length was both observed and predicted to be sufficient for homogeneity of the material to be assumed (Appendix A.1). If the path length is reduced to less than 1 mm, however, diffusion through the main soil matrix is fast compared to solute uptake by the organic material and solute uptake becomes increasingly independent of path length. This effect will be magnified as the concentration of organic matter in the cell is decreased or as the size of the diffusive center is increased. In the original shale deposit, deposits composed dominantly of organic material were observed which were several millimeters in size and several hundred microns wide. Under these conditions, R_{om} will become the dominant mechanism controlling solute uptake for centimeter sized structural units.

One problem with the present approach is that it still assumes only a single value for K_{oc}. Actual sorption coefficients are highly dependent on the nature of the organic matter deposits (Xing, 1994). For the given shale, K_{oc} of the test compounds is at least a factor of five greater than that of a surface soil (Qualizza, 1994). Presently, there is no way to determine how the nature of organic matter differs within the short, µm scale.

Thus actual variations in retardation coefficient may be much greater within the clay pores than is reported in this study.

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Chapter 5

Synthesis

In this thesis, it was stated that diffusion is fundamental in controlling transport of organic contaminants in fine textured deposits and aggregates. An attempt was made to link rates of sorption with rates of diffusion in aggregates. Measurement of diffusion, however, can be complicated by the heterogeneous nature of a natural material. This heterogeneous nature must be considered in the diffusion analysis in order to properly link the diffusion coefficient with measured rates sorption and transport in the deposit. During the course of this investigation, two major hypotheses were proposed based on problems encountered in linking the measured values with actual experimental data. These were:

1. That clay materials can act to restrict entry of larger hydrophobic molecules and ionic species into the clay pore space. This may result in lower measured diffusion coefficients when they are estimated based on free solution water outside the clay pore space. Restricted entry seems to result from the change in activity of the species as it enters the clay pore space from the free water solution (chapter 2).
2. That short term (week to month) rates of sorption measured for organic contaminants may be controlled by microaggregate diffusion. Microaggregate diffusion coefficients will be much slower than those predicted from the bulk diffusion coefficient due to the higher retardation coefficient for organic matter coated microaggregates than is measured for the bulk soil. This may result in

slow rates of sorption and desorption even for moderately sorbing hydrophobic organic species (e.g. anthracene) (chapter 4).

These concepts do suggest an avenue to re-evaluate literature data on rates of sorption of organic contaminants and diffusion measurements in clay textured materials. Some treatment of literature has been attempted in the body of the thesis. For most literature data, however, too many assumptions had to be made to obtain missing variables so most of literature data regarding these two hypotheses were disregarded.

Traditionally, diffusion measurements have been made by fitting a data set to a given diffusion model. Diffusion measurements, have usually been conducted using only one method of analysis. This type of analysis lends itself to the use of fitting parameters which have not been validated for a given test data set. In chapter 1, fitting parameters used in diffusion measurements are listed. For most literature data, concepts such as ion exclusion, surface diffusion, reduction in sorption with soil compaction or pore exclusiony have been used as fitting parameters to make a set of data fit to the diffusive flux model. These parameters have not been directly validated. Thus it is unknown whether the proposed theory is influencing solute flux or whether the value is simply an empirical formulae which aides in fitting the equation to a known data set.

For diffusion of anions in clays, it is still reasonable to assume that anion exclusion is occurring at the surface of the clay. This may limit the solute accessibility to the small clay pore space and result in an apparent reduction in solute concentration in the clay pore space. Because sorption of anions in the clay materials is generally lower than experimental error, it is impossible to tell if the apparent sorption coefficient is reduced by the compaction of the clay cell.

For some cations and for organic materials, both diffusion and apparent sorption in the clay seem to be affected by compaction (chapter 2). Surface diffusion has been used to explain this phenomenon, and may still be a possibility for cations. For hydrophobic organic moities, however, this seems untenable since most have a very low affinity for the surface of the clay material. Sorption here is dominantly within the organic matter regions. These regions are heterogeneously distributed through the soil and would not form a continuous path for diffusion through the soil. The apparent drop in solute concentration at the clay interface in several experiments (chapter 2) is also not explained by invoking the theory of surface diffusion.

To investigate microaggregate diffusion, reevaluation of literature data was attempted. Again, however, reevaluation of most literature data required too many assumptions about the nature of the material used which could not be directly quantified from literature results. In particular, this reevaluation required speculation on the distribution of organic materials within a ped for which data were not present in any sorption rate experiments found in the literature. In his 1990 thesis, Ball presents a very good discussion on how the application of contrasting assumptions about the nature of the geological material used in his study could be used to explain the same sorption rate data set. Unless some data are available on the distribution of organic materials in a given deposit, the microaggregate diffusion hypothesis becomes simply another empirical fitting function. Only with additional information can the validity of this hypothesis be tested.

For both hypotheses, therefore, evaluation of the literature required too many a priori assumptions which could not be verified for the given experiment. Because one of the main attempts for this thesis, as stated in chapter 1, was to avoid the use of untested fitting parameters, most of this evaluation was rejected from the main body of the thesis. When re-evaluations of literature data were conducted, however, some data sets revealed predictions about characteristics of the deposit which could be potentially verified by further experimental evidence. Since these areas did suggest possible ways of verifying proposed mechanisms of transport, some of this work has been included in the discussion.

5.1 Diffusion of Solute in the Clay barrier

Diffusion research on organic chemicals is a relatively new field of research, thus very little actual experimental data exist. Diffusion of inorganic chemicals through clays, however, has received more attention. There are still, however, some discrepancies between predicted and observed rates of diffusion.

Several researchers have suggested that cations may diffuse faster in clay materials than is predicted on the basis of aqueous phase diffusion alone (Berry and Bond, 1992; Cheung, 1990; Jensen and Radke, 1988; Kim et al., 1993; Muurinen et al., 1985, 1987; Staunton and Nye, 1983; Staunton, 1986). This has generally been explained by diffusion of sorbed ions along the surface of the clay . The sorptive energy of exchangeable cations is sufficiently low that it is believed that exchangeable cations may diffuse along the surface of the clay plate. As sorption of the cation increases, this pathway is believed to become a dominant diffusive pathway (Cheung, 1990). Surface diffusion studies, however, relied on predictions of sorption coefficients for the clay material under conditions that were different from those used in the diffusion experiment. In many instances, determination of surface diffusion was conducted by altering sorption of the inorganic ion by the clay material. Concentration of total dissolved ions in solution was increased for separate experiments to suppress sorption of the cation being studied. In these studies, it was found that the ionic concentration in solution had a minimal effect on the rate of diffusion of the test species but had a large effect on the ionic exchange. The lack of effect of the ionic concentration on the rate of diffusion was explained by the tendency of the sorbed species to diffuse along the surface of the clay.

