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# REDUCED TRANSPORT OF ORGANIC POLLUTANTS IN SOIL MODIFIED WITH HEXADECYLTRIMETHYLAMMONIUM

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## REDUCED TRANSPORT OF ORGANIC POLLUTANTS IN SOIL MODIFIED WITH HEXADECYLTRIMETHYLAMMONIUM

By

Ines Toro-Suarez

## A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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### ABSTRACT

## REDUCED TRANSPORT OF ORGANIC POLLUTANTS IN SOIL MODIFIED WITH HEXADECYLTRIMETHYLAMMONIUM

By

#### Ines Toro-Suarez

Groundwater use for drinking water in the U.S. justifies efforts to prevent or remediate groundwater contamination. This laboratory is developing a remediation technique that couples increased sorption of pollutants with microbial degradation. The overall objective of this research was to evaluate solute sorption during transport in Oshtemo Bt2 horizon soil exchanged with hexadecyltrimethylammonium (HDTMA). In the first part of this study, mechanisms of interaction between this soil and pentafluorobenzoic acid (PFBA) were evaluated.

Anion exchange of PFBA with cationic HDTMA, formed by HDTMA  $C_{16}$  alkyl moieties interacting by London dispersion forces, was demonstrated using  ${}^{36}Cl^-$  and anionic PFBA in a buffer solution (pH 5.4). A PFBA mass balance demonstrated ion-pair formation between PFBA dissolved in water and desorbed HDTMA. Adsorption at the soil/water interface, adsorption at the HDTMA/water interface and partitioning between water and the HDTMA phase were the mechanisms considered responsible for retention of PFBA by HDTMA remaining in the soil after column equilibration. Adsorption at the HDTMA/water interface was the major contributor to retention.

In the second part of the study, sorption coefficients (K) from water for naphthalene, benzene, and TCE were extrapolated from the predicted linear relationship between log K values obtained in water-methanol mixture from soil column breakthrough curves (BTCs), and the corresponding methanol fraction (Rao et al., 1985). These values were compared to sorption coefficients from sorption isotherms. The two methods did not coincide, and the relationship between log K obtained from batch isotherms and the corresponding methanol fraction was not linear.

Benzene sorption coefficients from water obtained from BTCs and batch isotherms in soil with the same organic carbon content were different. Benzene also did not follow the linear relationship between log K and methanol fractions (0 to 0.40) predicted by Rao's model. These results could be explained by methanol/HDTMA interaction and the need to redefine the phase ratio for HDTMA-modified soils. Evidence for methanol/HDTMA interaction was indicated by a strong affinity of methanol for the octane/water interface.

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## **CHAPTER 1**

## Introduction

It is estimated that more than 40% of the U.S. population utilizes groundwater as a source of drinking water and that 25% of all fresh water used in the U.S. is groundwater. Thus, it is important to understand and predict pollutant transport from the soil surface through the unsaturated and on saturated zones to groundwater (Bouchardet et al., 1989). The geologic materials through which these compounds move are very complex porous media. This porous medium has two major components: solid particles and free space between the particles and within their pores. Organic matter and minerals (present in clay, silt, and sand-sized particles) in different proportions constitute the soil solids. A dissolved organic compound entering the soil will move with the bulk flow or be retained due to interaction with the organic matter and/or the mineral components of the soil. It may also diffuse into the small pores of soil particles. Therefore, the main parameters to be considered in the study of the transport of organic compounds through natural porous media are: water flux, molecular diffusion of the compounds, organic carbon content of soil or aguifer material, and water solubility of the compounds. The behavior of a compound in a soil or aquifer material can not be accurately described unless all of these parameters are considered simultaneously.

To study the interaction of these variables at the laboratory level, soil and environmental scientists have normally used what they call miscible-displacement experiments. Miscible-displacement experiments are performed by passing a solution of the solute to be studied through a column filled with the material to be characterized (i.e., soil, sand, aquifer material, or sediments). The change in concentration is followed at the outlet of the column by collecting fractions for further analysis or by continuously feeding the outlet of the column through a concentration-sensitive detector. This method was the original form of chromatography and is also known as frontal chromatography. The response from frontal chromatography is transformed to obtain the effluent breakthrough curves (BTCs). Tiselius (1940) introduced the theory of frontal chromatography which served as a base for the further development of chromatography theories. These theories have been used to explain the behavior of compounds of environmental concern flowing through natural porous materials.

The overall objective of this research has been to evaluate the transport of organic contaminants in soil columns. The soil contained in the columns has been previously modified by substituting the native inorganic exchangeable cations with a quaternary ammonium cation, hexadecyltrimethylammonium (HDTMA). This has been shown in batch equilibration experiments to substantially increase the sorptive properties of the soil for nonionic organic contaminants (NOCs) (Boyd, et al., 1988, 1991; Lee et al., 1989). In the present study, miscible-displacement or frontal chromatography has been tools used to study transport of organic contaminants and the processes that influence their mobility. Thus, the purpose of this chapter is to indicate how environmental scientists have quantitatively related the chromatographic retention and dispersion parameters of the BTCs to physical and chemical characteristics of the system.

#### **Components of a Miscible-displacement Experiment**

The behavior of water flowing through a soil or aquifer material is of the same nature as that of any fluid flowing through a bed of stationary solid particles. For this reason, it is obvious that the same mathematical equations as models applied in general to study the movement of solutes through porous materials can be used to study the flow of organic contaminants through soil and aquifer materials. Thus, soil scientist have taken advantage of and improved the theories advanced by investigators in other related

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fields, such as the theories developed for chromatography and porous media (Nielson and Biggar, 1962). In this chapter the different aspects needed to study the behavior of organic contaminants flowing through geological materials will be considered in a systematic order.

### Selection of the Input Function.

In any chromatographic experiment, the type of chromatogram obtained (the response) depends on the shape of the sample input profile (the input function). Reilley et al. (1962) studied the chromatographic response corresponding to different input functions. Figure 1 shows the response profiles for the two most common types of input functions, the impulse and the step functions. In A, a concentration of the sample is introduced instantaneously in the column (impulse function). In B, the concentration of sample entering the column increases rapidly from zero to a finite value and remains constant at that value (step function). The step injection mode is referenced to as frontal chromatography. Chemical engineers and soil and environmental scientists have called this form of sample injection miscible-displacement, due to the fact that the sample is mixed in the porous medium at the same time that it moves through the column (Nielsen and Biggar, 1961).

Selection of the input function depends on the objectives of the analysis and the column diameter. During miscible-displacement experiments, the solid particles restrain, deflect, and disperse the flow. The form of the flow pattern is determined by the geometry of the interstitial pore space. The front of the zone advancing through the column is spread (dispersed) due to different velocities in the flow stream. The internal structure of the porous medium also influences the diffusion rates. Therefore, it is very important to know as many details as possible of the flow pathway (Giddings, 1965).

Two types of dispersion can occur. Radial dispersion occurs when a sample is injected in the impulse mode. Radial dispersion is much slower than axial dispersion at



Figure 1. Response and schematic representation of useful parameters for pulse (A) and step (B) input functions. From Riley, et al. (1962).

normal flow rates. Thus, the band of solute will travel through the column contained within a central core of the packing. Depending on the column diameter and the particle size diameters, the central core can be so contained that in many cases the solute never reaches the column wall. Knox (1977) quantified this phenomenon with chromatographic columns and called it the infinite diameter effect because the column behaves as it has a very large diameter. Axial dispersion occurs more rapidly close to the walls of the column. Therefore, in chromatography it is considered advantageous for the sample to avoid contact with the column walls because it decreases spreading in the signal. However, this is not the case when part of the objectives of the research is to study dispersion effects due to column packing, as is the case with soil and aquifer materials. This is one of the reason why during this type of research, it is more precise to use the step mode of injection. In this injection mode the sample volume is big enough that the solution will contact almost all the parts of the packing material. The other reason to use the step mode instead of the impulse mode during the characterization of the dynamic behavior of soils, is that due to the broad range of particle size present in these materials, wider bore columns must be used to minimize walls effect. With the impulse injection mode, the response or peak height of a compound decreases as its retention increases . This is a dispersion effect called the column dilution factor (Knox, 1977) and is greater in larger columns. In the step mode, the compound solution is introduced in the column until the response is equal to the input concentration. In studies with soil columns, the compound is sorbed in the column until it reaches equilibrium. The response of the solute concentration (Co) is established first outside of the column. Thus, equilibrium is assumed to be reached when the response of the compound eluting from the column is equal to the Co response. Therefore, to be able to use this equilibrium criterion, it is necessary to use the step injection mode. It is also possible to use the step method to study the effects in sorption caused by varying solute concentration (adsorption) isotherms) (Reilley et al., 1962).

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Now that the reasons for selecting the step function to perform the frontal chromatographic or miscible displacement experiments with soil columns has been established, the construction of the BTC will be considered.

#### **Breakthrough Curves**

Danckwerts (1953) studied the problems presented by steady- flow in different systems and showed how its behavior can be investigated and quantitatively specified. He defined the breakthrough curve (or "F- diagram") as the plot of F(t) vs vt/V, where F(t) is the fraction of concentration of the compound at the outlet of the column as a function of time and vt/V is the ratio between the total volume that has flowed through the column at time t and the volumetric water content. Lapidus and Amudson (1952) used a similar approach to represent the change in concentration at the outlet of the column but they used the total volume of fluid instead of the volumetric water content. Nielsen and Biggar (1962) adapted Danckwerts' procedure in their studies with soil columns, adopting the notation of C/Co for F(t) and referred to the volumetric ratio as pore volumes. This is still the most common notation used today.

Lapidus and Admundson (1952) were the first to demonstrate, with chromatographic columns, the influence of flow velocity and diffusion in the shape of the BTCs. Danckwerts also showed that his F- diagrams (BTCs) revealed a good deal of information about the behavior of the fluid flowing through the column. In Figure 2, taken from his paper, the shapes of different BTCs are presented. As he indicated, they represent different behavior of the fluid as influenced by the column packing. Figure 2a corresponds to the ideal behavior of a fluid through a column where elements of fluids which enter the column at the same time will move through it with constant and equal velocity on parallel paths and will leave the column at the same time. Figure 2b is indicating deviation from ideal behavior due to some mixing of the fluid in the column. Figure 2c corresponds to the shape of the BTC when perfect mixing of the fluid is



.

(a) Pinton flow;

(b) Piston flow with some longitudinal mixing; (c) Complete mixing;

(d) Dead water.

Figure 2. Danckwers' F-diagrams of fluid flow through columns. (Danckwerts, P.F., 1953).

occurring in the column, whereas Figure 2d represents the diagram obtained where there is dead water present in the system (stagnant water trapped in pores).

Nielson and Biggar (1962) indicated that if any solute flowing through the column is retained within the column by any chemical or physical process, the breakthrough curve will move to the right. This can be concluded by simple inspection of the compound BTC. Thus, the breakthrough curve is descriptive of the relative time taken for the displacing fluid to flow through the medium or for the solutes in the displacing fluid to come in chemical equilibrium with the medium.

#### **Hydrodynamic Dispersion**

The ideal behavior of a fluid flowing through a column is known as piston flow (Figure 2a). However, in reality the fluids are Newtonian in nature. There will always be some spreading in the column profile (Danckwerts, 1953). This longitudinal spreading is called hydrodynamic dispersion and is due to a continuous exchange of velocities in the flow stream. The configuration of the porous medium is very complex. It is constituted of cavities, pores of different sizes, channels, and micropores inside the particles, all randomly distributed in the medium. Therefore, different points in the flow stream have different velocities; this has been called the microflow pattern (Giddings, 1963). Spreading depends on how rapidly these velocities can be exchanged.

Two mechanisms determine how fast flow exchange occurs for a compound traveling through a column without interaction with solid material (tracer). The first one is molecular diffusion, a process by which a molecule can move from one flow path to another. The second mechanism has been called eddy diffusion, which occurs when the compound follows the flow path that randomly changes velocities during its travel through the column. In chromatography, hydrodynamic dispersion has been studied using a theory known as the coupling theory of eddy diffusion (Giddings and Robison, 1962). In porous media, it has been well established that if the macroscopic flow is

accepted as one-dimensional, the longitudinal dispersion may be described by the onedimensional diffusion equation in which the diffusion coefficient is replaced by the coefficient of dispersion (D).

$$\frac{\delta C}{\delta t} = D \frac{\delta^2 C}{\delta x^2} - U \frac{\delta C}{\delta x}$$
(1)

Where,

C(x,t) is concentration in solution (mol/cm<sup>3</sup>)

t is time (s)

x is distance from the inlet (cm)

D is the dispersion coefficient  $(cm^2/s)$ 

U is the linear velocity (cm/s)

Also the length of the bed is L and the initial solute concentration is Co.

When this equation is solved for a non-retained compound, we have the simple case of miscible displacement. In this case, the only effect that influences the movement of the tracer is the flow phenomenon. Any compound flowing through the system, whether it is retained or not, will sense this effect. Brenner (1962) gave solutions to equation (1) in a general form and in tables, where the dimensionless exit concentration is presented as a function of dimensionless time (T = Ut/L) for different Peclet numbers (by analogy with the convective heat) which defined as P = UL/4D where D is the axial dispersion coefficient. There are several techniques described in the literature to determine P from the BTC of a tracer. The two most common will be considered here. Hashimoto et al. (1964) determine P by fitting the BTC data of a tracer to the Brenner solutions by a least square method. Then, the best fit is obtained by interpolating in graphs such as the one presented in Figure 3. Rose and Passioura (1971) developed a method to determine P in which the data are transformed in a semilogarithmic form. The data fall on a straight

line, and P is determined from the slope. P is related to the effective diffusion coefficient, according to Brenners' definition, through the equation:

$$P = \frac{U1}{4D} \tag{2}$$

This equation can be solved with just the experimental data.

So far we have indicated only the effects of dispersion on the shape of the breakthrough curve for non-retained compounds. The shape of the BTC is also influenced by the sorption isotherm and the mass-transfer kinetics for compounds interacting with the media.

### Sorption Isotherms

The use of frontal chromatography to measure the sorption isotherm of solutes on solid surfaces is the oldest and, for many years, the most common application of this technique (Parcher, 1978). When a compound has a non-linear sorption isotherm, retention will change with concentration. For this reason, only frontal chromatography can be used for this process. To determine the adsorption isotherm, the amount of solute adsorbed in the solid material is determined at different concentrations (Gluckauf, 1945). As with any BTC, the effluent concentration from the column is monitored until it reaches a constant value equal to the inlet concentration. This indicates the saturation of the bed by the compound under study and the end of the sorption process. This method was recently employed by Thibaud et al. (1992) to investigate the adsorption equilibria of several volatile organic contaminants on soil. They determined the sorption capacity of each compound on the soil, at saturation, and compared to the adsorption capacity corresponding to a monolayer. They found that all the compounds studied had a BET type II adsorption isotherm and that the contaminants cover the whole surface uniformly. They also calculated, from the linear part of the adsorption isotherm, the



Figure 3. Brenner solution for equation 1 (Rose and Passioura, 1971)

molar heats of adsorption.

When a compound has a non-linear sorption isotherm, the boundaries of its BTC are either diffuse or self-sharpening depending of the curvature of the isotherm. Also, if sorption takes place but the amount retained changes with concentration, our computational procedure can produce only an empirical description of column behavior which may possibly be useful but certainly will have no immediate theoretical interpretation. In consequence, a condition that must be met to be able to use the convective-dispersive equation is that the compound under study should have a linear sorption isotherm in the medium. That is, the ratio of the amount of solute in the mobile phase to that in the stationary phase, the sorption coefficient ( $K_d$ ), should be constant and independent of solute concentration. Reilley, et al. (1962) concluded that if a compound has a linear isotherm in a partition chromatographic column, the retention time ( $t_T$ ) remains constant over the range of concentrations used. More importantly, the shape of response in each step, sorption and desorption, are symmetrical. Thus, if the sorption isotherm is linear, other factors will cause changes in the shape (symmetry) of the BTC.

