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IN THE UNSATURATED ZONE

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by

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ABSTRACT

TRANSPORT OF DISSOLVED VOLATILE ORGANIC COMPOUNDS IN THE UNSATURATED ZONE

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The main objective of this research was to explore the impact of individual transport mechanisms on the average velocity and extent of spreading of dissolved volatile organic compounds (VOCs) in the subsurface. Soil organic matter, pore-water velocity, and level of saturation were selected as the primary variables for investigation. Two nonionic organic compounds were employed: dimethylphthalate, as a nonvolatile compound, and benzene, as a volatile one. Tritium was also used and was verified to act as an ideal tracer.

Sorption and volatilization affect the transport speed of VOCs dissolved in the aqueous phase. This study showed that sorption-related retardation coefficients for the two nonionic organic compounds, as estimated from batch sorption isotherms and the properties of the soil matrix, were higher than their column-determined counterparts. The extent of deviation between the two techniques was independent of the organic carbon content of the soil. Although not specifically investigated experimentally, it was speculated that differences between the results of the two techniques were likely to result from either mixing differences or differences in particle spacing in the two systems.

It was also found that sorption-related retardation coefficients determined under dynamic flow conditions when the soil was partially saturated were higher than the values determined at full saturation. The increase in retardation was proportional to the decrease

in saturation. When the retardation coefficients were normalized to the same solid/water ratio, the values under the two flow conditions were similar for comparable pore-water velocities. This suggested that sorption-related retardation coefficients under unsaturated conditions can be estimated using a single value of the sorption distribution coefficient and assuming that the sorption capacity of the solids is unaltered by desaturation. The impact of volatilization on retardation of benzene was not significant under the conditions employed in this study. It was shown mathematically that this effect could be significant for higher volatility compounds and for low organic carbon soils.

The effects of dispersion in the liquid phase, diffusive transport in the air phase, and transport nonequilibrium on the extent of spreading of dissolved VOCs were also investigated. This study showed that the dispersivities of partially saturated soils were 2-3 times higher than the values obtained under saturated conditions. At low levels of saturation, however, spreading of benzene caused by dispersion in the liquid phase became negligible compared to that caused by diffusion in the air phase. Commonly accepted empirical relations overestimated the effective diffusion coefficient in the air phase.

This study revealed that there was no physical nonequilibrium, created by slow diffusion in and out of immobile water regions, during transport of solutes through partially saturated soils. However, sorption-related nonequilibrium during transport of nonionic organic compounds, under both saturated and unsaturated flow conditions, should be considered. The impact of changes in soil organic matter, pore-water velocity, and saturation on the extent of sorption nonequilibrium was investigated. The results showed that a 3-fold increase in soil organic matter slightly changed the extent of sorption nonequilibrium. It was also found that the mass transfer coefficient of nonionic organic compounds between equilibrium- and nonequilibrium-type sorption sites is dependent on the pore-water velocity, but not on soil organic matter. Changes in saturation did not appear to influence the values of the nonequilibrium parameters.

To my mother

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CHAPTER 1

OBJECTIVES AND REVIEW

1.1 Introduction

Dissolved volatile organic chemicals (VOCs) present in the subsurface are of concern because of their potential to produce adverse health effects. Currently, many of the accepted remediation strategies depend primarily on extensive water extraction or soil excavation. These may be inefficient and costly remedies. Identification of efficient, cost-effective approaches, however, depend on a thorough understanding of the fundamental mechanisms that control the transport and fate of these contaminants.

Subsurface transport mechanisms can be divided into two categories: those that leave the structure of a chemical unchanged, and those that transform the chemical into one or several products. The first category of processes includes transport and mixing within a given phase as well as transfer processes between different phases. Alterations of the structure of a compound may occur by chemical, photochemical, or biological transformation reactions. This study focuses on the first category of processes. It is not intended, by doing so, to undermine the impact the second category of processes may have on the ultimate fate of VOCs.

Figure 1-1a exemplifies a region within the unsaturated zone that is contaminated by a VOC. As shown schematically in Figure 1-1b, three distinct phases (solid, water, and air) are present under unsaturated conditions. In this figure, it is also conceptualized that a fraction of the water phase is relatively immobile. If a VOC is present in the flowing fraction of the water phase, the VOC is subjected to advection and dispersion within that fraction. In addition, the compound may transfer to the other phases and to the immobile water fraction. Transfer of the compound from the water phase (mobile or immobile) to the solid phase is referred to as

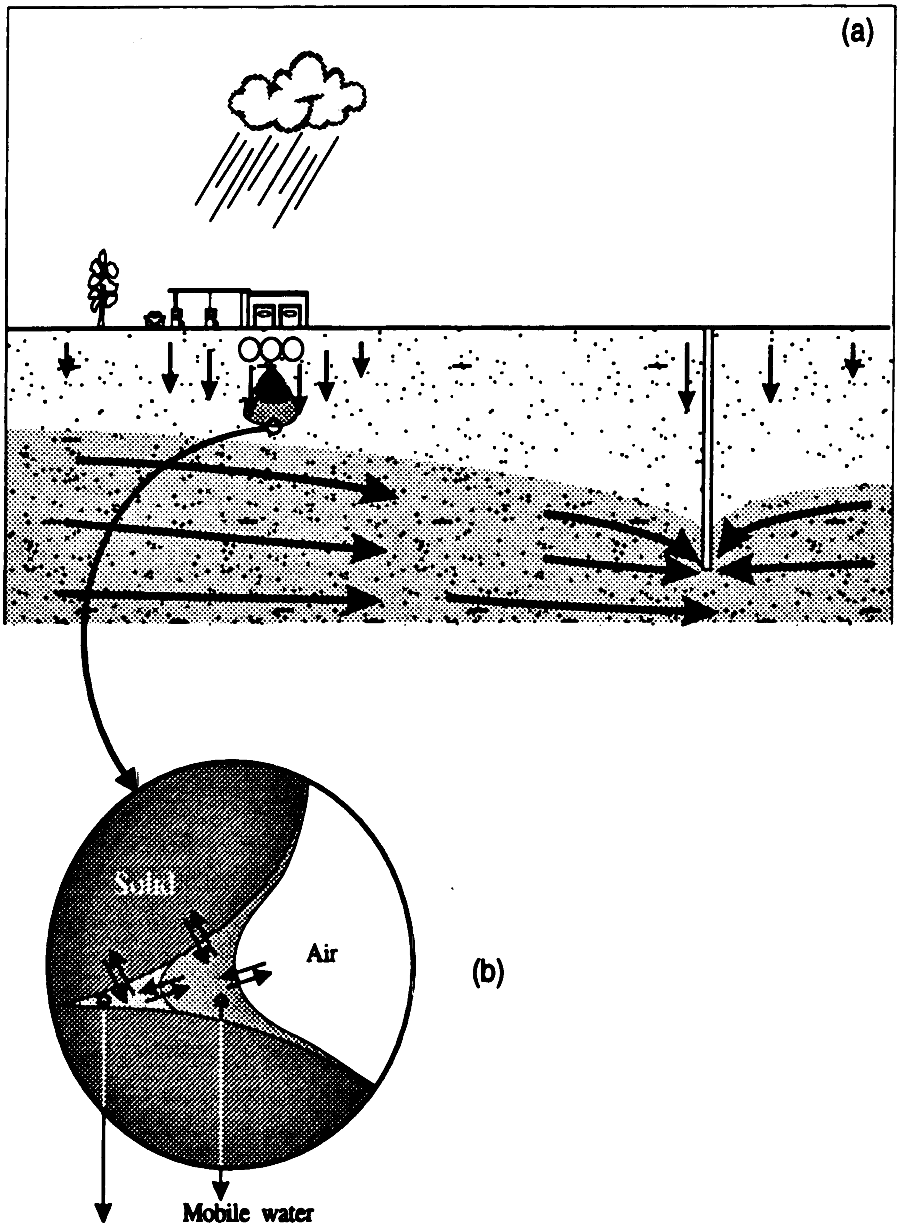

Figure 1-1. Schematic conceptualization of possible VOC transport and transfer mechanisms under unsaturated conditions

sorption, while that from the water phase to the air phase is volatilization. The volatilized part might be subjected to the same transport mechanisms as the one in the mobile liquid phase. Yet, the effect on the fate of the chemical might be totally different.

The impact of some of the above mentioned mechanisms on the transport of a VOC is presented in Figure 1-2. Advection is the mechanism by which chemicals are transported by the bulk motion of the flowing phase. As illustrated in Figure 1-2a, a nonreactive chemical present in the water phase moves at an average velocity equal to the average pore-water velocity. Due to hydrodynamic dispersion, however, part of the chemical plume migrates slightly faster, while part moves slightly slower than the average water velocity as shown in Figure 1-2b. Hydrodynamic dispersion is caused by two processes: mechanical mixing during fluid advection and molecular diffusion driven by concentration gradients.

The effect of sorption is demonstrated in Figure 1-2c. Sorption reduces the average velocity of the solutes with respect to that of the water molecules. The importance of sorption in retarding the transport of organic chemicals has led some investigators to suggest modification of soil materials as a means to reduce the migration of solute plumes (Boyd *et al.*, 1988; Lee *et al.*, 1989). Sorption may also have an effect on many natural transformation processes. Microorganisms, for example, are thought to be unable to assimilate and transform sorbed molecules compared to those in soil solution (Orgam *et al.*,1985). Chemical reactions may also be affected by sorption (Macalady and Wolfe, 1985).

In the absence of air flow, volatilization of VOCs results in an increase in VOC retardation as part of the dissolved VOC in the water phase partitions into the air phase. Theoretically, the increase in retardation is a function of Henry's constant and air saturation. Diffusive transport in the air phase does not affect retardation but results in an increase in VOC spreading. Figure 1-2d shows the impact of volatilization and air phase diffusion VOC transport.

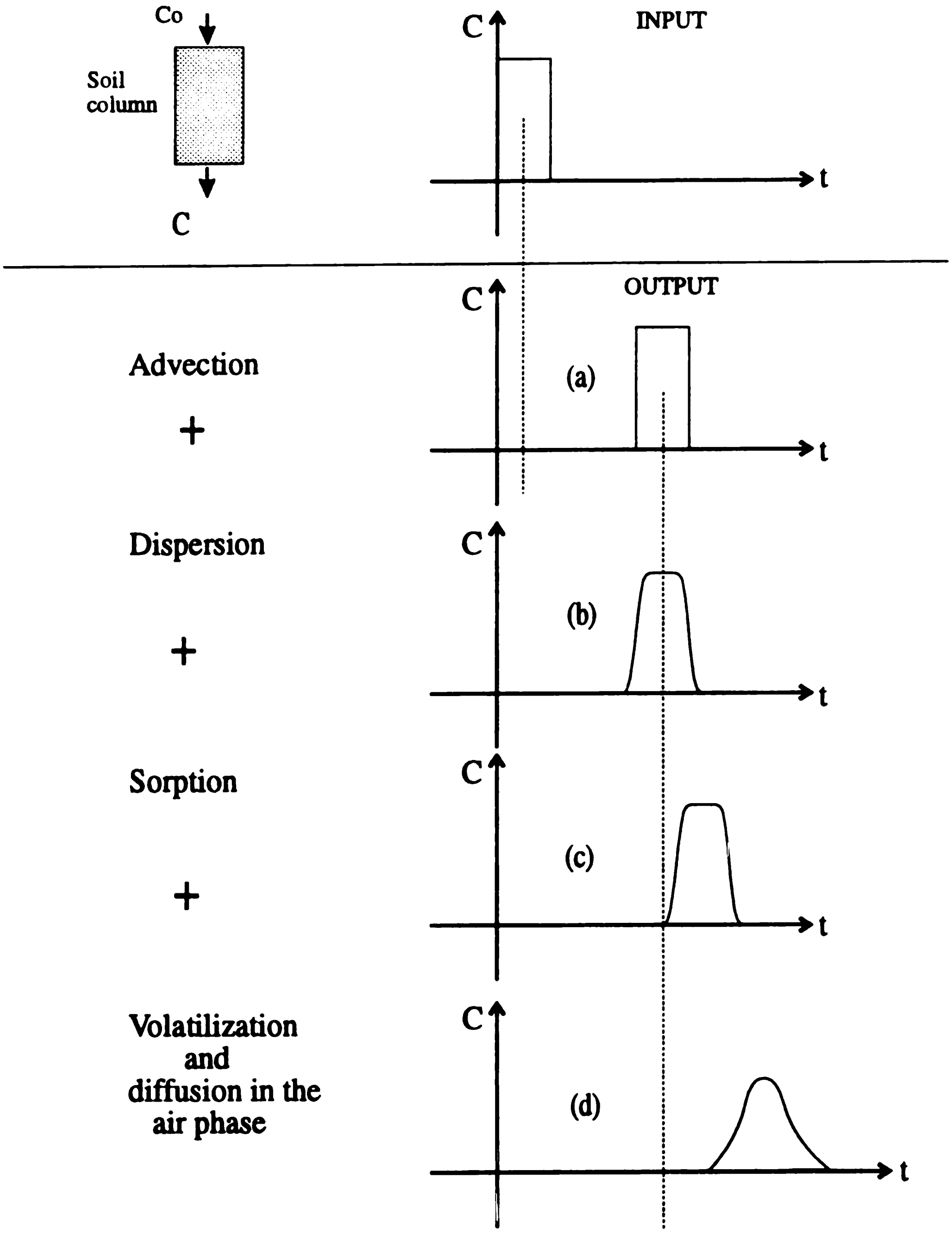

Figure 1-2 Impact of transport and transfer processes on VOC movement in unsaturated soil columns

Transfer processes of a VOC between different phases are commonly described as being in equilibrium. The use of this approach is applicable if the transfer time is much smaller than the mean residence time. The validity of this assumption under certain conditions is questionable. The impact of nonequilibrium in any of the transfer processes (i.e. sorption nonequilibrium, volatilization nonequilibrium , slow mass transfer into immobile water) is an enhanced spreading of the chemical and, therefore, an apparent increase in dispersion.

The main focus of this research is to explore the effect of some transport mechanisms on the mobility of VOCs in the unsaturated zone. The effect of sorption, advective-dispersive transport in the liquid phase, and diffusive transport in the air phase will be considered. Soil organic matter content and the degree of water saturation are chosen as the principle parameters of interest in this study. It is intended in this chapter to provide the reader with an overall review of the literature related to dispersion, sorption, volatilization, and diffusive transport in the subsurface environment. Subsequent chapters report the results of experimental research designed to increase our understanding of VOC transport in the vadose zone. The specific objectives of this research are as presented below.

1.2 Research objectives

This study was subdivided into four main areas of research. The results of each area are presented in a separate chapter. Each chapter is written to essentially stand alone and is in the process of being published.

The first area of research (Chapter 2) was designed to investigate the dispersive behavior of nonaggregated soils under unsaturated-flow conditions as compared to the conditions when the soil is fully saturated. In so doing, a better understanding of the appropriate conceptual representation of the geometry of the unsaturated pore volume would be gained. Our approach was to isolate any induced dispersion due to chemical nonequilibrium of the solute with the solid matrix or solute exchange between mobile and immobile water upon desaturation.

The second and third areas of research were designed to address the impact of organic matter and level of saturation on the ultimate sorption capacity of soil aquifers. In the second phase (Chapter 3), the discrepancy between batch- and column-determined retardation coefficients were investigated. It is also intended to determine if the extent of discrepancy is related to soil organic matter content.

The primary objective of the third phase (Chapter 4) was to determine the role of water saturation on the retardation of nonionic organic compounds (NOCs). To our knowledge, this study is the first to explore the impact of soil moisture content on the retardation coefficient under dynamic conditions. The influence of diffusive transport in the air phase on the movement of VOCs was also addressed.

The final area of research (Chapter 5) was designed to determine, on a quantitative basis, the impact of soil organic matter and water saturation on the degree of sorption nonequilibrium of dissolved nonionic organic compounds (NOCs). The influence of changes in pore-water velocity on sorption nonequilibrium was also investigated.

1.3 Review of dispersion processes

1.3.1 Theory of dispersion

Hydrodynamic dispersion in porous media refers to the spreading of a stream or discrete volume of contaminants as it flows through the subsurface. For example, if a set of particles is injected into porous media through which groundwater is flowing, the particles will spread longitudinally in the direction of flow (longitudinal dispersion) and transversely in the other direction (transverse dispersion).

Hydrodynamic dispersion is primarily caused by two mechanisms: mechanical dispersion and molecular diffusion. Mechanical dispersion on a microscopic scale is caused by three mechanisms (Freeze and Cherry, 1979): (1) deviation of velocity in individual pore channels from the average groundwater velocity, (2) diversion of flow paths around individual pore channels which results in variations in the average velocity among different pore channels, and (3) dispersive processes related to the tortuosity, branching and interfingering of pore channels. The first mechanism is usually referred to as dynamic and the other two as kinematic (Sahimi and Imdakm, 1988). Molecular diffusion, on the other hand, occurs due to natural thermal motion of dissolved constituents. Qualitatively, mechanical dispersion and molecular diffusion are analogous but the causes and the magnitude of their impacts vary. In fact, most of the time, one of the two mechanisms predominates. As reported by Shackelford (1991), diffusive mass transport is dominant at seepage velocities of ≤ 0.005 m/yr.

On a macroscopic scale, it is believed that hydrodynamic dispersion is caused by the presence of large-scale heterogeneity within the subsurface (Anderson, 1979; Anderson, 1984). Anderson (1979) reported values of hydrodynamic dispersion coefficients under field conditions that are 1000-10000 times larger than values reported in the laboratory. Moreover, the only dispersion that can be measured in the lab is that which is observable at the macroscopic scale. It is assumed that this macroscopic dispersion is a result of the microscopic processes previously described (Freeze and Cherry, 1979). In practice, the dispersion coefficient is used as an empirical parameter that includes all of the solute spreading mechanisms that are not accounted for in the transport model.

1.3.2 Modeling dispersion under saturated-unsaturated conditions:

Deterministic and stochastic have been used to describe solute transport in the subsurface. A model is regarded as stochastic if any of the variables in its mathematical expression are described by a probability distribution. A model is termed deterministic if all the variables are viewed as free from random variations. Stochastic models use variable velocity and dispersion coefficient. The reasoning behind the development of these models is the wide variability of soil properties in the field. Stochastic models are not reviewed in this chapter. Readers who are interested in the use of statistical approaches to characterize dispersion in porous media may refer to the work by Bear (1969), Greenkorn (1970), Scheidegger (1974), Sahimi *et al.* (1983, 1986), and Sahimi and Imdakm (1988).

Deterministic models assume that Darcy's Law applies, i.e. all water particles move at the same velocity through the media. Because this assumption neglects microscopic variations in fluid velocity, a transport component analogous to Fick's First Law is introduced to account for dispersion. The justification for the use of this type is given by Taylor (see Ficher *et al.*, 1979) in his study of laminar flow through pipes. Therefore, deterministic models use a constant dispersion coefficient to describe area-averaged solute movement.

The following section reviews the various forms of the dispersion coefficient reported to describe miscible displacement, and the flow and transport of contaminants in the saturated-unsaturated zones. The factors affecting dispersion in porous media are also discussed.

1.3.2.1 Dispersion under saturated conditions

Dispersion under saturated flow conditions has been modeled in two forms, namely: the advection-dispersion (AD) model, and mobile-immobile water (MIM) models.

AD Model:

Several investigators have concluded (Perkins and Johnston, 1963), or tactically assumed (Brigham *et al.*, 1961; Greenkorn, 1970) that dispersion in porous media is Fickian i.e., that the transport of a nonreactive solute can be described as:

$$\theta\frac{\partial C}{\partial t} = \theta D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} \qquad (1.1)$$

where, θ is the volumetric water content, C is the concentration, t is the travel time, D is the hydrodynamic dispersion coefficient, ν is the seepage velocity and x is the distance.

Brigham *et al.* (1961) studied the impacts of particle size, pack/core lengths and diameter, and phase velocity on dispersion using packs of glass beads and cores of sandstone. The authors found that dispersion in the sandstone cores was always higher than that in the packs of glass beads. This was thought to be due to pore-level heterogeneity in the sandstone cores. Moreover, dispersion was found to be independent of the sample length (samples of length ≈ 1-8 m) and diameter, except those of very small diameter where wall effects were important.

Perkins and Johnston (1963) reviewed various forms of the dispersion coefficient which were derived previously. The report presented the effects of particle size distribution, fluid density ratio, and turbulence on dispersion. According to Perkins and Johnston (1963), dispersion increases for soils with lower uniformity coefficients (well graded) and with nonuniformity of particle shape. Dispersion also increases when the displacing fluid is denser than the displaced one.

Greenkorn (1970) characterized dispersion in porous media which were composed of glass beads of several different sizes. The dispersion coefficient for homogeneous and linearly heterogeneous media was found to be of the form:

$$D = a\,v_o^{b} \tag{1.2}$$

where, a and b are empirical constants that decrease with the a decrease in the bead diameter. For heterogeneous media, Greenkorn (1970) found that increases in the permeability of the media increased dispersion and that the dispersion coefficient is a function of the slope of the particle size distribution curve.

Charlaix *et al.* (1987) depicted the effects of porosity on dispersion. They found that the hydrodynamic correlation length, dispersivity, which is a function of the pore size, was higher in consolidated media than that in unconsolidated ones. Gupta and Greenkorn (1974), found that dispersivity increases approximately linearly with an increase in clay content.

MIM Models:

Breakthrough curves (BTCs) predicted by the AD Model are nearly symmetrical. However, several experimental studies on aggregated soils under saturated flow conditions have shown strongly nonsigmoid and asymmetrical concentration distributions (for example, see van Genuchten and Wierenga, 1976, 1977; Nkedi-Kizza *et al.*, 1983; Hutzler *et al.*, 1986). This has lead to the development of the MIM models, which are also referred to as transport nonequilibrium models.

While the AD Model assumes that all the water participates in the flow and solute transport, the MIM models assume that a fraction of the water is relatively immobile and, therefore, does not participate in the flow. The immobile water fraction, however, affects solute transport as some mass of the solute diffuses into and out of the immobile water fraction. The mathematical formulation of the MIM models is usually written as (Coats and Smith, 1964):

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} = \theta_m D_m \frac{\partial^2 C_m}{\partial x^2} - \theta_m v_{om} \frac{\partial C_m}{\partial x} \qquad (1.3)$$

where, the subscripts *m* and *im* refer to the mobile and immobile water fraction, respectively, D_m and v_{om} are the hydrodynamic dispersion coefficient and average pore-water velocity of the mobile water, respectively. Other parameters are as previously defined.

To complete the model formulation another equation is used to describe the transfer of the solute between the mobile and immobile water regions. Two different approaches have been proposed: (1) a mass transfer approach and (2) a diffusion approach. In the Mass Transfer Model, a first-order kinetic transfer equation has been proposed as (Coats and Smith, 1964):

$$\theta_{im} \frac{\partial C_{im}}{\partial t} = \alpha (C_m - C_{im}) \qquad (1.4)$$

where, α is the mass transfer coefficient between the two water regions and other parameters as previously defined. Coats and Smith (1964) performed experiments on consolidated and where, α is the mass transfer coefficient between the two water regions and other parameters as previously defined. Coats and Smith (1964) performed experiments on consolidated and unconsolidated core samples and found that the MIM model with a first-order mass transfer coefficient is more accurate than the AD model. The authors calculated the dispersion coefficient using the following formulation:

$$D = 0.5\,\sigma\, d_p\, v_o \; ; \quad 2 < \frac{\sigma\, d_p\, v_o}{D_o} < 50 \tag{1.5}$$

where, d_p is the average particle size and σ is proportional to the degree of heterogeneity of the porous media. Coats and Smith (1964) warned against directly applying the dispersion coefficients determined by Eq.(1.5) to field studies due to possible scaling effects. According to Coats and Smith (1964), the effects of rate limitation in mass transfer between mobile and immobile water regions under field conditions could be negligible due to greater lengths and lower velocities than those observed in the laboratory experiments.

In the Diffusion Models, the geometry of the aggregate is specified and Fick's Law is then used to describe the concentration distribution within the specified geometry. For spherical aggregate geometry, the immobile volume-averaged concentration (C_{im}) is defined as (van Genuchten and Cleary, 1979; Rao *et al.*, 1980a: Crittenden *et al.*, 1986):

$$C_{im} = \frac{3}{\xi^3} \int_0^{\xi} C_\xi \, dr \tag{1.6}$$

where, ξ is the aggregate radius, r is the radial coordinate, and C_ξ is the local aqueous concentration inside the aggregate, which is determined using Fick's Law as follows:

$$\frac{\partial C_\xi}{\partial t} = D_\xi \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial C_\xi}{\partial r}\right) \quad ; \quad 0 \le r \le \xi \tag{1.7}$$

where, D_ξ is the effective pore diffusion coefficient in the immobile phase.

A third approach that has been utilized to describe the transport of solutes in soils containing an immobile water region is the Effective (Apparent) Dispersion Model. This approach assumes that local equilibrium between mobile and immobile regions may satisfactorily describe solute transport. The effects of diffusive mass transfer and hydrodynamic dispersion coefficient are combined to obtain an effective dispersion coefficient (D_{eff}) that can be used in the classical AD model. This approach is actually based upon the fact that nonequilibrium causes the spreading of the front of BTC which results in a higher dispersion coefficient.

D_{eff} has been expressed in different forms. Passioura (1971) presented a form of D_{eff} for nonreactive solutes in a system of spherical aggregates:

$$D_{eff} = D + \frac{(1-\phi)\, v_o^2\, \xi^2}{15\, D_e} \qquad (1.8)$$

where, D is the hydrodynamic dispersion coefficient, D_e is the molecular diffusion coefficient in porous spheres, ξ is the radius of sphere and ϕ is the porosity of the system. Other forms of D_{eff} have been given by De Smedt and Wierenga (1984) and Parker and Valocchi (1986).