For organic chemicals, surface diffusion cannot explain the rate of solute transport. Organic matter in soil does not form a continuous pathway, which would be necessary for surface diffusion to occur. Since the organic contaminant reacts only weakly with the mineral layer, this layer would act as a block to further surface diffusion. Thus, where a similar phenomenon has been observed it has been suggested that sorption in the compacted clay is not as great as that in an uncompacted soil (Myrand et al. 1992). This suggests that part of the clay material is not accesible to the diffusing species.

For anionic contaminants which do not sorb, or sorb very poorly on the soils, several researchers have found that diffusion rates measured on the basis of external solution concentrations can be lower than those predicted or measured from the concentration of solute within the clay pore space (Cheung, 1989; Muurinen, 1990; Oscarson et al, 1992; Sawatsky and Oscarson, 1991a,b). It has been suggested that this is due to anionic exclusion from the surface of the clay (Cheung, 1989). Anionic exclusion would result in a lower porosity available for solute diffusion than is available for water in the clay cell. Thus, the available porosity of the clay will be overestimated, resulting in a larger predicted diffusion coefficient than is actually observed.

Recently, it has been shown that surface diffusion is likely not an important phenomenon in the diffusion of several cations in bentonite clay (Oscarson, 1994). When actual sorption of Cs^+ in a clay textured material was accounted for, it was found that the rate of diffusion was similar to that predicted on the basis of theory and on the basis of within-clay diffusion measurements (Chapter 2). Similarly, when sorption measurements were conducted in the clay material, it was found that both an increase in soil/water ratios and compaction of the clay resulted in an apparent decrease in the measured sorption of Cs^+ in the clay material (Oscarson et al. 1994). This called in question earlier results suggesting surface diffusion as an important phenomenon controlling Cs^+ diffusion. Alternatively, the results do suggest two possibilities:

1. Sorption coefficients do actually decrease with compaction of the clay. It has been suggested that this is due to pore space which is inaccessible to the solute, thus limiting the surface area available for sorption (Oscarson et al., 1994).
2. There is an apparent decrease in sorption coefficients resulting from the exclusion of solute from the clay pore space. Unlike point 1, this point suggests that solute concentration is not eliminated from the clay pore space but is lower than that in the bulk solution over a wide range of pore sizes. An overall exclusion of solute from the clay pore space results in a lower observed pore solution concentration than is present in the external solution. This lower pore

solution concentration will be controlling the amount of sorption in the soil. Since the solute concentration is higher in the external solution, a higher amount of sorption will be predicted on the basis of the external solution than actually takes place within the clay cell.

Reference can be made to figure 5.1 to illustrate the difference between the two hypotheses. Although both hypotheses assume that the solute concentration change within the clay pore space is described by a continuous curve, different assumptions are made over the range at which solute concentration changes are acting.

Hypothesis 1 tends to assume that solute concentration changes will occur only within the first few nanometers of the clay surface. The zone in which solute concentration is changing with distance from the clay surface is is relatively narrow. Thus, solute access will be relatively unrestricted in most clay pores larger than a few nanometers in size. For pores smaller than this, the clay pore space is virtually inaccessible to the solute molecule.

Hypothesis 2 accepts a much longer zone over which solute concentration is changing within the clay pore space (tens to hundreds of nanometers). Thus much of the clay pore space will fall into the affected zone. This will a reduction in the average concentration of the solute within the clay pore space. By this theory, there is a continuum of solute concentration from very low in the small clay pores to equal to that of the bulk solution concentration in the largest clay pores. The concentration however, can be represented by a value averaged over all clay pore sizes.

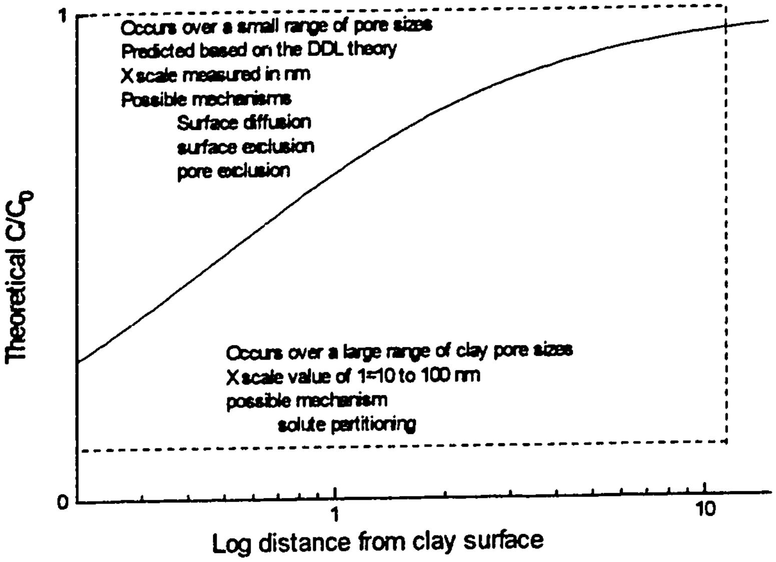

Figure 5.1. Theoretical models for solute concentration near the clay surface.

In chapter 2, it was suggested that hypothesis 2 is likely controlling diffusion in the clay. Since to a first approximation, sorption is a function of available clay surface area, very little pore space would need to be excluded to result in the observed decrease in sorption in the clay cell (Chapter 2). Alternatively, the apparent decrease in the Cs^+ sorption coefficient from that measured in batch reaction to that measured in compacted clay at the same soil:solution ratio seems to be of the same order of magnitude as the observed decrease in Cs^+ diffusion as measured by the steady state method. This is similar to present results for sorption and diffusion of naphthol and naphthalene in compacted shale material(Chapter 2). This would be the case if exclusion of solute at the surface of the clay was taking place.

At present, data is not available to accurately predict what is controlling the apparent decrease in sorption and diffusion across the clay barrier. Evidence, however, is sufficient to conclude that the effect is real and must be considered in developing boundary conditions and models. It cannot be automatically assumed that the surface solute concentration is similar to the clay pore concentration if this boundary condition has not been actually analyzed. According to this theory, diffusion may sometimes be slower than actually predicted by most diffusion models due to solute exclusion from the pore space.

In chapter 2, it was suggested that exclusion was taking place due to the change in solution activity between the external solution and that of the clay pore water. If the product of activity coefficients within the clay pore is greater than that of the external solution, preferential exclusion of molecules and ions from the clay pore space would be predicted in order to maintain equilibrium between the two phases. However, if the salt concentration of the external solution is increased, the activity coefficients of the two solutions (within pore and external) will become more similar and solute exclusion should be suppressed. Then both the predicted diffusion rate on the basis of the external solution concentration and the measured K_d should approach the value measured in the compacted clay.