#### **Retardation Factor (R)**

If linear reversible equilibrium sorption is assumed, sorbed and aqueous solute concentrations may be related using the partition or distribution coefficient,  $K_d$ , such that:

$$S = K_{d}C \tag{3}$$

where S is the concentration of solute sorbed by the soil (mg/kg) and C is the concentration of solute in solution at equilibrium (mg/L). Hashimoto et al. (1964) solved the diffusion equation for a column of finite length under the assumption of a linear

sorption isotherm. They defined a dimensionless factor that they called the retardation factor (R) expressed as:

$$R = 1 + \frac{\rho}{\theta} K_d \tag{4}$$

Where  $\rho$  is the bulk density and  $\theta$  the volumetric water content of the column. Thus, the difusion equation can be rewritten:

$$R\frac{\delta C}{\delta t} = D\frac{\delta^2 C}{\delta x^2} - U\frac{\delta C}{\delta x}$$
(5)

The retardation factor R is a quantitative index of a chemical compound's mobility, in that its value is equal to the ratio of the positions of the sorbed and non-sorbed solute in the soil column. For a non-sorbed solute, the value of the sorption coefficient  $K_d$  in the equation is equal to zero: hence, R = 1. For sorbed solutes, R is greater than one since the value of  $K_d$  is larger than zero. A compound with a large value of R has reduced mobility in soils.

Since there was a lack of a standard method to determine the retardation factor from BTCs, Nkedi-Kizza et. al. (1987) decided to evaluate four different methods. The compounds selected were diuron and atrazine, two pesticides with non-linear sorption isotherms. In the first method, the values of R was calculated from sorption isotherms in mixed solvents using the equation

$$R^{m} = 1 + \frac{\rho K^{m} C o^{(N-1)}}{\theta} \qquad O < N < 1$$
 (6)

Where m indicates that the eluent is not plain water but a mixed solvent solution. The values of  $K^m$ , the sorption coefficients for diuron and atrazine were obtained from the

sorption isotherms using the Freundilich equation,  $S = K C^N$ , for non-linear isotherms. In the second method they calculated  $R^m$  from a series of equations deduced by Rao et al. (1985):

$$R^{m} = 1 + \frac{\rho(OC)P^{m}}{\theta}$$

$$P^{m} = P^{w} \exp(-\alpha \sigma^{c} f_{c}) \qquad (7)$$

$$\sigma^{c} = \Delta \gamma^{c} \frac{(HSA)}{kT}$$

where, OC is the organic carbon content of the soil,  $P^{m}$  the solute sorption coefficient determined from the mix solvent and normalized by the soil organic carbon content,  $P^{W}$ is the solute sorption coefficient in the soil determined from water and also normalized by the soil organic carbon content,  $\alpha$  is a constant with a value of 0.83 for soils,  $\sigma$  is as defined in the equation, fc is the fraction of organic cosolvent,  $\Delta\gamma$  the interfacial tension between the hydrocarbon part of the solute molecule (HSA) and the solution. In the third method  $R^{m}$  was determined as the number of pore volumes at 0.5 of the input concentration. This method assumes symmetrical BTCs and is a common method used in chromatography to determine retention time for the impulse injection mode. In the fourth method, Nkedi-Kizza et al., (1985) tested a method previously suggested by Danckwerts (1953) based on the principle of mass conservation. R is equal to the area above the BTC (Figure 4) as given by:

$$R = \int_0^{P_{\max}} 1 - C^* \, dp \tag{8}$$

where, P is pore volumes and  $C^*$  is the relative concentration (C/C0). After comparing the four methods, they suggested method 4 as very reliable way to determine R from the solute BTC.



Figure 4. Graphical representation of R calculation using method 4 in Nkedi-Kizza, et al., 1987.

During the last five years, the value of R has very often determined from the first moment of the BTC. The temporal moment analysis was developed by Aris (1958) traditionally used in chemical engineering and chromatography. The first moment describes mean breakthrough time and is based in the statistical first moment, which physically corresponds to the mean of a cumulative density curve. To determine R by this method, the curve is digitized and the data are manipulated in the usual way as to obtain the BTC. The C/Co and pore volumes are tabulated and entered in a computer program. The output of the program gives the first moment. The R values are obtained from the formula:

$$R = M - \frac{1}{2} T_o \tag{9}$$

Where, M is the statistic first moment, and  $T_0$  the sample pulse size in pore volumes.

### **Non Equilibrium Parameters**

As it will be review in this section, many of the parameters required to run the bicontinuum model, used to study rate limiting process in porous media, can be obtained from BTCs obtained for the solutes in the porous material under study.

The early theory of chromatography assumed that equilibrium between adsorbent and adsorbate solution was immediately established (Wilson, 1940). Wilson (1940) was also the first to recognize that the sample band (impulse) may increase because the leading edge of the band migrates too slowly due to a low rate of desorption (non-equilibrium). However, the most comprehensive analysis of the nonequilibrium phenomena was carried out by Giddings in 1965. These rate-limiting or nonequilibrium processes, are also observed during transport of solutes in structured soils and aquifer materials. These rate-limiting process have been grouped into two general classes:transport-related and

sorption-related. Transport-related nonequilibrium (TNE) results from the existence of a heterogeneous flow domain. The influence of soil structure on solute transport was recognized more than 100 years ago (Schumacher, 1864). Non-uniform flow velocity in the field (preferencial flow, macropore flow, channeling etc.) has been generally accepted to result from non-unimodal pore-size distribution. To model this complex system, the porous medium is considered to have two domains: a mobile domain where advective flow occurs and an immobile domain in which the flow is minimal. The mobile-immobile concept for soils was first used by Gardner and Grooks (1956). Solutes are transported rapidly in the mobile domain and slow diffusive mass transfer also occurs between the mobile and immobile domain. Because solutes resident in the immobile domain move to the mobile domain by diffusion only, solutes in these systems are considered to be in a state of nonequilibrium or TNE.

Since the early sixties TNE in soils has been studied in experimentally obtained BTCs. Thus, in 1960 Biggar and Nielsen observed, in a soil column under unsaturated conditions, a delayed approach to relative concentrations (C/Co) values of either 1 or 0 (tailing, according to Giddings, 1963) in the BTC. They argued that under unsaturated conditions the large porous are eliminated for transport and the amount of water that does not move increase. This water has been called stagned water or immobile water. Transport-related nonequilibrium has also been observed in aggrated soils, which contain many micropores into where solutes move only by diffusion (Biggar and Nielsen, 1962). Transport-related nonequilibrium affects both sorbing and nonsorbing solutes; thus, since sorption related nonequilibrium is observed only for sorbing compounds, any transport study should start with a BTC for a nonsorbing solute (tracer).

Sorption-related nonequilibrium may result from chemical nonequilibrium or from rate-limited diffusive mass transfer. Chemical nonequilibrium is caused by rate-limited interaction between the sorbate and the sorbent. This possible source of nonequilibrium should be important in the interaction of polar organic compounds with natural soils.

However, for NOCs this type of interaction is considered unimportant, since organic matter that is the part of the soil interacting with them behaves as a partition medium. Three processes are considered today as responsible for nonequilibrium due to difusive mass transfer: film diffusion, retarded intraparticle diffusion, and intrasorbent diffusion (Brusseau et al., 1991).

Lapidus and Amudson (1952) solved the convective/dispersive equation with the purpose of studying longitudinal diffusion in ion exchange and other chromatographic columns. For the first case, they implied that equilibrium was estableshed at each point in the bed while in the second case they assumed the rate of sorption is finite and follows a first-order kinetics, described by a first-order rate constant  $(k_2)$ . Under equilibrium conditions, that as the flow velocity decreases diffusion begins to affect the system and smear out the response (Lapidus and Amundson, 1952). Hashimoto, et al. (1964) obtained a similar solution which included the longitudinal mixing process as well as equilibrium and linear adsorption during one-dimensional flow. Many analytical solutions to the convective/dispersive equation can be found in the literature for a variety of initial and boundary conditions (Van Genuchten and Parker, 1982). However, all the solutions are based in studing BTCs obtained from miscible displacement experiment. Some of the most recent approaches will be considered next.

Lee et al. (1988) evaluated sorption nonequilibrium during transport of trichloroethylene (TCE) and p-xylene through saturated columns of two aquifer materials. The BTC obtained with these compounds were used to evaluate a bicontinuum sorption model. As a secondary objective of their work, they also evaluated competitive sorption between TCE and p-xylene using BTC and batch isotherms data. Brusseau et al. (1991) designed experiments to determine the rate-limiting or nonequilibrium sorption of NOCs in natural sorbents. They also analyzed their miscible-displacement results (BTCs) using a first-order bicontinuum model. From the parameters required to run their model, they obtained P from the BTC of a tracer (tritiated water). The value of R and thus K,

was obtained from the first moment of the BTC. The solute pulse size  $T_0$  also is established when determining the BTC. Analysing their values of  $(k_1)$  and  $K_2$ , obtained from the BTCs, by a linear free energy relationship, they concluded that intraorganic matter diffusion was the major mechanism responsible for sorption nonequilibrium in soils.

### Conclusions

There is no doubt that miscible-displacement experiments are useful tools to characterize new sorbent materials. The transport behavior of a non-reactive tracer, in particular the shape of the BTC and the Peclet number, gives information on the porous medium. The sorptive properties can be determined from the value of R. Also, the mass-transfer behavior can be determined from the non-equilibrium parameters.

From the literature reviewed in general, an obvious observation is that, for the past forty years the same methodology has been used to study the interactions of chemical compounds in the environment. With little modification, the diffusional equation adapted by Lapidus and Amundson in 1952 is still used to study the flow of compounds through porous media. There has not been much cross fertilization of ideas from other disciplines, that give rise to new methodologies or provide insight into questions that persist, about the behavior of chemicals in the environment.

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# **CHAPTER 2**

Retention of Pentaflurobenzoate in Hexadecyltrimethylamonium Modified Soil by Anion Exchange and Ion-pairing.

# 2.1 Introduction

The native inorganic exchangable cations on soil clays can be replaced with quaternary ammonium cations by simple ion exchange reactions (Boyd, et al., 1988). This modification increases the organic carbon content of the soils and subsoils, and improves their sorptive properties for nonionic organic compounds (NOCs). Recently the sorptive characteristics of three different soils materials (Oshtemo Bt, Marlette Bt, St. modified bv the addition and Clair Bt) that have been of hexadecyltrimethylammonium bromide (HDTMA) in an amount equivalent to the CEC, have been studied. These studies have shown that the sorptive uptake of NOCs by the HDTMA-modified soils was greatly enhanced (Lee, et al. 1989). The improvement of the sorptive properties of the soil by chemical modification may be useful for reducing migration of organic contaminants through soils, subsoils, and aquifer materials that have low organic carbon content. Due to this potential application, the overall goal of this research is to characterize the transport behavior of NOCs through an organically modified soil, using columns packed with the chemically modified soil. For this study we have chosen HDTMA-modified Oshtemo Bt horizon soil material.

Conservative tracers are widely used to determine the hydrodynamic properties of a porous medium at the laboratory and field scale. A conservative tracer is a compound that does not react chemically or biologically during transport. Typically, the experimental evaluation of hydrodynamic dispersion consists of measuring the tracer

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concentration in eluent as a function of the number of pore volumes displaced through the column (breakthrough curve). When a conservative tracer moves as a plug through the column, the breakthrough curve should correspond to a vertical line (ideal piston flow). However, breakthrough curves always deviate from ideality (Fig. 1). This is commonly due to hydrodynamic dispersion, a process that results from mechanical mixing and molecular diffusion (Drever, 1988; Freeze and Cherry, 1979; Giddens, 1965).

Many compounds have been used as conservative tracers in transport studies to determine the Peclet number (P) of soils and aquifer materials. The Peclet number is a dimensionless parameter that describes the effect of diffusion on the overall dispersion of the column. The Peclet number is defined as P = uL/4D, where u is the fluid linear velocity, L is the column length and D the axial dispersion coefficient of the fluid. Pentafluorobenzoic acid (PFBA) has been widely used as a consrevative tracer since 1984 when it was evaluated with five other compounds (Bowman, 1984) to assess their suitability as tracers in laboratory and field studies of soil water movement. PFBA and two other fluorinated compounds have the advantage that their diffusion coefficients are approximately 60 percent lower than Br<sup>-</sup>. This is a very important consideration in the determination of dispersion coefficients in porous medium. Another advantage, specifically for PFBA, is that its pKa is 1.48, which means that it will be essentially completely anionic in most soils.

For our studies of solute transport in soil columns containing HDTMA-modified soils, PFBA was selected for use to determine P. Although PFBA was expected to behave as a non-retained tracer, it was strongly retained in the column. Two possible mechanisms were identified that might account for the strong retention of PFBA in the HDTMA-modified soil: anion exchange due to reverse charge formation (De Vivo and Karger, 1979; Joycock and Ottewill, 1963) or ion-pairing of PFBA anion with the HDTMA cation (Knox and Laird, 1976; Sood, et al., 1976), with subsequent sorption of the neutral PFBA-HDTMA ion pair by the nonpolar alkyl tail of HDTMA.

The objective of this work was to determine the most likely mechanism(s) by which PFBA is retained in the HDTMA-modified soil. This study is the first attempt to understand the mechanism of interaction between quaternary alkyl ammonium modified soils and organic acids. The elucidation of this mechanism is environmentally significant because organic acids are often highly mobile in soils and subsoils. The retention of organic acids, e.g. pentachlorophenol and 2,4-D, by such modified soils may be used to reduce their transport and hence their potential for ground water contamination.

#### 2.1 Materials and Methods

#### HDTMA-modified soil.

An Oshtemo Bt2 horizon (coarse-loamy, mixed, mesic Typic Hapludalfs) was used to prepare hexadecyltrimethylammonium (HDTMA) modified soil. A 500-g of soil material was mixed with 1000 ml water. Then an aqueous solution of HDTMA (8.2 g in 3000 ml) was added in an amount equal to the stoichiometric cation exchange capacity of the soil (Table 1). The suspension was stirred overnight, then transfered to centrifuge bottles and centrifuged at 2,603xg for 20 min. The supernatant was removed using gentle vacuum suction, and the bottles were refilled with 225 ml water. This procedure was repeated three times to remove any excess HDTMA. After the washing process, the soil was air dried.

# <sup>14</sup>C-HDTMA-modified soil.

The same basic procedure just described was used to prepare the  ${}^{14}C$ -HDTMAmodified soil except that, 0.1 ml of  ${}^{14}C$ -HDTMA (specific activity 55 mCi mmol<sup>-1</sup>) was also dissolved in the water and added to the soil together with the HDTMA required to satisfy the CEC of the soil.

Particle Size (%) Sand Silt Clay	89 5 6
CEC (mmol/Kg)	45
рН	5.8
Organic Carbon Content (%)	0.1

Table 1. Properties of Oshtemo Bt horizon soil

### **Cation Exchange Capacity.**

Method 1. The first method used for the CEC determination was reported by Lee et al. (1989). In summary, the CEC was taken as the summation of extractable cations:  $Al^{3+} + Ca^{2+} + Mg^2 + K^+ + Na^+$  (non buffered) or  $H^+ + Ca^{2+} + Mg^{2+} + K^+ + Na^+$  (buffered).  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $K^+$ , and Na<sup>+</sup> were exchanged with 1N ammonium acetate at pH 7 and then determined by atomic absorption. Al<sub>3+</sub> was extracted with 1M KCl and determined by titration with a standarized base.

Method 2. Cation exchange capacity also was measured by ammonium saturation and sodium displacement. The soil was saturated with 1M NH<sub>4</sub>OAc (pH 7). Entrained solution was displaced with ethanol one time, and the entrained NH<sub>4</sub><sup>+</sup> concentration in the ethanol was measured by steam distillation. Adsorbed NH<sub>4</sub><sup>+</sup> was displaced by reacting the soil with an excess of NaCl. Ammonium was determined by steam distillation. Admonium was determined by steam distillation. Ammonium not neutralized by the acid was back titrated with standarized H<sub>2</sub>SO<sub>4</sub> or HCl.