The applicability of the effective dispersion concept requires that mean residence times be large enough to mitigate differential gradients between mobile and immobile regions (Parker and Valocchi, 1986). Rao *et al.* (1980b) found that the limiting condition on Eq. (1.8) is:

$$\frac{(1-\phi) D_e\, L}{\xi^2\, v_o} > 0.3 \qquad (1.9)$$

where L is the length.

As mentioned earlier the mobile-immobile water models has been utilized to describe solute transport in aggregated media. However, Schulin *et al.* (1991) presented data for saturated experiments with aggregate packing that was adequately described by the advection-dispersion model combined with an equilibrium ion-exchange isotherm. Schulin *et al.* (1991) used the mobile-immobile water model and found no significant improvement in data fitting over the AD model.

1.3.2.2 Dispersion under unsaturated conditions:

Most of the deterministic models used to describe solute transport under unsaturated flow conditions are based upon models previously developed for saturated conditions. The AD model (Smiles *et al.*, 1981; Bond *et al.*, 1982; Bond, 1986; Schulin *et al.*, 1987; Seyfried and Rao, 1987; James and Robin, 1986), the MIM model with first-order mass transfer coefficient (van Genuchten and Wierenga, 1977; Guadet *et al.*, 1977; De Smedt and Wierenga, 1984; Bond and Wierenga, 1990), and the MIM model with specified pore geometry (Gierke *et al.*, 1990) have been used for simulating unsaturated miscible displacement experiments.

Although the use of the MIM models under saturated cases is usually associated with aggregated media, the models have been used under unsaturated conditions for nonaggregated media (De Smedt *et al.*, 1986; Bond and Wierenga, 1990). Bond and Wierenga, 1990 indicated that the suitability of using the AD model for unsaturated nonaggregated porous media depends on the applied flow conditions. They presented steady and unsteady unsaturated miscible displacement experiments and found that the AD Model satisfactorily described unsteady flow experiments but a MIM model is needed to account for the tailing in the BTCs of the steady flow experiments. Several investigators, however, presented data for nonaggregated porous media under steady unsaturated flow conditions which were successfully described by the AD model. This point is reviewed in more detail in Chapter 2.

There have been several derivation to describe dispersion in unsaturated soils. The formula developed by Bear (1969):

$$D = a\, v_o^b + D_e \qquad (1.10)$$

has been used and found satisfactory by some investigators. For example, Kirda *et al.* (1973) found that D could be modeled with $a = 0.545$ and $b = 1.355$ for $v_o \geq 0.01$ cm/min, Yale and Gardner (1978) found that $a = 0.216$ and $b = 1.0$ for $0.01 < v_o < 0.28$ cm/min, Biggar and Nielsen (1976) used $a = 2.93$ and $b = 1.11$. Eq. (1.10) was used by others (Schulin *et al.*, 1987; De Smedt and Wierenga, 1984) to model dispersion using the MIM model provided that only the mobile fraction of water is responsible for solute dispersion. De Smedt and Wierenga (1984) found that the AD model could be used to describe unsaturated BTCs if dispersion coefficients of about 20 times larger than those for comparable saturated experiments were used. The use of such an approach is similar to the use of the effective dispersion model, since both hydrodynamic dispersion and diffusional exchange between the mobile and immobile water fractions are lumped into one parameter.

1.3.3 Comments on dispersion in the unsaturated zone:

Dispersion in porous media has been characterized by a number of researchers from different disciplines but the general form is still ambiguous. The primary reason for this is the inability to include the effects of phase saturation on dispersion. In addition, a more confounding and persistent problem is correlating the laboratory-scale with the field-scale studies where the discrepancies arise due to the fact that the movement of water through unsaturated zone is three-dimensional and not one-dimensional (see, for example, Gelhar *et al.*, 1985), and the existence of large scale heterogeneity in the field.

Several forms of the dispersion coefficient, however, have been derived but were case specific. Dispersion has also been characterized using statistical mechanics, but these derivations still need to be rigorously verified using laboratory and field data. Thus, there still lacks a unique formulation for the dispersion coefficient in the unsaturated zone.

1.4 Review of sorption processes for NOCs

Most existing models that deal with the sorption of dissolved organic compounds in the saturated zone assume that sorption can be described by the use of a partitioning coefficient determined by experiments on the basis of batch studies. Linear, equilibrium submodels are usually used for modeling purposes. This may be adequate under certain conditions, but usually it is used to simplify model analysis and to reduce the required computation time. In contrast, kinetic approaches requires quantitative treatment of the microscopic transport steps and detailed specification of the geometry of the solid phase (Rubin, 1983). Although such detailed knowledge is impossible for aquifer materials (Valocchi, 1985), an adequate understanding of sorption kinetics is necessary to develop efficient processes to destroy, immobilize, or separate organic pollutants from the soil matrix.

The conceptual formulation of the various models that deal with the transport of dissolved organic contaminants through the subsurface are reviewed in the following sections. Before doing so, a brief idea about the nature of the sorptive interaction of NOCs is given below.

1.4.1 Mechanisms of sorption of NOCs:

There are two schools of thought on the nature of the sorptive interaction of NOCs. One assumes that sorption occurs by hydrophobic partitioning between soil solution and soil organic matter (see for example, Chiou, 1989). The other (Mingelgrin and Gerstl, 1983), however, regards this mechanism as unproved and that the evidence is insufficient to exclude surface adsorption. Chiou (1989) has outlined the arguments that support the partitioning mechanism. These include the ability to model the sorption of organic solutes at high relative concentration using linear isotherms, the noncompetitive nature of the interaction of binary solutes, the observed low heats of sorption, and the fact that the interaction of organics with soil is similar to partitioning of the chemicals into organic solvents. Recently, Murphy *et al.* (1990) investigated the sorpitivity of carbazole, dibenzothiophene and anthracine on hematite and kaolinite coated with natural humic substances up to a mass percent carbon of 0.5% and found nonlinear sorption isotherms. They concluded that the actual physio-chemical mechanism is adsorption onto the surface of the organic carbon phase rather than partitioning into the organic phase.

The tendency of NOCs to partition onto the soil phase has been usually modeled using a linear equilibrium model as:

$$q = K_D C_e \qquad (1.11)$$

where, q is the amount of sorbate per unit mass of sorbent, K_D is the distribution coefficient and C_e is the equilibrium concentration of sorbate in the aqueous phase. Contaminant transport can also be expressed on an organic carbon basis as (Karickhoff *et al.*, 1979):

$$K_{oc} = K_D / f_{oc} \qquad (1.12)$$

where, f_{oc} is the fraction of sorbent as organic carbon and K_{oc} quantifies the degree of hydrophobicity of the compound. Several investigators have developed empirical relationships to estimate the K_{oc} value based on the octanol-water partition coefficient (K_{ow}) or the water solubility of an NOC (see schwarzenbach *et al.*, 1993). The K_{oc} value of a given NOC may vary over an order of magnitude for different soils. Such variations may be attributed in part to compositional differences in the soils organic matter (Mingelgrin and Gestl, 1983; Garbarini and Lion, 1986). For example, Garbarini and Lion (1986), in examining the capacity of selected components of soil organic matter to sorb trichloroethylene and toluene, observed that the use of a sorbent oxygen content as well as its carbon content yields a more accurate prediction of K_{oc} than relationships that rely solely on the organic matter content of the sorbent. The authors warned, however, against directly applying the relationships they determined to soil with low organic carbon content due to the possible influence of the mineral matrix. For low-organic carbon mineral systems, investigations have shown that K_{oc}-K_{ow} relationships (where K_{oc} is calculated by assuming no mineral contribution to sorption) tend to deteriorate below an f_{oc} of 0.001 (Schwarzenbach and Westall, 1981 ; Mackay *et al.*, 1985). This suggests that mineral surfaces contribute (under certain conditions) to the sorption of NOCs. Karickhoff (1984), in reviewing sorption of organic pollutants in aquatic systems, proposed a multiple sorptive model in which sorption onto mineral surfaces and partitioning into soil organic matter contribute to the sorption of NOCs. Mineral contribution to sorption, as discussed by Karickhoff (1984), tends to occur with high sorbate polarity and/or low organic carbon content of the sorbate, especially with coincident high clay content.

The value of K_{oc} has also been shown to be influenced by the nature of the mineral-organic association (Garbarini and Lion, 1986; Murphy *et al.*, 1990). Murphy *et al.* (1990) observed that a given humic substance exhibited a different sorptivity for the tested compounds on the different humic substances-coated mineral surfaces. They attributed this to the effect of the mineral surface on the interfacial configuration of the humic substances by either altering the size of the hydrophobic domains on the humic molecule or the accessibility of these domains to the tested organic compounds.

Sorption linearity appears to depend also on the concentration of an NOC in the aqueous phase. At low aqueous phase concentration, sorption isotherms are reasonably linear. Karickhoff (1981) attributed this to the independence of the fugacity coefficient upon concentration. At high NOC concentration, nonlinear isotherms have been noticed (Rao and Davidson, 1979; Means *et al.* 1980; Schwarzenbach and Westall, 1981). Means *et al.* (1979, 1980) found that the use of Freundlich sorption model gives more accurate fitting of polycyclic aromatic hydrocarbons isotherms. The Freundlich model is usually given as:

$$q = K_D C_e^{\,n} \qquad (1.13)$$

where, *n* is a constant (≠1). Nonlinearity affects the shape of solute BTC (Brusseau and Rao, 1989). For *n* >1, breakthrough front will be spreading and elution front will be self-sharpening. The effect, however, will be opposite for *n* <1. The effect of the latter may mask the effect of nonequilibrium, since nonequilibrium tends to spread the front of BTC.

1.4.2 Effect of moisture content on sorption of NOCs:

Most of the work dealing with the sorption of NOCs was conducted under conditions where the solid surface is fully covered by water. Little is known about the impact of changes in water coverage on the ultimate sorption of hydrophobic organic compounds. The results presented by Spencer and Claith (1970) and those of Chiou and Shoup (1985) showed that under very dry conditions the adsorbed concentration of hydrophobic organic compounds would be higher than that obtained with the water phase present. Chiou and Shoup (1985) also found that if the water content is increased such that it is greater than what is required to provide solid surface coverage, then sorption is independent on further increase in water content. The above findings, however, are in contrast with the findings of Peterson *et al.* (1988) for the sorption of trichloroethylene (TCE) on a porous aluminum oxide surface coated with humic acids. Peterson *et al.* (1988) observed a nonlinear increase of TCE sorption coefficient over the examined moisture contents (the high end of which corresponds to 2.4 monolayers of water). They attributed the increase in K_d to either the possibility of the existence of very small fractions of dry sites or that moist solid surface, which is completely covered with water, has a sorptive binding strength greater than that when all the pore space is saturated with water.

Experimental observation of vapor phase sorption of NOCs on dry soils and clays have shown that these materials have a sizable capacity to absorb organic vapors, which is strongly related to the absorbent external surface area as determined by the Brunauer-Emmett-Teller (BET) Model (Call, 1957; Chiou and Shoup, 1985; Pennell *et al.*, 1992a). The observed sorption isotherms were highly nonlinear and corresponds to type-II BET which is characteristic of vapor condensation to form multilayer adsorbates (Chiou and Shoup, 1985; Pennell *et al.*, 1992a). It has also been found that sorption is primarily due to mineral adsorption to solid surface rather than partitioning into soil organic matter (Pennell *et al.*, 1992a). For the case where the mineral surface is totally covered by organic matter, linear sorption isotherms have been found (Peterson *et al.*, 1988). This would suggest that under such conditions of complete coverage of the mineral surface by the organic matter phase, partitioning into soil organic matter is the controlling factor. In addition, vapor phase sorption on dry clays have been found to be influenced by exchangeable cation species (Jurinak, 1957; Pennell *et al.*, 1992b) and cation exchange capacity (Pennell *et al.*, 1992b). Such variation in the sorption uptake was attributed to variation in BET surface areas. However, Pennell *et al.* (1992b) observed higher sorption of *p*-xylene on Ca-, Na-, and Li-Kaolinite than what would be accounted for based on BET surface area. They suggested the possibility of having specific interactions between *p*-xylene and exchangeable cations.

Sorption isotherms of water vapor by dry soils has also been shown to be nonlinear and of the BET-type, but with higher sorption capacity than organic vapors (Chiou and Shoup, 1985; Pennell *et al.*, 1992b). The high sorption capacity of water can be explained based on the strong polar interactions with polar minerals (Chiou *et al.*, 1983). Pennell *et al.* (1992b) concluded that sorption of water on Ca- and Na-kaolinite is related to the hydration energy of exchangeable cations. It would be expected, therefore, that water effectively competes with NOCs for mineral adsorption sites. This has been noticed by many investigators (Spencer and Claith, 1970; Chiou and Shoup, 1985; Peterson *et al.*, 1988; Pennell *et al.*, 1992a; 1992b). Chiou and Shoup (1985) noticed that in addition of the dramatically reduced sorption capacities of benzene, *m*-dichlorobenzene, and trichlorobenzene in the presence of water vapor, the isotherms for organic vapor at relative humidity (RH) of 50% or more are practically linear. Moreover, at RH of 90% the sorption capacities fall into a range close to those found in aqueous systems. Nonlinear BET isotherms, however, have been reported by Shonnard *et al.* (1993) for the sorption of benzene and dichloromethane at RH of 25% and 33%, and by Pennell *et al.* (1992a) for the sorption of *p*-xylene at RH of 67% and 90%. On the other hand, Pennell *et al.* (1992b) noticed small reduction in *p*-xylene with increasing RH. The authors attributed the continuation of sorption of *p*-xylene in the presence of water to the possible existence of a considerable fraction of surface sites not covered by water.

Although the effect of moisture content on the sorption of NOCs is well established, the specific mechanisms responsible for the sorption at RHs above what is required to provide surface coverage by at least a monolayer of water remain unclear. Call (1957), for example, studied the effect of RH on the sorption of ethylenedibromide on several soils and clay minerals. Call (1957) suggested that sorption on wet soils is attributed to dissolution in sorbed water films and adsorption at the gas-liquid interface. In contrast, Chiou and Shoup (1985) postulated that hydrated soils behave as a dual sorbent in which the mineral surface acts as a conventional solid adsorbent and the organic matter as a partition medium. Pennell *et al.* (1992a) , however, demonstrated that mechanisms in addition to what have been proposed by Chiou and Shoup (1985) must be considered to account for vapor sorption of *p*-xylene in the unsaturated zone. They concluded that a multimechanistic approach should be utilized for such purposes which include: " a) adsorption on mineral surface, b) partitioning into the soil organic matter, c) dissolution into sorbed water films, and d) adsorption on the gas-liquid interface".

Little is known about the effect of soil moisture content on the sorption of NOCs under dynamic conditions. The findings of Chiou and Shoup (1985) and those of Peterson *et al.* (1988), although in conflict with each other, do not incorporate the impact of changes in vertical velocity associated with changes in soil water content. Soil water content and velocity are positively correlated. A decrease in vertical velocity will retard the downward transport of the chemical. However, a decrease in water content increases the fraction of air-filled pores, resulting in creation of additional dead-end pores which rely on diffusion process to attain equilibrium with the displacing solution (Gupta *et al.* 1973).

1.4.3 Modeling sorption in soil aquifers:

The one-dimensional equation describing solute transport through a homogeneous soil column, under steady-state conditions, is given as:

$$\frac{\partial C}{\partial t} + \frac{\rho}{\theta}\frac{\partial q}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - v_o\frac{\partial C}{\partial z} \tag{1.14}$$

where, q is the concentration in the solid phase, and other parameters are as defined previously.

Prior to solving Eq. (1.14), a submodel was required to describe the sorption rate. For a linear equilibrium sorption reaction, Eq. (1.14) in a nondimensional, scaled form reduces to

$$R\frac{\partial C}{\partial T} = \frac{D}{v_0 L}\frac{\partial^2 C}{\partial Z^2} - \frac{\partial C}{\partial Z} \tag{1.15}$$

$$R = 1 + \frac{\rho K_D}{\theta} \qquad (1.16)$$

where C is the normalized solute concentration, L is the length of the column, T is the normalized time = $v_0\ \theta\ t/L$, and R is the retardation coefficient.

The existing equilibrium transport models, however, have been less than satisfactory for simulating solute transport under several conditions (van Genuchten and Wierenga, 1977; Gaudet *et al*, 1977 ; Gupta *et al.*, 1973; Krupp and Elrick, 1968). The observed asymmetry and tailing of BTCs using soil columns has been attributed to slow solute sorption reaction or slow mass transfer with respect to advective flow of the pore-water. Nonequilibrium submodels are presented in the following sections.

Two general types of models have been developed to simulate sorption kinetics; 1) sorption-related models and 2) transport-related models (Brusseau *et al.*,1989). The sorption-related models result either from chemical nonequilibrium or intrasorbent diffusion. Transport-related models, also referred to as physical nonequilibrium models, assume the existence of mobile and immobile water regions with solute transfer between the two water regions. These models have been discussed in detail in section (1.3.2.1). Sorption-related models are discussed in the following section.

Chemical nonequilibrium models:

All the chemical nonequilibrium models assume that the sorption reaction is the rate-limiting process. The derivations of these models ignore the existence of mobile-immobile water regions and assume that all the water contributes to chemical transport. The difference among the chemical nonequilibrium models is in the nature of the sorption rate a sorbate undergoes. In the one-site first-order model, all the soil sites are assumed to be kinetically controlled. The equation that describes the rate of sorption is given as (van Genuchten *et al.* 1974):

$$\frac{\partial q}{\partial t} = k_f \frac{\theta}{\rho} C^n - k_r q \qquad (1.17)$$

where, k_f and k_r are the forward and reverse rate coefficients, respectively. This mathematical formulation implies that sorptive exchange is limited by only one of many important processes including binding by single class of sorbing site. It was found that this model does not fit experimental data well (Wu and Gschwend, 1986), especially at high pore-water velocity (van Genuchten, 1974, Pignatello, 1989).

Kinetic sorption data always shows a rapid initial uptake followed by a slow approach to equilibrium (Wu and Gschwend, 1986; van Genuchten and Wierenga, 1976; Khan, 1973). This finding has been utilized in developing the two-site chemical nonequilibrium models. In these models, sorption on one of the sites is assumed to be instantaneous, while sorption on the other site is kinetically controlled (Cameron and Klute, 1977). The mathematical formulation of the sorption rates are (Brusseau and Rao,1989):

$$\frac{\partial q_1}{\partial t} = FK_D \frac{\partial C}{\partial t} \qquad (1.18)$$

$$\frac{\partial q_2}{\partial t} = \gamma [(1-F)K_D C - q_2] \qquad (1.19)$$

where, F is the fraction of the instantaneous sorption sites, γ is a first-order rate constant and q_1 and q_2 are the amount sorbed on the instantaneous and kinetically controlled sorption sites. The model was found to be more successful than the one-site model in fitting column BTC data (Wu and Gschwend, 1986; Cameron and Klute, 1977). Unfortunately, the model retains three fitting parameters (γ, K_D, F) which cannot be estimated by independent means. In addition, the model was found inadequate to describe the BTC of 2,4-dimethylammonium salt and atrazine (Rao *et al.*, 1979).

Intrasorbent diffusion:

Intrasorbent diffusion involves the diffusive mass transfer of sorbate within the matrix of the sorbent. This can be separated into two classes; intraorganic matter diffusion (IOMD) and intramineral diffusion (Brusseau and Rao, 1989; Brusseau *et al.*, 1989). Given that organic matter is the predominant sorbent for HOCs, intramineral diffusion is not likely to be important (Brusseau *et al.*, 1989; Wu and Gschwend, 1986).

The conceptualization upon which the IOMD model is based requires that soil organic matter has a three dimensional structure, and that diffusion within the organic matter matrix is the rate-limiting process. Evidence of the last requirement has been given by Brusseau *et al.* (1991), Bouchard *et al.* (1988) and Nkedi-Kizza *et al.* (1989).

The mathematical formulation of an IOMD model is similar to the formulation of the Transport-nonequilibrium models, discussed in section 1.3.2.1, except that all the water present is considered mobile.

1.4.4 Comments on modeling sorption in soil aquifers

Brusseau and Rao (1989) and Brusseau *et al.* (1991) discussed the appropriateness of using chemical nonequilibrium models for the transport of NOCs. They stated that "the assumption of two significant types of sorption sites may not be viable," and that the nature of the hydrophobic reaction "results in hydrophobic sorption being a rapid process". Furthermore, experimental evidence of physical, not chemical, contribution to nonequilibrium is given by Wu and Gshwend, 1986: The lack of temperature dependence was interpreted as evidence that a physical process was being manifested; the dependence of sorption rate on particle size is consistent with a diffusive mechanism. The effect of diffusion into the organic matter in causing nonequilibrium is also experimentally supported by Bouchard *et al.* (1988).

Significant differences exist between different model hypotheses for the transport and transfer processes of organic chemicals in the soil. Because of the number of parameters associated with each model, verification of specific process hypothesis has been confounded. Usually, complex models with many parameters can achieve good agreement with experimental observations if parameters are adjusted to the data. However, this agreement does not constitute a test of the model hypotheses, but merely demonstrates the versatility of the model to describe outflow shapes or soil profiles. Nkedi-Kizza *et al.* (1984) showed, for example, that the mobile-immobile water model and the chemical nonequilibrium model with two different types of sorption sites had the same mathematical form. Thus, their optimum fit to any single concentration-time or concentration-depth record will be identical, even though they have been built on physically distinct hypotheses. It is imperative, therefore, to devise independent means of measuring the model parameters by a method other than simultaneous curve-fitting with other parameters. Efforts in this regard are very limited and are restricted to porous media with well defined structure (Rao *et al.*, 1980).

The assumption that a single process is responsible for the observed nonequilibrium results in a lumped kinetic term for systems where nonequilibrium is affected by more than one process. This limitation has recently led to the development of other transport models which account for more than a single nonequilibrium process (see Brusseau *et al.*, 1989). The main limitation of these models is still the large number of transport parameters that, in most of the cases, cannot be determined independently.

One of the transport parameters related to sorption is the retardation coefficient. This parameter is either determined using batch or column technique. However, results reported using the two techniques for modeling sorption under saturated conditions are ambiguous. This has been discussed in more details in Chapter 3. Studies regarding retardation under unsaturated conditions are very limited. As discussed earlier, Previous work focus on determination of changes in distribution (partitioning) coefficient with changes in moisture content under static conditions. It is not straightforward, however, to determine how the distribution coefficient changes with saturation under dynamic conditions. The difficulty arise due to the fact that under dynamic conditions *R* (not K_D) is the parameter that can be determined from an unsaturated column study. To obtain K_D from the value of *R* one needs to know the value of the solid/water ratio, i.e. ρ/θ at that level of saturation. The value of θ can be determined gravimetrically, the amount of solid that participated in the sorption process could be different from that when the column was fully saturated. Determination and changes of *R* with saturation is the primary topic of Chapter 4 of this study.

1.5 Review of volatilization and air phase transport processes

The earliest model of VOC transport in the unsaturated zone was developed by Jury *et al.* (1983, 1984a, b, c). The model incorporates the effects of volatilization, leaching, and degradation to describe the major loss pathways of pesticides. The model which assumes linear reaction and equilibrium conditions, was intended for use as a screening tool to assess behavior under prototype conditions rather than to make precise predictions under specific circumstances. Baehr (1987) and Mendoza and McAlary (1990) provided numerical solutions for transport of organic vapors in the unsaturated zone. Their model does not incorporate water mobility and assume instantaneous and equilibrium conditions. Gierke *et al.* (1990) developed a one-dimensional transport model to simulate the transport of VOCs in unsaturated soil columns. The model takes into consideration advective-dispersive transport in both liquid and gas phase and accounts for sorption. The model, however, has not been experimentally validated using a sorptive medium. Moreover, independently determined gas dispersion coefficient and Henry's constant were altered in the description of the column data. This emphasizes the need for a better understanding of the role of volatilization and transport in the air phase as a function of saturation. The following sections review volatilization and transport of VOCs in the air phase. Section 1.5.3 addresses the impact of volatilization and diffusive transport in the air phase on retardation and dispersion of VOCs.

1.5.1 Volatilization of VOCs

The importance of volatilization of VOCs and vapor transport in the subsurface has only recently been appreciated. Wilson *et al.* (1981) presented the results of a laboratory investigation of the transport of organic pollutants in soil columns. By infiltrating organic solutions in unsaturated columns, they found that 30 to 90% of the organic mass was lost to volatilization during percolation.

The partitioning between dissolved and vapor phases for an organic compound is generally described through the equilibrium relation known as Henry's law. Henry's law states that the partial pressure of a compound above the water phase, P_i is proportional to the mole fraction of the compound in the water phase, X:

$$P_i = k_H X \tag{1.20}$$

where k_H is Henry's constant. Henry's law is obeyed very well for sparingly soluble, noneloectrolyte compounds assuming an ideal gas phase (Noggle, 1985). Using the ideal gas law:

$$P_i V = nR_c T \tag{1.21}$$

where V is the volume of the air phase, n is the number of moles of the compound, R_c is the universal gas constant, and T is the temperature. Eq. (1.20) may now be expressed in the dimensionless form:

$$G = K_H C \tag{1.22}$$

where G is the concentration in the air phase, C is the concentration in the liquid-phase and K_H is the dimensionless form of the Henry's constant (= $k_H / R_c\ T$).