When a literature search was conducted to find data on diffusion coefficients with solutions of varying ionic potential in similar clay deposits, very little data was found. What was available generally reported large variations in diffusion measurements which would tend to hide other trends in the data. One study on Cl^- did reveal that solute diffusion did increase with increasing salt concentration (Muurinen et. al., 1989). This, however, could also be explained by the suppression of the diffuse double layer at the surface of the clay with increasing salt concentration. For Cl^-, no observable sorption occurs so it is impossible to tell if the apparent sorption coefficient is similar to that predicted from a loose clay at a similar soil/solution ratio. This would be more telling in separating out the possibility of exclusion from the clay surface from that of the concentration reduction model. If solute exclusion is only occurring near the clay platelet, the average pore solution concentration should still be near that of the external solution. In this case, the effective porosity may be lower than the actual porosity, but the sorption on the clay should still be predicted reasonably well by batch equilibrium experiments. If solute is being excluded from the clay barrier due to a change in activity, both diffusion and sorption will be affected. An increase in external salt concentration, however, should cause the predicted and observed values to begin to merge. There is some suggestive evidence from earlier studies on Cs^+ that this is indeed what is happening (Jensen and Radke, 1988; Muurinen et al. 1985, 87). In papers where surface diffusion was used to explain the difference in predicted and observed breakthrough curves, it can be suggested that what was actually being observed was a change in the apparent sorption coefficient, K_d for Cs^+. If this is the case, then this model would suggest that whereas the apparent sorption coefficient was much higher in batch equilibrium experiments than in the clay cell for solutions containing low salt concentrations, the two values tended to merge as the salt concentration increased. In addition, the agreement between the predicted effect on the apparent sorption coefficient for Cs^+ based on the present model (Chapter 2) and that observed experimentally by Oscarson (1994) does suggest that this interpretation may be valid. The data set, however, is too limited to support the present theory. This is particularly true when it is considered that measured diffusion coefficients may vary by as much as a factor of 2 to 3. Thus proof of this theory would require a much more detailed comparison between measured and calculated diffusion coefficients.

5.2 Microaggregate diffusion in the organic material

In chapters 3 and 4, it was suggested that the aggregate hierarchy model may be important in describing the heterogeneous distribution of organic matter in a soil material, and therefore, may be important in determining rates of diffusion within soil aggregates. An example of the aggregate hierarchy model is illustrated in figure 5.2. The terms for this particular example have been borrowed from Dexter (1988). Although some terminology will change depending on the literature source, the general size relationships described in the figure seem to remain constant.

Most of the following discussion is centered around the argument that organic matter or organo-mineral aggregates are particularily prevelant in the soil in the range of 10 to 30 μm in size. This would place these aggregates within the cluster and small microaggregate size range according to the aggregate hierarchy model. Although it is recognized that the 10 to 30 μm size range is rather narrowly defined given the qualitative data present on soil organic matter distribution, it was found that this size range was sufficient to explain most rates of sorption for hydrophobic organic chemicals reported in the literature.

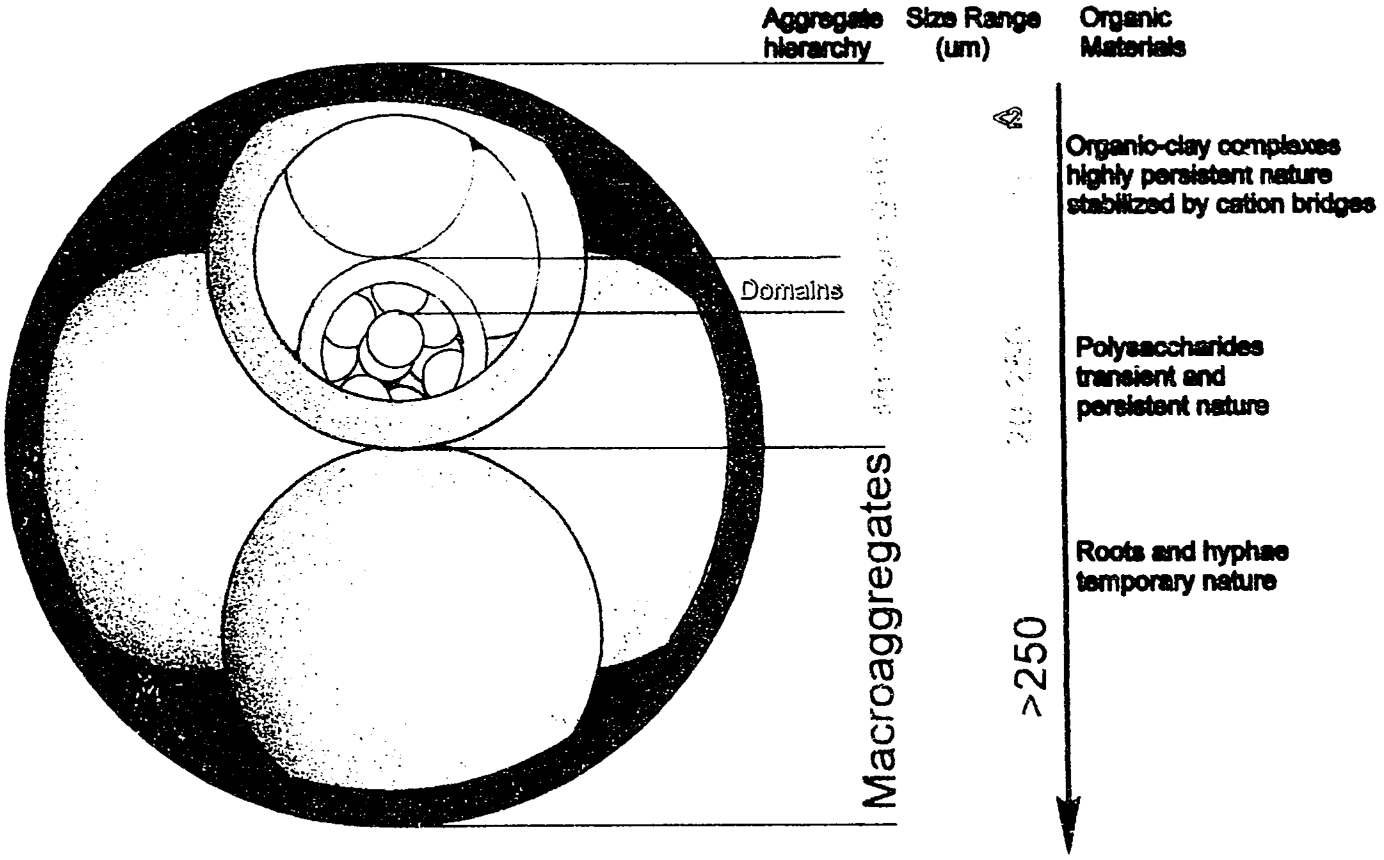

Figure 5.2 A pictorial example of the aggregate hiearchy model as described by Dexter (1988).