Method 3. Cation exchange capacity was also measured by  $Mg^{2+}$  saturation and  $Ba^{2+}$  displacement. The soil was reacted once with 0.5 M MgCl<sub>2</sub>, twice with 0.1 M MgCl<sub>2</sub>, and once with 0.05 MgCl<sub>2</sub>. The first three supernatant solutions were discarded, the

0.05 M MgCl<sub>2</sub> solution was saved, and the entrained Mg<sup>2+</sup> concentration was determined by atomic absorption spectroscopy. Adsorbed Mg<sup>2+</sup> was calculated as the difference between the total moles of BaCl<sub>2</sub>-extractable Mg<sup>2+</sup> and the number of moles of entrained Mg.

# Anion Exchange Capacity

The anion exchange capacity of the HDTMA-modified soil, was determined by  ${}^{36}$ Cl<sup>-</sup> (ICN Biomedicals Inc., activity 0.772 mCi/ml) adsorption. Twenty ml of 0.007 N CaCl<sub>2</sub> with  ${}^{36}$ Cl<sup>-</sup> activity ranging from 6.0 x 10<sup>4</sup> to 1.2 x 10<sup>4</sup> dpm per ml were added to 1 g of HDTMA modified Oshtemo soil. The samples were prepared in triplicate and a blank (no soil) was prepared for each  ${}^{36}$ Cl<sup>-</sup> concentration. The samples were shaken for 24 hours, after which the solid and liquid phases were separated by centrifugation. The  ${}^{36}$ Cl<sup>-</sup> in 0.5 ml of supernatant was measured by liquid scintillation counting. The amount of Cl<sup>-</sup> exchange was obtained by difference between the total  ${}^{36}$ Cl<sup>-</sup> activity present in the blanks after equilibration and the total activity present in the supernatant. The following equation expresses to the equilibrium exchange reaction between  ${}^{35}$ Cl<sup>-</sup> and  ${}^{36}$ Cl<sup>-</sup> in the modified soil where (aq) and (ex) denote aqueous and exchanger-phase species, respectively:

$$^{35}Cl^{-}(ex) + {}^{36}Cl^{-}(aq) = {}^{36}Cl^{-}(ex) + {}^{35}Cl^{-}(aq)$$
$$Keq = \frac{[{}^{36}Cl^{-}(ex)][{}^{35}Cl^{-}(aq)]}{[{}^{35}Cl^{-}(ex)][{}^{36}Cl^{-}(aq)]}$$

The equilibrium constant of the isotopic reaction (Keq) is always equal to one. The anion exchange capacity (AEC) of the soil is equal to the  $[^{35}Cl^{-}(ex)]$  since  $^{35}Cl^{-}$  is 99.9 % of the Cl present. The value of AEC was calculated from the slope of a linear plot of  $[^{36}Cl^{-}(ex)]$  versus  $[^{36}Cl^{-}(aq)]$ , with  $[^{35}Cl^{-}(aq)] = 0.007$  N for this experiment:

$$[{}^{36}Cl^{-}(ex)] = \frac{[{}^{35}Cl^{-}(ex)]}{[{}^{35}Cl^{-}(aq)]} [{}^{36}Cl^{-}(aq)]$$

#### **Equilibrium Sorption Isotherms.**

Sorption of PFBA from water and a buffer (pH 5.4) on the HDTMA-modified soil was measured by the batch sorption isotherm method. The buffer solution was a mix of of KH<sub>2</sub>PO<sub>4</sub> and NaOH at concentrations of 0.5 N and 0.05 N respectively. Duplicate 1-g soil samples (for PFBA/water) or 2-g soil sample (for PFBA/buffer) were weighed into glass Corex centrifuge tubes, mixed with 25 ml of the PFBA solution, and closed using teflon lined screw caps. Initial PFBA concentrations were between 50 ppm and 1,000  $\mu$ g/ml. For each concentration, a no-soil blank was prepared. The samples were shaken for 24 hrs and then centrifuged at 9,681xg for 30 min in a Sorvall RC5-C centrifuge at 24 °C. The aqueous-phase concentration of PFBA (Ce) was determined using a diode-array UV/VIS spectrophotomer (Hewlett Packard, model 8452A; Palo Alto, Ca). The amount of PFBA sorbed in the HDTMA-modified soil (Q) was determined by difference between initial (Co) and equilibrium (Ce) PFBA concentration in the aqueous phase. The sorption isotherm was obtained by plotting Ce as the independent variable and Q as the dependent variable.

The pH of the Co and Ce solutions were determined using an Orion Research digital ion analyzer, model 701 A (Cambridge, MA.)

# **HDTMA Desorption.**

The amount of  ${}^{14}C$ -HDTMA desorbed during the adsorption isotherm experiment was determined by removing triplicate 1-ml aliquots from each of the supernatant solutions. The amount of  ${}^{14}C$  present in these samples was measured in a liquid



scintillation analyzer (TRI-CARB, model 1500, Canberra-Packard, Zurich, Switzerland). The amount desorbed was calculated based on the known activity of the <sup>14</sup>C-HDTMA modified soil.

# 2.3 Results and Discussion

In our initial experiments to characterize the hydrodynamic properties of the soil column, we observed that PFBA was strongly retained by the HDTMA-modified Oshtemo soil. This result was unexpected because PFBA is commonly used as a conservative tracer in solute transport studies in soil columns. Also, PFBA retention was unexpected because the pH of the 50 ppm PFBA solution was 4.8, which is slightly more than three log units above the pKa of PFBA (1.48). At this pH, the compound is essentially completely ionized (anionic) in solution and thus expected to be non-retained by the soil column.

#### Interaction by Anion Exchange.

One possible explanation for the retention of PFBA is the presence of excess positive charge in the HDTMA-modified soil, known as reverse charge formation. DeVivo and Karger (1970) observed that kaolinite and montmorillonite reversed their charge from initially negative to positive by measuring the changes in zeta potential or electrophoretic mobility during the reaction of the clays with dimethylammonium bromide (EHDA-Br). Jaycock and Ottewill (1963) presented a model to explain the charge reversal that they observed during the interaction of colloidal silver iodide with ionic surfactants. DeVivo and Karger (1970) used this model to explain their results. Essentially, a monolayer of cationic surfactant is adsorbed by electrostatic forces neutralizing the negatively charged surface of the clay. A second layer of surfactant is then absorbed via non-polar interactions among hydrophobic chains of the surfactant. Completion of a second layer of surfactant, with ammonium groups pointing toward the solution, results in a positively charged interface.

Based on the results above and the well known fact that CEC is not a fundamental quantity but rather an operationally defined parameter (Drever, 1988; Rhoades, 1982), it was postulated that the original method used (sum of exchangeble bases  $+Al^3$ ) may have overestimated the HDTMA-accessible CEC resulting in the addition of an excess amount of HDTMA during the soil modification. Addition of HDTMA beyond the CEC of the soil could result in charge reversal, with the source of positive charge originating from ionized HDTMA held by non-polar interactions with the C-16 alkyl moieties of HDTMA adsorbed to cation exchange sites of the soil.

This hypothesis is suported by the  ${}^{36}$ Cl (Fig. 2) and PFBA (Fig. 3) adsorption data, which are summarized in Table 2. The PFBA AEC was equated with the PFBA adsorption maxima (Arrows in Fig. 3). These results indicate that there is an excess of positive charge in the HDTMA-modified soil, probably because the amount of HDTMA added to the soil (45 mmole/Kg) exceeded the number of exchange sites accessible to HDTMA.

Experimental Source	AEC (mmol/K g)	Sat. Cov. (meq/100 g)
36 <sub>Cl</sub> -	9.0 ± 0.24	
PFBA in Buffer		7.9 ± 0.54
PFBA in Water		$16.4 \pm 0.1$

Table 2. Anion exchange capacity (AEC) and amount of HDTMA at saturation coverage in an HDTMA modified soil.

To further evaluate this possibility, the CEC of the Oshtemo soil was measured by two other methods described in the methods section. The CEC values obtained in each case are reported in Table 3. The variability observed among the measured CEC



Figure 2.  $^{36}Cl^{-}$  - Anion exchange on HDTMA-modified soil



Figure 3. PFBA adsorption isotherms on HDTMA-modified Oshtemo soil

values is due, in addition to the expected analytical error, to the different methods of CEC determination. In the soil, the exchangeable cations adsorbed on negative charges present in the aluminosilicate clay structure, at mineral edges (hydroxyl groups), and in acid functional groups of the organic matter. Of these soil components, only the charge present in clay minerals with isomorphic substitution is considered to be permanent. The rest of the surface charge is variable, meaning that its magnitude depends, among other factors, on pH, ionic strength, dielectric constant in the medium, and nature of the anion and cation in the solution phase. Of the methods reported here, only method 3 uses unbuffered saturating solution. This is considered an advantage because the natural soil pH is not significantly altered (Rhoades, 1982). Also, methods 1 and 2 use  $NH_4^+$  to replace the native cations; this can result in high CEC values in soils containing vermiculites and weathered micas, as is the case with Oshtemo Bt, because  $NH_4^+$  can replace structural  $K^+$  from clay interlayers. In method 3, the index cation is  $Mg^{2+}$ , a cation that is common in most soils and will not displace  $K^+$  from micas. Therefore, method 3 is considered to be the most precise of the analytical methods used. The way this method corrects for the amount of entrained saturating solution, is highly recommended for precise determination of CEC (Rhoades, 1982). These arguments support the conclusion that a 50 % excess [(4.5-3.0/3.0) mmol/100 g) of HDTMA was added to the Oshtemo soil during modification. If all the excess HDTMA was retained by tail-tail interactions, this could provide an anion exchange capacity of about 1.5 meq/100 g, which is intermediate between the measured values reported in Table 3.

A separate independent measure of CEC (method 4) was obtained from the difference between the organic carbon content of the modified soil and the organic carbon of the native soil. This CEC value was corrected for the  ${}^{36}$ Cl<sup>-</sup>CEC. This yields a CEC value of 2.2 meq/100 g, which is below any of the measured CECs. This suggests that some HDTMA may have become bound by tail-tail interactions even before HDTMA fully satisfied the soil CEC.

Method	CEC mmol/K g	рН	Sat. Cat.	Entrain correction
1	45	7	NH4 <sup>+</sup>	Yes
2	38 ± 0.2	7	NH4 <sup>+</sup>	No
3	$30 \pm 0.1$	N.A. <sup>a</sup>	Mg <sup>2+</sup>	Yes
<b>4</b> b	$31 \pm 0.3$ (22 ± 0.2)			

Table 3. Comparison of CEC values obtained by different methods.

<sup>a</sup>Not adjusted

<sup>b</sup>Calculated from of organic carbon contents of modified and native soil.

Value in parenthesis is corrected for the measured anion exchange capacity.

The agreement between the value of AEC calculated from the <sup>36</sup>Cl<sup>-</sup> experiment and from the PFBA/buffer adsorption isotherm was good, supporting the conclusion that anion exchange is responsible for the binding of PFBA by the HDTMA modified soil. The proposed anion exchange reaction is between Br<sup>-</sup> associated with HDTMA cations held by tail-tail interactions and the PFBA anion. The shape of the adsorption isotherm is characteristic of ion-exchange reactions (type-I) where the added ion is strongly preferred.

Interaction by Ion pairing. Another possible interaction will be the formation of an ion-pair between the two ions, creating a neutral molecule in solution which would be sorbed by nonpolar interactions with the HDTMA-coated surface. However, during the PFBA adsorption isotherms experiments, <sup>14</sup>C-HDTMA modified soil was used, and the determined <sup>14</sup>C-HDTMA desorbed remained essentially constant at the different levels of PFBA. These findings argue against the formation of ion-pairs because if the HDTMA cation is ion-pairing with PFBA its concentration in solution should decrease with increasing concentrations of PFBA.

A different PFBA sorption isotherm behavior was observed in the non-buffered system (Fig. 3). The maximum amount of PFBA adsorbed was 16.4 mmol/Kg, approximately double the value observed with <sup>36</sup>Cl<sup>-</sup> and PFBA/buffer systems (Table 3).

Sorption of PFBA in the non-buffered systems, apparently results from the formation of ion-pairs between PFBA and HDTMA, that has desorbed into the aqueous phase. Knox and Laird (1976) and Haney, et al. (1976) independently introduced the concept of using hydrophobic ions with long alkyl chains as ion-pairing reagents to improve the chromatographic behavior of ionizable compounds. Knox and Laird (1976) used HDTMA to ion-pair with the -SO<sub>3</sub>H group in a wide range of sulfonic acids. They assumed that the neutral ion pair was extracted from the water-rich environment onto the organic phase covering the porous material in the column. By analogy, HDTMA ion pairs could be attracted to the surfaces of HDTMA-exchanged clays. The neutral ion pairs could either be disolved in the HDTMA medium or adsorbed at the HDTMA/water interface; either sorption process would result in the removal of PFBA from solution. The amount of HDTMA desorbed in the blanks (soil plus water) during the PFBA/water sorption experiments with <sup>14</sup>C-HDTMA modified soil, was 14 mmol Kg<sup>-1</sup>. This exceeds the amount of HDTMA held by tail-tail interactions, which was estimated as 9 mmol Kg<sup>-1</sup> based on the <sup>36</sup>Cl<sup>-</sup> anion exchange capacity (Table 2), and is about one-half of the total (initially) soil-bound HDTMA (31 mmol Kg<sup>-1</sup>; Table 1). The <sup>36</sup>Cl<sup>-</sup> AEC capacity was about 5 mmol Kg<sup>-1</sup> less than the amount of  $^{14}$ C-HDTMA desorbed, which means that 5 mmol kg<sup>-1</sup> of HDTMA desorbed from cation exchange. The desorption in pure water of 50 percent of initially bound HDTMA is consistent with other HDTMA desorption experiments in batch or column studies where about one-half of the original organic carbon consistently remains in soil (see chapter 4). Although the desorption chemistry of HDTMA is not well understood, we postulate that the water- desorbable HDTMA originates form HDTMA held by tail-tail interactions and some HDTMA held by ion-exchange at variable charge sites or on external surfaces of clay minerals, present in the soil. Desorption of the former fraction is indicated by the observation that after exposure to pure water, the soil loses its AEC.

The amount of HDTMA desorbed into solution decreased as the concentration of PFBA increased. HDTMA apparently forms ion-pairs with PFBA, and the ion-pair may be either sorbed or adsorbed. To test the ion-pairing sorption hypothesis, we performed a HDTMA mass balance. Assuming the amount of HDTMA desorbed by water is constant and that the decrease in solution is due to formation of ion-pairs with PFBA (1:1), then the amount of HDTMA determined in solution plus the amount of HDTMA-PFBA ion- pairs (equal to the amount of PFBA sorbed) should equal the amount of HDTMA desorbed into water. This mass balance was performed in each tube of the PFBA sorption-from-water experiment, and the results (Fig. 4) indicate such an equivalency up to an initial PFBA concentration of 300 ppm (pH 3.1). At higher initial PFBA concentrations (500 to 1,000 ppm) and concurrently lower pHs (2.8 to 2.4), the amount of HDTMA in solution combined with the amount forming ion-pairs is higher than the amount of HDTMA originally released in pure water. This has been interpreted as protonation on the oxide/hydroxide surfaces which depends on the ionic strength and pH of the solutions (Rhoades, 1982; Drever, 1988). Thus, the protonated hydroxide will desorb extra HDTMA into solution which can also ion-pair with PFBA.

#### 2.4 Summary

Due to the reaction of Oshtemo soil with HDTMA, it was found that, some of the native exchangeable cations are replaced by an ion exhange reaction with the quaternary ammonium cation HDTMA. It was also found that the  $C_{16}$  alkyl moieties of the exchanged HDTMA can interact with additional HDTMA, probably by London dispersion forces. This interaction exposes the quaternary ammonium heads reversing the normally negative charge of the soil to positive.