In almost all models describing vapor and dissolved phases, Henry's law is assumed to apply at all times, i.e. the phases are assumed to be in equilibrium, and the relationship is assumed to apply over the entire concentration range. Thus, Henry's constant may be calculated from two properties of organic compounds: its vapor pressure and solubility in water. The first expresses the equilibrium relationship between a solid or liquid compound and its gaseous concentration, and the second expresses that between the compound and its concentration in water. If a compound is both at equilibrium with the gas phase and the water phase, then the respective concentrations in the gas and water phases must be at equilibrium, and thus the ratio of these respective concentrations should yield the Henry's law constant

$$K_H = G_{sat} / C_{sat} \tag{1.23}$$

where the subscript *sat* refers to the saturated state of the phase. Since both vapor concentration and solubility are temperature dependent, K_H is a function of temperature. In general, K_H increases by a factor of two to three for each 10 °C rise in temperature. However, for an isothermal simulation, solution concentration in the two phases are assumed to be proportional and one of them may be eliminated from the transport equations using Eq.(1.23)

Although virtually all models representing these two phases assume the equilibrium form of Henry's law (Jury and Ghodrati, 1989), it is probable that a mass transfer limitation occurs in the transfer from the bulk water to the water-air interface, across the interface, or from the interface into the bulk air. Gierke *et al.* (1990) concluded from model comparisons to experimental observations of trichloroethene transport with water flow through unsaturated soil columns that the rate of mass transfer across the air-water is fast. Similar conclusion was also reached by Gierke *et al.* (1992) for their toluene vapor transport experiments through unsaturated soil columns. The level of saturation that has been measured in the work of Gierke *et al.* (1990, 1992) was less than 64%. Jury and Ghodrati (1989) indicated, however, that air-water mass transfer may be limited at relatively high soil water contents.

The rates of transfer from the bulk water to the interface and from the interface to the bulk air are generally considered much slower than the rate across the interface itself (McCarty, 1983). Under this condition, the interfacial concentration in the water C_{int} is in equilibrium with the interfacial concentration in the air G_{int} and thus

$$K_H = G_{int} / C_{int} \tag{1.24}$$

Mass transfer parameters between the water and the air phases have not been studied in unsaturated soils. Several studies, however, have been conducted in the field of air stripping and packed-tower operations. McCarty (1983) reviewed the removal of organic substances from water by air stripping and showed that the overall mass transfer coefficient of the compound, α_i, from water to air takes the form:

$$\frac{1}{\alpha_i} = \frac{1}{\alpha_{il}} + \frac{1}{\alpha_{ig} K_H} \tag{1.25}$$

where α_{il} is the liquid transfer coefficient, and α_{ig} is the gas transfer coefficient. The above equation shows that the overall mass transfer rate depends on the rate of transfer from the bulk water to the air-water interface and the rate of transfer from the interface to the bulk air. Eq. (1.25) also illustrates that mass transfer will be liquid-phase controlled for compounds with very large K_H since the last term in the equation becomes negligible, but will be gas-phase controlled for very small K_H. For intermediate values of K_H, mass transfer will be gas- as well as liquid-phase controlled.

The other parameter that needs to be determined is related to the area of contact of the phases, the geometry of the phase interfaces, and the distribution of the phases within the pores. Application of the theories that has been developed to predict mass transfer rates across interface boundaries were limited, in this regard, to very simple systems (Pfannkuch, 1984). In view of the difficulties in characterizing interface mass transfer processes in porous media in terms of fundamental parameters, a simplified approach is usually used. A first-order expressions in which the mass transfer driving force is proportional to the difference between the concentration in the two phases is employed. The proportionality constant is an overall mass transfer coefficient reflecting the contribution of the geometry of the soil and the distribution of the phases in the pores. Gierke *et al.* (1990), for example, used the following form to describe mass transfer of VOCs between air and water

$$\theta_a \frac{\partial G}{\partial t} = \alpha_i \, a_{int} \left[\frac{G}{K_H} - C \right] \tag{1.26}$$

This equation is similar to Eq. (1.4) used to describe mass transfer between the mobile and immobile water regions. Gierke *et al.* (1990) used a correlation developed by Turek and Lange (1981) for trickle bed reactors to estimate the value of $\alpha_i \, a_{int}$.

1.5.2 Transport of VOCs in the air phase

VOC dissolved in the water phase will volatilize and migrate through the gas phase in the unsaturated zone by both diffusive and advective processes. It is common in modeling miscible transport of VOCs in the vadose zone to assume a static gas phase. Pinder and Abriola (1986) questioned the validity of neglecting gas phase advection in modeling the transport of highly volatile organics in the vadose zone. Kell (1987) investigating the transport of pentane in dry laboratory sand columns, noted significant advective transport. Kreamer *et al.* (1988) suggested, however, that vapor-phase advection is small and can be neglected unless air pumping is present or unless there is a rapidly fluctuating water table.

Advection in the air phase may also be caused by density gradients arising from the high vapor pressure and molecular weights of some organic liquids. Abriola (1989) reviewed modeling multiphase transport of organic chemicals in porous media, and warned against not incorporating convection (density effect) of the air phase in modeling VOC transport in the vadose zone. Density-driven gas flow models were developed by Falta *et al.* (1989) and Mondoza and Frind (1990). Density variations with gas composition were found to have a significant impact on dense vapor (relative vapor density > 1.2) transport in soils with permeability greater than 10^{-11} m^2.

In the absence of vapor pressure and high density gradients, gaseous diffusion is expected to be the major mechanism for vapor transport. Diffusive processes may include ordinary diffusion, thermal diffusion, and counter diffusion resulting from evaporation of soil water (Weeks *et al.*, 1982). Among all, ordinary gaseous diffusion is the mechanism of greatest importance in the unsaturated zone (Weeks *et al.*, 1982). This mechanism is a result of a concentration gradient within the unsaturated region.

As coefficients of molecular diffusion in the gas phase are four to five orders of magnitude compared to those of diffusion in the liquid phase, ordinary gaseous diffusion may be a significant transport mechanism for VOCs in the unsaturated zone. Weeks *et al.* (1982) detected significant downward diffusion of fluorocarbons into the unsaturated zone. Mendoza and McAlary (1990) predicted that a TCE vapor plume in a permeable sandy material will spread tens of meters in the unsaturated zone within a few months by molecular diffusion and possibly by density-driven advection. Gierke *et al.* (1990) concluded that vapor diffusion is an important transport mechanism for TCE in sand with average pore-water velocities less than 0.43 cm/day. Therefore, volatilization and subsequent gas phase transport and gas-water partitioning, under certain transport conditions, may result in increased water phase contamination in both saturated and unsaturated zones.

1.5.3 Dispersion and retardation of VOCs under unsaturated conditions

Conservation of mass of a nondegradable VOC through homogeneous porous medium is expressed as:

$$\frac{\partial}{\partial t}(\theta_w C + \theta_a G + \rho\, q) + \Delta \cdot [J_w + J_a] = 0 \qquad (1.27)$$

where, J_w and J_a are water and air flux, respectively. All other symbols are as defined previously. If equilibrium conditions are valid to describe mass partitioning between air, water, and solid phases, then G and q can be written in terms of C as shown in Eq (1.22) and Eq. (1.11), respectively.

Under the assumption that ordinary diffusion is the prevailing transport mechanism in the air phase, then water and air flux may be expressed as:

$$J_w = \theta_w v_o C - \theta_w D \Delta C \tag{1.28}$$

and

$$J_a = -D_a \Delta G \tag{1.29}$$

where, D_a is the effective diffusion coefficient in the air phase. Terms in Eq.(1.28) are identified earlier. For nonreactive vapors in moist soils, Millington and Quirk (1961) showed that D_a can be calculated from the free-air diffusion coefficient (D_a^{air}) using the following relationships:

$$D_a = \theta_a \tau_a D_a^{air} \tag{1.30}$$

$$\tau_a = \frac{\theta_a^{7/3}}{\phi^2} \tag{1.31}$$

Sallam *et al.* (1984) indicated that Eq.(1.31) is an approximate representation. They found that a coefficient of 2.1 rather than 7/3 provided better agreement with experimental data. Neilsen *et al.* (1984) pointed out that significant differences in estimated diffusion coefficients occur depending on the assumed model. They present a pore distribution model to estimate the diffusion coefficient of radon. Peterson *et al.* (1988) found that the gaseous diffusion coefficient predicted empirically by Eqs. (1.30) and (1.31) can be in error by as much as 400%.

Eq.(1.27) can be written in terms of air phase concentration, liquid phase concentration (Baehr, 1987), or total concentration (Jury *et al.*, 1983). Baehr (1987) considered stagnant liquid phase, and Jury *et al.* (1983) neglected hydrodynamic dispersion. In terms of liquid phase concentration, Eq.(1.27) may be written as:

$$\left(1 + \frac{\theta_a K_H}{\theta_w} + \frac{\rho\, K_D}{\theta_w}\right)\frac{\partial C}{\partial t} = \left(D + \frac{K_H D_a}{\theta_w}\right)\frac{\partial^2 C}{\partial x^2} - v_o \frac{\partial C}{\partial x} \tag{1.32}$$

$$\frac{\partial C}{\partial t} = \frac{1}{R}\left[(D_{eff})\frac{\partial^2 C}{\partial x^2} - v_o \frac{\partial C}{\partial x}\right] \tag{1.33}$$

where, D_{eff} is an overall effective dispersion coefficient. Since dispersion affects only the spreading of the BTC but not the mean of the curve, then R is a measure of retardation.

Retardation and diffusive transport of VOCs in the air phase at various levels of saturation are discussed in more detail in Chapter 4.

1.6 Validity of local equilibrium assumption

Several studies have addressed the problem of developing criteria for the applicability of local equilibrium assumption (LEA) (Valocchi, 1985; Parker and Valocchi, 1986; Jennings and Kirkner; 1984; Bahr and Rubin, 1987). Jennings and Kirkner (1984) used Damkohler I number (D_a), which is the ratio of an average transit time to reaction time, in a study of multicomponent transport affected by surface reactions and solution phase complexing. They concluded that LEA is applicable when the smallest D_a exceeds 100, and reasonable approximation can be achieved when D_a exceeds 10. However, the authors cautioned that the smallest D_a criteria is applicable to the boundary conditions they used and modification of the criteria may be needed for other boundary conditions. Valocchi (1985) argued that the use of Damkohler numbers as criteria may not be sufficient as other parameters may influence the validity of LEA.

Valocchi (1985) and Parker and Valocchi (1986) used the first, second and third temporal moments to evaluate the impact of nonequilibrium upon solute transport and assess the differences between nonequilibrium and equilibrium models. In the temporal moment method, developed by Aris (1958), the first three moments correspond to the mean, degree of spreading and degree of asymmetry of the BTC, respectively. Valocchi (1985) and Parker and Valocchi (1986) examined several nonequilibrium models of a solute that undergoes linear sorption reaction. Fractional deviations in the second and third central moments of the BTCs for equilibrium and nonequilibrium models have been used to quantify the applicability of LEA.

Valocchi (1985) compared the behavior of two physical and chemical nonequilibrium models to that of a local equilibrium model. The derived moments indicate that nonequilibrium does not affect the mean breakthrough of a solute (all models have the same first temporal moment). However, expressions of the second and third moments illustrate the enhanced spreading and asymmetry created by nonequilibrium conditions. The criteria used by Valocchi (1985) for assessing the deviation from nonequilibrium is given by the E parameter defined as:

$$E=\frac{U_{neq}-U_{eq}}{U_{neq}} \tag{1.34}$$

where, U_{neq} and U_{eq} are the nonequilibrium and corresponding equilibrium moments. When E parameter = 0, solution to nonequilibrium and equilibrium models will be exactly similar.

The most benefit of using the temporal moment method is that evaluation of transport models can be made without knowledge of the analytical or numerical solution to the transport models. A major limitation of the use of the method, however, is that its dependency upon Laplace transformation makes its applicability restricted to linear problems.

Bahr and Rubin (1987) developed a method termed SKIT, separation of the kinetically influenced term, to identify the term or terms responsible for departure from local equilibrium. The authors proposed four steps to develop a SKIT equation: (1) write the system of mass balance equations describing the transport problem, (2) obtain substitution expression for the sorbed species, (3) differentiate the expressions obtained in step 2, and (4) substitute the differentiated expressions into the original mass balance equation. Note that step 2 needs to be modified in case of compounds that undergo volatilization. Once developed, the SKIT equation will be a sum of an equilibrium equation and one or more kinetically influenced terms, as shown in the following nondimensional equation developed by Bahr and Rubin (1987):

$$\frac{\partial C}{\partial T}=D\frac{\partial^2 C}{\partial Z^2}-\frac{\partial C}{\partial Z}-\frac{1}{P_D}\left[\left(\frac{1}{1+\frac{D_{a1}}{D_{a2}}}\right)\frac{\partial C}{\partial T}-\frac{1}{P}\frac{\partial^2 C}{\partial Z^2}+\frac{\partial C}{\partial Z}\right] \tag{1.35}$$

where, P_D is equal to the sum of two Damkohler numbers (D_{a1} and D_{a2}). Eq. (1.37) shows that the kinetically influenced term is a product of ($1/P_D$) and a differential facter. Bahr and Rubin (1987) proposed using P_D as a criterion for quantifying the validity of using LEA. To quantify the departure of a nonequilibrium model from local equilibrium a parameter ε is proposed which is defined as:

$$\varepsilon = \frac{q}{q_{eq}} \tag{1.36}$$

When $q = q_{eq}$ solution to nonequilibrium and equilibrium models will be exactly similar. A major limitation of the use of the SKIT method is that kinetic data are necessary to make a feasible prediction of the departure from LEA. Another limitation is that it can not be applied to all transport models.

1.7 Summary

Several transport and transfer mechanisms may affect the movement of dissolved VOCs in the unsaturated zone including, advection and dispersion in the water phase, sorption, volatilization, and advection and dispersion in the air phase.

Dispersion in porous media has been characterized by a number of researchers from different disciplines but the general form is still ambiguous. The primary reason for this is the inability to include the effects of phase saturation on dispersion. A more confounding and persistent problem is correlating laboratory-scale with field-scale studies where the discrepancies arise due to the fact that the movement of water through unsaturated zone is three-dimensional and not one-dimensional and the existence of large scale heterogeneities in the field.

One of the transport parameters related to sorption is the retardation coefficient. This parameter is determined using either a batch or column technique. Reports vary as to the relationship between the results obtained by the two techniques. In addition, extrapolation of the results of either technique to describe retardation under unsaturated conditions are yet to be verified. Determination of the impact of water content on the sorption distribution coefficient was limited to static-type experiments and at levels of saturation that do not contribute to flow. Little is known about the effect of soil moisture content on the sorption of NOCs under dynamic conditions.

Several factors are potential causes for nonequilibrium during VOC transport in the unsaturated zone including: slow diffusion between mobile and immobile water regions, slow chemical reaction, slow diffusion into the matrix of soil organic matter, or slow partitioning into or from the air phase. Tremendous efforts have been expended in developing nonequilibrium transport models which assume one or more of the above factors as the rate-limiting process. Unfortunately, verification of specific process hypotheses has been confounded. Adequate understanding of the cause and reasonable quantification of the extent of nonequilibrium is necessary to develop efficient processes to destroy, immobilize, or separate organic pollutants from the soil matrix.

In the absence of vapor pressure and high density gradients, volatilization may enhance retardation of VOCs and gaseous diffusion is expected to be the major mechanism for vapor transport. As coefficients of molecular diffusion in the gas phase are four to five orders of magnitude higher than those in the liquid phase, ordinary gaseous diffusion may be of significant importance.

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CHAPTER 2

EFFECT OF WATER SATURATION ON DISPERSIVITY AND IMMOBILE WATER IN SANDY SOIL COLUMNS

2.1 Introduction

The normalized one-dimensional advection-dispersion (AD) equation describing solute transport through a homogeneous soil column, under steady-state conditions, is given by Eqs. (1.15) and (1.16), in which *D* is the hydrodynamic dispersion coefficient which has commonly been expressed by Eq. (1.10). The first term on the RHS of Eq. (1.10) is referred to as mechanical dispersion. This is primarily caused by two mechanisms; one kinematic and the other dynamic (Sahimi *et al.*, 1983). The kinematic mechanism results from a variation in the length of streamlines that traverse the length of the column. The dynamic mechanism results from a variation in the speed of fluid movement from one streamline to the next. Longitudinal spreading of solutes in porous media may also be caused by the existence of nonequilibrium processes during solute transport. This spreading should not be incorporated into the dispersion coefficient if this coefficient is to be referred to as the hydrodynamic dispersion coefficient.

Two unsettled issues have been reported for experiments conducted under steady-state, unsaturated conditions: the first regarding the shape of BTCs and the second regarding differences in the dispersive behavior compared to the case when the porous media is saturated. Table 2.1 summarize the results of some of these experiments. The two issues are discussed below in more detail.

Table 2.1. Review of some experimental investigations of dispersion in unsaturated soil columns under steady flow conditions

Investigator	tracer	soil description	column length cm	D_{sat} cm²/day	D_{unsat}/AD cm²/day	D_{unsat}/MIM cm²/day	AD model fit	MIM model fit compared to AD fit	Shape of BTCs
Schulin et al., 1987	Br^- ^3H	50-55% stones undisturbed	50, 42	NA	$4v_o+0.5$	$2.31v_o+0.5$	good	no better	symmetrical at low v_o
De Smedt and Wierenga, 1979	Cl^-	100μm dia glass beads	30	$1.2+.021v_o$	$20D_{sat}$	$0.021v_o+1.2$	poor	better	tailing
De Smedt and Wierenga, 1986	^3H	0.02-0.05 cm packed sand	100	$0.094v_o$	$7.3v_o$	$0.63v_o$	good	better at low v_o	some tailing
Yale and Gradner, 1978	Cl^-	0.025 cm dia packed sand	23	NA	$0.216v_o+ 4.6$	NA	good (with transverse dispersion)	NA	symmetrical
Bond and Wierenga, 1990	^3H	92.8% sand, 2.5% silt, 4.7% clay. packed	30	NA	$D_{unsat}/AD > D_{unsat}/MIM$			better	small tailing
James and Rubin, 1986	Cl^-	90% sand, 7% silt and 3% clay packed	10 sat. 15 unsat.	$0.194v_o$	$\cong 0.059\ v_o$	NA	good (with anion exclusion)	NA	No tailing

Note: AD and MIM stand for advective-dispersive and mobile-immobile water models, respectively, sat. and unsat. mean saturated and unsaturated flow conditions, respectively, and NA means not available.

Some experiments under unsaturated flow conditions have shown nonsigmoid and asymmetrical concentration distributions (van Genuchten and Wierenga, 1976, 1977; Nkedi-Kizza *et al.*, 1983; De Smedt and Wierenga, 1979, 1984, 1986; Bond and Wierenga, 1990). Such observations are inconsistent with the use of the simple AD model and led to the development of other transport models that use one of the following approaches: (i) models that incorporate a diffusive interchange of solute between mobile and immobile zones of specified geometry (van Genuchten *et al.*, 1984), (ii) models that incorporate a first-order mass transfer of solute between mobile and immobile water regions (Deans, 1963; Coats and Smith, 1964; van Genuchten and Wierenga, 1976), and (iii) an AD model with a modified (lumped) dispersion coefficient (Baker, 1977). The use of approach (i) requires detailed knowledge of the geometry of the porous media. Approach (ii) is simpler and provides simulations similar to those obtained using the diffusion based models (Parker and Valocchi, 1986). The system of normalized equations describing approach (ii) for a linear, equilibrium sorption is (van Genuchten and Wierenga, 1976):

$$\beta R \frac{\partial C_m}{\partial T} + (1-\beta) R \frac{\partial C_{im}}{\partial T} = \frac{D_m}{L v_{o_m}} \frac{\partial^2 C_m}{\partial Z^2} - \frac{\partial C_m}{\partial Z} \tag{2.1}$$

$$(1-\beta) R \frac{\partial C_{im}}{\partial T} = \omega \, (C_m - C_{im}) \tag{2.2}$$

where C_m and C_{im} are the average relative concentrations in the mobile and immobile water regions, respectively. R is as defined before, D_m and v_{om} are the dispersion coefficient and average pore-water velocity of the mobile water, respectively. β is a dimensionless partition variable and ω is the normalized mass transfer coefficient. β and ω are defined as :

$$\beta = (\theta_m + f \rho K_D) / (\theta + \rho K_D) \tag{2.3}$$

$$\omega = \alpha L / v_{om} \theta_m \tag{2.4}$$

where θ_m is the volumetric water content of the mobile region, f is the fraction of sorption sites in the mobile region and α is the average mass transfer coefficient between the mobile and immobile water regions. When R= 1 (i.e. K_D is zero), β reduces to the fraction of mobile water (i.e. θ_m/θ). Evidence of the existence of stagnant (immobile) water regions was clear for some investigators (Krupp and Elrick, 1968; Gupta *et al.*, 1973; De Smedt and Wierenga, 1979; De Smedt and Wierenga, 1984; Bond and Wierenga, 1990; and others). Other researchers have shown the suitability of using the AD model without considering the existence of an immobile region (Biggar and Nielsen, 1976; Yale and Gardner, 1978; James and Rubin, 1986; Schulin *et al.*, 1987; Seyfried and Rao, 1987). James and Rubin (1986), for example, were able to describe chloride transport through unsaturated sand columns using an AD model that included anion exclusion. Their support for the existence of anion exclusion is the difference in the shape of saturated BTCs of chloride from those of tritium.

The other unsettled issue is the change in the mechanical dispersion when the soil is desaturated. Application of the capillary tube model of Aris (1956) would predict that for the same average pore-water velocity the dynamic part of mechanical dispersion will be reduced as the media is desaturated. This is because the possible range of pore sizes is reduced as the larger pores are emptied. Experimental results reported by James and Rubin (1986) are in agreement with this analysis. However, results reported by Yale and Gardner (1978); De Smedt and Wierenga (1979, 1986); in addition to those (not listed in Table 2.1) of Biggar and Nielsen (1976) and De Smedt and Wierenga (1984) have shown an increase in dispersion for partially saturated media as compared to the fully saturated case. De Smedt and Wierenga (1984) assumed that hydrodynamic dispersion retains the same value, at a given pore-water velocity, regardless whether the media is saturated or unsaturated. They attributed the increase in dispersion of their unsaturated experiments to the existence of a physical nonequilibrium situation created by solute exchange between mobile and immobile water regions. Yale and Gardner (1978), however, reported symmetrical BTCs with what appears to be higher mechanical dispersion under unsaturated conditions. Yale and Gardner (1978) speculated that this occurred because of a wider variation in the pore-water velocity distribution when the soil is desaturated.

The purpose of this chapter is to investigate the dispersive behavior of non-aggregated soils under unsaturated flow conditions as compared to when the soils are fully saturated. In so doing, a better understanding of the appropriate conceptual representation of the geometry of the unsaturated pore volume will be gained. Our approach is to isolate, if it exists, any induced dispersion due to chemical nonequilibrium of the solute with the solid matrix or due to solute exchange between mobile and immobile water regions. This will then allow quantifications of changes in mechanical dispersion as the media is desaturated. We will expand the work of Yale and Gardner (1978) to natural soils and that of James and Rubin (1986) to a tracer that does not undergo anion exclusion. The unsaturated experiments will be conducted over a range of saturations using three soils having similar grain size distributions.

2.2 Materials and methods

Soil from the A and B horizons of Oakville sand (mixed, mesic Typic Udipsamments) and from the B horizon of a Pipestone sand (mixed, mesic Entic Haplaquods) were used in the experiments described below. Soil samples were air-dried and ground to pass through a 0.85-mm sieve. Samples were characterized for pH, cation-exchange capacity (CEC), organic matter, and particle size (see Table 2.2). Sample pH was determined on a 1:1 sample-water suspension (Eckert, 1988), CEC was determined by a method outlined by Warncke *et al.* (1980), organic matter content was determined using the wet digestion technique (Schulte, 1988), and particle size distribution was determined by the hydrometer method. The differences in the pH values among the three soils are considered very slight. Variations in the CEC might be due to variations in the organic matter content. Similar grain size distributions were also found among the sand fractions of the three soils (not shown in Table 2.2). About 53% of each soil sample was found to have a medium size (250-500 um), 30% within the fine sand range, and 12% within the coarse range.

Table 2.2. Properties of Packed Soils.

soil	pH	CEC meq/100g	organic carbon %	sand %	silt %	clay %	θ cm^3/cm^3	ρ g/cm^3	K cm/hr
Oakville A	6.8	5.9	2.25	94.5	3.5	2.0	0.408	1.587	33.62
Pipestone	5.7	4.2	1.57	95.0	3.1	1.9	0.383	1.636	37.16
Oakville B	6.0	1.8	0.70	94.5	4.0	1.5	0.353	1.587	39.46

The soil columns were constructed of glass cylinders (5.45 cm ID x 30.2 cm long) with Teflon end-plates. A porous stainless-steel plate (Soil Measurement Systems, Tucson, AZ) that functions as a capillary barrier was attached to the outflow end of each column. The columns could be operated in either a saturated or an unsaturated mode. Tensiometers (Soil Measurement Systems, Tucson, AZ) were used to measure soil-water suction at one-third and two-thirds the column length. This was necessary to establish a unit hydraulic gradient for the unsaturated experiments. The aqueous phase was applied to the top of the column using a precision constant flow pump (Harvard Apparatus Inc., South Natick, MA). A modified column setup of the one reported by Annable *et al.* (1993) has been used in this study as shown in Figure 2.1.