Microaggregate diffusion stopped being considered as a possible option to explain short term (hours to weeks) rates of sorption around 1990. Prior to this, several researchers had considered the option that rates of sorption were actually measured rates of aggregate diffusion (Karickhoff and Morris, 1985; Wu and Gschwend, 1986, 1988). The reasons for rejecting the intra-aggregate diffusion model for explanation of rates of sorption included:

1. Rates of sorption were slower than those predicted by aggregate diffusion rates using any reasonable aggregate path length (e.g. Brusseau and Rao, 1989a).
2. Solute breakthrough curves for non-sorbing solutes are described reasonably well by a simple solute transport model. (Brusseau and Rao, 1989a). This suggests a limited amount of diffusion-controlled region within the deposit since this region would act on non-sorbing and sorbing species alike.
3. Rates of sorption seemed to be tied to overall K_d and not to K_{oc} suggesting both the presence of organic matter and the path length are important parameters in predicting solute sorption (Brusseau and Rao, 1989b). A model where organic matter is dominantly regionalized into certain aggregates would suggest that sorption parameters would be controlled by K_{oc} and not K_d.
4. A lack of correlation between the calculated mass transfer coefficient and the rate of solute uptake (Brusseau and Rao, 1989b).
5. The discovery of extremely slow rates of diffusion, even for deposits which have very low sorption coefficients (e.g. Ball, 1990, K_d<10).

Thus, rates of diffusion are now being investigated using an intra-organic matter or intra particle diffusion model. For long term desorption studies, it seems reasonable to conclude that rates of desorption are too slow to be explained without some sort of chemical or physical interaction between the solute and the reactive stationary phase (e.g. Pignatello, 1990a,b; Steinberg et al. 1987). In addition, interactions of substituted organic solutes (e.g. 1-naphthol, present study) cannot be explained by a pure aggregate diffusion model. However, if organic matter in most soils exists as a dominant surface coating in particular aggregates, much of the short term rate data could be explained by a simple aggregate diffusion model without invoking more complex intra-organic matter or intra-particle models. Thus it may be valuable to reevaluate some of the data using an intra-aggregate model, assuming a regionalization of organic matter on the micro scale.

In his Ph.D. thesis, Ball (1990) suggests that a pore diffusion model could account for rate data presented by Brusseau and Rao(1989b) even if the length scale did remain constant. Ball (1990) points out that the use of non-reactive tracers to obtain evidence for a physical non-equilibrium model will tend to be in error as values of $\frac{\rho_a}{n}K_d$ become larger. In a comment on the paper by Brusseau et al., (1989), Ball et al. points out that the data used by Brusseau and Rao cannot be used to exclude a pore diffusion model. The model used by Brusseau and Rao fails to account for potential retardation due to sorption. Thus, their model adequately accounts for changes in transport rates due to changes in the value of D_e, but the measured rate of sorption is actually dependant on the value, D_e/R_d. Since the model used by Brusseau does not account for the value of R_d, the comparison between predicted rates of sorption based on the model and observed rates of sorption is invalid. Wu and Gschwend (1986) have already suggested the use of a pore diffusion model to explain rates of sorption. In their model, an intra-aggregate porosity of 13% is assumed, which is very close to predictions here as well as average porosities of water stable silt sized aggregates suggested in the agricultural engineering literature (Chapter 3). The major differences between their model and the one proposed here is that they assume a constant K_d for all aggregates with the path length given by the average size of the aggregate whereas in this study, it is suggested that K_d will vary from the sorption coefficient for the general mineral matrix (K_m) to the organic matter sorption coefficient (K_{om}) with an average path length somewhere between 2 and 250 µm (or the size given by water stable microaggregates). Where aggregates are stabilized dominantly by the presence of organic materials, retardation at the pore surface will be controlled by K_{om}. Thus, diffusion rates in the microaggregate could be as much as two orders of magnitude lower than that predicted by Wu and Gschwend based on the use of K_d. As well, aggregate size will become important at scales less than 250 µm where regionalization is most dominant.

Since little is known about actual organic matter distribution, some a priori assumptions will have to be made. These will include

1. Density in the organic matter dominated aggregate is similar to that predicted for silt sized aggregates (1.8 (measured) to 2.15 (literature), Chapter 3).
2. Where organic matter is dominant, microaggregate diffusion will be dominantly controlled by K_{om} since most pores will be coated with organic materials.
3. Average tortuosities in the aggregate will be about 0.1.

4. Oades has proposed a hierarchical concept for water stable aggregates (Chapter 4). Within this concept, water stable microaggregates are distributed in very distinct size regions. Thus, rather than being distributed across the entire region from 2 to 250 μm, the aggregate size which is important for this study, (i.e. the main aggregate size which is stabilized by organo-mineral clay complexes) may be distributed over a fairly narrow size range. Thus, a single path length will be assumed to describe the average aggregate size.

Point 4 is particularly problematic. A single path length may cause some errors in prediction. It is a reasonable approximation provided the range of aggregate size is limited (Wu and Gschwend, 1988). This assumption will, however, tend to cause error in predicted rates of sorption as the size range becomes larger. Thus if aggregate size actually varies over 2 orders of magnitude (i.e., anywhere from 2 to 250 μm), significant errors may be introduced. Additionally, decomposition of organic matter in a deposit has been shown to break down larger aggregates first and have little influence on the smallest microaggregates (2 to 20 μm) (Chapter 4). Thus the average path length will also be influenced by the amount of organic matter present in the deposit and the average age of the organic material within the deposit. This general model, however, will allow for some predictions on the nature of the distributed material which can be verified experimentally.

In soils used by Brusseau and Rao, (1989b), materials represent either surface soils or sediments. Thus most will contain a large fraction of water stable microaggregates. Although many materials were mechanically altered prior to the experiments, alteration was sufficiently mild that most of the microaggregates (less than 250 μm size fraction) would have remained intact. If some microaggregates are coated with organic material, the resultant diffusion coefficient will be approximately

$$D_a = \frac{D_0 \tau_a}{R_{om}} \qquad 5.1$$

with

$$R_{om} = 1 + \frac{\rho_a}{n} K_{om} \qquad 5.2$$

Here, D_a is the microaggregate diffusion coefficient and R_{om} and K_{om} define the retardation coefficient and sorption coefficient in the organic matter coated aggregate respectively.