When PFBA, a widely use non-reactive tracer, was dissolved in a buffer solution at a pH in which it is completely ionized, the negatively charged acid anion replaced Br<sup>-</sup> anions present in the soil neutralizing the HDTMA positive charges. However, when PFBA is dissolved in deionized water, the HDTMA interacting by weak dispersion forces is desorbed from the soil and forms ion pairs with PFBA. These ion pairs interact with the adsorbed HDTMA by dissolving in it or by adsorption at the HDTMA/water interface.

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#### **CHAPTER 3**

Interfacial Adsorption as a Major Mechanism Contributing to Pentafluorobenzoic Acid Retention During Transport on a Hexadecyltrimethylammonium Modified Soil

## 3.1 Introduction

Quaternary methyl ammonium ions of the general form  $[(CH_3)_3NR]^+$  or [(CH<sub>3</sub>)<sub>2</sub>NRR']<sup>+</sup>, where R and R' correspond to large hydrocarbon groups, effectively displace native inorganic cations from the cation exchange sites of soils (Boyd et al., 1988a, Lee at al., 1989). The replacement of the hydrated metal by alkylammonium cations, increases the organic carbon content of the soil and changes the nature of the the mineral surfaces from hydrophilic to organophilic. As a result, soils modified with quaternary ammonium cations have been shown, under equilibrium conditions, to have greatly enhanced capabilities for removing nonionic organic compounds (NOC) from water (Lee et al., 1989). Improvement of the sorptive properties of soils for NOCs due to this chemical modification was demonstrated for both high and low clay content soils (Lee et al., 1989) and for the major types of 2:1 clay minerals commonly found in soils and Boyd, 1991). and subsoils (Jaynes For subsoils treated with hexadecyltrimethyammonium ions, sorption coefficients for common ground water contaminants were increased by over two orders of magnitude. Organic-matternormalized sorption coefficients of HDTMA-treated subsoils versus native surface soils showed the HDTMA-derived sorption phase was 10 to 30 times more effective on a unitmass basis than natural soil organic matter (Lee et al. 1989). The HDTMA-derived sorptive phase of modified soils and clays, like natural soil organic matter, acts as a partition phase for NOCs (Boyd et al., 1988b; Jaynes and Boyd, 1991).

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The ability to enhance the sorptive properties of soils and subsoils for NOCs substantially reduces the transport potential of these compounds. This suggests an approach for creating a sorbent zone <u>in situ</u> that could reduce down-gradient pollutant concentrations in water (Boyd et al., 1991). The feasibility of underground injection of organic cations to create a sorptive zone that could intercept an advancing contaminant plume and immobilize the contaminants therein has been demonstrated (Burris and Antworth, 1992). Due to the potential applications of this technology for in-site remediation and contaminant plume management, the behavior of the NOCs under dynamic conditions was evaluated in this research using columns filled with hexadecyltrimethylammonium (HDTMA) modified soil.

The first step in a comprehensive study with soil columns is to determine the contribution of column packing and flow phenomena (molecular diffusion and eddy diffusion) to the total dispersion of solutes. This is known as the hydrodynamic dispersion and is often evaluated with nonreactive tracers (see chapter 2). In this approach, the Peclet number (P) is estimated from the effluent breakthrough curve of a nonreactive tracer. The apparent diffusion coefficient (D\*) then can be determined using the equation  $P = uL/4D^*$ , where u is the linear velocity, and L is the column length. Knowing  $D^*$ , equation (1) can be applied to obtain  $D_1$ , the coefficient of hydrodynamic dispersion:

$$D_1 = \alpha_1 u + D +$$

where  $\alpha_1$  is the dynamic dispersivity, u is the linear velocity of the fluid in the porous medium (Freeze and Cherry, 1979).

Recently, pentaflourobenzoic acid (PFBA) has been used as a nonreactive tracer to describe the movement of ground water under a wide set of conditions. Bowman and Gibbens (1990) recommended PFBA as a nonreactive tracer, after it was compared with several other fluorinated benzoic acids. While it is generally accepted that no perfect nonreactive tracer exists, PFBA has many desirable characteristics (e.g., biological and chemical stability, low diffusion coefficients, etc.) and it has been rapidly accepted as a tracer for soil column studies. Lee et al. (1991) compared the behavior of PFBA and  ${}^{3}\text{H}_{2}\text{O}$  as nonreactive tracers to estimate P and concluded that the two compounds function equally well. Brusseau et al. (1991) also used PFBA and  ${}^{3}\text{H}_{2}\text{O}$  as nonreactive tracers to determine the P value of soil columns filled a wide range of organic carbon contents (0.034 - 3.41%). They also found this compound functioned well as a nonreactive tracer in all the soils studied . However, as reported in Chapter 2 of this dissertation, PFBA was unexpectedly found to be strongly retained in a column filled with hexadecyltrimethylammonium (HDTMA) modified soil.

The purpose of this research was to identify the mechanism(s) responsible for the strong retention of PFBA in the HDTMA-modified soil column. In a previous study, we found that PFBA dissolved in a buffer solution interacts with the HDTMA-modified (Oshtemo Bt) soil. This occurred because excess positive charge was created during the reaction of HDTMA with the soil. When HDTMA was added to the soil, some of the native exchangeable cations of the soil are replaced with HDTMA by simple ion exchange reactions. Additionally, HDTMA is adsorbed by a non-electrostatic mechanism when the C-16 alkyl moieties interact by London dispersion forces with the C-16 alkyl moieties of HDTMA previously adsorbed by ion-exchange. This results in cationic quaternary ammonium head groups at the modifier-water interface, and creates anion exchange capacity in the modified soil. The positively charged head groups may then interact with negatively charged PFBA, leading to its adsorption from solution.

Our previous results also indicated that, in non-buffered (deionized) water, PFBA can ion-pair with HDTMA desorbed from the soil and be removed from the solution as a neutral species by sorption to the HDTMA-derived organic phase still associated with soil. These results were obtained in batch systems under equilibrium conditions with a

freshly modified soil. Studies of the desorption of HDTMA from the modified soil performed with seven different columns (see chapter 4) revealed that under certain conditions as much as 50% of the originally bound HDTMA desorbed from soil, leaving a very stable and strongly adsorbed HDTMA fraction in the soil. It was also concluded that HDTMA was desorbed during column pre-equilibration with water, which occurred prior to introduction of PFBA into the column. Thus, the excess positive charge of HDTMA-modified soil observed in batch buffered experiments was not present in the HDTMA soil contained in the pre-equilibrated soil columns. Therefore, anion exchange could not account for HDTMA retention in the columns. Additionally, since no more HDTMA was desorbable from the pre-equilibrated columns, PFBA could not be retained as an HDTMA-PFBA ion-pair.

In contrast to the retention of PFBA in our HDTMA-modified soil columns, Lee et al. (1991) and Brusseau et al. (1991) reported that PFBA behaves as a nonreactive tracer even with natural soils containing high organic carbon contents. The difference in reaction of PFBA in natural soils and the HDTMA-modified soil may be related to the more nonpolar character of the HDTMA-derived sorption phase. The very low polarity of the HDTMA partition phase is illustrated by the fact that  $K_{OM}$  values for NOC sorption on modified soils and clays are nearly equal to  $K_{OW}$  values, whereas  $K_{OM}$  values for NOC sorption on nature soils are typically about 10 times less than  $K_{OW}$  (Bydetal, 1988; Lee et al., 1989; Boyd and Jayne, 1991). The low polarity of the HDTMA-derived phase creates a defined interface with water, such as occurs between two inmiscible liquids (e.g. hexane-water), as compared to natural soil organic matter where polar functional groups may interact with water diffusing the interface.

Bjerrum (1926) postulated that in a medium of low dielectric constant, such as hydrocarbons, ions of opposite electrical charge associate by columbic forces creating ion pairs with a net electrical neutrality. Ion pairs can also be formed in aqueous bulk phase but they have the tendency to move to phases with lower dielectric constants (Tomlinson et al., 1978). Previous research (Kaiser and Valdmanis 1981; Westall et al., 1985; Jafvert et al., 1990; Lee et al., 1990) has evaluated the distribution of chlorophenols between octanol and water. These studies found that at high pH, where compounds such as pentachlorophenol (PCP) are almost completely ionized, the amount of phenolate transfer from the water to the octanol phase increases with the solution ionic strength. These authors generally agreed that ion pairing between phenolate and the cations in solution was one of the mechanisms responsible for the increased partitioning into octanol. Transfer of organic ions from one phase to another, or from solution to the interface, or diffuse layers between the two phases were also mentioned as possible mechanisms. However, as Jafvert et al. (1990) recognized, it is difficult to distinguish between these mechanisms using data from conventional distribution experiments.

By drawing an analogy between octanol and the HDTMA-derived partition phase of modified soils (Boyd et al., 1988 a, b; Lee et al., 1989; Jaynes and Boyd, 1991) the mechanism postulated for phenolate partition between octanol and water could be responsible for the strong retention of PFBA in HDTMA-modified soil. The goal of this research was to evaluate the contribution of three potential mechanisms of retention: (1) the interaction of PFBA with possible active sites in the Oshtemo soil; (2) the formation of PFBA-electrolyte ion pairs followed by partitioning of the neutral species into the liquid-like environment created by the hydrocarbon tails of HDTMA exchanged in soil and (3) PFBA adsorption at the HDTMA/water interface with its hydrophobic part oriented towards the HDTMA-derived phase and its carboxyl moiety oriented to water where counter ions from the bulk solution can be transferred to the double layer to maintain neutrality. To study the possible interaction of PFBA with the native soil, PFBA retardation factor was obtained in column filled with Oshtemo soil. To assess the contribution of PFBA ion-pair distribution in the solvent-like environment created by the exchanged HDTMA, the partition coefficient of pentafluorobenzoate in octanol/water system was determined. To evaluate the adsorption of the anionic PFBA at the HDTMA/water interface, adsorption of PFBA at the interface between octane and water was studied using the drop weight method (Adamson, 1960).

#### **3.2 Materials and Methods**

All the solutions were prepared with reverse osmosis deionized water, polished through a Milli-Q system (Milliport, Milford, MA). Octane and octanol were purchased from Fluka (Ronkoma, NY) and PFBA from Aldrich Chemical Co. (Milwaukee, WI). Hexadecyltrimethylammonium bromide was obtained from Sigma Chemical Co. (St. Louis, MO), and <sup>14</sup>C-HDTMA-Br, labelled on the terminal carbon of the hexadecyl chain, from Moravek Biochemical Inc. (La Brea, CA); it had a specific activity of 55 mCi mmol<sup>-1</sup> and a radiochemical purity of > 98%. All chemicals were used without further purification.

# HDTMA-modified soil.

An Oshtemo Bt2 horizon (coarse-loamy, mixed, mesic Typic Hapludalf) was used to prepare the hexadecyltrimethylammonium (HDTMA) modified soil. The soil (500 g) was mixed with 1000 ml water while an aqueous solution of HDTMA (8.2 g in 3000 ml) was added in an amount equal to the cation exchange capacity of the soil (Table 1). The suspension was stirred overnight, then transferred to centrifuge bottles and centrifuged at 2,603 g for 20 min. The supernatant was removed using a gentle vacuum suction, and the bottles were refilled with water (225 ml). This procedure was repeated three times to remove any excess HDTMA. After the washing process, the soil was air dried.

# <sup>14</sup>C-HDTMA-modified soil.

The basic procedure used to prepare the HDTMA-modified soil, described above, was also used to prepare the <sup>14</sup>C-HDTMA modified soil. In addition to the HDTMA

required to satisfy the soil CEC, 0.1 ml of  $^{14}$ C-HDTMA solution was dissolved in the aqueous solution added to the soil suspession containing 100 g of soil.

Particle Size (%) Sand Silt Clay	89 5 6
CEC (mmol/Kg)	45
рН	5.8
Organic Carbon Content	0.1

 Table 1. Properties of Oshtemo Bt horizon soil

#### Miscible Displacement Experiments

Miscible displacement experiments were used to determine the hydrodynamic dispersion of the column (Peclet number) containing nonmodified soil and to determine the retention of PFBA in the HDTMA-modified soil.

A schematic diagram of the miscible displacement system is presented in Figure 1. The system consists of two glass bottles, one containing the solute (the sample) and the second the elution solvent. Two single piston pumps (Model 302, Gilson Medical Electronics Inc.) and (Model 510, Waters Ass.) are used in the constant pressure mode for sample and solvent delivery. The pumps are connected to the column through a fourway solvent selection valve (Model 5020, Reodyne). The inlet of the column is also connected to the four way solvent selection valve. The outlet of the column is connected to a flowthrough ultra-violet/visible variable-wavelength detector (Holochrome, Gilson). The column is connected to the system with low dead-volume Teflon fittings and tubing. The various connections are kept as short as possible to minimize extra-column





contribution to dispersion. Changes in concentration as sensed by the detector were registered on a chart recorder (ABB model SE 120).

Three columns were used during these experiments. One was filled with nonmodified Osthetemo Bt horizon soil and two with the HDTMA-modified Oshtemo soil, one with <sup>14</sup>C-HDTMA and the other nonlabeled. The column filled with the nonlabeled modified soil was used to obtain the BTC for PFBA/buffer solution, and the labeled one to obtain a soil equilibrated under similar conditions as those used when the BTC was performed.

The column used was a borosilicate glass preparative column (Candies, Chromaflex) with an internal diameter of 2.5 cm and a length of 5 cm. Bed supports consisted of woven Teflon (FE) diffusion mesh and a Teflon (TEE) filter membrane (extra-fine pore--2.5 um) mesh and a 0.45- $\mu$ m nylon filter membrane. The fraction of air-dried HDTMA-modified soil that passed a 1-mm diameter sieve was used to fill the columns. The columns were dry-packed using the "rotate, bounce and tap method" (Knox 1976) widely used for packing materials with particle sizes higher than 40  $\mu$ m. The dry material was packed to obtain a uniform bulk density.

For pre-equilibration, the columns were connected, in standing vertical position, to a piston pump (Model 302, Gilson Medical Electronics, Inc.). The columns were equilibrated with pure water until steady-state water-saturation conditions were established.

A buffer solution containing a mixture of 0.5 N potasium phosphate monobasic and 0.05 N NaOH (pH 5.4) filtered through a 0.45- $\mu$ m Millipore system and degassed with helium was used to prepare a PFBA solution (50 mg L<sup>-1</sup>) and to elute the column. After determining the inlet solution UV deflection in the recorder (Co-response) at 235 nm, the BTC of PFBA was measured by displacing the sample solution through the column, at a linear velocity of 90 cm h<sup>-1</sup>. The sample was displaced until the detector

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response reached Co. Then the eluent was switched to plain buffer solution. The column was eluted until the effluent UV response was equal to the original base line.

# **HDTMA** desorption

During the column experiment with the  $^{14}$ C-HDTMA-modified soil, eluent was collected and its volume determined. The  $^{14}$ C-activity in these solutions was determined in triplicate by LSC.

# **Octanol/Water Partition Coefficient**

Equal volumes of buffer solution (0.5 N KH<sub>2</sub>PO<sub>4</sub> and 0.05 N NaOH) and octanol (Fluka, Ronkoma, N.Y.) were allowed to equilibrate for four days. PFBA was dissolved in the octanol-saturated buffer solution to obtain a concentration of 500  $\mu$ g m<sup>-1</sup>. Three 20-ml glass vials were filled with 15 ml of the PFBA/buffer solution and allowed to equilibrate in an incubation chamber (New Brunswick Sci., Edison, N.J.) at  $25 \pm 1^{\circ}$ C. Then, 5 ml of water-saturated octanol was added to each of the vials, which were sealed with teflon-lined septa. The vials were stirred for 48 hrs. in an incubation chamber (25  $\pm$  1°C) at approximately 200 rpm. A sample of the octanol layer was removed from each vial using a Paster pipette, and a sample from the water layer was drawn off with a long stainless steel needle connected to a glass syringe to avoid disturbing the octanol layer. The PFBA concentrations in the two layers were measured using a diode array UV/VIS spectrophotometer (Hewlett Packard, model 8452A). The Kow was calculated as the ratio of the concentration of PFBA in octanol to the concentration of PFBA in the buffer solution. Also,  $Na^+$  and  $K^+$  were extracted back in water from 1 ml aliquot of the octanol phase. The Na<sup>+</sup> and K<sup>+</sup> concentration in the water extract as well as in the water phase, were determined in a plasma emission spectrophotometer (Spectra Span, model VB).