A sample from each soil was uniformly packed in a soil column. All the soil columns were initially evacuated and then wet from the bottom very slowly with 0.01 N

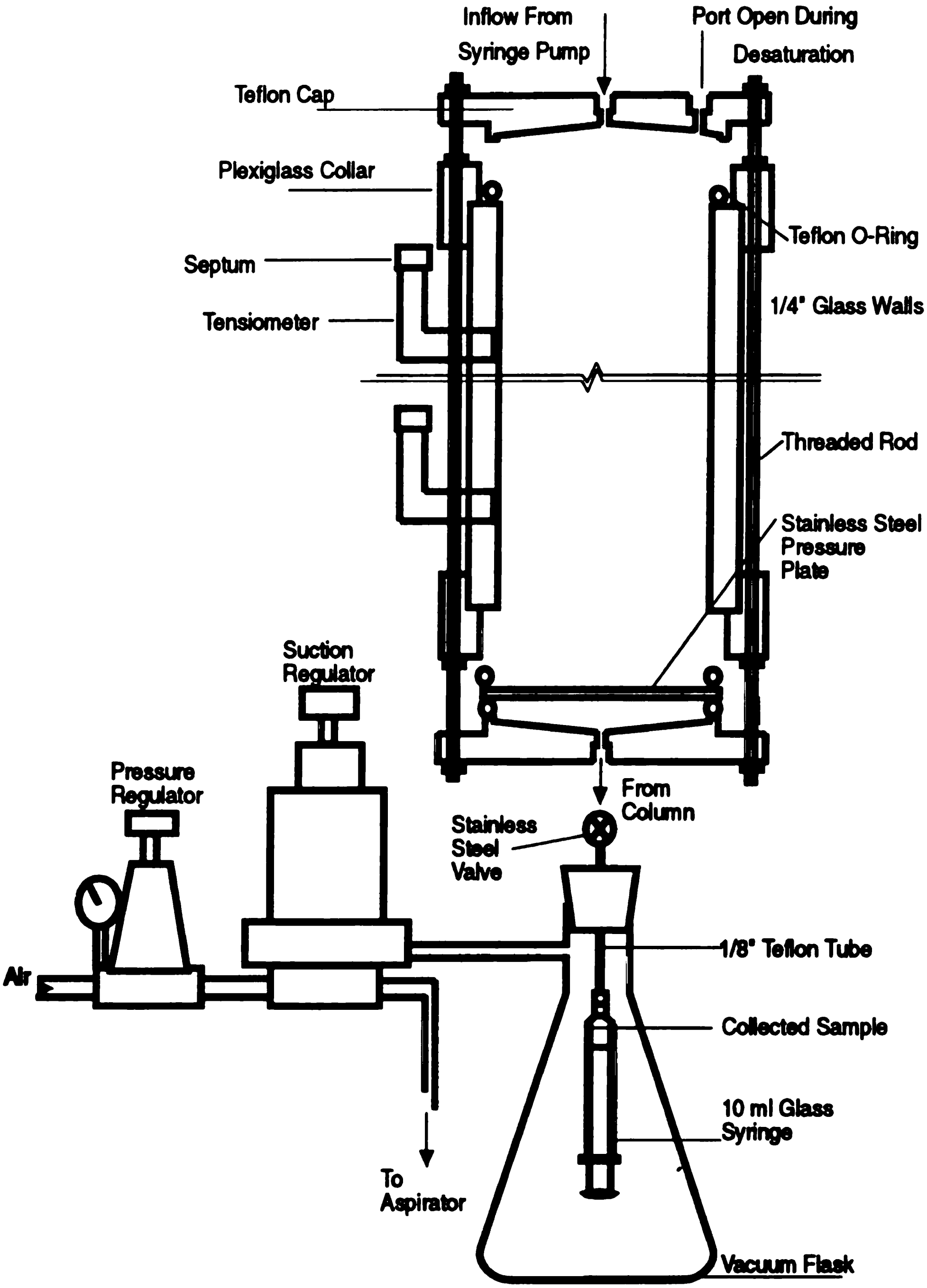

Figure 2.1 Schematic diagram of the unsaturated soil column with the sample collection device

$CaCl_2$ solution until they were completely saturated. The soil columns were weighed to determine the saturated moisture content (θ). Saturated hydraulic conductivity (K) was determined using the constant head method. Column bulk density (ρ), θ, and K values are listed in Table 2.2. Flow of a 0.01 N $CaCl_2$ solution was established at different velocities less than or equal to K by adjusting the delivery rate from the syringe pump for the saturated experiments or the applied suction and delivery rate to obtain a unit hydraulic gradient for the unsaturated flow experiments. In the later case, water content or degree of saturation was determined by column weight.

To verify that a uniform saturation had been established along the depth of the soil columns, Metea soil (83% sand, 11% silt, 6% clay), classified as loamy, mixed, mesic Arenic Hapludalfs, was packed in a 30.2 cm column, and unit hydraulic gradients were established at several degrees of saturation. The column was then sacrificed to measure the water content distribution along the length of the column. The water content distribution was compared with the mean value determined by difference between the weight of the column at that saturation and the dry weight of the column. This is presented in Figure 2.2 for a saturation of 43.2%. Some variations in actual water distribution along the length of the column can be seen in the figure. The upper part of the column is drier than the lower part. This might be due in part to a 5 mbar higher suction detected in the upper tensiometer compared to the lower one, or due to redistribution of the water along the length of the column between the time the flow stopped and the time the column was segmented. The largest detected difference from the average was 4%. In all the unsaturated experiments conducted for the soils listed in Table 2.2 except for the first unsaturated experiment of each soil, the difference in the tensiometers readings never exceeds 3 mbar. At an applied suction pressure of 7 mbar at the pressure plate for the first unsaturated experiment of each soil, no negative pressure was detected in the

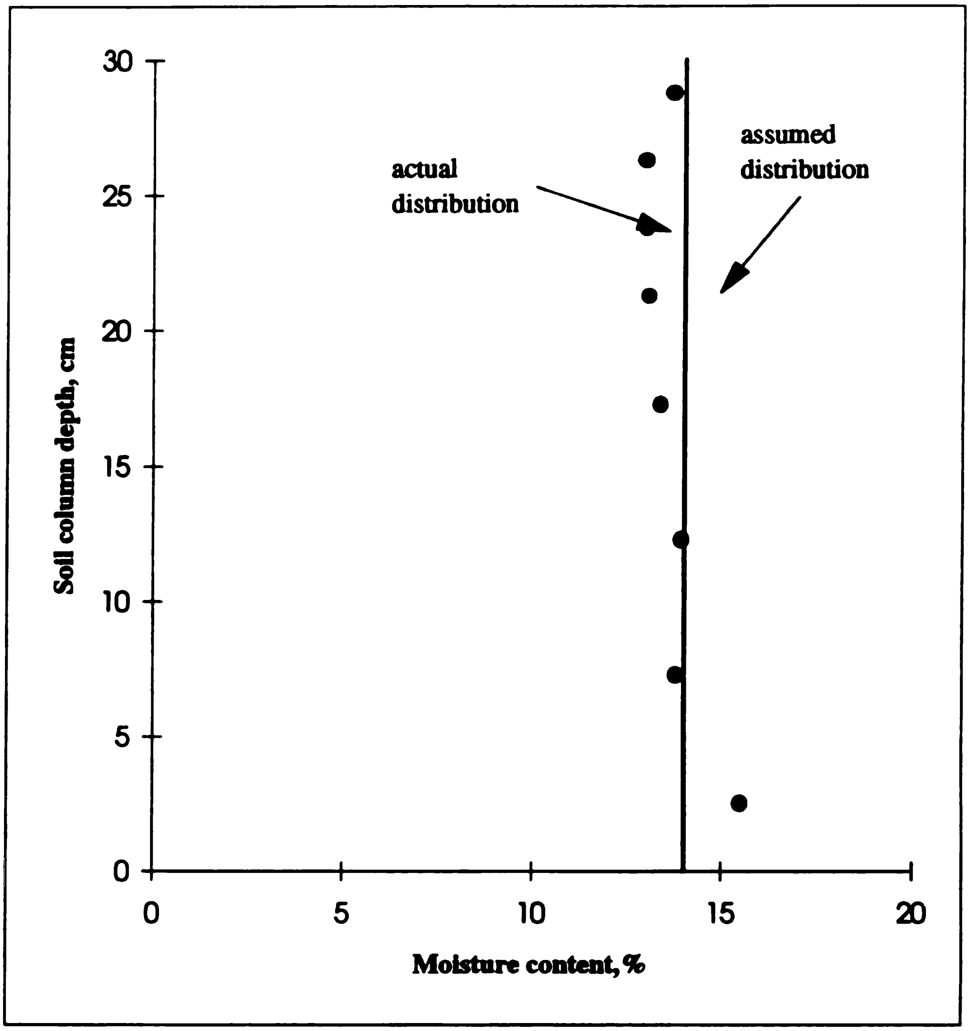

Figure 2.2 Water distribution along the depth of a Metea soil column at a negative pressure of 55 mbar

tensiometers. It is assumed, therefore, that a uniform moisture content was established along the depth of the column for the conducted unsaturated experiments.

Tritiated water was injected either in the form of a pulse input for a fixed period of time or as a step increase that was maintained until the effluent concentration reached the input concentration. A fraction collector was used to collect effluent samples for the step-increase studies, which were only used for saturated flow. In the pulse input experiments, effluent samples were collected using clean glass syringes attached to the outlet of the column as shown in Figure 2.1. Effluent samples were analyzed for tritium by liquid scintillation counting. At the end of each experiment, the columns were displaced by a tracer-free calcium chloride solution, until the effluents were free from any detectable amount of tracer.

Retardation coefficients (*R*) for tritiated water were determined by measuring the area above the BTC for a step input (Nkedi-Kizza *et al.*, 1987). Short columns (5.45 cm ID x 10.2 cm long) packed with either Oakville B soil or Oakville A soil were employed. Injected tritium concentration was identical to the one used in the long column experiments. Experiments were conducted at four different saturated flow rates that cover the range of flow rates used for the saturated-unsaturated long column experiments.

2.3 Results and discussion

To determine the dispersive behavior of a porous media, any induced spreading as a result of chemical or physical nonequilibrium has to be isolated. Chemical nonequilibrium is caused by slow solute interaction with all or some specific sites of the solid matrix. Physical nonequilibrium, however, results from slow solute diffusion in and out of relativley stagnant water regions. This might be created by the nature of the structure of the media, i.e. aggregated vs. nonaggregated, or the flow conditions, i.e. saturated vs. unsaturated. The following section focuses on the interaction of tritium with the solid matrix. This is necessary to determine *R*, which is one of the transport parameters that needs to be used in Eqs. (1.15), (1.16), and (2.1). The value of *R* will determine if verification of the existence of chemical nonequilibrium is necessary. The second section focuses on data analysis using two models: one assumes that the system is operating under physical equilibrium and the other accounts for the presence of physical nonequilibrium. The last section compares the values of hydrodynamic dispersion coefficient under unsaturated conditions to that under saturated ones.

2.3.1 Role of chemical interaction

R values are usually determined by either batch or column experiments. Since tritium is commonly thought to function as an ideal tracer (Wierenga and van Genuchten, 1989), the batch equilibration method may not be sensitive enough to measure small values of K_D (van Genuchten and Wierenga, 1977). Under these circumastances, the use of soil column technique becomes preferable over batch experiments.

Table 2.3. Retardation of tritium in saturated short columns

Oakville B		Oakville A	
v_0 (cm/hr)	*R*	v_0 (cm/hr)	*R*
17.267	0.999	17.257	1.045
5.180	0.982	5.177	0.999
2.302	0.993	2.283	1.087
0.575	0.976	0.571	1.001

Table 2.3 shows the values of R measured in this study for tritium at a range of average flow velocities similar to the range used in the saturated and unsaturated experiments; all values are very close to 1.0. These results are consistent with the findings of Wierenga and van Genuchten (1989). Values different from 1.0 have been reported by some investigators, however. Seyfried and Rao (1987), for example, found that R for tritium is 1.10-1.18 for column experiments. Sorption of tritium is thought to be due to isotopic exchange with crystallatic hydroxyls of clay particles (Wierenga *et al.*, 1975; van Genuchten and Wierenga, 1977). Nkeddi-Kizza *et al.* (1983) and Schulin *et al.* (1987), after fitting the AD model with D and R as unknowns to tritium data, noticed some dependency of R on flow velocity, with lower R values at higher velocities. Schulin *et al.* (1987) attributed their higher than previously reported values of K_D, i.e. 0.025 cm^3/g for less than 2mm dia. soil fraction, to a possible small error in determining θ. R values reported by Nkeddi-Kizza *et al.* (1983) ranged between 0.626 and 1.33. Values less than 1.0 are thought to be an indication of the existence of a "physical nonequilibrium" situation between the mobile and immobile water regions (Nkeddi-Kizza *et al.*, 1983).

For the soils under investigation, and within the range of flow velocities employed there was no evidence of either a positive or negative retardation of tritium to the soil matrix. Since retardation is not a function of column length (Wierenga and van Genuchten, 1989), a value of R=1.0 was used in fitting the BTCs generated from the long column experiments to the AD and MIM models. Since R=1, any nonequilibrium present during tritium transport through the soil columns cannot be attributed to slow chemical interaction.

2.3.2 Role of physical nonequilibrium

BTCs for the saturated-unsaturated experiments were analyzed first using the AD model which assumes that the system is under physical equilibrium. The unsaurated BTCs were then analyzed using the MIM to determine parameter values for the immobile water fraction and mass transfer coefficient.

The AD model: Tritiated water was injected through saturated soil columns at flow velocities ranging from approximately the magnitude of the saturated hydraulic conductivity (≈ 37 cm/hr) to about 0.2 cm/hr. The conditions for these experiments are listed in Table 2.4. Generated BTCs were analyzed to determine D using the nonlinear least squares inversion program CXTFIT of Parker and van Genuchten (1984) with R=1 and v_o and T_o are as given in Table 2.4. D values are accompanied by their 95% confidence limits. Similarly the AD model was fit to the unsaturated experimental data. Values of D along with the conditions of the unsaturated experiments are listed in Table 2.5. Values in parenthesis represent 95% confidence limits as estimated by CXTFIT. A typical BTC for each soil column is shown in Figure 2.3 for the saturated experiments and in Figure 2.4 for the unsaturated ones. For comparison of dispersion under saturated and that under unsaturated flow conditions it is useful to employ the same range of pore-water velocities. Therefore, the first saturated experiment of each soil, i.e. SB1, SP1, and SA1 is not included in the discussion of this chapter since the average pore-water velocities of these experiments (> 30 cm/hr) are beyond the range of the unsaturated flow velocities..

The values of D obtained using the AD model for the saturated and unsaturated experiments are plotted versus the average pore-water velocity for each soil as shown in Figure 2.5. Small air saturations as noticed in experiments USB1, USP1, and USA1

Table 2.4. Experimental conditions and dispersion coefficients for the saturated flow experiments

Experiment	Tracer Application	v_o, cm/hr	Normalized Pulse Time, *To*	*D*, cm^2/hr
Oakville B				
SB1	pulse	36.47	2.186	18.040±8.04
SB2	step increase	14.76	-	8.022±2.40
SB3	pulse	7.29	2.20	3.275±2.05
SB4	step increase	1.84	-	0.668±0.22
SB5	step increase	0.99	-	0.289±0.06
SB6	pulse	0.73	2.17	0.203±0.11
SB7	step increase	0.25	-	0.114±0.01
Pipestone				
SP1	pulse	33.60	2.08	18.780±7.17
SP2	step increase	13.62	-	8.592±1.79
SP3	pulse	6.72	2.09	2.900±0.34
SP4	step increase	1.70	-	0.687±0.10
SP5	step increase	0.91	-	0.233±0.08
SP6	pulse	0.67	2.05	0.159±0.07
SP7	step increase	0.23	-	0.127±0.04
Oakville A				
SA1	pulse	31.55	1.95	20.870±3.45
SA2	step increase	12.79	-	9.440±0.99
SA3	pulse	6.30	1.96	5.371±2.14
SA4	step increase	1.60	-	0.846±0.09
SA5	step increase	0.85	-	0.382±0.11
SA6	pulse	0.62	1.91	0.220±0.07
SA7	step increase	0.21	-	0.138±0.03

Table 2.5. Experimental conditions and the results of fitting the AD and MIM models to the unsaturated flow experiments

Exp.	v_0, cm/hr	*To*	S%	AD Model		MIM model			
				D, cm^2/hr	SSE	*D*, cm^2/hr	β	ω	SSE
USB1	18.738	2.16	95.6	8.53	0.16	8.05	0.98	0.0023	0.160
				(±2.89)		(±2.65)	(±0.08)	(±0.238)	
USB2	9.180	2.56	71.0	9.17	0.09	7.85	0.923	0	0.004
				(±2.78)		(±0.54)	(±0.006)	NA	
USB3	2.735	1.69	50.6	2.53	0.09	2.09	0.937	0	0.005
				(±0.55)		(±0.11)	(±0.004)	NA	
USB4	1.014	2.21	47.8	1.32	0.20	0.71	0.897	0	0.006
				(±0.43)		(±0.05)	(±0.005)	NA	
USP1	17.496	2.12	96.0	11.63	0.11	11.84	1.0	0.00012	0.100
				(±2.35)		(±2.42)	NA	(±6.326)	
USP2	8.397	2.42	72.0	14.24	0.05	14.42	1.0	0.0009	0.042
				(±2.91)		(±2.70)	NA	(±3.223)	
USP3	2.562	1.64	55.4	2.81	0.11	2.80	1.0	0.0012	0.102
				(±0.62)		(±1.75)	NA	(±4.37)	
USP4	1.026	2.30	43.6	0.66	0.35	0.67	1.0	215370	0.329
				(±0.33)		(±0.34)	NA	NA	
USA1	16.506	1.94	95.5	11.98	0.13	12.16	1.0	0.0042	0.112
				(±3.62)		(±2.86)	NA	(±4.627)	
USA2	7.272	2.08	78.0	11.22	0.01	10.73	0.983	0	0.010
				(±1.12)		(±0.99)	(±0.009)	NA	
USA3	2.155	1.38	58.5	3.75	0.03	3.80	1.0	0.0063	0.029
				(±0.38)		(±0.37)	NA	(±2.833)	
USA4	0.806	1.80	52.2	0.76	0.01	0.76	1.0	1947	0.011
				(±0.06)		(±0.06)	NA	NA	

(S>95%) do not appear to cause a change in the dispersivity of the media as shown in Figure 2.5. De Smedt and Wierenga (1984) observed that porous media at 90% saturation or above have identical dispersive behavior to fully saturated ones. Figure 2.5 shows, however, that for any saturation (S) ≤ the saturation of US2 experiments, the dispersion coefficient is higher than its value if the media is saturated. This behavior has been noticed by other investigators as previously shown in Table 2.1. When a linear regression of the form $D=av_0$ is used to fit the saturated data and the unsaturated data for saturation less than or equal to that which corresponds to US2 experiments, we found that the ratio $a_{unsat}/a_{sat} \cong 1.9\text{-}2.8$. The results of the regression are presented in Table 2.6 along with the r^2 of the regression given in parenthesis.

This ratio is much lower than the ones reported by De Smedt and Wierenga (1979 and 1984). Their ratios were 20 and 73, respectively. The higher ratios were attributed to the existence of a physical nonequilibrium situation created by the presence of immobile water regions under unsaturated conditions, while all the water is considered mobile for the saturated cases. Therefore, part of the increase in D is caused by this nonequilibrium situation. Their evidence for the presence of an immobile water region, as shown also by Bond and Wierenga (1990), is the tailing and asymmetry of the BTCs. The extent of tailing and asymmetry has been shown to be a function of, among other parameters, the average pore-water velocity. Our BTCs, as shown in Figure 2.4, appear to be symmetrical with no noticeable tailing. This indicates that dead end pores either do not exist or do not play a significant role in causing physical nonequilibrium in the transport of tritium. Therefore, non-equilibrium considerations cannot be used to explain the higher D values in this study. The MIM model was used, however, to confirm this observation.

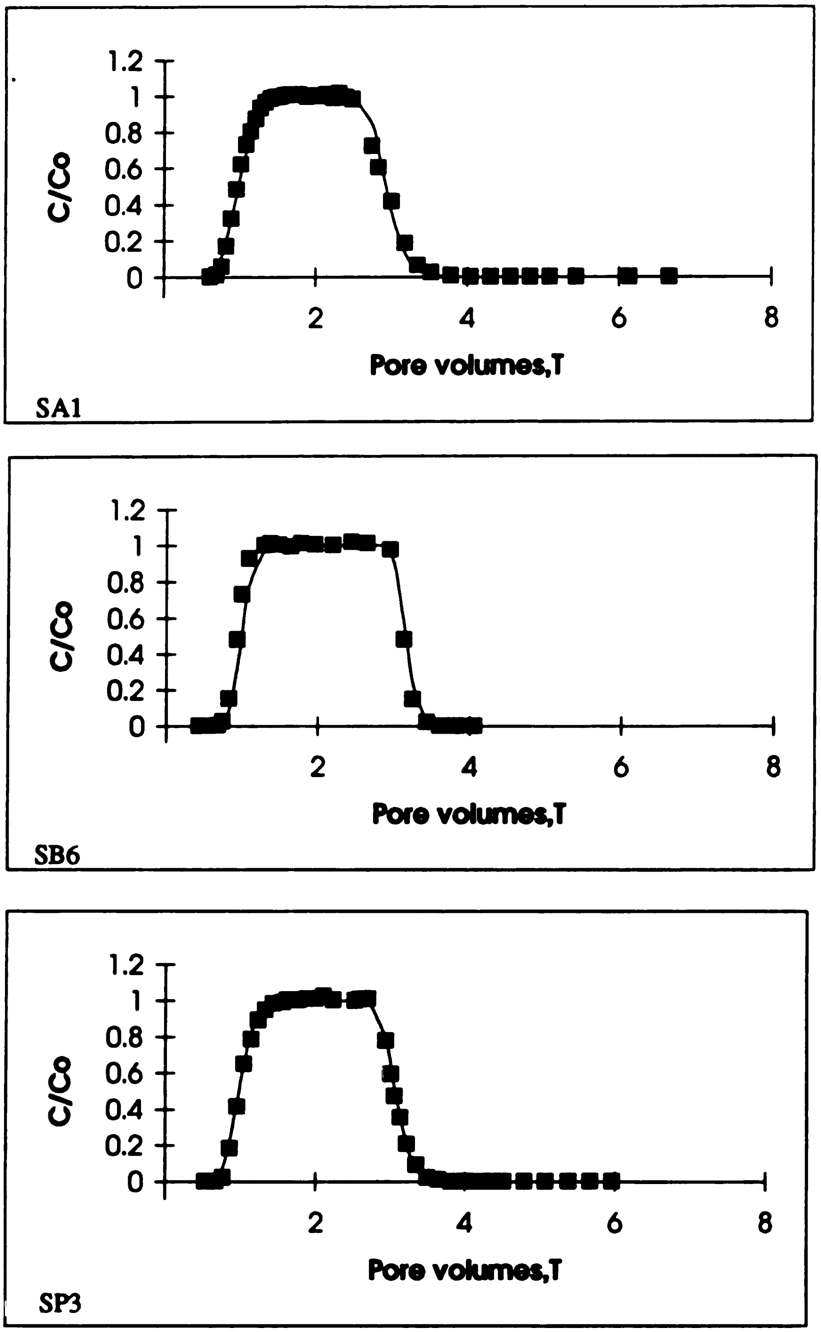

Figure 2.3 Selected BTCs from the pulse input saturated flow experiments. Dots are experimental data, and solid lines are simulations with the AD model using parameter values listed in Table 2.4

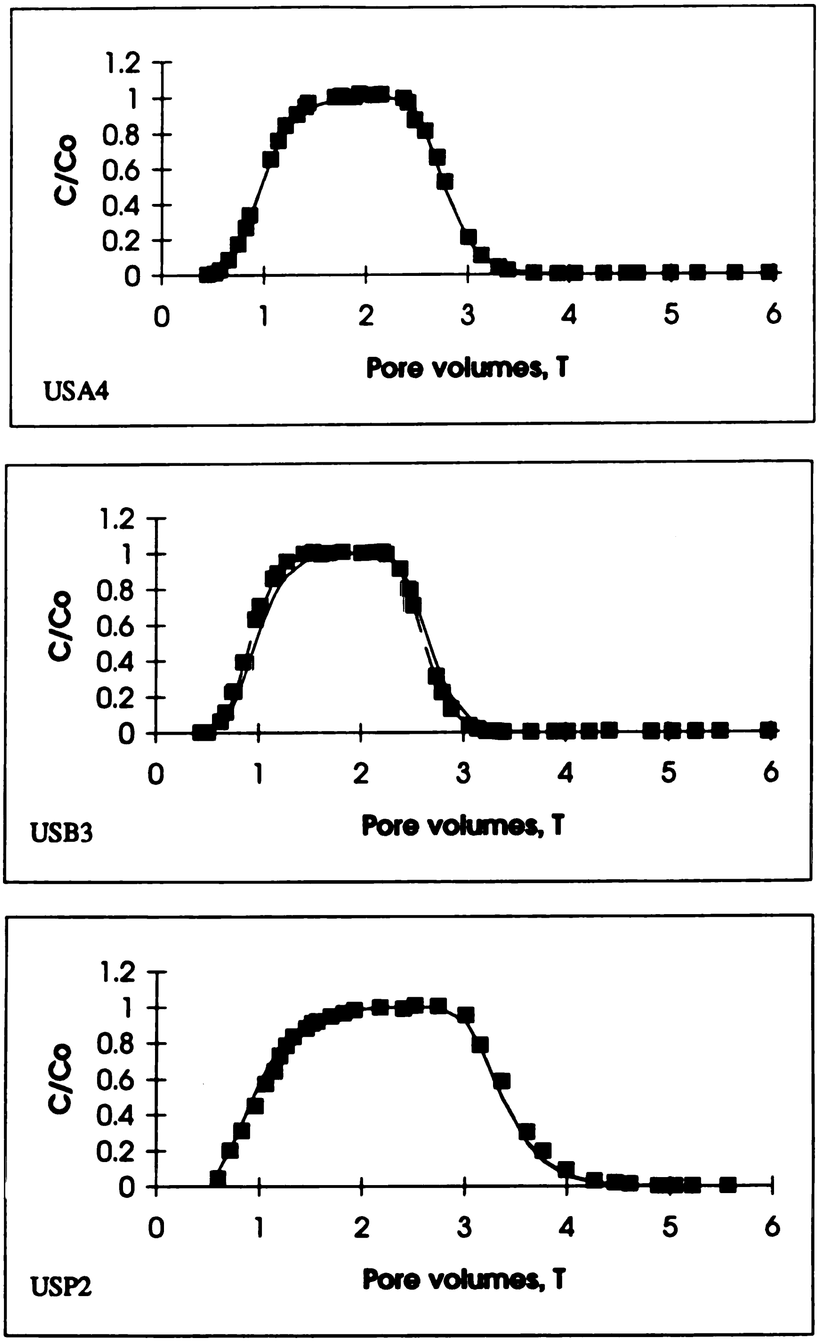

Figure 2.4 Selected BTCs of the unsaturated experiments. Dots are experimental data, solid lines are simulations with AD model and dashed lines are simulation with MIM model. Simulation parameter values are as listed in Table 2.5

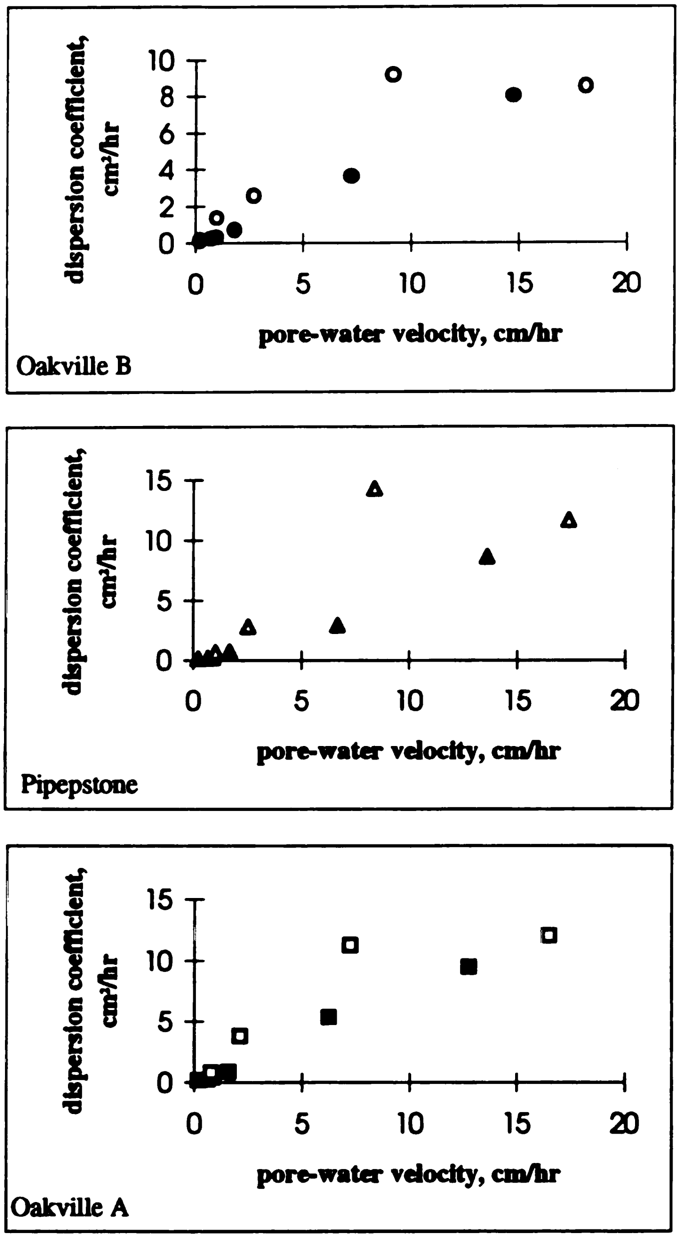

Figure 2.5 Dispersion coefficient for the three soils under saturated (closed symbols) and unsaturated (open symbols) conditions

The MIM model: Numerical experiments using CXTFIT to determine MIM parameters for data generated with the MIM model under conditions similar to those observed in our lab experiments showed parameter value errors of about 4% due to inaccuracies in the numerical integration. The relative error (STOPER) in subroutine ROMB (which handles the required numerical integration) of CXTFIT was reduced to $5*10^{-7}$ instead of the reported value of $5*10^{-5}$ and the number of iterations was adjusted so that convergence was achieved to improve this situation. Parameter value errors of less than 0.16% were then obtained. Several initial values of β and ω were tried to obtain the values listed in Table 2.5. Selection of the shown optimized values was based on the lowest value of sum of square errors (SSE) without violations of physical reality. The following constraints have been imposed on the optimized values to avoid violations of physical reality: $D \geq 0$, $\omega \geq 0$, and $0 \leq \beta \leq 1.0$.