The two site model used by Brusseau and Rao can be considered an approximate solution for the diffusion model (Brusseau and Rao, 1989a). The two site model predicts that solute uptake from a batch equilibration experiment will be given by (Karickhoff and Morris, 1985),

$$f_u(t) = 1 - (1 - X_1)e^{-k_2 t} \qquad 5.3$$

where $f_u(t)$ is the fraction of solute taken up at time t, X_1 is the fraction taken up by the fast phase in the two site model and k_2 is the rate coefficient for the slow uptake phase. This is very similar to the approximate solutions for diffusive uptake of solute in a planar, cylindrical or spherical geometry (Crank, 1975) where,

$$\frac{M_t}{M\infty} = 1 - \sum_{n=1}^{\infty} \chi_n e^{-\beta_n D_a t / L^2} \qquad 5.4$$

Here, M_t is the solute mass uptake by the aggregate, $M\infty$ is the maximum mass of solute uptake, χ and β are fitting parameters which are dependent of the aggregate geometry and L is the path length. For large values of D and t, this will reduce to,

$$\frac{M_t}{M\infty} = 1 - \chi e^{-\beta D_a t/L^2} \qquad 5.5$$

For a microaggregate diffusion model, the measured rate coefficient will, therefore, be a function of D_a and the average path length or,

$$k_2 = \beta \frac{D_a}{L^2} \qquad 5.6$$

D_a is the apparent diffusion coefficient, which can be defined as,

$$D_a = \frac{D_0 \tau_a}{R_a} \qquad 5.7$$

with R_a being the apparent retardation coefficient, here suggested to be some unknown combination of retardation due to sorption at mineral and organic matter surfaces in the pore and, for a linear sorption isotherm,

$$R_a = 1 + \frac{\rho}{n} K_a \qquad 5.8$$

where K_a is the apparent sorption coefficient. Combining equations 5.6, 5.7, and 5.8,

$$k_2 = \frac{D_o \beta \tau_a}{L^2} \frac{1}{1 + \frac{\rho}{n} K_a} \qquad 5.9$$

For large values of K_a, this will reduce to,

$$\log k_2 = \left(\log \frac{D_o \beta \tau_a}{L^2} - \log \frac{\rho}{n} \right) - \log K_a \qquad 5.10$$

Brusseau and Rao (1989b) found a reasonable relationship between the rate and the partition coefficient with,

$$\log \mathbf{k}_2 = 0.301 - 0.668 \log \mathbf{K}_d \qquad 5.11$$

where K_p was the overall partition coefficient. They suggested that an aggregate model could not be used to explain the data because the mass transfer coefficient predicts that the sorption coefficient will have little effect on the sorption rate in the deposit. The mass transfer coefficient is given by,

$$\mathbf{m} = \frac{\beta \mathbf{D}_0 \tau_a}{\mathbf{L}^2} \qquad 5.12$$

which only considers solute flux at the aggregate boundary. Based on equation 5.10, the rate of change in solute concentration will be given both by mass transfer coefficient and sorption within the deposit. Thus the LFER relationship proposed by Brusseau and Rao could also be considered an approximation for equation 5.4. For non-hydrated molecules, free water diffusion coefficients will be approximately inversely related to the molecular volume (Wilke and Chang, 1955). If the diffusion coefficient of benzene is assumed to be 1020 $\mu m^2 s^{-1}$ (Bonali and Witherspoon, 1968), the free water diffusion coefficient for test compounds will tend to be within a range of 100 to 1000 $\mu m^2 s^{-1}$. If a spherical diffusion model is employed, the value for α is approximately π^2 (see equation 6.30, Crank, 1975). If we substitute values for $\tau_a = 0.1$, density =2.15, than the first term of equation 5.10 using the numerical value of 0.31 (equation 5.11) predicts an average particle radius of between 3 and 8 μm. Several problems may exist with this approach

1. The sorption coefficient is related to K_d, not K_{om}

2. The value for the slope of the log-log relation was found to be 0.7 (equation 5.11) whereas the present formula predicts a slope near 1(equation 5.10).

The slope of 0.7 is likely due to the error in approximation of equation 5.4 in order to obtain the two-site rate model. If it is assumed that the data can be explained by a diffusion into the aggregate according to equation 5.4, the latter terms in the summation will become increasingly important over longer periods of t as diffusion in the aggregate decreases. Thus, as the retardation coefficient increases, the actual value of k from the two site model will only be valid for large values of t. Because rate data is generally collected over a limited time period, this tends to cause an overprediction in the actual value of k for small diffusion coefficient (see, for example, Karickhoff and Morris, 1985, fig 5). A similar phenomenon may also occur in column experiments using pulses of contaminant which are in contact with the column for limited periods of time. Again, the two site rate model will approximate the data reasonably well only for large values of D and t.

As mentioned earlier, one of the original reasons for rejecting the aggregate diffusion model was that rates of sorption seemed too slow to be controlled by microaggregates present in the soil (e.g. Brusseau and Rao, 1989a). Karickhoff and Morris (1985), attempted to evaluate the significance of their measured rates of sorption assuming a diffusion based model. Using a 10 μm path length, which is similar to that of the most water stable aggregates, they predict that diffusion coefficient within the aggregate of 10^{-11} to 10^{-13} cm^2 s^{-1} would be necessary to explain results based on equation 5.4. If sorption by the material is accounted for, predicted diffusion coefficients will still be between 10^{-8} and 10^{-9} cm^{-2}s^{-1}. For an average free water diffusion coefficient of around 10^{-}

^{6} cm^{2}s^{-1}, an unreasonably large tortuosity factor would still be required to explain the data. If, however, retardation is being controlled by the organic matter fraction at distances within the 10 µm scale, the predicted diffusion coefficients will be within a factor of 10 of the free water diffusion coefficient (table 5.1). High values seem to be recorded only for soils with less than 1% organic matter. This factor may be due to a breakdown in the size of the smaller aggregates at very low organic matter contents. Although much of this discussion is presently speculative, it is quite reasonable to assume a very heterogeneous distribution at the 10 µm scale length.

Table 5.1. Predicted effective diffusion coefficients from rate data given by Karickhoff and Morris, 1985.