#### **Interfacial Adsorption of PFBA**

Equal volumes of octane and 0.5 N KH<sub>2</sub>PO<sub>4</sub> buffer (pH 5.4) were equilibrated for 48 hrs. A series of PFBA solutions were prepared in buffer saturated with octane solution and equilibrated for four days with an equal volume of octane saturated with buffer. Using these solutions, the interfacial tension at the octanol/water (buffer) and air/water (buffer) interfaces was measured by the drop method. The interfacial tension measurement apparatus consisted of a micrometer, syringe, capillary tube and container. A buffer solution containing PFBA was delivered to the end of one capillary tube from a syringe, whose plunger is operated by a micrometer. The tip of the capillary must be ground smooth so that the end is sharp, regular, free from any nicks, and perpendicular to the tube.

The syringe was previously calibrated to determine the volume of liquid per unit of micrometer scale. As the liquid is delivered from the capillary to the immiscible second phase, a drop forms and eventually breaks away, and the volume of the drop is determined by reading the micrometer.

Absorption spectra of the bulk solutions were measured by a Hewlett Packard (Model 8452A) Diode Array spectrophotometer to determine PFBA concentrations at equilibrium. This value was used to correct PFBA initial concentration. T h e densities of water and organic solutions were measured using a pycnometer with a 2 ml volume.

The interfacial tension  $\gamma$  was obtained from the equation

$$\gamma = \frac{V(d_1 - d_2)gf}{r}$$

where  $d_1$  and  $d_2$  are the densities of the immiscible liquids studied, V is the volume of the drop, g is the gravitational acceleration, f a correction factor (from Hrakins-Brown table), and r the radius of the tip of the capillary. The change of interfacial tension as a function of change in solute concentration (PFBA) was used to construct the first type adsorption isotherm, described in detail in the Results and Discussion section.

#### 3.3 Results and Discussion

#### Oshtemo Bt horizon soil PFBA interaction

To evaluate possible interactions between PFBA and the native soil, a BTC of PFBA dissolved in 0.01 N CaCl<sub>2</sub> was obtained in a column filled with the unmodified soil. Figure 2 shows the BTC obtained with this column, where the relative concentration at the column outlet is plotted against the number of column pore volumes. The calculated retardation factor for PFBA was 1.0, which indicates that the compound is moving with the front of the solvent and is not being retained by the soil. The shape of the BTC is sigmoidal and symmetric indicating that nonequilibrium, as would be indicated by tailing is not present in the system.

#### **PFBA** interactions with the HDTMA-modified soil

In contrast to the observed behavior of PFBA in columns filled with the unmodified Oshetmo Bt horizon soil, we observed retention of PFBA in the HDTMA-modified soil. This is shown clearly in Fig. 3 which presents the BTC for PFBA (Co 50 mg/ L or 0.24 mM in  $KH_2PO_4$  buffer at pH 5.4) in the HDTMA-modified soil column. The calculated retardation factor was equal to 57.4 pore volumes. It is interesting to note that it took 26.2 pore volumes for the outlet concentration to be above the detector signal detection limit. Some tailing is observed in the complete BTC (sorption and desorption) indicating the presence of some mass transfer nonequilibrium.



Figure 2. Breakthrough Curve of PFBA in Oshtemo Bt horizon soil

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Figure 3. Breakthrough Curve of PFBA/Buffer in HDTMA-modifed Oshtemo Bt horizon soil

Previous studies on sorption characteristics of NOCs in HDTMA-modified clays and soils conducted under equilibrium conditions have shown that the organic matter normalized partition coefficients ( $K_{om}$ ) of NOCs sorbed by HDTMA-modified subsoils were 10 to 30 times greater than those observed on native surface soils. In the former case, the organic sorption phase is composed almost entirely by HDTMA whereas in the latter case it is natural soil organic matter. The interacting hydrocarbon moieties of HDTMA exchanged in soil clays forms a more effective partition phase for NOCs than natural soil organic matter, which contains an abundance of polar oxygen functional groups such as hydroxyls and carboxyls. In comparison, the hydrocarbon tails of HDTMA form a phase that closely resembles a reverse-phase chromatographic material (e.g.  $C_{18}$ ) where the long hydrocarbon tails covalently bonded to the -SiOH functional groups of silica gel (Snyder and Kirkland, 1978) form an organic phase that is compositionally similar to the HDTMA-derived phase. Thus, the theory and behavior of organic acids in reverse-phase chromatography may be useful in understanding the interaction of anionic PFBA with the HDTMA-modified soil.

Since the development of partition chromatography (Martin and Synge, 1941) organic acids have been studied in non-polar chromatographic materials using a simplified model, where the compounds are assumed to partition between the polar mobile phase and the nonpolar stationary phase covering the solid support. However, these studies have largely ignored the role of interfacial adsorption in retention. Ion-pair formation between hydrophobic acids and quaternary alkylammonium ions was used by Wahlund (1975) as a method to separate hydrophobic acids in reversed-phase chromatographic columns. Partitioning of ion pairs between water and the nonpolar phase, previously covered with 1-pentanol, was the assumed mechanism.

Adsorption of the PFBA at the HDTMA/water interface is considered here as a plausible mechanism to account for the strong retention of PFBA. Martin (1961) was the first to suggest that solute adsorption at the gas-liquid interface can contribute to

retention in gas-liquid chromatography. Adsorption of polar or ionic compounds at the interface between the nonpolar stationary phase and the gas phase, in reverse phase gas chromatographic systems, was later demonstrated by Berezkin (1978). For reverse phase high pressure liquid chromatography, however, no report was found where interfacial adsorption has been experimentally evaluated.

To account quantitatively for the strong retention of PFBA by HDTMA-modified soil, we attempted to consider separately the contribution of PFBA (or PFBA ion pairs) dissolution into the HDTMA phase and contribution of interfacial adsorption. To evaluate the magnitude of these two processes, the total retention of PFBA in the HDTMA-modified soil was compared to (a) PFBA partitioning between octanol and water, and (b) the interfacial adsorption of PFBA in octane-water mixtures.

Model solvent selection Under the conditions in which the BTC experiment was initially conducted, the compound was completely ionized. This was because the pH of the system was 4.8 which is 3 units greater than the pKa of PFBA (pKa = 1.48). Thus, in the model binary solvent systems evaluated (octanol/water and octane/water) pH was equal to or above 4.8, so that PFBA in the aqueous phase was completely ionized. During the interfacial adsorption experiments phosphate buffer (pH 5.4) was used to keep PFBA completely dissociated. At pH values where acidic compounds are nearly completely ionized (pH > pKa + 2), the formation of ion pairs has been shown to increase with ionic strength (Kaiser and Valdmanis 1981; Westall et al. 1985; Jafvert et al. 1990; Lee et al. 1990). Although the high ionic strength of the buffer solution used in these experiment ( $\mu = 0.55$ ) would favor the formation of ion-pairs, we attempted to minimize ion-pair formation by using monovalent cations in the buffer solution (0.5 N potassium phosphate nonobasic and 0.05 N NaOH).
The octanol-water partition coefficient (Kow) of PFBA was determined to be 0.04. To establish if ionic pentafluorobenzoate or neutral ion pair had been transferred to octanol, the presence of cations in the buffer solution, and in the octanol fraction, was determined. The presence of Na<sup>+</sup> in the octanol phase (Table 1) indicates that PFBA was probably transferred to the octanol phase as an ion pair with Na<sup>+</sup> from the buffer solution. The concentration of Na<sup>+</sup> in octanol (36.5 mg  $L^{-1}$ ) was higher than the PFBA concentration (20.5 mg  $L^{-1}$ ) indicating that excess Na<sup>+</sup> had partitioned into the octanol fraction. Evidence for both ion pairs and free ions in water-saturated octanol was also reported Westall et al. (1990) in a study of the distribution of several strong electrolytes between water and octanol. It is noteworthy that  $K^+$ , present in the buffer solution at a concentration 10 times higher than Na<sup>+</sup>, was not detected in the octanol phase. Westall et al. (1990) also found that Na<sup>+</sup> more readily partitioned into octanol, consistent with the size of the hydrated ions and the Bohr model. Since PFBA is a hard ligand, it is expected to complex more strongly with a harder metal ion (Na<sup>+</sup>) that has lost its hydration shell in a medium with a lower dielectric constant (octanol) than in water. Another important factor may be the size of the ion:  $Na^+$  is smaller than  $K^+$ , and it will be more readily complexed with a ligand having a small bite (aperture) like PFBA. At this point, we can only speculate about the reasons why Na<sup>+</sup> is more favorably transfered in the octanol phase. However, this finding is interesting enough to justify further research.

Using the experimentally-determined Kow value, the maximum amount of PFBA retained by the soil as a result of ion-pair partitioning was calculated as an estimate of the contribution of this mechanism (PFBA partitioning into the HDTMA organic phase) to the overall retention of PFBA in the soil column. The distribution coefficient of PFBA in the soil is defined as:

$$K_{OM} = \frac{[PFBA]_{HDTMA}}{[PFBA]_{hadler}}$$

where  $[PFBA]_{HDTMA}$  is equal to the total number of  $\mu g$  of PFBA per unit volume of HDTMA (ml) and  $[PFBA]_{buffer}$  is the number of  $\mu g$  of PFBA per ml of water contained in the column. If we assume that  $K_{OM}$  for PFBA in the soil is equal to  $K_{OW}$  (Jaynes and Boyd 1991) and we know the HDTMA content of the soil, the total number of mmols of PFBA retained by the soil in the column (soil loading capacity) can be obtained as follows:

$$K_{OM} = \frac{[\mu g \ PFBA/ml \ HDTMA]}{[\mu g \ PFBA/ml \ water]}$$

The volume of HDTMA present in the column is estimated from the density  $(\rho)$  of hexadecane:

$$Vol HDTMA = \frac{HDTMA \text{ weight}}{\rho \text{ hexadecane}}$$

The HDTMA content of the soil (0.3%) is estimated from the equilibrated solid organic carbon content (0.4%) minus the initial organic carbon content of the soil (0.1%). Knowing the mass of organic carbon in a mole of HDTMA (228 g), then the number of moles of HDTMA in 100 g of soil = 0.3 gC/228 gC = 0.0013 moles/100 g. Assuming that PFBA will dissolve only in the hexadecane tails, the weight of the sorptive phase in 100 g of soil will be the number of moles times hexadecane molecular weight (226.45 g), or 0.0013 moles times 226.45 g/mole = 0.299 g per 100 g of soil. The weight of hexadecane in the experimental column containing 45.42 g soil is 0.136 g. The volume of HDTMA in the soil column then is obtained by dividing the weight of HDTMA by the density of hexadecane: 0.136 g/0.773 g/ml = 0.176 ml. The denominator of the distribution coefficient is:

$$[\mu g PFBA/ml water] = \frac{[Total \ \mu g \ PFBA - X]}{water \ content \ (ml)}$$

Where X equals the mass of PFBA retained by the column or the loading capacity of the column, and total  $\mu g$  PFBA (in the column) is equal to the PFBA input concentration (52.2  $\mu g/ml$ ) times the volumetric water content (10.36 ml). Therefore:

$$[\mu g \ PFBA/ml \ water] = \frac{[(10.36 \ ml \ x \ 52.2 \ \mu g/ml) \ - \ X]}{10.36 \ ml}$$

Thus, assume  $K_{ow}$ , determined experimentally as 0.04, is equal to  $K_{om}$ , then:

$$K_{OM} = 0.04 = \frac{[X/0.176 \ ml]}{[(540.79 \ \mu g - X)/10.36ml]}$$

Solving the equation for X:

$$X = 0.366 \ \mu g \ or \ 1.73 \ x \ 10^{-6} \ mmoles$$

These results indicate that the HDTMA-modified soil column could retain a maximum of 0.366  $\mu$ g PFBA or 1.73 x 10<sup>-6</sup> mmoles by partition interactions, if all of the above assumptions are true.

# **Role of Interfacial Adsorption in PFBA Retention**

The most common way for studying adsorption of organic compounds at liquid/air or liquid/liquid interfaces is based on measurement of the interfacial tension. We used the drop-weight method to evaluate the potential for adsorption of PFBA at the interface between water and the HDTMA-derived organic phase (referred to hereafter as the "hexadecane-water interface") of the modified soil.

Model Selection. Octanol-water has been used since 1964 (Fujita et al.) as a model system to predict certain behavior of organic pollutants in the environment, as for example NOC partitioning into soil organic matter and the bioaccumulation is NOCs.

We used the drop-weight method to evaluate the adsorption of PFBA at the octanol/water interface. Table 2 summarizes the PFBA adsorption data in the equilibrated octanol/water system and at the air/water interface.

System	Surface tension (γ <sub>0</sub> ) mN/m	Surface tension ( $\gamma$ ) mN/m	Surface pressure $(\gamma_0 - \gamma)$ mN/m
octanol/water (0.05 M PFBA)	8.75	8.56	0.19
air/water (plus 0.05 M PFBA)	72.39	63.21	9.18
air/water (saturat. with octanol)	72.39	37.51	34.88
air/water (saturat. with octanol plus 0.05 M PFBA)	72.39	37.51	34.88

Table 2. Surface tension measurement at the air-water and octanol-water interface.

Interfacial tension at the octanol/water interface  $\gamma_0$  was equal to 8.75 mN/m. The addition of PFBA (0.05 M) did not substantially change the interfacial tension ( $\gamma$ ) of the



Figure 4. Change in interfacial adsorption  $(\gamma)$  as a function of concentration.

octanol/water system ( $\gamma_0 - \gamma = 0.19$ ). Apparently the high surface activity of octanol obscures the surface activity of PFBA at the octanol/water interface due to the competition between two amphiphilic compounds. The surface activity of octanol, and the competition between octanol and PFBA, was clearly observable at the air/water interface. The surface tension at the air/water interface ( $\gamma_0$ ) is equal 72.39 mN/m. If 0.05 M PFBA was dissolved in the aqueous phase instead of octanol the decrease in surface tension ( $\gamma_0 - \gamma$ ) was only 9.18 mN/m. If octanol saturated water is used instead of pure water to determine the surface tension ( $\gamma$ ) at the air/water interface, the value decreases to 37.51 mN/M ( $\gamma_0 - \gamma = 34.88$ ), due to the high surface activity of octanol. Thus, if PFBA is added to water saturated by octanol, the surface tension at the air/water interface does not change significantly (Table 2). This precludes the use of octanol-water mixtures as a model to study PFBA adsorption at the interface between water and the HDTMA-derived organic phase. Thus, octane water was selected as the model system to study the interfacial adsorption of PFBA at the hexadecane/water interface of the HDTMA modified soil.

Figure 4 represents changes in octane/water interfacial tension as a result of increasing PFBA concentration in solution. As the graph shows, the octane/water interfacial tension increases as a function of PFBA concentration indicating that PFBA is a surface-active compound. When the adsorption isotherm is plotted as  $\Gamma$ , where  $\Gamma$  is the excess of particles of a substance adsorbed per unit of suface area of interface in relation to the concentration of the same substance present in the bulk solution (Gibbs, 1906) versus the PFBA concentration (Fig. 5), the maximal value of Gibbs surface excess ( $\Gamma_{\rm m}$ ) is obtained. The value of  $\Gamma_{\rm m}$  corresponds to the coverage of the interface by a monolayer of PFBA. The minimal interfacial area per adsorbed PFBA molecule can be calculated from the equation:



Figure 5. Excess surface concentration ( $\Gamma$ ) vs PFBA concentration.

$$\Gamma = (AN_A)^{-1}$$

where  $N_A$  is Avogadro number and A is the interfacial area per adsorbed molecule. Thus, in the compact layer of the electric double layer at the octane/water interface

$$A_{\mathbf{m}} = (\Gamma_{\mathbf{m}} N_A)^{-1}$$

where  $A_m$  is the minimal area per adsorbed PFBA molecule. This value, calculated from the  $\Gamma_m$  obtained from figure 5, is given in Table 3.