Table 2.6. Linear regression results between *D* and v_0

	Dispersivity (cm)	
Soil	Saturated	Unsaturated
Oakville B	0.531(0.99)	0.996(0.99)
Pipestone	0.588(0.97)	1.630(0.97)
Oakville A	0.754(0.99)	1.552(0.99)

The MIM model was fit to the unsaturated experimental data. Values of *D*, β, and ω are listed in Table 2.5. Values in parenthesis represent 95% confidence limits as estimated by CXTFIT. When the optimized β is greater than 1.0 or ω is 0 or large, no confidence interval is estimated.

Fitting the MIM model to the Pipestone and Oakville A data did not result in a significantly better representation of the experimental results as can be seen from the SSE values. The optimized β for all the unsaturated experiments of Pipestone and Oakville A soils were greater than 1.0 but less than 1.018, except for USA2 which was 0.983. Values greater than 1.0 have been replaced by 1.0. This should not alter the values of SSQ, since the way CXTFIT estimates SSE for any $\beta \geq 1$ is, in fact, based on $\beta = 1$. With $\beta=1$, the value of *D* predicted using the MIM model should be identical to the value predicted using the AD model. Therefore, the added complexity of the MIM model is not necessary to explain tritium movement in these two soils.

Use of the MIM model for Oakville B soil shows a value of β that ranges between 0.89-0.93 with high certainty as noticed in the confidence intervals listed in Table 2.5. Error propagation methods were used to estimate the uncertainty in the calculated values of v_0. This has been found to be around 1.4%. Therefore, the 10% immobile water fraction noticed for Oakville B soil cannot be explained based on experimental error in determining average pore-water velocity. De Smedt and Wierenga (1984) and Schulin *et al.* (1987) found that about 85% of the water content in their experiments is mobile. Bond and Wierenga (1990) found 96% to be mobile. It can also be seen in Table 2.5 that β is independent of the degree of saturation and the average pore-water velocity. This was also noticed by De Smedt and Wierenga (1984), Schulin *et al.* (1987) and Bond and Wierenga (1990). In earlier studies (Bond and Wierenga, 1990, for example) use of the MIM model was justified because the small, non zero values of ω required to achieve better fit produce a mass transfer effect that is evidenced in the tailing and asymmetry of the data. The values of ω as estimated by CXTFIT for the unsaturated experiments on Oakville B soil were found to be 0. For $\omega=0$, there is no mass transfer from the mobile to the immobile water region and any immobile water present is isolated from the flowing fraction. This is an equilibrium situation in which the MIM model reduces to:

$$\beta\frac{\partial C_m}{\partial T} = \frac{D_m}{Lv_{om}}\frac{\partial^2 C_m}{\partial Z^2} - \frac{\partial C_m}{\partial Z} \tag{2.5}$$

This equation is similar to the AD equation, with the exception that the BTC will be shifted to the left for $\beta<1$. It is expected, therefore, that the predicted BTCs will exhibit no tailing and the use of the MIM model becomes unnecessary. However, The use of the AD model without accounting for β will influence the value of D predicted, since the optimization scheme used to estimate model parameters is such that it will force the model simulation to go through the data points as much as possible. Owing to the inadequacy of the AD model to describe the experimental data in this case, the model simulation will, as a matter of necessity, yield higher D values in order to shift the BTC to the left. This of course, will be associated with a higher degree of uncertainty in D and a higher SSE value compared to the ones obtained using the MIM model as can be seen in Table 2.5. Suggesting a need for a 2-parameter model to describe the generated data.

2.3.3 Dispersivity under saturated-unsaturated flow conditions

After isolating the effect of nonequilibrium on dispersion, De Smedt and Wierenga (1986) found that the dispersivity for the unsaturated media is about 7 times higher than that when the media is saturated. Yale and Gardner (1978) also noticed what seems to be a more dispersive unsaturated media. The above findings and ours are in conflict with the expectation deduced from the capillary tube model for unsaturated media, i.e. less dispersion due to narrowing the range of pore sizes available to flow. A possibility for this contradiction is that the conceptualization upon which the capillary tube model was built upon might be successful in describing the contribution of the dynamic mechanism of dispersion, it neglects, however, the contribution of the kinematic mechanism as part of mechanical dispersion. It is well to consider this point further.

As the media is desaturated, changes in orientation of flow paths will occur. The effect of such changes is a more tortuous, irregular pore sequences that are not oriented in the principal direction of flow (Corey *et al.*, 1963). This will increase the contribution of the kinematic mechanism to dispersion. A capillary tube model that treats a porous media as a bundle of capillary tubes that do not intersect each other cannot account for such an increase. A more appropriate model, from this point of view, is one that involves a random network of connected pores. Sahimi and Imdakm (1988) gave an explanation of dispersion in unsaturated media using random walk and percolation theories. To model the distribution of immiscible fluid, the authors used the concepts of random percolations. They predicted that, for the case where thin films of the wetting phase that coat the surface of the nonwetting phase are taken into account, hydrodynamic dispersion increases with desaturation until a saturation of ≈ 0.4, after which it decreases and becomes very small at saturation close to 0. We presented in Figure 2.6 the dispersivity values as a function of wetting phase saturation for the three soils used. As previously indicated, the dispersivity of the media at saturation of about 95% is similar to that of the fully saturated case. The model of Sahimi and Imdakm (1988) shows, however, an immediate increase in dispersivity as saturation is reduced. With the limited number of data points available for saturation of < 95%, it seems that there is an increase followed by a decrease in dispersivity as saturation decreases. This is consistent with the numerical observations of Sahimi and Imdakm (1988). More experimental data are needed, however, to draw a firm conclusion.

The contradiction between our findings and those of James and Rubin (1986) is hard to explain, but may be attributed to differences in the experimental procedure. James

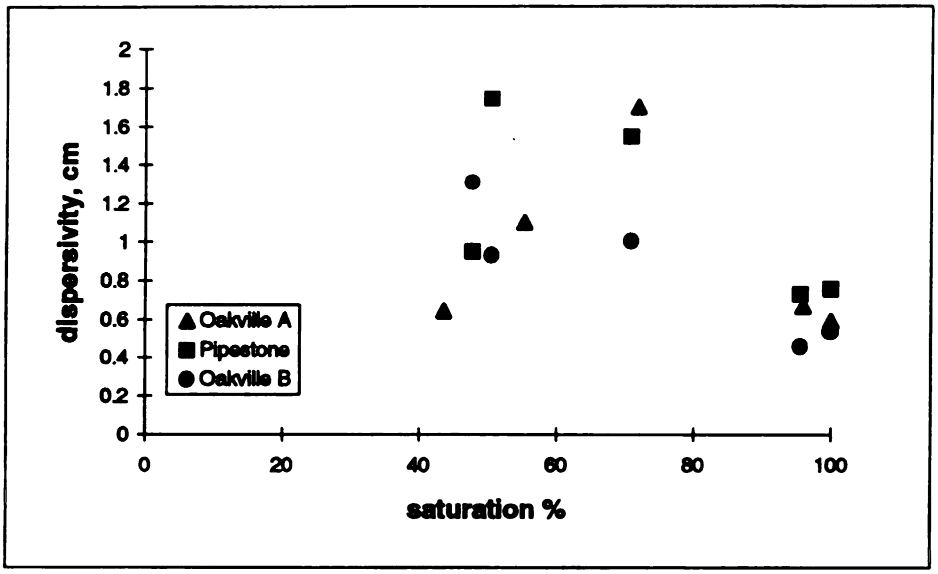

Figure 2.6 Dispersivity of three nonaggregated soils at various levels of saturation

and Rubin (1986) evaluated the dispersion coefficient for the unsaturated experiments by determining chloride concentration along the soil profile at an average soil length of 15 cm. Their evaluation of dispersion coefficient for the saturated experiments was based on collecting effluent samples from a 10-cm length column. According to James and Rubin (1986), apparatus induced dispersion has been accounted for. Differences between their results and ours are possibily due to differences in the column length and flow rates used. Corey *et al.* (1963), for example, found that dispersion for unsaturated soil increases as the column length increases. The same finding was also noticed for their saturated experiments at high flow rates, but not at low rates. Meanwhile, it has been demonstrated that at short distances the dispersion coefficient rises sharply for saturated media, but the rate of increase falls off rapidly (Han *et al.*, 1985). Yet, it is not known how the rate of increase changes under unsaturated conditions. A study that investigates the dispersive behaviour of both saturated and unsaturated soil at different column lengths using the same tracer and same technique of sampling would be helpful answering the above question.

2.4 Summary and Conclusions

Two conflicting issues have been reported for the transport of nonsorbing tracers through nonaggregated media under steady, unsaturated conditions: the first is whether there is physical nonequilibrium created by slow solute diffusion into relatively stagnant water regions, the second is whether the dispersivity increases, remains the same, or decreases as the media is desaturated.

In this study, we investigated the dispersive behavior of three nonaggregated sandy soils using an ideal tracer over a range of saturation and found that the dispersivity of unsaturated soil is about 1.9-2.8 times higher than when the soil is fully or nearly saturated. This behavior contradicts the expectation deduced from the capillary tube model which treats the porous medium as bundles of tubes that do not intersect each other. It suggests, however, that a model which accounts for intersection of capillary tubes could represent the geometry of the unsaturated pore volume more appropriately. We speculated that the increase in dispersivity under unsaturated conditions is a result of an increase in the tortuous path length.

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We also concluded that there was no evidence of mass transfer limitation in the transport of tritium through the media. For two of the soils used in this study, there was no evidence of immobile water regions. There is a possibility, as noticed for the third soil, for some immobile water that is totally isolated from the flowing fraction and did not produce physical nonequilibrium in the system.

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CHAPTER 3

COMPARISON BETWEEN RETARDATION COEFFICIENTS OF NONIONIC ORGANIC COMPOUNDS DETERMINED BY BATCH AND COLUMN TECHNIQUES

3.1 Introduction

It is generally believed that the primary sorption mechanism for dissolved nonionic organic compounds (NOCs) is hydrophobic partitioning to the soil organic matter matrix and that the ultimate extent of sorption is a function of the degree of hydrophobicity of the compound and the fraction of organic matter on the soil (Chiou, 1989). Investigators, however, found that for low-carbon soils (< 0.1%), the relationship between sorption capacity and soil organic carbon content tends to deteriorate and that the contribution of mineral surfaces to sorption of NOCs should be considered (Schwarzenback and Westall, 1981; Karickhoff, 1984; Mackay *et al*, 1985).

The impact of sorption is to reduce the average velocity of the contaminant relative to that of water. The normalized 1-D advection-dipersion equation describing transport of NOCs through a homogeneous soil column, under steady-state conditions is usually written as:

$$R\frac{\partial C}{\partial T}=\frac{1}{P}\frac{\partial^2 C}{\partial X^2}-\frac{\partial C}{\partial X} \qquad (3.1)$$

where C is the normalized concentration, T is the dimensionless time = $v_o t/L$, v_o is the average pore-water velocity, t is the time, L is the length of the column, X is the normalized length = x/L, x is the length, P is the Peclet number = $v_o L/D$, D is the hydrodynamic dispersion coefficient, and R is the retardation coefficient defined as:

$$R = 1 + \frac{\rho K_D}{\theta} \tag{3.2}$$

in which ρ is the bulk density, K_D is the linear distribution coefficient and θ is the volumetric water content.

Proper determination of R can have a significant impact on managing and preventing groundwater contamination. In the laboratory, retardation coefficients are customarily determined by either batch or packed column experiments. The advantages and disadvantages of the column and batch approaches have been discussed by Kool *et al.* (1989) and Jackson *et al.* (1984). Reports vary as to the relationship between values of R determined by the two techniques; good agreement (MacIntyre *et al.*, 1992; Nkedi-Kizza *et al.*, 1987; Lee *et al.*, 1988), slight differences (Bouchard *et al.*, 1988; Celorie *et al.*, 1989), and high deviations (up to 100%) (MacIntyre and Stauffer, 1988; Lion *et al.*, 1990; Bilkert and Rao 1985) have all been reported.

Similarity of R's in the work of MacIntyre *et al.* (1992) between the two methods was attributed to relatively rapid kinetics and linear nature of the sorption isotherms. Bilkert and Rao (1985) noted that the high discrepancy between the two values may be a consequence of failure to reach local equilibrium in the column. While, the independence of K_D on velocity in the work of MacIntyre and Stauffer (1988) did not allow them to attribute this to nonequilibrium, neither were they able to resolve the cause. The degree of sorption nonequilibrium of NOCs has been shown to increase with the increase in soil organic matter content (Bouchard *et al.*, 1988). Therefore, if failure to attain equilibrium is the cause of discrepancy between batch and column coefficients, then the deviations between the two methods will increase with increases in soil organic matter.

Several other factors have been offered to explain disagreement between batch- and column-determined retardation coefficients including: loss of sorbent particles through column end retainers, column flow variations, column flow channeling (MacIntyre *et al.* 1992), mixing differences between the two methods (Schweich *et al.* 1983), reductions in soil particle spacing (Celorie *et al.*, 1989), differences in soil/water (S/W) ratio between batch and column experiments(Lion *et al.*, 1990), and the use of undisturbed columns and homogenized soil samples if spatial variability in sorption occur along the depth of the column (Chrysikopoulos *et al.* 1990).

The above factors can be categorized into two groups: sorption-related factors including sorption nonequilibrium, nonlinearity, and nonsingularity, and sorption-nonrelated factors. If discrepancy between the two methods is caused by sorption-nonrelated factors, the use of one of the techniques may become inappropriate. For example, if the discrepancy is a result of differences in the S/W ratio, mixing differences, particle spacing, or homogenized batch samples, then the assumption that batch-determined parameters can be applied to dynamic systems will not be valid. On the other hand, if the discrepancy is caused by loss of sorbent particles through the column end retainer, column flow variations, or column flow channeling, then the use of a column technique for determination of sorption coefficients becomes questionable. Prior to answering such questions, identification whether the discrepancy is sorption-related or sorption-nonrelated becomes essential.

The purpose of this paper is to compare batch and column retardation coefficients and to assess the impact of the possible factors that are previously reported to cause discrepancy between the results of the two techniques. No literature was found that considered the impact of changes in soil organic matter on the degree of discrepancy between batch- and column-determined retardation coefficients. If the discrepancy is sorption-related, then the extent of deviation between retardation coefficients determined by the two techniques will be dependent on the amount of soil organic carbon. In this study, three aquifer materials of similar texture but different organic matter are utilized. Earlier studies focused on comparing the results of the two techniques using aquifer materials of low organic carbon content. Discrepancy between the two methods may not be noticeable on these materials. The aquifer materials employed in this study have relatively medium to high organic carbon.

3.2 Experimental Procedure

The same soils described in Chapter 2 are employed in this phase of study. The properties of the long soil-columns are presented in Table 3.1. Two nonionic organic compounds have been chosen: Benzene and dimethylphthalate (DMP). Both benzene and DMP were obtained from Aldrich Chemical Co. in pure forms (99+%). ^{14}C-labeled benzene mixed with cold benzene was used in all the experiments and was analyzed by liquid scintillation counting. DMP was analyzed by a Gilson HPLC using 50% water/50% acetonitrille as the mobile phase.

Table 3.1. Properties of packed columns

Soil	Organic carbon (%)	ρ g/cm^3	θ cm^3/cm^3
Oakville A	2.25	1.587	0.408
Pipestone	1.57	1.636	0.383
Oakville B	0.70	1.587	0.383

Table 3.2 shows some of the properties of the two compounds. Reported experimental and calculated values of octanol/water partition coefficient (K_{ow}) for benzene did not exhibit a wide range. It is not clear why the values for DMP vary significantly. Values in the upper range are usually the ones calculated based on established empirical relations (see Veith *et al.*, 1978). The ones in the lower range are commonly the ones that have been determined experimentally (Leyder and Boulanger, 1983). We determined the K_{ow} for the two compounds using a method similar to the one reported by Chiou *et al.* (1979). The only difference between their method and the method we utilized is the phase in which the compounds are initially dissolved. We found that the value for benzene is consistent with the one previously reported and that for DMP is close to the one reported in the lower range and it depends on the initial concentration in the aqueous solution.

Table 3.2. Some properties of the used organic chemicals

Compound	Molecular Weight	Solubility @ 20°C, mg/l	log K_{ow}	D_w(c) $\times 10^5$ cm²/s
Benzene	78	1780(a)	2.13(b)	1.1
DMP	194	1744(a)-5000(d)	1.53(e)-2.11(b)	0.78

(a) Verschueren, 1983.
(b) Veith *et al.*, 1978. K_{ow} is the octanol/water partition coefficient.
(c) McCarty, 1983. D_w is the molecular diffusion coefficient in the water phase.
(d) Callahan *et al.* (1979).
(e) Leyder and Boulanger (1983).

Sorption experiments were conducted using both batch and saturated-flow experiments. The experimental conditions for the saturated experiments, sample collection, and column size and material were the same as the one reported in Chapter 1. Among the saturated experiments, only pulse type experiments were conducted. The column experiments were conducted at several flow rates. Both benzene and DMP were originally dissolved into 0.01N $CaCl_2$ deaired, deionized water before injection into the columns. Initial concentration of the compounds was ≈30 mg/l (< 2.5% solubility limit). To inhibit biodegradation, 0.05 % sodium azide was dissolved in the prepared water solution. This concentration of inhibitor was recommended by Russell and McDuffie (1986) for DMP. The effectiveness of the biocide was verified by a recovery of 95% of the compounds when a mass balance was performed for the saturated experiment with the lowest flow rate. No adsorption, relative to tritium, of the two compounds to the column material was noticed when a saturated experiment using a 10-cm long column filled with clean glass beads was conducted. No evidence of hydrolysis of DMP was detected as DMP and phthalic acid, which has a different retention time in the HPLC method, were monitored in the effluent samples.

Batch experiments included kinetic studies and equilibrium isotherms. A 14-day sorption rate study was conducted to estimate the time required to achieve equilibrium for each sorbent/sorbate combination. In addition, 3-day and 14-day sorption isotherms were performed to evaluate potential differences resulting from the slightly asymptotic behavior observed in the rate studies. In the batch experiments a fixed S/W ratio of 1/1.5 g/ml was used. 15 g soil was added first to 25-ml Corex centrifuge tubes (volume when full ~ 28 ml) . For the rate experiments, ~22.5 ml of 0.01N $CaCl_2$ deaired deionized water containing 0.05% sodium azide and 30 mg/l benzene and DMP was added to each tube. The isotherms were set-up similarly, except that the initial concentration was varied over a range from about 5 mg/l to approximately 7% of solubility. After being filled with these solutions, the tubes were immediately capped with Teflon-lined screw caps and tumbled end over end for the desired period of time. Phase separation was accomplished by centrifugation 4000 rpm for 30 minutes. Aqueous samples collected using glass syringes were then analyzed for benzene and DMP concentration. The amount sorbed by soil was determined by difference. Blank tubes were tested to verify that no sorption to the tube material occurred. The exact amounts of soil, organic compound-free water solution and organic compound solution added to each tube were determined by difference in tube weight between subsequent steps. In addition, a 14-day sorption isotherm of benzene and DMP on Oakville A soil with a S/W ratio of 1/6.5 was also conducted to evaluate whether the solid/solution ratio affected sorption in this system.

3.3 Data analysis

Retardation coefficients for benzene and DMP on the three aquifer materials have been determined by batch and column techniques. In the batch technique, a sorption isotherm is constructed and the slope of the isotherm along with the properties of the soil aquifer, i.e. ρ and θ, are utilized to estimate R. In the column technique, a dimensionless breakthrough curve (BTC) of the chemical is used to determine R using: (1) the number of pore volumes at which $C=0.5Co$, (2) the area above the curve for a step input, or (3) the mean (first moment) of the BTC for a pulse input. The three cases are schematically shown in Figure 3.1 a, b, and c, respectively. Other column techniques that have been used for the determination of R are reviewed by Jacobson *et al.* (1984).

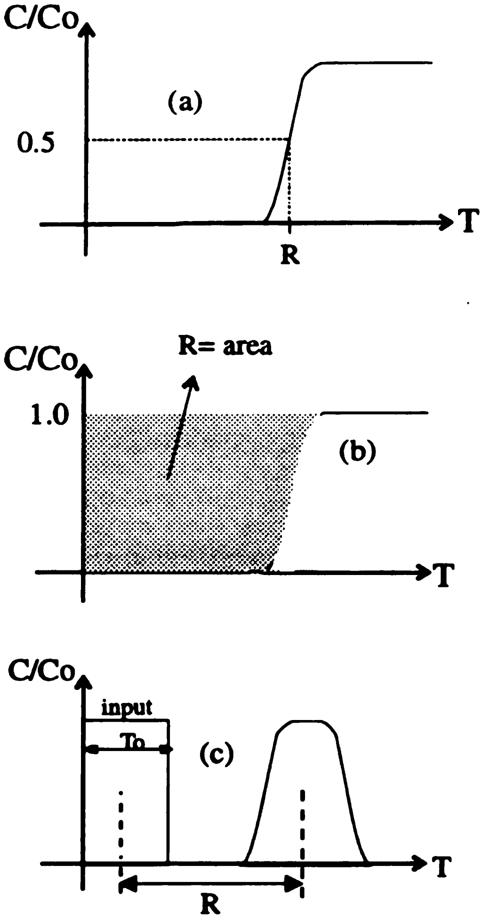

Figure 3.1 Retardation factors determined from column BTCs: (a) R=T @C/Co=0.5, (b) the area above the BTC, and (c) the mean of BTC.

Retardation coefficients computed by the above three column methods will be identical for symmetric BTCs (Bouchard *et al.*, 1988). For asymmetric BTCs , retardation factor determination using $C=0.5Co$ are inappropriate (Nkedi-Kizza *et al.*, 1987; Bouchard *et al.*, 1988). Asymmetry of BTC is caused by solute nonequilibrium which may either be transport- or sorption-related or both. Transport-related nonequilibrium is due to slow solute diffusion in an out of "immobile" water regions. Sorption-related nonequilibrium may be due to slow chemical reaction or slow diffusive transport within the sorbent or the intraparticle pores. For more details about nonequilibium transport models, the reader is referred to the excellent review by Brusseau and Rao (1989).