Compound	Measured K_d	% Organic Matter[1]	log R_{om}	Predicted D_e ($\mu m^2\ s^{-1}$)[2]
Hexachlorobenzene	7300	3.56	6.60	27
	1100	0.26	6.92	670
	1100	0.19	7.05	761
	32000	5.23	7.08	21
	28000	5.23	7.02	20
	2600	2.55	6.30	33
	3500	2.08	6.51	147
	2600	2.61	6.29	17
Pentachlorobenzene	8100	5.23	6.48	17
	7100	5.23	6.42	28
	2200	2.55	6.22	35
Pyrene	2900	5.23	6.03	11
	1300	2.55	6.00	50
Trifluralin	120	1.24	5.28	61
	23	0.19	5.38	200
	950	5.23	5.55	5

[1] Assuming percent organic matter = 1.72x percent carbon

[2] Based on equation 5.9. D_e is assumed to be $D_0\tau_a$, l is 20 µm, density is 2.15 Mg m^{-3}, and α is π^2.

5.3 Future Research

When this project is compared with literature research on the rate of movement of organic contaminants in soils, there seem to be three separate levels of resolution which are controlling desorption and transport of organic contaminants in soils. The three levels of resolution suggested here are as follows:

1. Diffusion within the macroaggregate (>1 mm in size). At this level, the soil material can be considered to behave as a relatively homogeneous medium. Thus use of an average sorption coefficient for the entire material (Chung et al. 1993; Wu and Gscwhend, 1986) or aqueous solubility where a separate oily phase exists (Feng et al. 1994) will likely lead to a good prediction of the rate of transport and degradation from the aggregate. Diffusion through the pore space at this level will behave as a simple self diffusion system with a fixed pore structure. At this level of resolution, dominant pore size is sufficiently large (μm size range) that hindered diffusion can be ignored. Only for macromolecules (about 100 nm in size or larger) will hindered diffusion become important.
2. Diffusion into the microaggregate (Chapter 4). In this instance, diffusion will still be through a fixed, large pore system. However, the deposit can no longer be assumed to be homogeneous. Since the mineral-organic matter complexes will tend to control uptake of organic contaminants in most deposits, the specific distribution pattern of this material in the deposit will be critical in controlling solute uptake. The sorption coefficient within this factor will be equal to or somewhat greater than the average K_{om} for the deposit. There is

now no way to determine how variable this factor is from one deposit to the next. However, since some literature suggests that the 20 μm fraction seems to be the most water stable, this may be a relatively standard size controlling sorption in the deposit. Thus, this size range might be used as a reference point to test if microaggregate diffusion may be controlling sorption rates in the deposit.

3. Transport and sorption within the sorptive phase. This phase at present is poorly understood. However, there does seem to be a long term sorptive uptake or desorptive release from the deposit which cannot be explained by diffusion in larger pore spaces. Sorption at this level may be controlled by intraparticle diffusion (Ball, 1990), some form of intraorganic matter diffusion (Brusseau and Rao, 1989a,b) or some form of rate controlled chemisorption. Some features about sorption in this phase are that there seems to be a much stronger temperature dependence on the rate of desorption (Steinberg et al. 1988) and the deposit shows an increasing sorption coefficient with time (Pignatello, 1990a,b). The polymer diffusion model proposed for intraorganic matter diffusion could result in a hindered movement of organic chemicals especially for highly collapsed, very hydrophobic portions of the organic moiety. Additionally, movement in small micropores could be subject to hindered diffusion which could require an activation energy for release. This phenomenon would tend to be much more temperature dependent as it will be affected by activated diffusion.

At present, prediction of levels 2 and 3 are based on a limited data set which is available for only certain test compounds. If, however, these levels of resolution can be clearly defined, it will become much simpler to define situations under which different features are controlling the fate of organic contaminants. This type of system should hopefully lead to better prediction and better testing of parameters in the soil system.

5.4 References

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Appendix

Estimation of the effect of microaggregate diffusion on early breakthrough in the soil column

If sorptive material is not distributed uniformly through the deposit, early breakthrough of contaminants and a lag to attainment of steady state conditions may result during diffusion measurements. This will result from the probability of a given path for diffusion of the contaminant through the deposit in passing through an average length of organic material. If the path followed by the contaminant does pass through less than the average percent organic material in the deposit, the organic contaminant will arise at the collection reservoir prior to the predicted breakthrough time. However, contaminant migration may also be retarded more than predicted due to the contact with more than average organic material in the deposit. In present results, a small amount of early breakthrough was observed in diffusion cells, but this generally accounted for only about 1% of the final steady state breakthrough concentration in the cell. If organic matter is predicted to be heterogeneously distributed, the predicted breakthrough from the cell should also fall within this observation and early breakthrough should not be overpredicted. Alternatively, the size of the predicted organic matter microsites would have to be smaller in order to conform to predicted results.

The distribution of organic material within microsites in the soil material will also influence rates of sorption in an aggregated medium. If organic material is distributed non-uniformly throughout the aggregates, there will be a critical aggregate size beyond which the sorption rate will become nearly independent of aggregate size and dependent only on the microsite distribution of organic material within the aggregate. This size range will be a function of the distribution of organic material in the aggregate and the size of the aggregate.

To test the validity of predicted diffusion coefficients based on the proposed theory, an equation was developed to predict the breakthrough of a solute from a cell where sorptive centers are distributed in discrete zones within the deposit. Predicted breakthrough curves were then compared against experimental results to determine if early breakthrough was predicted due to the uneven distribution of sorptive centers in the deposit.

A.1 Model development

A theoretical model of the shale material is shown in figure A.1. To model the shale deposit, it was assumed that the organic material in the shale was regionalized in spherical regions, 20 μm in size. An average path length between separate centers of organic material was then given by the percent distribution of organic material in the deposit. The basic assumptions of this model are:

1. The medium consists of a non-sorbing matrix with discrete centers of sorption, 20 μm in diameter distributed throughout.
2. Solute movement in the background matrix will be described by diffusion through a non-sorbing clay medium.
3. Solute transfer within the sorbing organic matrix will be described by diffusion into a sphere with a retardation coefficient equal to R_{om}.