Table 3. Adsorption parameters of anionic PFBA in the octane-water system at 22°C.

System	Γ <sub>m</sub> 10 <sup>-10</sup> M/cm <sup>2</sup>	A <sub>m</sub> Ų/mol	a	-∆G kJ/mole	ρ
PFBA (0.5M KH <sub>2</sub> PO <sub>4</sub> + 0.05 M NaOH)	0.716	231.84	0.455	23.73	0.63

The PFBA adsorption parameters at the octane/water interface can be calculated from the general form of the adsorption isotherm of amphiphilic compounds (Markin et al., 1992):

$$\frac{\theta[p - (p - 1)\theta]^{p-1}}{p^p(1-Q)^p} \exp(-2a\theta) = X_A^B \exp[-\Delta G^0/RT]$$

where p is the number of adsorbed octane molecules substituted for by one molecule of PFBA, a is the attraction constant between the particles adsorbed, X is mole fraction of PFBA,  $\Delta G^0$  is the standard Gibbs free energy of adsorption at equilibrium, and  $\theta$  is the surface coverage.

Using the software *Mathematica* (Wolfram Research), the adsorption parameters p, a, and  $\Delta G^0$  were calculated and are shown in Table 3. These data are consistent with anionic PFBA adsorbed at the octane-water interface with the COO<sup>-</sup>-groups oriented into water and screened from the electric double layer by inorganic cations such as H<sup>+</sup>, K<sup>+</sup>, and Na<sup>+</sup>. The phenyl rings of PFBA are present in hydrophobic octane phase interacting due to Van der Waals forces; this is the source of the resulting attraction constant of 0.455. The interaction energy, 23.73 kJ per mole (5.68 Kcal/mol) corresponds to the sum of all Van der Waals forces between the adsorbed moieties.

### Estimation of Anionic PFBA Retention Due to Interfacial Adsorption

To integrate the results obtained in the octane/water system with the results observed in the BTC, it has been assumed that, at the moment when PFBA started to elute from the column, a compact layer of PFBA has been formed at HDTMA/water interface of the soil. Therefore, the minimum area  $A_1$  covered by a molecule of PFBA at the compact layer in the model octane-water system was used to calculate the surface area of the soil covered by the anionic PFBA, as shown below.

The number of molecules retained by the soil before any PFBA elution occurs was calculated as follows:

## V [PFBA] = mass of PFBA adsorbed at the base line

where V (271.53 ml) is equal to the number of base line pore volumes before PFBA elution commenced multiplied by the volume of one pore volume. The input concentration of PFBA [PFBA] =  $52.2 \ \mu g/ml$ . Therefore,  $251.53 \ ml x \ 52.20 \ \mu g/ml$  =  $14173.75 \ \mu g$ , or 0.067 mmols. Multiplying by Avogadros's number gives the corresponding number of molecules:

$$6.02 \times 10^{-23}$$
 molecules/mol x 0.067 mmol/1000 = 40.243 x 10^{10}

Now, the number of molecules is multiplied by the area covered per molecule (Table 3) at the compact layer: so,  $4.024 \times 10^{19}$  molecules. 231.84 A<sup>2</sup>/molecule = 9,330.1 x 10<sup>21</sup> A<sup>2</sup> To convert this value to square meter we divide by  $10^{20}$ :

$$9,330.1 \times 10^{21} \text{ A}^2/10^{20} = 93.301 \text{ m}^2$$

Thus, the maximum surface area coverage by adsorbed PFBA per gram of modified soil, obtained after dividing by the column soil weight (45.42 g), yields a value of 2.05  $m^2/g$ .

In Table 3 the surface area of the soil calculated with the model value is compared to the value obtained using the BET method.

Table 3. Comparison between soil surface areas measured using N2 (BET) and estimated using PFBA

Method of Determination	Surface Area (m <sup>2</sup> /g)
BET	2.36
BTC base line and area cover/molecule	2.04

Interestingly, a very close agreement exists between the surface area calculated from the octane/water model and the  $N_2$  BET surface area of the modified soil. This would seem to be a reasonable result supporting the concept of interfacial adsorption of PFBA in the modified soil, realizing that the majority of surface area in this soil is due to clay mineral surfaces which are presumably covered with exchanged HDTMA.

Conder et al. (1969) established that the different contributions to gaschromatographic retention (partition, adsorption at solid/liquid and liquid/liquid interfaces) are additive, and we have adapted this idea and applied to our system. The retardation factor (R) calculated from the BTC first moment and expressed column pore volumes for anionic PFBA in the HDTMA-modified soil column will be:

$$R_{\text{total}} = (R) \text{Ad.Soil/water} + (R) \text{disol.} + (R) \text{Ads Liquid/liquid}$$

Where the total retention  $R_{total}$  obtained from the BTC is equal to 57.4 pore volumes, the retention due to interaction of PFBA with the native soil (R)<sub>Ad.Soil/water</sub> is 1 pore volume, the number of pore volumes due to dissolution (R)<sub>disol</sub> is equal to 3.4, and the number of pore volumes due to interfacial adsorption in the HDTMA/water interface (R)<sub>Ads lquid/liquid</sub> is equal to 26.2 pore volumes. The sum of all terms in the right side is equal to 30.6, which is 26.8 pore volumes smaller than the R<sub>total</sub>. The difference is approximately equal to the number of pore volumes due to interfacial adsorption. This could conceivably be accounted for by the formation of a second PFBA layer at the interface. At any rate, these results suggest that among the different contributors to retention of PFBA in the HDTMA modified soil, adsorption of PFBA at the hexadecanewater interface of the HDTMA-soil is the primary mechanism accounting for the strong retention of PFBA.

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## CHAPTER 4

Directly Measured vs Predicted Sorption Coefficients During Transport for Nonionic Organic Compounds in a Hexadecyltrimethylammonium Modified Soil.

# 4.1 Introduction

Sorption and degradation (biological or chemical) of nonionic organic compounds (NOCs) cause decreased transport through soils, thereby reducing ground water contamination. Sorption of NOCs by soil and sediments in aqueous systems is controlled mainly by the organic carbon content of the sorbing material and by the water solubility of the NOC. With these facts in mind, this laboratory has been working to develop an integrated approach to remediate contaminated soils and aquifer materials. This approach consists of reducing transport of common ground water contaminants and then subsequently degrading them microbiologically (Nye et al., 1993). To reduce transport, the sorptive capability of sandy soils has been increased by exchanging the inorganic native cations of the soils with quaternary ammonium compounds (cationic surfactants) of the form  $(CH_3)_3NR$  where R is a large alkyl hydrocarbon. This method has been proven to increase the sorption of NOCs on surfactant treated B-horizon soils by over two orders of magnitude (Boyd et al., 1988). Sorption studies with these modified soils indicate that the surfactant-derived sorptive phases are 10 to 30 times more effective than native soil organic matter as partition media for NOCs (Lee et al., 1989).

The two tools most commonly used to study sorption behavior of organic compounds in soils and sediments are batch sorption isotherms and breakthrough curves (BTC). With these methods, the thermodynamic distribution constant, or the sorption coefficient, K, of the compounds are determined. The sorption coefficient in the batch method corresponds to the slope of the sorption isotherm constructed by plotting the concentration of the sorbed compound in soil versus its concentration in water contacting that soil at equilibrium. From the BTCs the retardation factor (R) of the compound, a parameter indicating the mobility of a solute eluted through a soil column, is obtained. K is determined from the R value by using the equation

$$R = 1 + \frac{\kappa \rho}{\theta} \tag{1}$$

where  $\rho$  is the bulk density and  $\theta$  is the volumetric water content of the soil. The phase ratio,  $\rho/\theta$ , is the ratio between the two phases in the system, in this case the solid phase and the liquid phase, in which the compound flowing through the system will be distributed. The basic difference between the two methods is that one value is obtained under equilibrium conditions (batch method) and the other under dynamic conditions (BTCs). However, since K is an equilibrium parameter the two values should be the same. For natural soils, in most cases, these values have been shown to be the same (Nkedi-Kizza et al., 1987; Wood et al., 1990). The results obtained with laboratory soil columns are considered to provide a better understanding of the transport behavior of NOCs through soil or aquifer materials.

Before this work, only batch sorption isotherms had been used to characterize the impact of chemical modification, with cationic surfactants, on the sorption capacity of soils. The first objective of this part of the study was to compare K values obtained during transport, i.e., from BTCs, with K values obtained from sorption isotherms. To obtain the BTC, a constant concentration of the compound must be fed into the column until equilibrium is obtained (step function injection mode). Based on the sorption coefficients obtained with the batch method, NOCs are expected to be highly retained in the soils and thus, their R values are expected to be high. This suggests an operational limitation to obtain the BTC directly from water, for volatile organic compounds,

because the elution volumes and hence elution times required are large. Nkedi-Kizza et al. (1985) suggested for solutes with low water solubility and large sorption coefficients that sorption coefficients from water can be estimated from BTCs obtained from mixtures of water and organic solvents using a model developed by Rao et al. (1985). This model predicts a log-linear relationship between K and the fraction of organic solvent in water ( $f_c$ ). This relationship was developed by combining the Karickhoff (1984) equation for sorption of hydrophobic organic compounds (HOC) from water on soils and sediments with a solubility model developed by Amidon et al. (1974) and Yalkosky et al. (1975). A summary of the theory is presented in the next section.

The theory was used by Nkedi-Kizza et al. (1985) to predict the sorption of diuron, atrazine and anthracene from water in five different soils. They used different proportions of methanol-water and acetone-water. They found that, as expected, a log-linear relationship exits between the K values of the compounds and the corresponding fractions (fc) of methanol-water. However, when different proportions of acetone-water were used as solvent mixtures, a quadratic relationship appeared to fit the data better.

The overall goal of this part of the study was to evaluate the retention of common ground water contaminants (benzene, naphthalene, and TCE) in soil columns containing quaternary ammonium cation modified soils. We compared the K values determined in columns filled with hexadecyltrimethylammonium (HDTMA) modified soil with the K values obtained in the same soil from batch equilibrium sorption isotherms. Because NOCs are strongly retained in the organically modified soils (Boyd et al., 1988; Lee et al., 1989), the approach was to use the log-linear relationship between K and  $f_c$  of watermethanol mixtures (Rao et al., 1985) to estimate K values in pure water by extrapolation. Because the K values, for the compounds above, obtained by extrapolation using the model did not coincide with the K values calculated from the sorption isotherms and also because it was observed that the organic carbon content of the soil was reduced significantly during the BTC experiments. The values of K from effluent BTCs were obtained directly from pure water and compared to the extrapolated Ks. Also, K values

were obtained by batch sorption isotherms using soil removed from the column at the end of the BTC experiments.

### 4.2 Theory

The model of Rao et al. (1985) was developed to describe quantitatively the sorption and transport of hydrophobic organic chemicals (HOC) dissolved in water and mixtures of water-organic solvents in sorbent materials such as soils and sediments. These sorbents are known to contain both mineral and organic constituents. However, based on Karickhoff (1984) findings, it was assumed that the surfaces in direct contact with the interstitial solution were predominantly hydrocarbonaceous in nature. The sorbate molecules were considered to be composed of hydrocarbon and polar moieties, with hydrocarbonaceous portions predominating. The theory considered sorbate-solvent and solvent-solvent interactions to be most important in describing HOC sorption on soils and sediments from single or mixed solvents. Sorption (sorbate-sorbent interaction) is assumed to be controlled by sorbate solubility in the solvent from which sorption occurs. Thus, the major theoretical assumption was that sorbate-solvent hydrophobic forces are responsible for sorption. Changes in sorbent physico-chemical properties due to solventsorbent interactions, as well as competition between solvent and sorbate for the sorbent surface, were neglected in the theory (Rao et al. 1985).

Karickhoff (1984) showed that for soil and sediments, the logarithm of the HOC sorption coefficient normalized by the soil organic carbon content (P<sup>W</sup>) is equal to:

$$\ln P^{W} = \alpha \ln X^{W} - \left(\frac{\Delta S_{f}}{RT}\right) (T_{m} - T) - \beta$$
 (2)

where  $\alpha$  and  $\beta$  are constants,  $X^{W}$  is the mole fraction solubility,  $\Delta S_{f}$  is entropy of fusion,  $T_{m}$  is the melting point (<sup>O</sup>K), T is temperature (<sup>O</sup>K) and R the gas constant (KJ/mol <sup>O</sup>K). Karickhoff (1984) found the values of  $\alpha$  and  $\beta$  to be 0.83 and 2.142, respectively, in soil and sediments.

Amidon et al. (1974) and Yalkowsky et al. (1975) modified the basic concept of solubility of Hildebrand et al. (1970), which was used to describe solvent-solute interactions in regular solutions, to study solubility in polar solvents. In an ideal solution all intermolecular forces are equal and there is no change in heat or volume during mixing. In a non-ideal solution, the deviation from ideal is known to arise as a result of the unequal intermolecular forces between solvent-solvent and solvent-solute molecules, and it is described by the activity coefficient (ac). Thus, the mole fractional solute solubility  $(X_2)$  is expressed as:

$$-\log X_2 = \log X_2^{ideal} + \log (ac)$$
(3)

The ac is considered to reflect the work required to remove the solute from its own environment  $(W_{22})$ , plus the work required to create a cavity in the solvent large enough to contain the solute molecule  $(W_{11})$ , plus the work gained after the molecule is inserted into the cavity  $(W_{12})$ . Mathematically the log of ac can be expressed as:

$$-\log (ac) = \frac{(W_{22} + W_{11} - 2W_{12})V_2\phi^2}{2.303RT}$$
(4)

where  $V_2$  is partial molal volume, and  $\phi_1$  is the solvent volume fraction. For regular solutions, where the size and polarity of the solvent do not differ greatly, Hildebrand et al. (1970) approximated the term  $W_{12}$  by the geometric mean of  $W_{11}$  and  $W_{22}$ . Thus, the equation for diluted solutions ( $\phi_1$ ) becomes:

$$\log (ac) = - (W_{11}^{1/2} - W_{22}^{1/2})^2 \frac{V_2}{2.303 RT}$$
(5)

where the square roots of the work terms are known as solubility parameters  $\delta_1$  and  $\delta_2$  of the solute and the solvent, respectively. When Yalkowsky et al. (1975) considered that for solutions in aqueous or polar solvents, the geometric mean approximation is not valid, they proposed a two dimensional analog of the equation of Hildebrand et al. (1970). Thus, instead of using the geometric mean approximation to obtain  $W_{12}$ , they

used the concept that the work required to remove a solute molecule from the bulk phase is equal to the work of cohesion of the solute. This work is equal to the surface area of the solute (A) times the surface tension of the solute ( $\gamma_1$ ). The work required to create a cavity of area A in the solvent is considered to be equal to the work of cohesion of the solvent, i.e.,  $A\gamma_2$ , where  $\gamma_2$  is the solvent surface tension. Also, the work involved in the insertion of the solute molecule into the solvent corresponds to the work of adhesion, which is equal to  $A\gamma_{12}$ , where  $\gamma_{12}$  is the interfacial tension between solute and solvent. Thus, they arrived at the equation:

$$-\log (ac) = -\frac{\gamma_{12}A_2}{2.303 RT}$$
(6)

Furthermore, considering that both interfacial tension and molecular surface area vary with structure, they adopted the approach of Langmuir (1911) of separating the contributions to interfacial tension of the nonpolar and polar portions of the molecule. Thus, equation 6 becomes:

$$-\log (ac) = \frac{\gamma_{1\rho}A_{\rho} + \gamma_{1k}A_{k}}{2.303 RT}$$
(7)

where  $\gamma_{1h}$  is the microscopic aliphatic hydrocarbon-solvent interfacial tension, and  $\gamma_{1p}$  is an analogous two-dimensional term dependent on the interaction between the solvent and the polar portion of the solute. Rao et al. (1975) adapted this basic concept of solubility. They expressed Yalkowsky mole fraction solubility for any crystalline solute in any pure solvent as:

$$\ln X^{j} = -\frac{\left[(\gamma^{j}HSA) + (e^{j}PSA)\right]}{kT} - \left(\frac{\Delta S_{f}}{RT}\right)(T_{m} - T)$$
(8)

where  $\gamma^{j}$  and  $\epsilon^{j}$  correspond to  $\gamma_{1h}$  and  $\gamma_{1p}$ , respectively; HSA and PSA correspond to  $A_{h}$  and  $A_{p}$ , respectively, according to Yalkosky et al. (1975) nomenclature; and k is the Boltzmann constant (kJ/K). They also used an extension of the cavity model developed by Yalkowsky et al. (1976) to predict HOC solubility in binary solvent mixtures which is expressed as a linear combination of terms representing the pair-wise interactions of each solvent with each topographic component of the solute molecule:

$$\ln X^{m} = \ln X^{w} + f_{c}[(\Delta \gamma^{c} HSA) + (\Delta \epsilon^{c} PSA)]/kT$$
<sup>(9)</sup>

where  $\Delta \gamma^{c} = (\gamma^{w} - \gamma^{c}); \quad \Delta \epsilon^{c} = (\epsilon^{w} - \epsilon^{c});$  and the superscripts w, m and c correspond to water, mixed-solvent, and organic miscible solvent (cosolvent), respectively.