Retardation coefficients were determined for Oakville B and Oakville A soils using two column lengths (10.4 and 30.2 cm) and different pore-water velocities. Those for Pipestone soil were determined using only the 30.2-cm long column. For the short column, a step increase in the concentration has been used and the experiment was terminated when the relative concentration of the effluent solution reached ≈1.0. Retardation coefficients were then evaluated by measuring the area above the BTCs. For the long columns, a pulse input of approximately 2 pore volumes has been injected. The columns were then flushed with compound-free solution. Retardation coefficients were then determined using two methods: (1) the mean of BTC, (Valocchi, 1985):

$$R=\frac{\int_0^\infty CT\,dT}{\int_0^\infty C\,dT}-0.5\,T_o \tag{3.3}$$

where T_o is the number of pore volumes of benzene/DMP-solution injected, and (2) a curve fitting technique using the nonlinear, least squares optimization program CXTFIT of Parker and van Genuchten (1984) subject to the modification employed in Chapter 1. In the curve fitting technique, BTCs were analyzed using a bicontinuum model that assumes instantaneous sorption for some portion of the porous media and is rate-limited for the remainder. The governing nondimensional equations describing the bicontinuum nonequilibrium model have been presented elsewhere (see, for example, Brusseau, 1992;

Brusseau *et al.*, 1991). Input parameter values for D are the same as the ones determined for tritium for the same experimental conditions of this study (see Chapter 1).

3.4 Results and discussion

Several factors have been tested for possible effect of causing discrepancy between batch and column retardation coefficients including sorption nonequilibrium, sorption nonlinearity, sorption nonsingularity, S/W ratio, column channeling, and column residence time. The impact and direction these factors may have on obtaining different retardation factors from the two techniques along with experimental findings regarding their effects on the retardation of benzene and DMP are discussed below. Batch experiments are utilized to investigate the effect of batch nonequilibrium, sorption nonlinearity, and S/W ratio. Column experiments are employed to determine the effect of column nonequilibrium, flow channeling, sorption nonsingularity, and column residence time. Comparison between values of retardation coefficients obtained by the two techniques are discussed in the last part of this section.

3.4.1 Batch sorption experiments

Rate study:

Sorption distribution coefficients are generally determined by mixing a certain amount of soil with an aqueous solution containing the targeted compounds. If the mixing time was not enough for the compound in the solution to reach equilibrium with that on the solid phase, then the distribution coefficient would be underestimated. This will result in a higher retardation coefficients using a column technique compared to those from a batch sorption isotherm.

The results of a batch rate study for benzene and DMP on Oakville A and Oakville B soils are presented in Figure 3.2. The figure shows a rapid sorption rate at initial times

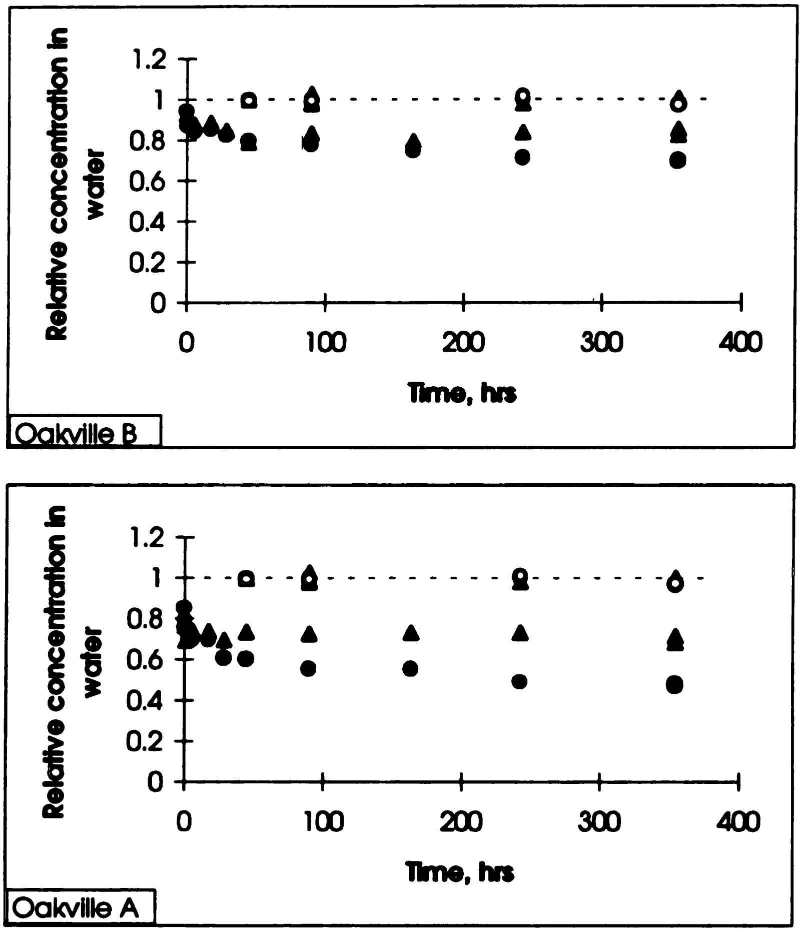

Figure 3.2 Batch rate study of Benzene (triangles) and DMP (circles). Open symbols for blank tubes.

and a much slower rate at later times. Similar behavior has been noticed by other researchers (Wu and Gschwend, 1986; Brusseau *et al.*, 1989). The figure also shows that at early times benzene and DMP are sorbed to the same extent and start to deviate (DMP being sorbed more) at later times. Benzene reached apparent equilibrium after approximately 40 hrs while it appeared that DMP continued to sorb over the entire mixing period. The slow continued sorption of DMP resulted in a greater total amount of this compound being taken up by the soil. This contradicts the expectation based on the K_{ow} values of the two compounds, i.e. higher or at least equivalent sorption of benzene, and suggests the possibility of another bonding mechanism, besides partitioning. Seip *et al.* (1986) also noticed higher retardation of DMP than benzene. They attributed this to the possible formation of hydrogen bonds between the oxygen atoms of DMP and the hydrogen atoms on the soil surface. Another possible mechanism is the formation of phthalate/soil organic matter complexes (Autian, 1973). Slow sorption of DMP may then be attributed to chemical nonequilibrium caused by the non-partitioning mechanism(s).

Sorption nonlinearity

The retardation coefficient defined by Eq. (3.1) is based on linear sorption behavior. Linearity is commonly observed at low aqueous concentrations, however, at high concentrations, nonlinear isotherms have been reported (Means *et al.*, 1980; Schwarzenbach and Westall, 1981). Means *et al.* (1980) used a Freundlich sorption model to describe the isotherms of polycyclic aromatic compounds. The Freundlich model is given as:

$$q = k C^{n} \tag{3.4}$$

where q is the amount sorbed at equilibrium with the aqueous concentration C, k and n are constants. A modified form of Eq. (3.2) results when the Freundlich model is used:

$$R = 1 + kn \frac{\rho k}{\theta} C^{n-1} \tag{3.5}$$

The implication of Eq. (3.5) is that retardation coefficients determined for a nonlinearly sorbed compound assuming a linear sorption isotherm will differ from those determined from a column BTC. The difference (higher or lower) depends on the value of *n* (less than 1 or greater than 1) and the injected solution concentration.

In this study sorption isotherms were determined for two different mixing times: 3 days and 14 days. The results using Oakville A and Oakville B soils are shown in Figure 3.3. For the 3-day sorption isotherm the two compounds are similarly sorbed on the low organic matter content soil, but deviate from each other on the high organic matter soil, with DMP showing slightly higher sorption than benzene. As noticed in the rate study, deviation between the two compounds becomes more clear at late times. This is also obvious for the 14-day isotherm. Figure 3.3 also shows that benzene reached equilibrium much earlier than DMP, since the 3-day and 14-day isotherms for benzene are identical.

The 14-day sorption isotherm data for the two compounds were fit to a linear sorption model with zero intercept. The values of the linear distribution coefficient (K_D) for the three soils and the associated correlation coefficient (r^2) are listed in Table 3.3. Although sorption linearity for the two compounds seems to be an appropriate assumption, the data were also fit to the Freundlich model.. The values of *k* and *n* for the nonlinear model are also shown in Table 3.3. The F-test was used to determine if a benefit is gained in selecting the nonlinear model over the linear one. The results of the F-test, as shown in Table 3.3, indicated some benefit in each case at the 95% confidence limit from fitting the isotherms data to the nonlinear model.

To determine retardation coefficients based on the batch sorption data, the nonlinear parameters have been utilized to obtain a linearized coefficient using the following equation (van Genuchten *et al.* 1977):

$$\int_0^{30} K_{\text{linearized}}\, C\, dC = \int_0^{30} k C^n\, dC \quad (3.6)$$

This requires that the areas under the isotherms over the range 0-30 mg/l for both the linearized and the nonlinear equations be the same. The value of 30 mg/l is selected because it is the concentration of injection fluid into the columns. Values of *R* estimated

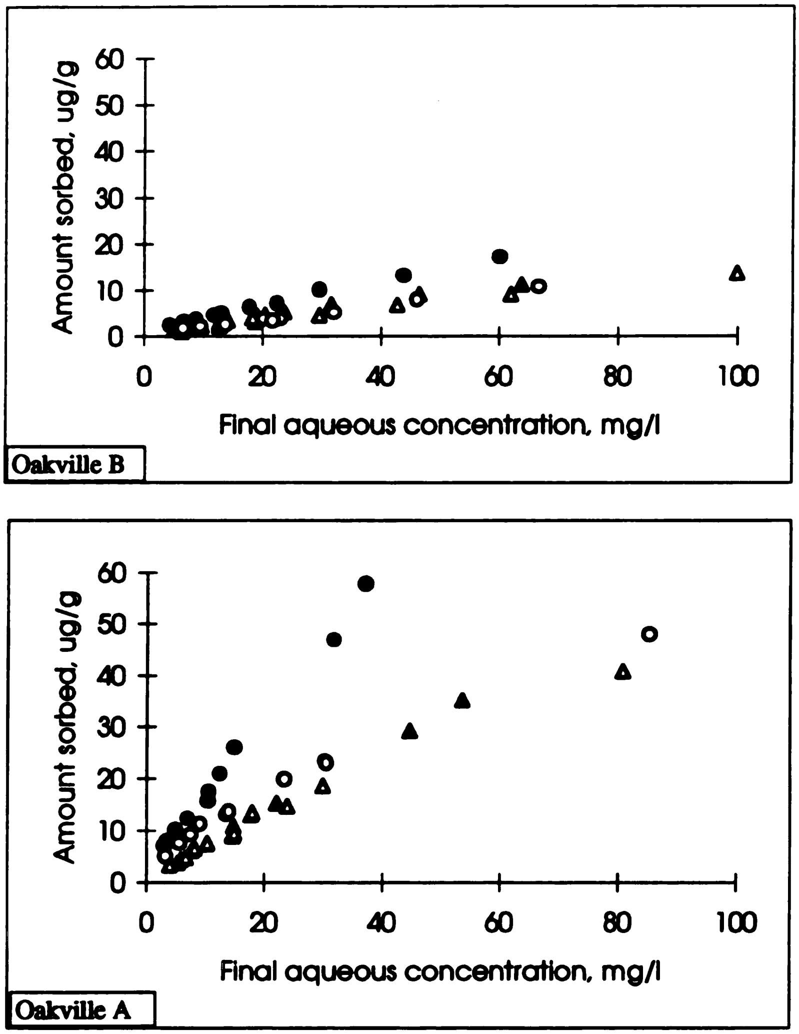

Figure 3.3 Batch sorption isotherm of DMP (circles) and benzene (triangles) after a 3-day (open symbols) and a14-day (closed symbols) mixing period

Table 3.3. Results of the linear and Freundlich type models

Soil	Compound	K_D	r^2	SSE	k	n	SSE	F	$F_{95\%}$
Oakville B	benzene	0.194	0.955	4.25	0.405	0.803	0.52	57.1	5.31
	DMP	0.303	0.967	6.87	0.579	0.825	0.77	63.1	5.31
Pipestone	benzene	0.518	0.966	13.8	0.695	0.866	7.24	7.25	5.31
	DMP	0.559	0.947	37.8	1.172	0.808	10.53	20.7	5.31
Oakville A	benzene	0.666	0.996	4.57	0.832	0.939	1.67	13.9	5.31
	DMP	1.554	0.987	35.02	2.119	0.906	16.82	9.31	5.31

SSE is the sum of square errors

using $K_{linearized}$, ρ and θ of the soil columns are listed in Table 3.4. In using the linear sorption coefficients instead of the linearized coefficients, it is estimated that the maximum error in R is about 12.0% for DMP on Pipestone and the average error is about 6%.

Table 3.4. Retardation coefficients based on batch results using the linearized sorption coefficient

Soil	Compound	$K_{linearized}$	R
Oakville B	benzene	0.229	2.03
	DMP	0.350	2.57
Pipestone	benzene	0.474	3.03
	DMP	0.674	3.88
Oakville A	benzene	0.697	3.71
	DMP	1.615	7.28

S/W ratio

Some investigators have suggested that the sorption distribution coefficient is dependent upon the S/W ratio used in the isotherm experiment, and possibly in the field as well (O'Conner and Connolly, 1980; Voice *et al.*, 1983; Di Toro, 1985). These investigators have all reported that K_D decreases with increasing solid concentration. The S/W in a soil column is about 4g/ml. This is much higher than those commonly utilized in batch experiments. The impact of this phenomenon on R would result in a lower retardation in columns when compared to those determined by batch techniques.

If such an effect is present and applicable to the system under study, one would need to employ a S/W ratio in batch studies similar to that found in a column in order to use the batch test for estimation of column retardation factors. This is difficult to accomplish, however, due to problems with phase separation at such high solids concentrations. To determine whether a solids concentration effect is operative for the solutes selected in this study, additional 14-day isotherms were conducted for both benzene and DMP at a S/W ratio of 1g/6.5ml and the Oakville A soil. These isotherms were compared to the corresponding isotherms with a S/W ratio of 1g/1.5 ml as shown in Figure 3.4. This data indicate that the S/W ratio does not effect the isotherm results for the two ratios used. This is also consistent with the findings of Lion *et al.* (1990) for phenanthrene using two S/W ratios (1:1 and ≈ 1:5 g/g).

3.4.2 Saturated column experiments

Column flow channeling

Flow channeling refers to the restriction of flow to some channels in the column, i.e. other available channels are much less conductive. Unless accounted for, flow channeling results in a shift to the left of a BTC, and therefore, a lower value of *R*. The presence of a flow channeling can be detected with the use of an ideal tracer for which *R* equals to 1.0. Values less than 1.0 are an indication of an inappropriate estimation of pore-water velocity based on the assumption that all the pores participate in the flow. Nkedi-Kizza *et al.* (1983) reported values of *R* for tritium, which is commonly thought to function as an ideal tracer, that are less than 1.0. They attributed that to the existence of a physical nonequilibrium created by the presence of mobile and immobile water regions.

Solution injected into the columns contained tritium in addition to benzene and DMP. Tritium data was analyzed and reported in Chapter 1. We found that the values of *R* ranged between 0.976-1.087. We concluded that there is no evidence of existence of immobile water in the columns. Therefore, any discrepancy between batch- and column-

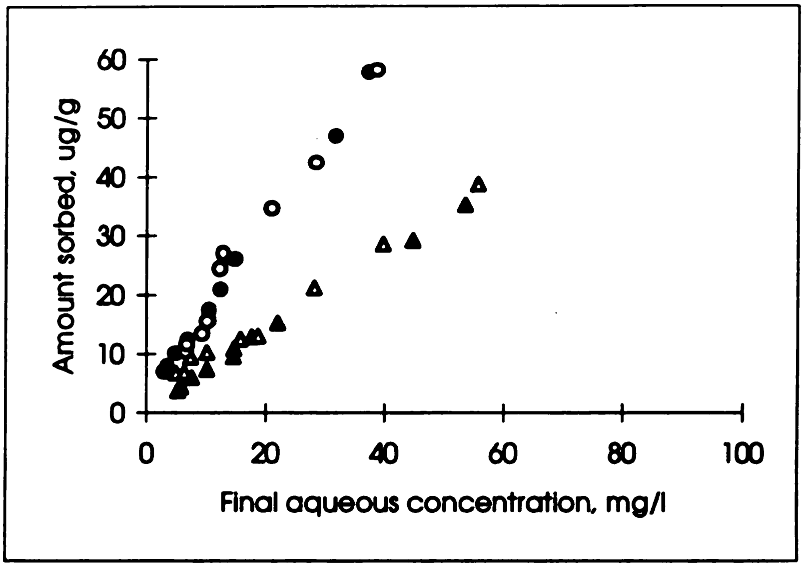

Figure 3.4 Sorption isotherm of DMP (circles) and benzene (triangles). Closed symbols for S/W ratio =1/1.5 and open ones for S/W ratio= 1/6.5

determined retardation coefficients must be attributed to other factor(s) but flow channeling.

Residence time in the column

Effect of hydraulic residence time in the column on the value of retardation coefficient for benzene and DMP has been investigated. Hydraulic residence time is a function of pore-water velocity and column length. The impact of the two parameters on *R* is presented below.

Values of *R* estimated by moment analysis (R_{moment}) and those by curve fitting (R_{fit}) for the long column experiments are reported in Table 3.5. Values in parenthesis are the 95% confidence limits as estimated by CXTFIT. Table 3.5 shows that the values of *R* determined using moment analysis are lower than the corresponding values determined by curve fitting. In addition, the values of *R* determined by moment analysis appear to increase with the reduction in pore-water velocity. The values of *R* determined by curve fitting, except for those of DMP on Oakville A soil, are not, however. Several investigators reported a leftward shift of BTC as the velocity increases or an apparent velocity dependence (inverse relation) of *R* (van Genuchten *et al.*, 1974; Schwarzenbach and Westall, 1981; Bouchard *et al.*, 1988) which is generally regarded as a result of nonequilibrium in the column. Brusseau *et al.* (1991) and Brusseau and Rao (1989) argued that the velocity dependent *R* is an artifact and that the first temporal moment is independent of the extent of nonequilibrium in the system. Therefore, the true value of *R* is independent of velocity, and the dependency of R determined using moment analysis is, in actuality, an artifact. There are several conditions, however, under which the use of temporal moment analysis may not yield the true value of *R*: (1) extreme nonequilibrium (Brusseau *et al.*, 1991), (2) experimental artifacts such as insufficient collection of effluent samples from soil column in a manner that not all the mass injected is accounted for, and (3) analytical limitations where it is difficult to accurately determine the contribution of peak tailing which is marginally greater than the analytical baseline (Lion *et al.*, 1990). Each of the above conditions would result in underestimation of the column retardation.

For all the experiments on Oakville B soil, effluent samples were collected until the concentration of the compounds reached its detection limit and a mass balance was verified. Yet, differences between the two determined values of *R* exist. Hence, discrepancy cannot be due to failure to account for all the mass injected. On the other hand, inspection of Table 3.5 indicates that existence of extreme nonequilibrium is likely to be the cause of the discrepancy, since the deviation between the values of *R* determined by the two methods narrows down as the velocity decreases. This is expected since the extent of nonequilibrium will be less at lower velocities.

Table 3.5. Retardation coefficients determined from BTCs using first moment analysis and curve fitting technique

				Benzene		DMP	
Exp.	v_o, cm/hr	T_o	D, cm^2/hr	R_{moment}	R_{fit}	R_{moment}	R_{fit}
SA1	31.55	1.95	20.87	2.14	2.46 (±0.14)	2.32	2.95 (±0.16)
SA2	6.3	1.96	5.37	2.16	2.78 (±0.84)	2.83	3.28 (±0.25)
SA3	0.62	1.91	0.22	2.27	2.73 (±0.17)	3.35	4.03 (±0.19)
SP1	33.6	2.08	18.78	2.23	2.76 (±0.34)	2.2	2.83 (±0.29)
SP2	6.72	2.09	2.90	2.27	2.74 (±0.19)	2.33	2.92 (±0.21)
SP3	0.67	2.05	0.16	2.41	2.75 (±0.14)	2.68	2.77 (±0.06)
SB1	36.47	2.18	18.04	1.37	1.64 (±0.18)	1.50	1.85 (±0.17)
SB2	7.29	2.20	3.27	1.36	1.62 (±0.16)	1.51	1.70 (±0.06)
SB3	2.17	2.17	0.20	1.52	1.65 (±0.03)	1.71	1.73 (±0.04)

Velocity dependent *R* for sorption of DMP on Oakville A soil, even with the use of a model that incorporates the effects of nonequilibrium, may signify the existence of an additional sorption process that is observable when relatively slow velocities are used. Alternatively, the observed increase in retardation at lower velocity could be due to inadequacy of the used nonequilibrium model to describe the effect of velocity on the BTCs. Schwarzenbach and Westall (1981) observed a similar trend and suggested the use of a continuous distribution of mass transfer coefficients. The different values of mass transfer coefficients for the case where sorption rate-limitation is due to diffusive transport, as interpreted by Schwarzenbach and Westall (1981), would correspond to different diffusion path lengths.

Sorption nonsingularity

Discrepancy between batch- and column-determined retardation coefficients may result due to improperly interpreting column data. For example, if the applied boundary conditions did not permit the effluent relative concentration to reach 1.0 due to relatively small pulse size or extensive tailing, then retardation coefficients are either determined using the number of pore volumes at C/Co=0.5 or temporal moment analysis. Constraints on using the former method has been discussed. The later method considers both sorption and desorption paths. If sorption nonsingularity exists, then retardation coefficients from batch technique, where only sorption path is usually considered, will be different from their column counterparts (assuming other factors to be ineffective). Nonsingularity has been noticed in the work of van Genuchten *et al.* (1977) for 2,4,5-T. van Genuchten *et al.* (1977) found that the linearized K_D desorption > K_D adsorption. If this is the behavior for DMP and benzene, then one would expect higher retardation based on temporal moment analysis of a pulse input compared to the ones estimated from the area above the BTC.

Retardation coefficients for DMP on Oakville A soil for the two column lengths are presented in Figure 3.5a. The values for the long column experiments are those determined by temporal moment analysis and the values for the short column are the ones determined from the area above the curve. Figure 3.5a shows that the values for the short column are higher than those for the long column at comparable pore-water velocity. There is a possibility that the behavior noticed in Figure 3.5a is due to different column lengths used rather than sorption nonsingularity. To investigate this point, the values of R determined using number of pore volumes at C/Co=0.5 for the two columns are compared. The results are presented in Figure 3.5b and indicated that the values of R for

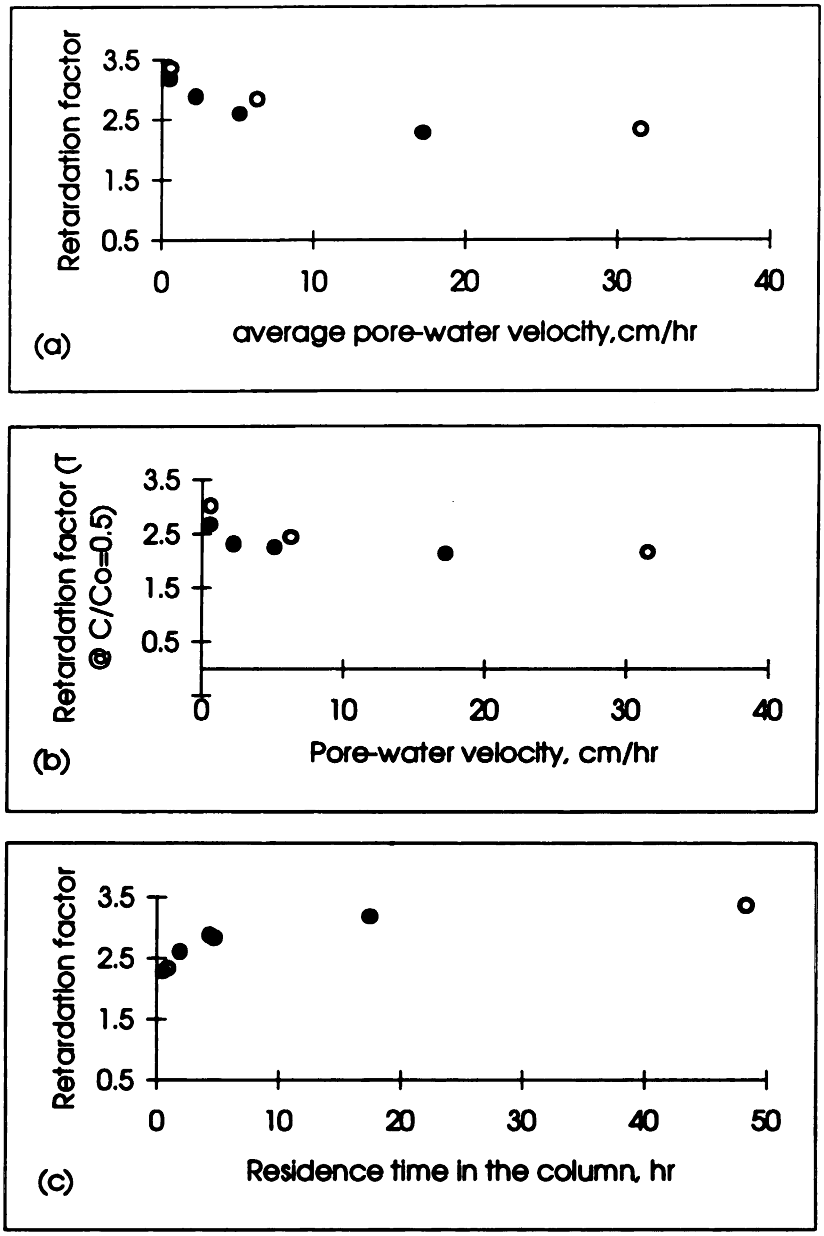

Figure 3.5 Retardation factors as influenced by pore-water velocity and hydraulic residence time for DMP on Oakville A soil. Closed symbols for short column and open ones for long column.

the long column are still higher than those for the short ones. Therefore, the difference in *R* cannot be attributed to sorption nonsingularity. Brusseau (1992) also observed that sorption of 1,4-dichlorobenzene, tetrachloroethene, *p*-xylene and naphthalene on three aquifer materials is not affected by nonsingulatrity. The other possibility is a dependency of *R* on the column length. To explore this, values of *R* shown in Figure 3.5a are plotted Vs. the residence time as illustrated in Figure 3.5c. Clearly, there is no difference between the values of *R* for the two column lengths at the same residence time.