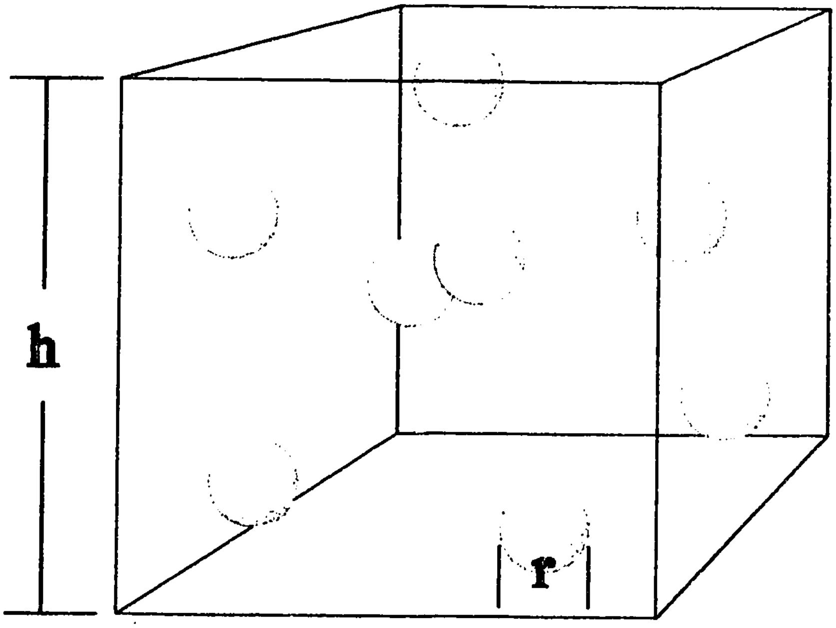

Figure A.1 Theoretical model of the shale material. Shale material is divided into 2 phases, a non-sorbing minera background phase in which spherical sorbent particles of diameter=20 um are contained

4. Solute will be transferred from the background matrix to the surface of the sorbing matrix by diffusion through the background matrix.

The change in solute concentration in the background matrix with time will then be described by,

$$\frac{\partial C_1}{\partial t} = D_e \frac{\partial^2 C_1}{\partial x^2} - D_e \frac{A}{\delta}(C_1 - C_a) \qquad \text{A.1}$$

given the following initial and boundary conditions,

$$\begin{aligned} &C_1(x,0) = 0; \\ &C_1(0,t) = C_0; \\ &C_1(b,t) = 0 \end{aligned} \qquad \text{A.2}$$

where C_1 is the concentration of solute in the background matrix, A is the surface area of the sorptive matrix per unit volume of soil, δ is the average path length from the background matrix to the surface of the sorptive matrix, C_a is the solute concentration at the surface of the sorptive matrix and b is the soil pore space at the collection reservoir in the diffusion cell.

Solute movement in the spherical sorptive matrix will be given by,

$$R_a \frac{\partial C_2}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 D_e \frac{\partial C_2}{\partial r} \right) \qquad \text{A.3}$$

with initial and boundary conditions,

$$\begin{aligned} &C_2(r,0) = 0; \\ &\left.\frac{\partial C_2}{\partial r}\right|_{r=0} = 0; \\ &D_e \left.\frac{\partial C_2}{\partial r}\right|_{r=a} = \frac{D_e}{\delta}(C_1 - C_a) \end{aligned} \qquad \text{A.4}$$

Here, C_2 is the solute concentration in the aggregate, R_a is the retardation coefficient (here assumed to be R_{om} or retardation in an organic matter coated matrix), and a is the surface area of the sorptive center.

In order to solve the two equations, the solution was obtained within the Laplace domain. The solution in the time domain was then obtained by numerical inversion of the Laplace transform (Cheng et al, 1994).

The Laplace transformation of equation A.3 is,

$$s\overline{C}_2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D_a \frac{\partial \overline{C}_2}{\partial r}\right) \tag{A.5}$$

where $D_a = D_e/R$. Solving for the initial and boundary conditions,

$$\overline{C}_2 = \overline{C}_a \frac{a}{r}\frac{e^{qr} - e^{-qr}}{e^{qa} - e^{-qa}} \tag{A.6}$$

with

$$q = \sqrt{s/D_a} \tag{A.7}$$

and a=aggregate radius. Differentiating with respect to r, the resultant equation at the aggregate surface will be,

$$\left.\frac{d\overline{C}_2}{dr}\right|_a = \overline{C}_a\left(q\coth(qa) - \frac{1}{a}\right) \tag{A.8}$$

For the background matrix, the Laplace transform of equation A.1 will be

$$s\overline{C}_1 = D_e \frac{\partial^2 \overline{C}_1}{\partial x^2} - \frac{AD_e}{\delta}\left(\overline{C}_1 - \overline{C}_a\right) \tag{A.9}$$

Given the boundary condition at the aggregate surface (A.4 and A.8),

$$\left.\frac{\partial \bar{C}_2}{\partial r}\right|_{r=a} = \bar{C}_a\left(q\coth(qa)-\frac{1}{a}\right)=\frac{1}{\delta}\left(\bar{C}_1-\bar{C}_a\right) \tag{A.10}$$

Therefore, solving the equation,

$$\bar{C}_a = \frac{\bar{C}_1}{\delta\left(q\coth(qa)-\frac{1}{a}\right)+1} \tag{A.11}$$

Substituting A.11 into equation A.13 and simplifying, we have

$$\bar{C}_1 = B_1 e^{px} - B_2 e^{-px} \tag{A.12}$$

where B1 and B2 are integration constants and,

$$p^2 = \left(\frac{s}{D_e} + \frac{A\left(q\coth(qa)-\frac{1}{a}\right)}{\delta\left(q\coth(qa)-\frac{1}{a}\right)+1}\right) \tag{A.13}$$

solving for B_1 and B_2 given boundary conditions A.2,

$$\begin{aligned} B_1 &= -\frac{C_0}{s}\frac{1}{e^{2pb}-1} \\ B_2 &= \frac{C_0}{s}\frac{e^{2pb}}{e^{2pb-1}} \end{aligned} \tag{A.14}$$

Values for B_1 and B_2 can then be substituted into equation A.12. After simplification,

$$\bar{C}_1 = \frac{C_0}{s}\left(\frac{e^{p(b-x)} - e^{-p(b-x)}}{e^{pb}-e^{-pb}}\right) \tag{A.15}$$

Solute flux at the outlet is then,

$$\bar{J} = -D_e \left.\frac{\partial \bar{C}}{x}\right|_b = 2C_0 \frac{p}{s}\frac{1}{e^{pb}-e^{-pb}} \tag{A.16}$$

A.2 Solute breakthrough through the diffusion Cell

In the original model, no attempt was made to account for the f factor as proposed in chapter 2. Exclusion of solute from the clay pore space was not considered and the boundary condition at the surface of the clay was considered to be the same as that within the source solution. For this treatment, it was found that the predicted solute breakthrough time and time to reach steady state conditions was greater than that observed in experimental results. By inclusion of the factor, f, of 0.4 (chapter 2), predicted solute breakthrough time and time to steady state seemed to conform to observed results.

Based on the proposed model, fig. A.2 shows the predicted solute breakthrough for the 4 mm sized clay cell used in the earlier diffusion experiments. Predicted curves are compared against actual measured solute breakthrough for 1-naphthol. Similar results were found for naphthalene breakthrough in the weathered shale deposit.