Rao et al. (1985) extended the Karickhoff (1984) sorption equation to mixed solvents:

$$\ln P^{m} = -\alpha \ln X^{m} - \left(\frac{\Delta S_{f}}{RT}\right)(T_{m} - T) - \beta \qquad (10)$$

By substituting  $\ln X^{m}$  as defined by Yalkosky et al. (1976) in equation 9, they obtained the following equation:

$$\ln P^{m} = -\ln X^{W} + \frac{f_{c}[(\Delta \gamma^{c} HSA) + (\Delta \epsilon^{c} PSA)]}{kT} - \left(\frac{\Delta S_{f}}{RT}\right)(T_{m} - T) - \beta$$
<sup>(11)</sup>

Next, Rao et al. (1985) defined the term

$$\sigma^{c} = \frac{\left[(\Delta \gamma^{c} HSA) + (\Delta \epsilon^{c} PSA)\right]}{kT}$$
(11b)

Combining Eq.(2) with Eq.(11a) and (11b) gives

$$\ln P^{m} = \ln P^{w} - \alpha \sigma^{c} f_{c} \tag{12}$$

The above equation expresses the log-linear relationship between the normalized sorption coefficient and the fraction of organic cosolvent. Rao et al. (1985) extended the concept of retardation factor to considered the effect of cosolvents on the transport of HOCs in soils:

$$R_{\rm m} = 1 + \frac{\rho K_{\rm m}}{\Theta_{\rm m}} \tag{13}$$

where  $R_m$  is the solute retardation factor in a mixed solvent system,  $K_m$  is the nonnormalized sorption coefficient and  $\theta_m$  is the liquid phase content (cm<sup>3</sup> / cm<sup>3</sup>) They generalize Eq (11) for the non-normalized sorption coefficient and substituted in Eq (12) rearranged giving:

$$\log (R_{_{\rm I\!M}} - 1) = \log(R_{_{\rm I\!W}} - 1) - \alpha \, \sigma^c f_c \tag{14}$$

This equation predicts an exponential decrease of  $(R_m - 1)$  with increasing  $f_c$  and was the equation used in this research to obtain K in water by extrapolation.

### 4.3 Materials and Methods

All solutions were prepared with reverse osmosis deionized water, purified further through a Milli-Q system (Milliport, Milford, MA). Benzene and TCE, both 99 % purity, were purchased from Aldrich Chem. Co. (Milwaukee, WI); naphthalene and hexadecyltrimethylammonium bromide, both 99 % purity, from Sigma Chem. Co. (St. Louis, MO); methanol, high purity, from Burdick & Jackson (Muskegon, MI); and octane from Fluka (Ronkoma, NY). <sup>14</sup>C-HDTMA-Br, labelled on the terminal carbon of the hexadecyl chain, was obtained from Moravek Biochemicals, Inc. (La Brea, CA); it had a specific activity of 55 mCi mmol<sup>-1</sup> and a radiochemical purity of > 98 %. All chemicals were used without further purification.

### HDTMA-modified soil.

An Oshtemo Bt2 horizon (coarse-loamy, mixed, mesic Typic Hapludalf) was used to prepare the hexadecyltrimethylammonium (HDTMA) modified soil. The soil (500 g) was mixed with 1000 ml water, after which an aqueous solution of HDTMA (8.2 g in 3000 ml) was added in an amount equal to the cation exchange capacity of the soil (Table 1). The suspension was stirred overnight, then transferred to centrifuge bottles and centrifuged at 2,603 g for 40 min. The supernatant was removed using gentle vacuum suction, and the bottles were refilled with water (225 ml). This procedure was repeated three times to remove any excess HDTMA. After the washing process, the soil was air dried.

Table 1. Properties of Oshtemo Bt horizon soil

Particle Size (%) Sand Silt Clay	89 5 6
CEC (mmol/Kg)	45
рН	5.8
Organic Carbon Content (%)	0.1

# <sup>14</sup>C-HDTMA-modified soil.

The basic procedure used to prepare the nonradioactive HDTMA-modified soil was also used to prepare the <sup>14</sup>C-HDTMA modified soil. In addition to the HDTMA required to satisfy the soil CEC, 0.8 ml of <sup>14</sup>C-HDTMA solution (3 mCi in 31 ml ethanol) was dissolved in the aqueous solution added to the soil suspension containing 800 g of soil. The resulting specific soil activity and organic carbon content were determined with 50 mg of finely ground soil samples. Triplicate samples of the soil were combusted at 1020<sup>o</sup>C in a Carbon Nitrogen -Mass spectrometer (CN-MS) analyzer (Roboprep, Europa Scientific, U.K.). The CO<sub>2</sub> released from the samples was split, a small portion was used in the mass spectrometer for carbon analysis, and the rest was collected in liquid scintillation vials and analyzed on a Packard 1500 TriCarb Liquid Scintillation Analyzer (Packard Instrument Co., Downer's Grove, IL). The obtained disintegration per minute (dpm) values were corrected for background levels.

## Miscible Displacement Experiments

Miscible displacement experiments were used to determine the hydrodynamic dispersion (Peclet number) and the retardation factor (R) of the column containing nonmodified soil and all the columns containing the HDTMA-modified soil used during this study.

A schematic diagram of the miscible displacement system is presented in Figure 1. The system consisted of two glass bottles, one containing the solute (the sample) and the second containing elution solvent. Two single piston pumps (Model 302, Gilson Medical Electronics Inc.) with water were used in the constant pressure mode for sample and solvent delivery. The pumps were connected to the column through a four-way solvent selection valve (Model 5020, Reodyne). The inlet of the column was also connected to the four-way solvent selection valve, and the outlet of the column connected to a flowthrough (Holochrome, Gilson) ultra-violet/visible variable-wavelength detector. The column was connected to the system with low dead-volume Teflon fittings and Teflon tubes. The various connections were kept as short as possible to minimize extracolumn contributions to dispersion. Changes in concentration as sensed by the detector were registered on a chart recorder (ABB model SE 120).

The column for the miscible displacement experiments performed with the native Oshtemo Bt horizon soil was a borosilicate glass preparative column (Beckman, Altex Division) with an internal diameter of 2.5 cm. The column length was adjusted to 5 cm, using a moveable plunger. Bed supports consisted of woven Teflon (TFE) diffusion mesh and a Teflon (TFE) filter membrane (extra-fine pore--2.5  $\mu$ m). For the miscible displacement experiments performed with the HDTMA-modified soil, fit-bed columns were used. They were also made from glass borosilicate (Candies, Chromoflex), with an internal diameter of 2.5 cm., and a fit length of 5 cm. Bed supports consisted of woven FE teflon diffusion mesh and a 2.5- $\mu$ m Teflon filter membrane together with a 0.45- $\mu$ m nylon filter membrane. The fraction of air-dried, non-modified or HDTMA-modified soil that passed a 1-mm diameter sieve was used to fill the columns. The



Figure 1. Schematic diagram of miscible-displacement system

columns were dry-packed using the "rotate, bounce and tap method" (Knox 1976) widely used for packing materials with particle sizes higher than 40  $\mu$ m. The dry material was packed to obtain a uniform bulk density.

For pre-equilibration, the columns were connected, in standing vertical position, to a piston pump (Model 302, Gilson Medical Electronics, Inc.). The non-modified column was equilibrated with a 0.01 N CaCl<sub>2</sub> solution until steady-state water saturation conditions were established. The modified columns were equilibrated in the same way but with pure water. Columns specification are summarized in Table 2.

 Table 2. General characteristics of the columns

Length (cm)	5	
Diameter (cm)	2.5	
Input flow rate (ml/min)	3.0	
Linear velocity (cm/hr)	91.8	
Input flow rate (ml/min) Linear velocity (cm/hr)	2.5 3.0 91.8	

To obtain the BTCs in the native Oshtemo Bt horizon soil, a 0.01 N solution of CaCl<sub>2</sub> filtered through a 0.45  $\mu$ m Millipore system and degassed with helium was used to prepare solute samples. After determining the sample solution UV deflection (Co) outside of the column at the specific selected wavelength for each solute, the BTC was measured by displacing the sample solution through the column at a linear velocity of approximately 90 cm h<sup>-1</sup>. The sample was displaced until the detector response reached Co. Then the eluent was switched to 0.01 N CaCl<sub>2</sub>. The column was eluted until the effluent UV response was equal to the original base line. The same basic procedure was used to obtain the BTC through the HDTMA-modified soil column, with the only difference that the solutions were prepared in pure water or different proportions of methanol water mixtures.

## Benzene BTCs with pressurized system

The same basic apparatus (Fig. 1) and the same basic procedure were used to run miscible displacement experiments through an HDTMA-modified soil column with water and different proportions of methanol and water. However, the solvent-sample delivery system consisted of two glass lined bottles connected through a valve to a He tank which degassed the solutions and maintained the head space slightly pressurized to control evaporation of solvent and indirectly of solute. For the last part of this research, seven columns were gradually equilibrated with increasing proportion of methanol (0 to 40 %) in water and used to obtain benzene BTCs. At the end of each experiment each column was unpacked and the soil air dried and used to determine benzene sorption isotherms, described below.

### Organic carbon mass balance

During the experiments with the HDTMA-modified soil, eluent from each step of the experiment was collected, its volume determined, and the solutions analyzed for <sup>14</sup>C-activity in triplicate by LSC. These data were added together and compared to the specific activity of the soil at the beginning of the experiments and at the end of the experiments. After the experiment, the soils from each of the seven columns were air dried and the soil specific activity and organic carbon content were determined in them. For these analyses, the same procedures described above to obtain the <sup>14</sup>C-HDTMA modified soil organic carbon content and specific activity were followed.

# **Sorption Isotherms**

Batch sorption isotherms from water were measured for solutes (benzene, naphthalene and TCE) in the native Oshtemo Bt soil. For the HDTMA-modified Oshtemo Bt soil, batch sorption isotherms were measured for all solutes in increasing proportions of methanol-water ( $f_c$ ). In addition, benzene sorption isotherms were measured on air-dry HDTMA-treated soil that was removed from the columns at the end

of the BTC experiments. Different soil:solution ratios (1:1 to 1:5) were used for the experiment depending upon  $f_c$ . Larger soil:solution ratios were used at higher  $f_c$  in order to improve the precision of the measurement. Duplicate samples were prepared in 5 ml glass amber tubes with increasing concentrations of <sup>14</sup>C-labeled solute, up to 75 % the water solubility of the solute. The tubes were closed with teflon-lined screw-tops and shaken for 24 h. Following this equilibration period, the solid and liquid phases were separated by centrifugation (1,993 x g) and 1 ml aliquots of the supernatant were analyzed by liquid scintillation counting (LSC). The concentration of solute sorbed in the soil (Q) was determined from the difference between initial and final solution-phase concentrations.

## **Methanol Interfacial Adsorption**

Equal volumes of octane and water were equilibrated for 48 hours. A series of methanol solutions were prepared in octane-saturated water and equilibrated for four days with an equal volume of water-saturated octane. Using these solutions, the interfacial tension at the octane/water and air/water interfaces was measured by the drop weight method.

The interfacial tension measurement apparatus consisted of a micrometer, syringe, capillary tube, and container. A water solution containing methanol was delivered to the end of one capillary tube with a syringe, with the plunger operated by a micrometer. The tip of the capillary had to be ground smooth so that the end was sharp, regular, free from any nicks, and perpendicular to the tube.

The syringe was previously calibrated to determine the volume of liquid per unit of micrometer scale. As the liquid was delivered from the capillary to the immiscible second phase, a drop formed, and on the break away, the volume of the drop was determined by reading the micrometer. The methanol concentration after equilibrium was determined by gas chromatography (G.C) analysis of 0.5 ml taken from the head space of 10 ml sealed vials containing 1 ml aliquots of the different solutions. The G.C. was equipped a flame ionization detector at a temperature of  $150^{\circ}$ C, and a DB-624 column with 3  $\mu$ m film thickness, 30 m x 0.543 mm at a temperature of  $60^{\circ}$ C. The injection port temperature was  $100^{\circ}$ C.

The densities of water and organic solutions were measured using a picnometer with a 2 ml volume.

### 4.4 Results and Discussion

## Estimation of K

To overcome the experimental limitations expected when dealing with strongly retained volatile organic compounds, the linear relationship between log  $K_m$  and  $f_c$ , predicted by the model of Rao et al. (1985), discussed in the theory section was used to estimate the sorption coefficients of several solutes from water ( $K_w$ ). Thus, to obtain  $K_w$ , the logarithms of the solutes' sorption coefficients obtained from BTCs and batch equilibrium isotherms in mixtures of methanol-water were linearly extrapolated until  $f_c = 0$ .

Five NOCs were used in preliminary tests, benzene, naphthalene, toluene, pxylene and TCE. Among them, naphthalene had the lowest water solubility (30 ppm) and was therefore most strongly retained in the column, requiring higher proportions of methanol to obtain the BTCs. This allowed use of a wider range of methanol concentrations which provided a more rigorous test of the proposed log-linear relationship between  $K_m$  and  $f_c$ . Log  $K_m$  values for naphthalene as a function of  $f_c$ , obtained by the two methods as well as the log  $K_w$  obtained by the batch method, are presented in Figure 2. The logarithm of  $K_m$  values estimated from the BTCs decreased linearly as a function of  $f_c$ , for the range of  $f_c$  value studied (0.5 to 0.65). A linear equation fitting these data was used to obtain the  $K_w$  value of naphthalene, which was ca. 1280. However, the naphthalene  $K_w$  value measured directly using the sorption isotherm method (100.9) is approximately one order of magnitude smaller than the value calculated by direct extrapolation assuming a log-linear relationship between  $K_m$  and  $f_c$ 



Figure 2. Log of naphthalene sorption coefficients (K) at different fraction of methanol(fc).

over the entire range of methanol concentrations. The  $K_w$  values obtained by the two methods correspond physically to the equilibrium distribution constant of the compound between the HDTMA-modified soil and the interstitial water and therefore, their values should be the same.