3.4.3 Batch/column retardation coefficients

The main purpose of this study is to compare between batch-determined retardation coefficient and those determined using column BTCs. We will compare between distribution coefficients listed in Table 3.4, where sorption nonlinearity has been accounted for, with those corresponding to the values of *R* determined from curve fitting for the column experiment (Table 3.5). The reason for comparing between distribution rather than retardation coefficients is to exclude the effect of different bulk density and moisture content among the columns. The values of *R* from the column were averaged for each sorbate-sorbent combination, except that for DMP on Oakville A soil where the value at the lowest flow rate was considered. This reduces the impact of hydraulic residence time on *R* and allows closer comparison with the batch-determined values for DMP on Oakville A soil.

Figure 3.6 shows the percentage difference in $K_{linearized}$ for the two compounds using the three soils. In the figure *Kb* and *Kc* refer to batch- and column-determined linearized distribution coefficients, respectively. Figure 3.6 reveals that even after accounting for sorption nonlinearity and hydraulic residence time there is still a difference between batch and column distribution coefficients. The one determined from the batch are higher by an average of 46% for benzene and 90% for DMP than those from the column. Also, the difference in the deviations between the two compounds is similar (about 40%), and is independent of the amount of soil organic matter.

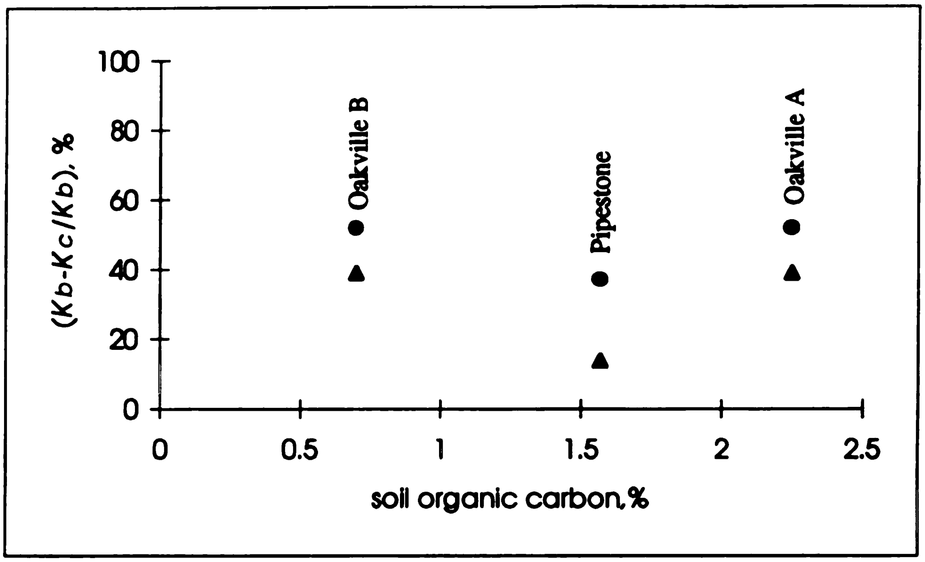

Figure 3.6 Comparison between batch/column sorption distribution coefficients for aquifer materials with different organic carbon content. Circles for DMP and triangles for benzene.

Figure 3.6 also shows that for the soil with intermediate carbon content, the difference between the distribution coefficients is lower than that for the soils with low and high organic matter. For the latter soils, the difference is identical for each compound; 61% for benzene and 107% for DMP. This makes it difficult to draw any conclusion regarding whether there is a trend in changes in distribution coefficients with changes in soil organic carbon. However, similar differences in deviations between the two compounds using the low and high organic matter soils suggests an independence on soil organic matter.

Among the other possible factors that cause discrepancy between batch- and column-determined retardation coefficients which are not investigated here are: loss of sorbent particles through column end retainer (MacIntyre *et al.*, 1992) and effective accessibility to sorption sites in batch as compared to column (Schweich *et al.*, 1983; Celorie *et al.*, 1989). Loss of soil material from the column will have an impact if either loss of particles occur or the aqueous solution is a good extractor of the soil organic matter. Water solution are not good extractor of soil organic matter (Hayes, 1985). On the other hand, loss of soil particles from the column is highly unlikely given the direction in which the column experiments were conducted; starting with the one that has the highest flow rate and ending with the one that has the lowest. In this direction, one would expect a decrease in *R* with the decrease in pore velocity if the sorbent is lost during the experiments. Our results do not show this to be the case.

Although not proven experimentally, mixing differences between the two techniques becomes a potential explanation for this discrepancy. It is possible that mixing in a batch tube either created sorption sites that are not accessible during transport through the soil column (Schweich *et al.*, 1983) due to soil abrasion, or reduction in soil particle spacing results in less surface area which is accessible by solute for sorption (Celorie *et al.*, 1989). Experimental confirmation of the above factor is needed. A soil column can be equilibrated with a certain aqueous concentration, then soil samples from the column are mixed in batch tubes with aqueous solution in which the concentration of the compound is equal to equilibrium concentration of the aqueous phase in the column. A decrease in the aqueous-phase concentration after mixing would be an indication of further sorption due possible sorption sites that are inaccessible during column transport. Further investigation to elucidate whether the cause of this discrepancy is soil abrasion or a result of reducing particle spacing is needed. We propose applying the same mechanical forces used for batch mixing to the intended-to-be-used soil samples prior to packing in the soil column. Similarities in batch- and column-determined retardation coefficients would indicate that the originally noticed discrepancy is due to mixing differences. If discrepancy still exists, then the cause will be due to reducing particle spacing. Had this been the case, accurate determination of retardation factors in the laboratory would necessitate subjecting soil packed columns to similar confining pressures as those present in the field. Indeed, experiments where column-determined retardation factors as a function of confining pressure may serve as a direct verification if particle spacing is the cause of discrepancy between retardation coefficients obtained by batch and column techniques.

3.5 Summary and conclusion:

The impact of previously reported factors that cause discrepancy between batch- and column-determined retardation coefficients have been assessed. Batch and column experiments on three sandy aquifer materials of 0.7, 1.57, and 2.25% organic carbon content have been conducted. Variations in soil organic matter allows determination whether the discrepancy is sorption-related or not. Batch-determined retardation coefficients for benzene and DMP are higher than their column-determined counterparts. Sorption nonequilibrium, S/W ratio, sorption nonsingularity, and column flow channeling are not the cause of this discrepancy. Sorption nonlinearity has a minor impact. Column hydraulic residence time has a significant impact on the value of retardation coefficient for DMP using the high organic matter soil but not on the other sorbate-sorbent combinations.

After accounting for sorption nonlinearity and considering the value of *R* at the lowest velocity when residence time was a factor, batch-determined distribution coefficients were 16-107% higher than column-determined values. The extent of deviation between the two values was independent of the amount of soil organic matter. This discrepancy may be attributed to mixing differences between the two techniques. Further investigation is proposed to resolve this issue.

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CHAPTER 4

RETARDATION OF NONIONIC ORGANIC COMPOUNDS UNDER UNSATURATED FLOW CONDITIONS

4.1 Introduction

The retardation coefficient (*R*) represents the average speed of contaminant transport in subsurface environment relative to that of groundwater. This parameter is usually expressed as:

$$R = 1 + \frac{\rho \, K_D}{\theta_w} \tag{4.1}$$

where, K_D is the linear sorption distribution coefficient, ρ is the soil bulk density, and θ_w is the volumetric water content. Retardation coefficients can be estimated using a value of K_D determined in a batch experiment and a knowledge of the bulk properties of the aquifer. This approach has been widely used for contaminant transport under saturated conditions, although recent evidence suggests that batch distribution coefficients may not translate directly to dynamic conditions (see Chapter 3). This approach has also been used for unsaturated conditions, however, there is no consensus on the effect of water content on *R*.

We can identify three potential causes for deviation of the value of *R* from that determined when the soil is fully saturated. First, the value of K_D determined using a traditional sorption isotherm or saturated soil columns might be different from that when the soil is partially saturated. It is still unclear how the sorptive capacity of the soil changes above a moisture content which corresponds to a surface coverage. Chiou and Shoup (1985) found that, beyond a monolayer of water coverage, sorption will maintain a level which is independent on further increase in water content. The above findings, however, are in contrast with the findings of Peterson *et al.* (1988) for the sorption of trichloroethylene (TCE) on a porous aluminum oxide surface coated with humic acids. Peterson *et al.* (1988) observed a TCE sorption coefficient of about 2 and 3 orders of magnitude higher than that found under fully saturated conditions at water surface coverage that corresponds to 1.6 and 2.4 monolayers of water, respectively. They attributed the increase in K_D to either the possibility of existence of very small fractions of dry sites or that moist surfaces, which is completely covered with water, have a sorptive binding strength greater than that when all the pore space is saturated with water.

The specific mechanisms responsible for the sorption of organic compounds at relative humilities above what is required to provide surface coverage by at least one monolayer of water remain unclear. Call (1957) suggested that sorption of ethylenedibromide on wet soils is attributed to dissolution in sorbed water films and adsorption at the gas-liquid interface. In contrast, Chiou and Shoup (1985) postulated that hydrated soils behave as a dual sorbent in which the mineral surface acts as a conventional solid adsorbent and the organic matter as a partition medium. Ong and Lion (1991) concluded that that sorption of TCE vapor at field capacity can be accounted for by dissolution of the compound in the water bound to the soil surface and partitioning into the soil organic matter. Pennell *et al.* (1992) suggested a multimechanistic approach to account for vapor sorption of *p*-xylene in the unsaturated zone that includes: adsorption on mineral surfaces, partitioning into the soil organic matter, dissolution into sorbed water films, and adsorption on the gas-liquid interface.

The second potential cause for deviation is that most of the work dealing with sorption of NOCs in the unsaturated zone was conducted under static conditions (batch experiments) and at saturation that corresponds to or below field capacity. Little is known about the effect of soil moisture content on sorption of NOCs under dynamic conditions. Under these conditions, it is the value of R (not K_D) that can directly be determined from a column BTC. Determination of K_D using the measured value of R requires knowledge of the ratio (ρ/θ_w) at that saturation. This ratio defines the ratio of the amount of solid that actively participated in the sorption process to the volume of flowing water present within a unit volume of the aquifer. Although it is straightforward to determine the value of this ratio under saturated conditions, it is not known how this ratio is altered upon desaturation. As the soil is desaturated, the larger pores are known to be emptied first. An element which contains these pores would have lower density than one which contains only smaller pores. The impact of this is a higher solid/water ratio within a volume containing the small pores, and consequently a greater amount of contaminant sorption. This is based on the assumption that sorption is restricted to solid grains constructing the pore channels that contains the flowing water. It is possible that solid grains constructing other pore channels would also act as sorbents.

A third possible cause must be considered for volatile NOCs which can partition into the air phase under unsaturated conditions. Assuming no advective air movement, and equilibrium sorption and volatilization, the 1-D transport equation of dissolved VOCs in terms of liquid-phase concentration can be written as (Baehr, 1987):

$$(1 + \frac{\theta_a K_H}{\theta_w} + \frac{\rho\ K_D}{\theta_w})\frac{\partial C}{\partial t} = (D + \frac{K_H D_a}{\theta_w})\frac{\partial^2 C}{\partial x^2} - v_o\frac{\partial C}{\partial x} \qquad (4.2)$$

$$\frac{\partial C}{\partial t} = \frac{1}{R}[(D_{eff})\frac{\partial^2 C}{\partial x^2} - v_o\frac{\partial C}{\partial x}] \qquad (4.3)$$

where, D_{eff} is an overall effective dispersion coefficient, D is the hydrodynamic dispersion coefficient, D_a is the effective diffusion coefficient in the air phase, θ_a is volumetric air content, θ_w is volumetric moisture content, and R is a measure of retardation. The contribution of volatilization to retardation depends, therefore, on the volumetric air content (θ_a) and Henry's coefficient (K_H).

The objective of this study was to investigate the role of saturation on the retardation of NOCs. Miscible displacement experiments on packed soil columns were performed. To our knowledge, this study is the first to report the effect of saturation on retardation under dynamic conditions. A volatile and a nonvolatile organic compound were employed. The nonvolatile compound was used to determine the impact of changes in K_D and the ratio (ρ/θ_w) on changes in R. Inclusion of the volatile compound then allowed evaluation of the impact of volatilization on retardation. Three soils with different organic matter content were utilized.

4.2 Materials and methods

Three natural nonaggragated soils were employed in this study. The soils have similar textures but the organic carbon content on these soils varied: 0.7% for Oakville B, 1.57% for Pipestone, and 2.25% for Oakville A soil. Other properties of the soils used can be seen in Table 2.2. Dimethylphthalate (DMP) was chosen as a nonvolatile organic compound and benzene as a volatile one. ^{14}C-labelled benzene was analyzed by liquid scintillation counting, and DMP was analyzed by HPLC. Some of the physical properties of the two compounds were described previously (Table 3.2).

Pulse-type miscible displacement experiments were conducted at four levels of saturation. Uniform saturation along the length of the packed soil columns was achieved by adjusting the flow rate and the applied suction at the bottom of the column such that equal tensiometer readings at 1/3 and 2/3 the depth of the column were achieved. A pulse input of 1.38-2.56 pore volumes containing benzene and DMP at a concentration of approximately 30 mg/l was injected. The columns were then flushed with compound-free groundwater. The experimental conditions, characteristics of the injected solution, column setup, and sample collection were the same as the one reported in Chapter 2. The experimental conditions are also listed in Table 4.1.

4.3 Data analysis

Retardation coefficients for DMP and benzene at each level of saturation were determined using (1) first temporal moment analysis (Valocchi, 1985):

$$R = \frac{\int_0^\infty CT\, dT}{\int_0^\infty C\, dT} - 0.5\, T_o \tag{4.4}$$

where, C is the normalized effluent concentration, T is the pore volume, and T_o is the number of pore volume of solution containing tracers that was injected into the column, and (2) a curve fitting technique using the nonlinear, least squares optimization program CXTFIT of Parker and van Genuchten (1984) subject to the modification employed in Chapter 2. In the curve fitting technique, BTCs were analyzed using a bicontinuum model that assumes instantaneous sorption for some portion of the porous media and rate-limited sorption for the remainder. The governing nondimensional equations describing the bicontinuum nonequilibrium model have been presented elsewhere (see, for example, Brusseau, 1992; Brusseau *et al.*, 1991). Input parameter values for D are the same as those determined for tritium, as reported in Chapter 2, for the same experimental conditions employed in this study. In the case of benzene, the value of D, R, the fraction of instantaneous sorption sites (β), and the Damkohler number (ω) were determined by curve fitting for all the experiments except those with saturation> 95%. For the experiments with saturation > 95%, D of tritium was utilized, and the other three parameters were determined by curve fitting. This was done since the contribution of diffusive transport in the air phase above that saturation, as will be shown latter, can be neglected.

The value of R determined by the above two approaches and the amount of compound recovered are listed in Table 4.1 for DMP and Table 4.2 for benzene. The amount of tracer recovered is estimated by dividing the area under the BTC by the number of pore volumes injected (T_o). It is obvious that the amount of tracer recovered decreases with an increase in soil organic matter content. This could be due to not collecting effluent samples over longer period of time. Although the experiments were terminated when the concentration in the effluent was ≤ 0.06 C_o, some of the tracer was not accounted for because of the long tailing noticed in the BTCs of benzene and DMP on Pipestone and

Oakville A soils. Extensive tailing could be due to slow diffusion out of the sorbent. An example of this behavior is presented in Figure 4.1. To evaluate the effect of tailing the curve was extended to $C/C_0 = 0$ using the slope of the last three data points. The area under the extended portion is equivalent to 11.37% of the mass of the compound. This compares favorably with the 15% of the mass that was not accounted for by only considering the main portion of the pulse (recovery of DMP for experiment USA3 was 85% in Table 4.1). The impact of not accounting for this mass would be a reduction in the value of *R* determined by moment analysis. For the above example, an 11% increase in *R* results when the extended portion is considered. Therefore, the values of *R* determined by moment analysis would be slightly higher if the total mass is accounted for. It is not surprising, therefore, to see that the retardation coefficients determined by curve fitting are higher than those determined by moment analysis. Other factors that would lead to

Table 4.1 Experimental conditions and values of *R* for DMP under unsaturated conditions

Exp.	v_w, cm/hr	*S*, %	T_0	*D** for ^{3}H cm^2/hr	mobile water*	*R* *1st moment*	*R* *fit*	Recovery
Oakville B								
USB1	18.74	95.6	2.16	8.05	0.98	1.36	1.55	0.99
USB2	9.18	71.0	2.56	7.85	0.92	1.59	1.57	0.99
USB3	2.73	50.6	1.69	2.09	0.94	1.98	2.21	0.94
USB4	1.01	47.8	2.21	0.71	0.90	2.46	2.88	0.94
Pipestone								
USP1	17.50	96.0	2.12	11.84	___	2.12	2.64	0.91
USP2	8.40	72.0	2.42	14.42	___	2.71	3.36	0.90
USP3	2.56	55.4	1.64	2.80	___	4.07	4.55	0.89
USP4	1.03	43.6	2.30	0.67	___	5.34	5.86	0.93
Oakville A								
USA1	16.51	95.5	1.94	12.16	___	2.32	2.83	0.89
USA2	2.27	78.0	2.08	10.73	___	2.55	3.38	0.87
USA3	2.16	58.5	1.38	3.80	___	4.19	5.46	0.85
USA4	0.81	52.2	1.80	0.76	___	5.40	7.29	0.82

* As reported in Table 2.6

erroneous *R* determined by moment analysis have been discussed in Chapter 3. Hence, the values of *R* determined by curve fitting were used in all subsequent analyses.

Table 4.2 Values of *R* for benzene under unsaturated conditions

Exp.	**Recovery**	***R*** ***1st moment***	***R*** ***fit***	D_{eff}* cm^2/hr	D_{eff} (Eq.3) cm^2/hr
Oakville B					
USB1	0.93	1.36	1.63	(8.05)	8.051
USB2	0.95	1.59	1.58	11.40	9.05
USB3	0.94	2.05	2.07	13.14	32.69
USB4	0.90	2.37	2.94	16.44	44.36
Pipestone					
USP1	0.89	2.22	2.87	(11.84)	11..841
USP2	0.93	2.81	3.33	6.54	16.066
USP3	0.94	3.97	4.10	8.23	19.85
USP4	0.88	4.43	5.64	8.88	76.67
Oakville A					
USA1	0.91	2.08	2.57	(12.16)	12.161
USA2	0.90	2.35	3.14	6.40	11.32
USA3	0.89	3.45	4.53	5.28	15.43
USA4	0.87	3.99	5.34	7.10	26.98

***Values as determined by curve fitting. Values in parenthesis are those of tritium reported in Table 2.6**

To account for the immobile water detected in columns packed with Oakville B soil as noticed in Chapter 2, retardation coefficients were normalized relative to those of tritium by dividing the value of *R* by the percentage of mobile water. In the discussion that follows, the normalized retardation coefficients are used and are still denoted as *R*.

In the unsaturated experiments, the moisture content and flow velocity are coupled. In order to be able to identify the effect of saturation on *R*, knowledge of the impact of flow velocity, if it exists, is essential. Several investigators reported a leftward shift of BTCs as the velocity increased or an apparent velocity dependence (inverse

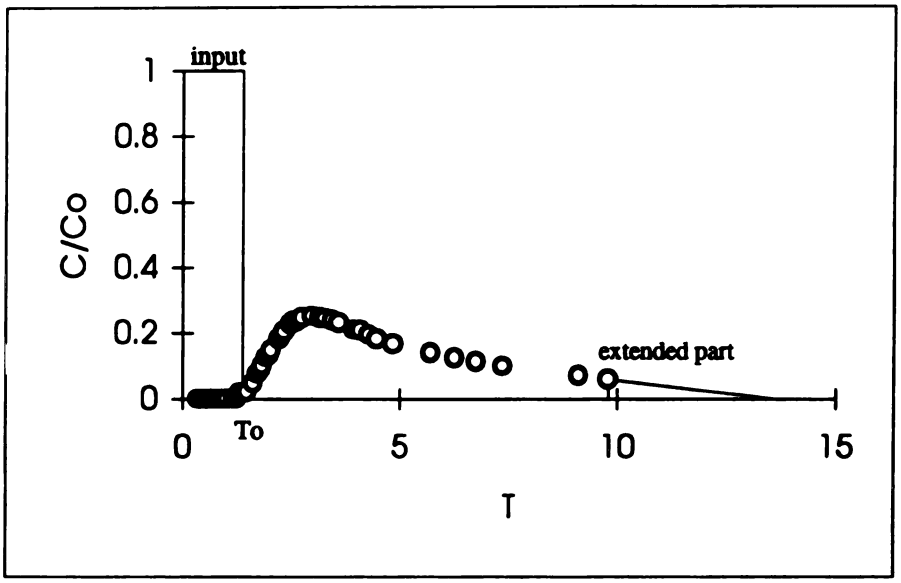


Figure 4.1 BTC of DMP on Oakville A subject to the conditions of experiment USA3.

relation) of *R* (van Genuchten *et al.*, 1974; Schwarzenbach and Westall, 1981; Bouchard *et al.*, 1988). In Chapter 3, we determined retardation coefficients for benzene and DMP using the same soil columns utilized in this study with a range of average pore-water velocity that covers the range of pore-water velocity of the experiments reported here. We found that *R* is not a function of velocity for the different sorbate-sorbent combinations except for the combination of DMP on Oakville A soil. The values of *R* at various pore-water velocities under saturated conditions as reported in Chapter 3 were adopted in this study.

4.4 Results and discussion

Three factors may cause deviations between *R* determined when the soil is fully saturated and those when the soil is partially saturated: (1) changes in the value of K_D, (2) changes in the solid/water ratio, and (3) volatilization into the air phase. DMP, a nonvolatile NOC, was used to assess the impact of the first two factors, and benzene was employed to investigate the role of volatilization on retardation. The data for DMP are discussed in the following section and those for benzene are presented in the subsequent one.

4.4.1 Effect of saturation on retardation

Table 4.1 shows that the values of *R* determined by curve fitting increase with reductions in saturation. The same trend was not noticed, except for DMP on Oakville A soil, under saturated conditions. For DMP on Oakville A, the values of *R* determined under saturated and unsaturated conditions as a function of pore-water velocity are plotted in Figure 4.2. The figure shows that the increase in *R* as the soil is desaturated is higher than would be expected as an effect of velocity, especially at low saturation.

The percentage increase in *R* over that expected for saturated conditions is plotted against saturation in Figure 4.3. Values of R under saturated conditions were estimated by linear interpolation for the same pore-water velocity. It can be seen that a decrease in saturation caused an increase in retardation, up to approximately 100% increase at the lowest saturation (40%). A linear function was used to fit the data in Figure 4.3 excluding those of US1, since the saturation for these experiments was higher than 95%. The best fit was found to be:

$$\begin{aligned} \frac{\Delta R}{R_{sat}} &= -2.81S(\%) + 212.7 \qquad && S \leq 74\% \\ &= 0 && S > 74\% \end{aligned} \tag{4.5}$$

with a correlation coefficient of 0.8. The line intersects the x-axis at a saturation of 0.74. We assumed that there was no increase in *R* above that saturation. The above relationship (Eq.(4.5)) is presented as a solid line in Figure 4.3. It is interesting to note that the data from all three soils is reasonably well represented by this relationship, suggesting that changes in *R* with saturation are not related to the organic matter content.

Unfortunately, the use of packed soil columns does not directly allow distinguishing if the increase in *R* is due to an increase in K_D or an increase in the solid/water ratio upon desaturation. When desaturated, the solid/water ratio may fall within two limits. The lower limit is equivalent to the one used when the soil is saturated. This means that the reduction in the moisture content is accompanied by similar reduction in the amount of soil that actively participates in the sorption process. In this case, the ratio (ρ/θ_{wsat}) where θ_{wsat} is the saturated water content maintains the same value. As we discussed in the introduction section, one would expect a solid/water ratio which is higher than its value under saturated conditions even if sorption is restricted to those solid walls constructing the active pores. Therefore, the assumption upon which the lower limit is established could be considered conservative. The upper limit would be to assume that all the solids in the column are active as sorbents, regardless of saturation. In this case, the reduction in saturation is not accompanied with a reduction in the amount of sorbent, and the solid/water ratio would be ($\rho/S\theta_{wsat}$). One might visualize that under this assumption

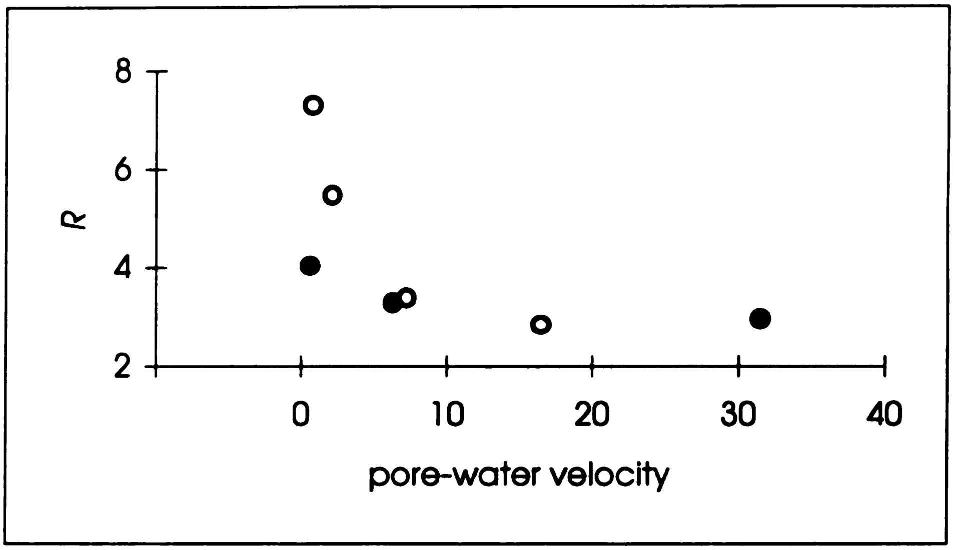


Figure 4.2 Retardation coefficients of DMP on Oakville A soil under staurated (closed symbols) and unsaturated (open symbols) flow conditions.