When 20 μm sized sorptive center is used in the deposit (assumed concentration =2.7% of the total deposit), very little deviation from ideal behaviour is predicted. The use of a sorptive center does predict a slight amount of early breakthrough in the first 48 hours of the experiment and some tailing, although the total expected deviation is well within experimental error. As the size of the sorptive center is increased, however, considerable deviation from ideality will occur (fig A.2, 50μm size particles).

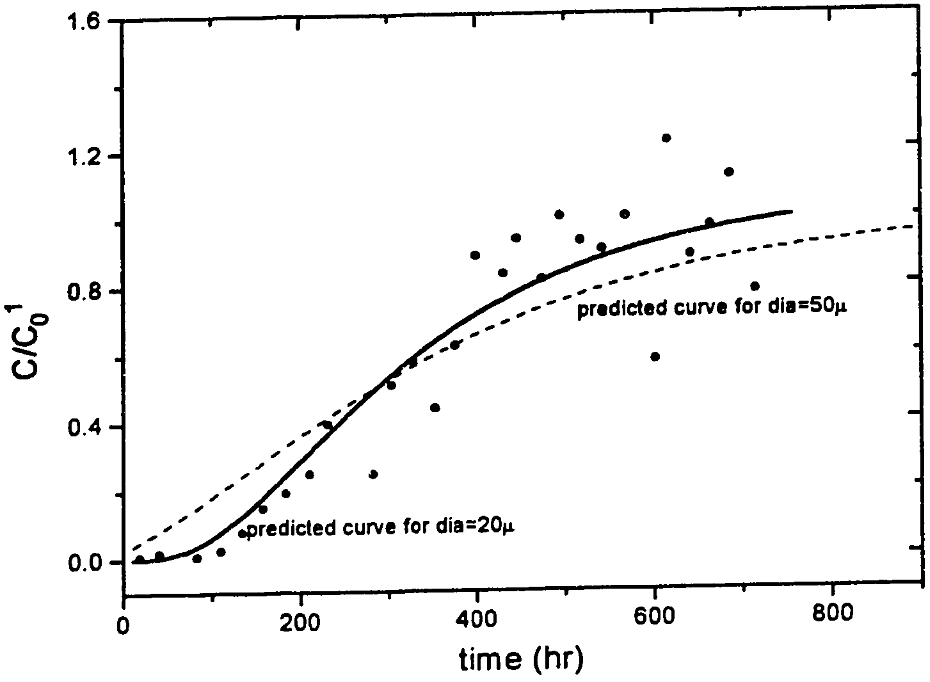

Figure A.2. Predicted diffusion of 1-naphthol through the clay cell using a 4 mm clay cell and predicted microaggregate size of 20 and 50 µm.

Size of the deposit and number of sorptive centers will be important in determining the deviation from ideal behaviour. As the cell length is decreased from 4 mm to 1mm (fig A.3), the model predicts considerable early breakthrough in the deposit but also much longer time periods until actual steady state within the cell is established. At this stage, the rate of solute uptake by the cell becomes much more dependant on the nature and location of the sorptive center than on the average solute uptake by the shale material. This will also be the situation as the percent organic matter is decreased, decreasing the probability of solute interaction with a given sorptive center.

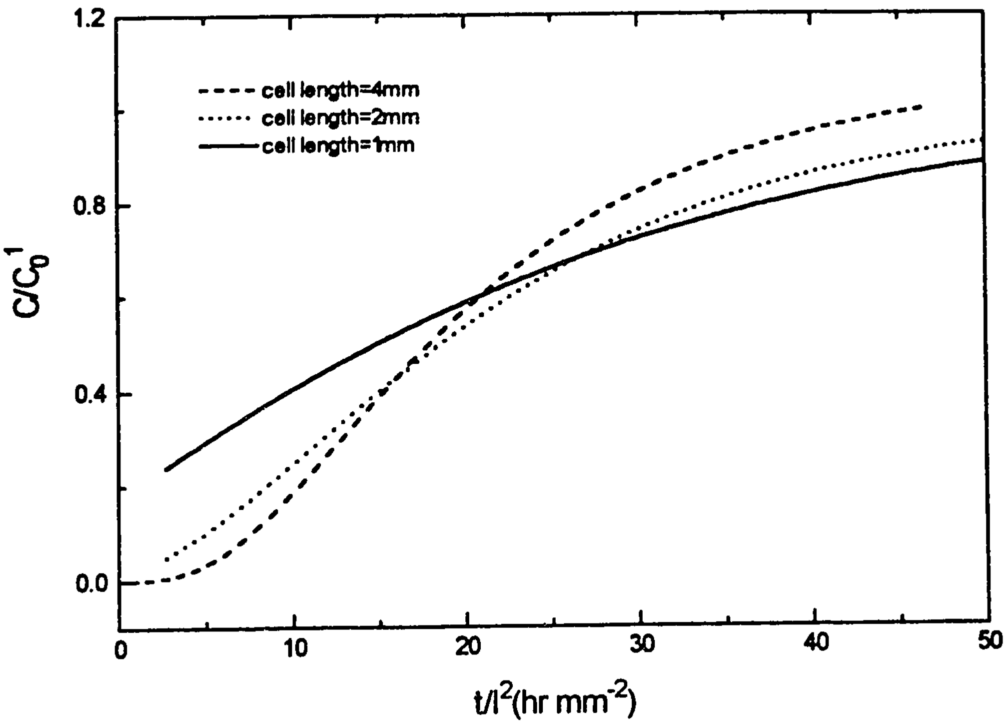

Figure A.3 Predicted solute flux by diffusion through the clay cell as a function of cell length. $^1C_0$=the maximum predicted flux through the clay cell at t=∞

The results of this treatment seem to conform to predicted results obtained from the diffusion experiment. If the predictive equation is correct, the use of a narrower diffusion cell should result in considerable early breakthrough. This could potentially be used as a test for heterogeneous distribution of organic material since the degree of early breakthrough will be a function of the size of the sorptive microsites and the concentration of sorptive material within the deposit. The predictive equation also suggests that for path lengths of 1mm or less diffusion into an aggregate will become increasingly dependent on the microsite distribution of organic material and not the aggregate size. This has important implications in the measurement of rates of sorption in any study conducted on soil material where the >2mm size fraction has been removed. Thus, in these studies, the aggregate size distribution should not be an important factor in the rate of sorption if the organic material is distributed in microsites of approximately 20 μm in diameter. Only if the aggregate size is reduced below that of the predicted microsite size will the rate of sorption again become dependent on the size of the material.

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