An important observation is that the values of  $K_m$  obtained by the two methods are very close in value in the range of methanol concentrations 0.5 to 0.65 used to obtain the BTCs, although they do not coincide exactly. In the lower range of methanol concentrations, where  $K_m$  values were only obtained from sorption isotherm, the log of  $K_m$  values were not linearly dependent on  $f_c$ . Negative deviations from linearity were observed below  $f_c = 0.5$ . Similar results were obtained for benzene and TCE as shown in figures 5 and 6. Deviation from linearity has been observed before with natural soils when acetone has been used as cosolvent (Nkedi-Kizza et al., 1985), with other binary solutions (Morris et al., 1988), and with reversed phase chromatographic materials (Dorsey and Dill, 1989). To verify the real behavior of the system, BTCs were obtained from water over a complete range of  $f_c$  values, including pure water ( $f_c = 0$ ).

BTCs were obtained for two solutes with the relatively high water solubilities  $(S_w)$ , benzene  $(S_w = 1,790 \text{ mg/L})$  and trichloroethylene (TCE)  $(S_w = 1,100 \text{ mg/L})$ . The higher water solubilities of benzene and TCE as compared to naphthalene manifests lower K values and enables the determination of BTC in pure water as well as watermethanol mixtures. We were also able to control solute evaporation, a common problem found with volatile compounds, using a new chromatographic commercial pump where the solvent reservoir is pressurized, which minimizes volatilization of the solutes during elution times associated with low  $f_c$  values (including pure water). In Figures 4 and 5, the BTCs, from water, for benzene and TCE obtained with the HDTMA-modified Oshtemo soil are compared with the BTCs, also from water, obtained for the same compounds in a column filled with the native Oshtemo soil. A shift to the right of the natural Oshtemo soil BTCs is observed in the BTCs of both compounds in HDTMA-modified soil. This shift in the BTCs corresponds to an increase in the R factor for the over the entire range of methanol concentrations. The  $K_w$  values obtained by the two methods correspond physically to the equilibrium distribution constant of the compound between the HDTMA-modified soil and the interstitial water and therefore, their values should be the same.

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Some physical and chemical properties of the native and HDTMA-modified Oshtemo soil are given in Table 4. The only apparent changes in the HDTMA-modified soil are a significant increase in the organic carbon content of the soil and a slight decrease (2x) in surface area of the soil. Thus, the increased retention is most likely due to the increase in organic carbon content in the soil produced by the exchange of inorganic cations by HDTMA which manifests higher sorption coefficients and hence larger R values.

Parameter	Benzene		TCE		
	Oshtemo	HDTMA-Osh	Oshtemo	HDTMA- Osh	
R	1.15	6.2	1.36	6.6	
K <sub>w</sub> (BTC)	0.04	1.3	0.09	1.4	
K <sub>w</sub> (batch)	0.05±0.005	3.0±0.09	0.08±0.00 5	2.9±0.05	

Table 3. Retardation factor (R) and sorption coefficient ( $K_w$ ) obtained from BTC.  $K_w$  obtained from batch sorption isotherm.

BTCs and sorption isotherm were experiments used to obtain K's for benzene and TCE in the HDTMA-treated soil for a range of methanol-water mixtures ( $f_c$  from 0 to 0.4). Figures 6 and 7 summarize the log of  $K_m$  values calculated by the two different methods over the  $f_c$  range. The  $K_w$  values obtained from the sorption isotherms and the BTCs are different and the relationship between the log of  $K_m$  and  $f_c$  is not a straight



Figure 4. Effect of HDTMA soil modification in benzene breakthrough curve (BTC) in water



Figure 5. Effect of HDTMA soil modification on TCE breakthrough curve (BTC) in water



Figure 6. Benzene sorption coefficient (K) obtained from BTCs and sorption isotherms in different fraction of methanol (fc).



Figure 7. TCE sorption coefficient (K) obtained from BTCs and sorption isotherms at different proportions of methanol (fc)
line as predicted by the model of Rao's et al., (1985). It was observed that the organic carbon content in a sample of soil obtained from the column at the end of the miscible displacement experiments was substantially different from the organic carbon content of the freshly modified soil. Difference in the organic carbon content of the soil used to obtain the BTC and the sorption isotherms with certainly give different  $K_w$  values. Experiments were later designed to study this possibility.

Soil Properties	Natural Soil	HDTMA-modified Soil
Org. Carb. Cont. (%)	$0.1 \pm 0.01$	$0.8^{*} \pm 0.02$
Surface Area (m <sup>2</sup> /g)	$5.4 \pm 0.1$	$2.4 \pm 0.08$
Column Properties		
Bulk density ρ (g/cm <sup>3</sup> )	1.61	1.60
Porosity $\theta$ (cm <sup>3</sup> /cm <sup>3</sup> )	0.4	0.4

Table 4. Properties of the native soil and HDTMA modified Oshtemo soil and of soil columns prepared with these soils.

<sup>6</sup> Organic carbon content prior to elution with water or water-methanol mixtures.

The observed deviation from linearity in the relationship between log  $K_m$  and  $f_c$  may be related to fundamental differences in the chemical composition of the sorptive phases in native and HDTMA-modified soils. Natural organic matter has a much more polar nature than the HDTMA-derived sorptive phase in the modified soil, which is comprised of the  $C_{16}$  alkyl hydrocarbon matter. Polar functional groups (-COOH, -OH, -NH<sub>2</sub>) present in the soil organic matter in either the ionized or nonionized form can interact strongly with water. This interaction decreases the interfacial resistance between the organic matter and aqueous phase and in effect eliminates a well-defined interface.

These types of interactions, however, do not likely exist between the non-polar hydrocarbon tails of HDTMA and the polar water, giving rise to a more defined interface between the HDTMA hydrocarbon tails and the intersticial water. The nature of this interface is similar to that between two immiscible liquids (e.g., hexane and water) and that present between water and reverse-phase chromatographic material where hydrocarbons are covalently bonded to the Si-OH functional groups of silica. Amphiphilic molecules such as alcohols have high affinity for these interfaces where they orient according to the polarity of their functional groups (Davis and Rideal, 1961). This creates the possibility of interaction between methanol with the HDTMA-modified soil. Examples of analogous solvent-sorbent interactions have been found in the chromatographic literature (Wahlund, 1979; Scott and Kucera, 1977; Schoenmaher, 1983). Since solvent-sorbent interactions were explicitly ignored in the development of the theory of Rao et al. (1985), interaction of methanol with the organic sorptive phases of the modified soil (sorbent) may explain the deviation of our data from the log-linear relationship predicted by their model. The next section present results of experiments in which we have further explored the possibility of solvent/sorbent interaction.

## Possible interaction of methanol with the HDTMA on the soil

The replacement of inorganic adsorbed cations by HDTMA, which has a long hydrocarbon ( $C_{16}$ ) chain, separate soil and water by a nonpolar phase. The presence of a sorptive phase comprised of nonpolar hydrocarbon chains that do not interact with water creates a well defined interface between sorbed HDTMA and water. Solute molecules transported to this interface by convective water flow in a column filled with the HDTMA-modified soil will need to cross the interfacial barrier to contact the nonpolar hydrocarbon phase. For HOCs there are two cooperative forces that help them overcome the interfacial barrier: the Van der Waals attractive forces between the solute molecules and the hydrocarbon tail of the HDTMA, and the repulsive hydrophobic force created when a HOC tries to enter in the water and disrupt its hydrogen bond network.

In contrast to HOCs, amphiphilic molecules have a strong tendency to accumulate at the interface, where they can orient themselves with their non-polar part interacting with the hydrocarbon tail and the polar part oriented to the water. This orientation at the interface decreases the interfacial barrier between the water and the hydrocarbon phase. Methanol is an amphiphilic molecule and alcohols are well known as surface active compounds (surfactants) (Davies and Rideal, 1961). The interfacial adsorption of methanol could affect the sorption of NOCs by HDTMA-modified soils in methanolwater systems. For this reason, the interfacial adsorption of methanol was studied using the immiscible solvent system octane-water as a model for the HDTMA-water interface in the HDTMA-treated soil.

Table 5. Summary of methanol adsorption parameters at the octane-water interface.

	СМС	A <sub>m</sub>	- Δ G
System	(%)	Å <sup>2</sup> /molecul	Kj/mole
		e	
Methanol in octane-water	35.8	19.4	5.33

The results indicate that methanol, as a surface active compound, decreases the interfacial tension between water and octane as a function of concentration (Fig. 8). The decrease in the interfacial tension is nearly linear and follows Henry's adsorption isotherm. The adsorption parameters of methanol at the octane-water interface obtained from these mesurements are summarized in Table 5. The formation of a single compact layer is observed at a methanol concentration of 35.8%. The surface area covered (cross sectional) by each molecule at this point is equal to 19.4 Å<sup>2</sup>. The low energy of interaction (5.33 kJ/mole) indicates that the particles are interacting by London dispersion

forces. The concentration of methanol at compact layer is considered to be the critical micelle concentration (CMC). Above the CMC molecules of methanol start to interact with each other in the aqueous phase forming micelles. The observed interfacial adsorption of methanol in an octane-water system could by analogy occur at the HDTMA-water interface in the modified soils. This could affect the sorption of NOCs and in part be responsable for the relationship observed experimentally between the K values for benzene and TCE, and  $f_c$ . One possible mechanism is that the dissolution of methanol into the HDTMA phase, alone or in combination with the adsorption of methanol at the interface could increase the overall polarity of the sorptive phase. This would in turn cause lower sorption coefficients.

If we carefully look to all the results obtained for naphthalene, TCE, and benzene during the experiments (Fig. 2, Fig. 5, Fig. 6), two slopes can be discerned rather than the predicted log-linear relationship based on the work by Rao et al. (1985). In the HDTMA-modified soil-water system, the intercept between the two lines of different slopes occurs at  $f_c$  values between 0.2 and 0.3 (20 to 30 per cent). At  $f_c$  values above this, the K values are lower than those produced by an extension of the line relating K and  $f_c$  between 0 and 0.20 methanol. One possible explanation is that at these high methanol concentrations (>22 %) the dissolution of methanol into the HDTMA phase could increase the overall polarity of the sorptive phase and hence manifest lower sorption coefficients for NOCs.

The observation of an apparent CMC for methanol at a concentration of 35.8 % is also interesting. This suggests a physical change in the methanol-water system that might increase the solubility of the system for NOCs. For example, Kile and Chiou (1989) showed that the solubility enhancement of DDT due to the presence of surfactants is a two-stage process. Below the CMC, the monomeric surfactant slightly increases the solubility of the compound in water; however, above the CMC, a sharp increase in solubility enhancement was observed. With our system the solubility below methanol CMC may be different than above it. Although the CMC of 35.8 % is higher than the



Figure 8. Change of interfacial tension  $\gamma$  in the octane/water interface as a function of methanol concentration

intercepts of the experimental lines, it does suggest the possibility of two distinct regions of solubility. At higher  $f_c$  values relative solvency may increase and account for the change in slope observed experimentally in the plots of log K vs.  $f_c$ .

## Organic carbon mass balance

The results of the mass balance performed with the <sup>14</sup>C determined in solvent collected during the BTC and the organic carbon determined in the columns soil at the end of the BTC are summarized in Table 6. These results indicate that approximately half of the HDTMA initially present in soil remains adsorbed at the end of each experiment, regardless of methanol concentration. A plot of the amount of HDTMA released from the column at each step of the process (Figure 9) shows that after the equilibration process the amount of carbon eluted from the column is almost zero. These results allow us to conclude that after the equilibration period, a very stable material with an organic carbon content of about 0.4 percent is obtained which corresponds to about half the original HDTMA content. The results also allow us to be sure that the organic carbon content of the soil is the same during the miscible displacement experiments and the corresponding sorption isotherms.

Column	% left from mass balance	% left from org.carb.cont	org.carb.cont. (%) after BTCs
1	63.9	46.2	$0.37 \pm 0.001$
2	59.9	45.0	0.36 ± 0.003
3	57.8	46.2	0.37 ± 0.003
4	(*)	52.5	$0.42 \pm 0.14$
5	59.1	45.0	$0.36 \pm 0.01$
6	58.6	45.0	0.36 ± 0.003
7	53.8	43.8	$0.35 \pm 0.10$

Table 6. Summary of organic carbon present in the soil after BTC experiments from an initial organic carbon content in the soil of 0.8 %.

(\*) loss data

## Benzene K values from BTCs in pressurized system and sorption isotherms on equilibrated soil

The log K values for benzene obtained from BTCs in individual columns with methanol fractions ( $f_c$ ) ranging from 0 to 0.4 and from sorption isotherms on equilibrated soil removed from the columns after the BTC experiments are presented in Figure 10. As it was demostrated in the previous section, the organic carbon content of the soil was the same during the two determinations of K. However, it is observed in Figure 10 that the values of K obtained by the two methods is different. The gap between the values of K obtained by the two methods (see Fig. 6) has decreased using soils with the same organic but there is still an observable difference.

When the equation  $R = 1 + K \rho/\theta$  is used to determine K values from the BTC, the conventional approach is to use the bulk density ( $\rho$ ), which considers the whole mass of soil as one of the phases with where the compound is distributed. It is assumed



Figure 9. HDTMA desorption during miscible displacement experiments.



Methanol fraction



implicitly that the compound will be uniformly distributed throughout the soil. In the HDTMA-modified soil, the sorption of NOCs will occur in the nonpolar phase created by the HDTMA hydrocarbon tails present on the Oshtemo soil surface. This suggests that the whole soil density will not be the best descriptor of one of the phases where NOCs will be distributed, which means that nature of the phase ratio has changed. However, the K values were obtained from the BTCs were obtained using the traditional phase ratio applied to soil columns. We believe that this change in the nature of the phase ratio is responsible for the difference observed between the two values. However, since we have demostrated the possibility HDTMA/methanol interaction, calculation of this phase ratio will be a matter of further research.

As observed previously, there is a change in slope in the log of  $K_m$  versus  $f_c$  at about 22% methanol (0.2), probably explained by the solvent/sorbent interaction. For reverse-phase chromatographic materials, which we believe resemble the HDTMAmodified soil more than a natural soil does, a quadratic relationship between ln K and the fraction of organic solvent has been demostrated (Dill, 1987, Dorsey and Dill, 1989; Schoenmakers, et al., 1982). Dill (1987) developed a theory, based on lattice statistical thermodynamic theories, to account for retention and selectivity of solutes in reversephase liquid chromatography. In Dill's model the equilibrium constant (K) is given as a simple quadratic function of the percentage of organic solvent. Ying et al., (1989) applied the linearized form of Dill's equation to a data base of 346 data sets and found that 80% of the data sets had R<sup>2</sup> of 0.9 or higher and almost 50% with R<sup>2</sup> of 0.99 or higher. We fitted the benzene BTC data to linear and quadratic equations; the results are presented in Figure 11. A R<sup>2</sup> of 0.993 for the quadratic fit vs a R<sup>2</sup> of 0.982 for the linear indicates that the HDTMA-modified soil behaves more like a reverse-phase chromatographic material (e.g. C<sub>18</sub>) than a natural soil.

In summary, exchange of native cations in the soil by HDTMA increases retention of NOCs during transport. Sorption coefficients from BTCs run with methanol fractions ranging from 0 to 0.4 were used to demostrate that linear extrapolation of the relationship



Methanol fraction

Figure 11. Results of fitting benzene breakthrough curve data to a linear and quadratic equation

y = 0.346 - 2.47x - 3.29x^2

R^2 = 0.993

between log  $K_m$  and  $f_c$  can not be used to predict sorption coefficients of NOCs from water in the HDTMA-modified soil because the relationship deviates from linearity below 30 % methanol. Interaction between methanol and HDTMA is probably responsible for this behavior. It was also found that benzene sorption coefficients determined directly from water using BTCs and sorption isotherms are different. We believe that these values are different because  $K_w$  is calculated from the BTC using the phase ratio ( $\rho/\theta$ ) applied to natural soils. In the modified soil, the nature of the phase ratio appears to be different, although it is difficult if not impossible to calculate with the present level of knowledge. The relationship between log K vs  $f_c$  fits a quadratic better than a linear equation, reinforcing our belief that the modified soil resembles more a reverse-phase chromatographic material than a natural soil.

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