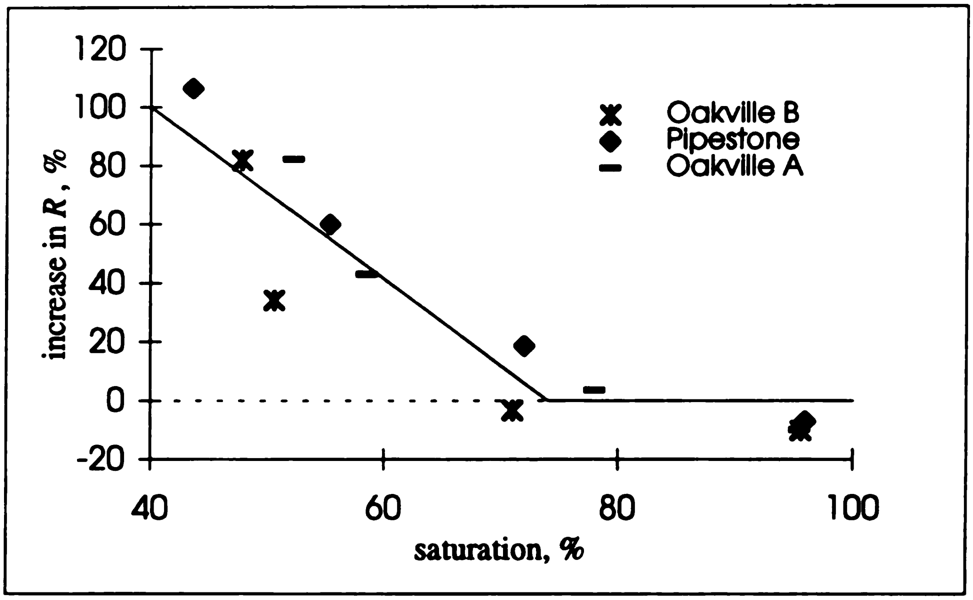


Figure 4.3 Percentage increase in *R* for DMP as a function of saturation.

the solid grains constructing the empty pore channels have a stagnant water film which is connected to the mobile water in the small pores. Accessibility of the compound to the grains in the large pores occurs through diffusion of the compound from the mobile water into the stagnant water covering these grains.

If it is assumed that sorption under unsaturated conditions is restricted to solid walls constructing the water-filled pores, and that the average bulk density of an element surrounding these pores does not deviate from that of the whole soil column, then the increase in R should be a result of an increase in K_D. However, if the average bulk density of the element surrounding the water-filled pores was higher than that of the soil column, or the solid grains constructing the large pores are active sorbents, then the above conclusion might not be valid unless the increase in R was higher than what would be expected based on full participation of all solid grains in the sorption process. Let us consider the case where all the solid grains actively participate in sorption, i.e. the upper limit of solid/water ratio. In order to compare between K_D under saturated and unsaturated conditions, the data needs to be normalized to the same solid/water ratio. For convenient comparison, we plotted $(R\text{-}1)S$ as a function of velocity as shown in Figure 4.4. The figure shows that the values for the unsaturated experiments are very close to the ones when the soil is saturated. For all the unsaturated experiments, the values are less than or equal to the saturated values, except at the lowest saturation where the values for the unsaturated case are slightly higher than the saturated ones. Therefore, if the assumption of full participation of all the solids in the sorption process is valid, one cannot then attribute the increase in R under unsaturated conditions to an increase in the value of K_D.

4.4.2 Effect of volatilization on retardation

The values of R for benzene determined by curve fitting are compared to the average values of R under saturated conditions. The percentage increase in R as a function of saturation is presented Figure 4.5. As was found for DMP, the deviations between the

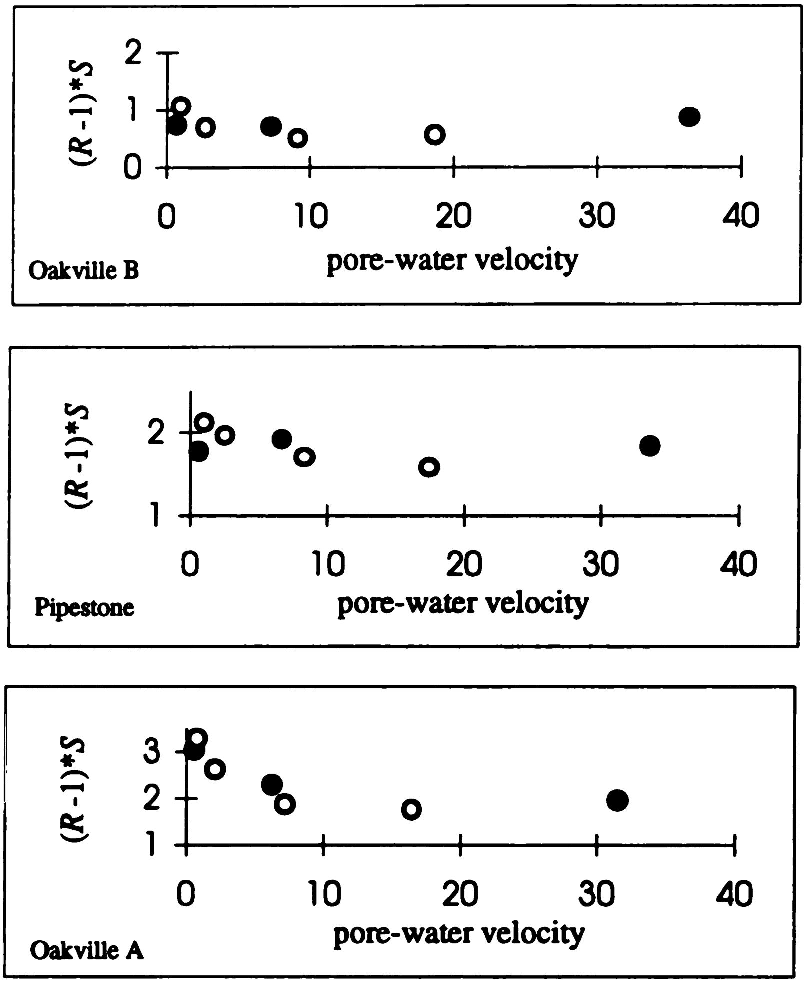


Figure 4.4 Retardation of DMP under staurated (closed symbols) and unsaturated (open symbols) conditions.

saturated and unsaturated values increase with decreases in saturation. Again, the increase in *R* appears to be independent of the soil organic matter content. Unlike DMP, part of the increase in *R* for benzene, as depicted by Eq. (4.2), is due to partitioning into the air phase.

Also shown in Figure 4.5 (solid line) is the relationship developed above for DMP (Eq. 4.5). Most of the data (excluding that at 95% saturation) were either on or above the line. This is because Eq.(4.5) does not account for an increase in *R* due to volatilization. The impact of volatilization on retardation, in this case, is not great. This is because of the low value of K_H and relatively high organic matter content of the soils. As depicted by Eq. (4.2), the contribution of volatilization to the overall retardation, for a given compound and at a certain saturation, will be constant for different soils. However, the percentage increase in *R* is dependent on the value of $\rho K_D/\theta$, and therefore, is dependent on the soil organic matter. To see this, the impact of volatilization on retardation is estimated for three VOCs: benzene, ethylbenzene, and cyclohexane on a nonsorbing ($\rho K_D/\theta = 0$) and a sorbing ($\rho K_D/\theta = 2$) aquifer materials with the use of Eq.(4.2) and is presented in Figure 4.6. The three compounds were selected because of their different K_H values. The value of K_H is 0.19 for benzene, 0.37 for ethylbenzene and 6.8 for cyclohexane (Corapcioglu and Baehr, 1987). As shown in Figure 4.6, the percentage increase in *R* is a function of K_H, θ_a and the extent of sorption. For compounds with relatively high K_H the impact of volatilization on retardation, as presented in Figure 4.6, becomes significant.

When normalized to the saturated solid/water ratio, the retardation coefficient, or specifically the parameter $(R-1)S$, of the unsaturated experiments coincides with the values determined for the saturated experiments, except at low saturation (Figure 4.7) where the values are slightly higher when the soil is partially saturated. This could be due to higher impact of volatilization on retardation at low saturation.

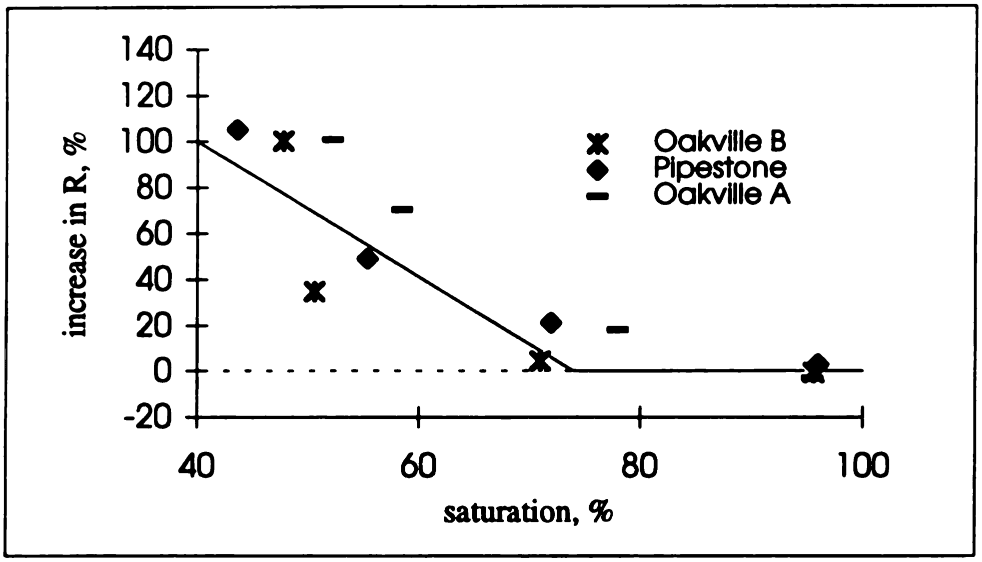
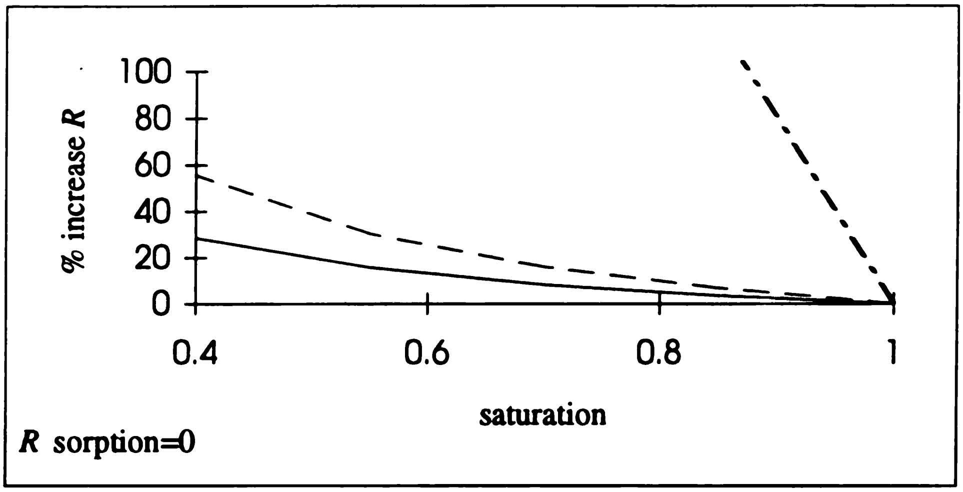


Figure 4.5 Percentage increase in *R* for benzene as a function of saturation. Solid line is the linear fit for DMP data of Figure 4.3.



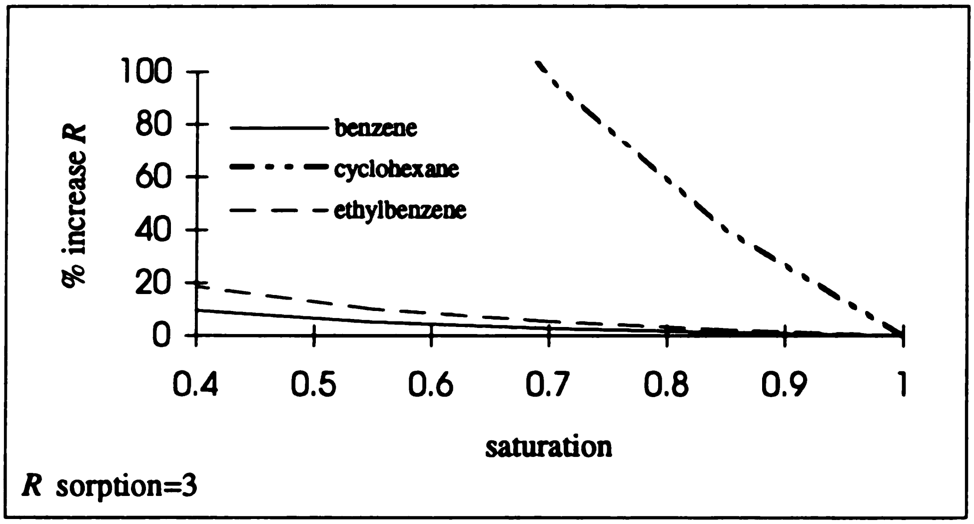


Figure 4.6 Theoretical estimation of the impact of volatilization on retardation of selected VOCs.

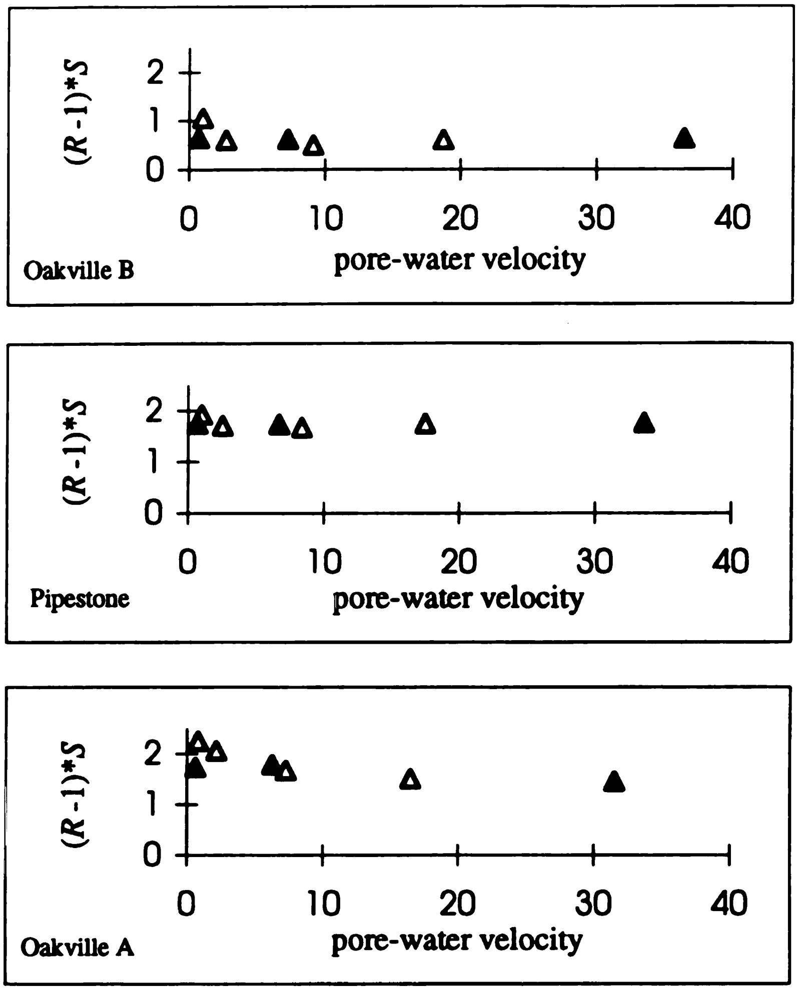


Figure 4.7 Retardation of benzene under staurated (closed symbols) and unsaturated (open) conditions.

4.4.3 Diffusive transport in the air phase

Although an investigation of the impact of diffusive transport in the air phase was not the purpose of the work presented herein, the results are amenable to some discussion of this topic. Figure 4.8 shows BTCs of benzene and tritium under saturated and unsaturated conditions. BTCs of benzene exhibit higher dispersion as the saturation decreases (Figure 4.8a). The increase in dispersion is not due to changes in velocity as shown in Figure 4.8c. In fact, a decrease in velocity should reduce dispersion, and on a normalized scale the BTCs should have the same Peclet number. The changes in the slope of BTC with desaturation is not detected by tritium, either (Figure 4.8b). Therefore, the increase in the slope of the BTCs can be attributed to diffusive transport in the air phase. Recall from Eq. (4.2) that volatilization has an impact on both dispersion and retardation. The increase in dispersion coefficient is a function of effective diffusion coefficient in the air phase (D_a).

For nonreactive vapors in moist soils, Millington and Quirk (1961) showed that D_a can be calculated from the free-air diffusion coefficient (D_a^{air}) using the following relationships:

$$D_a = \theta_a \tau_a D_a^{air} \tag{4.6}$$

$$\tau_a = \frac{\theta_a^{7/3}}{\phi^2} \tag{4.7}$$

For benzene, D^{air}, as estimated by the Hirschfelder-Bird-Spotz equation (Welty *et al.*, 1984) is 310 cm^2/hr. Eqs. (4.6) and (4.7) can now be used to determine the value of D_a at different levels of saturation. Adding the value of hydrodynamic dispersion coefficient determined from tritium BTCs, the value of the effective hydrodynamic coefficient (D_{eff}) of Eq.(4.2) can be determined. The estimated values of D_{eff} and those determined from curve fitting are presented in Table 4.2. Excluding US1 experiments, values of D_{eff} generally increases with the decrease in saturation. This is expected since the contribution of diffusive transport becomes dominant at lower saturation and the effect of hydrodynamic dispersion coefficient in the liquid phase becomes negligible as the velocity

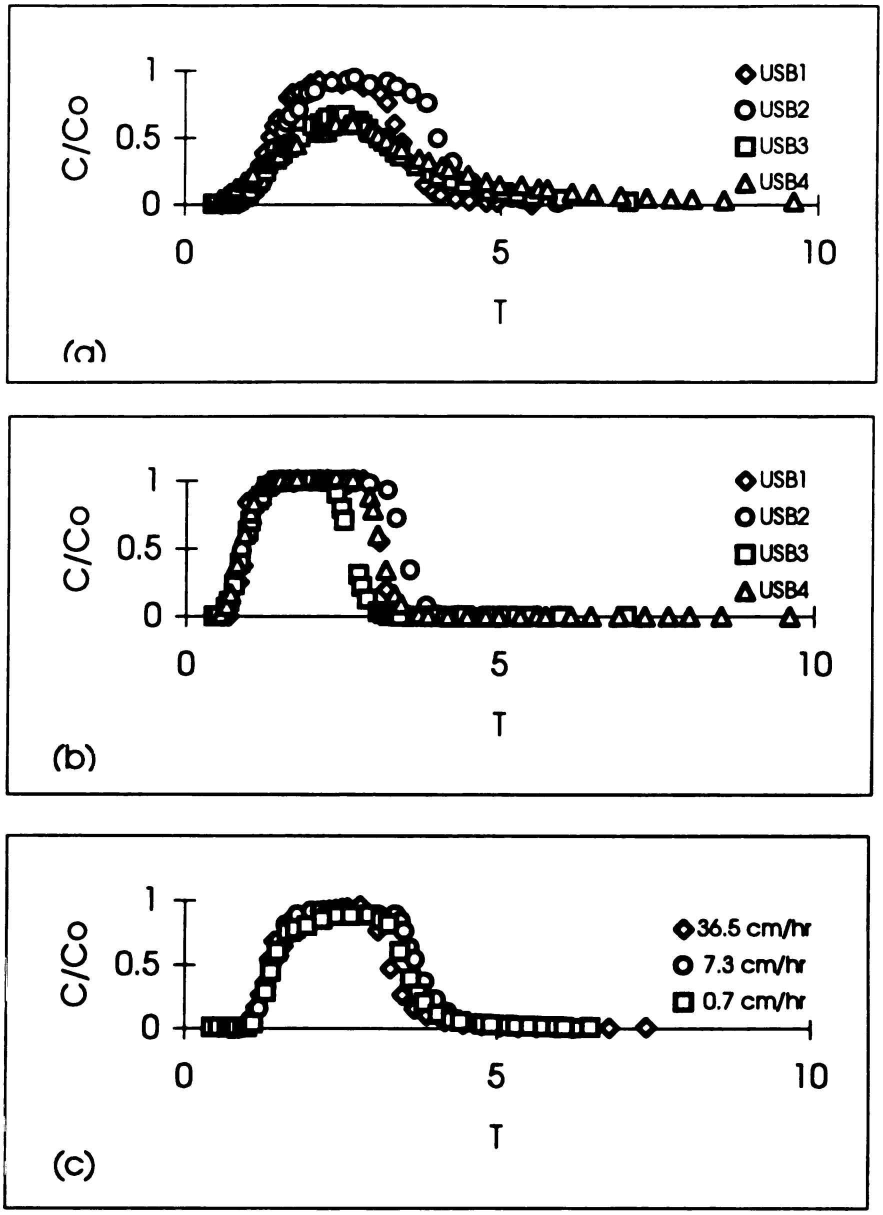


Figure 4.8 BTCs of benzene and tritium (a and b, respectively) at various levels of saturation subject to the experimental conditions indicated, and of benzene at various saturated velocities (c).

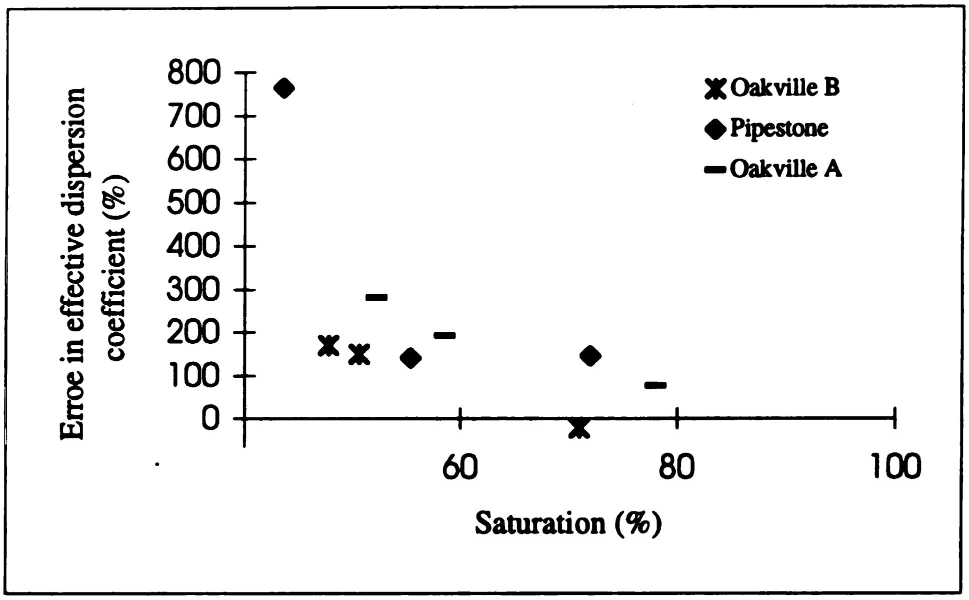


Figure 4.9 Error in the effective dispersion coefficient of benzene under unsaturated conditions.

decreases. Table 4.2 also shows that the values of D_{eff} estimated using the above relationships (Eqs. (4.6) and (4.7)) are higher than the corresponding values found in this study. Figure 4.9 shows that the percentage error could be as high as 700%, with an average value of about 200%. The figure also shows that the error increases at lower saturation. Peterson *et al.* (1988) found that the gaseous diffusion coefficient predicted empirically can be in error by as much as 400%. They attributed that to the uncertainty associated with the empirical relationships (Eqs. (4.6) and (4.7)) and the Hirschfelder-Bird-Spotz equation. Gierke *et al.* (1990) found a similar error and needed to reduce the predicted gas dispersion coefficient for TCE by a factor of 10 in order to be able to describe their column data.

4.4.4 Practical implications

The practical implications of the above findings is that retardation under unsaturated conditions can be predicted based on a single value of K_D. There are two alternatives. First, one could use the same solid/water ratio as determined for saturated conditions. In this case $R_{unsat} = R_{sat}$. Second, one could assume that the amount of solid sorbent remains the same, and therefore, $R_{unsat} = \{(R_{sat} - 1)/S\} + 1$. The later approach would result in a higher retardation upon desaturation. In this study, most of the data collected is in agreement with the later approach. The assumption that retardation is not function of saturation, however, is more conservative since it does not underestimate the average speed of the compound. The second approach can be employed for volatile chemicals given that the contribution of volatilization to retardation is not great (< 10%). If the impact of volatilization is high, its contribution to R could become important especially for low organic carbon aquifers.

4.5 Conclusions

Three factors could result in deviation of R under unsaturated flow conditions from those when the soil is fully saturated: (1) changes in the value of K_D, (2) changes in the solid/water ratio, and (3) volatilization into the air phase. In this study we determined *R* for benzene and DMP under dynamic conditions using packed soil columns over a saturation that varies from 43-100%. The values of *R* for the two compounds under unsaturated conditions were compared to the one determined in Chapter 3 when the soil was saturated.

Retardation coefficients under unsaturated conditions are generally higher than those when the soil is saturated. The deviations were found to decrease with increasing saturation. A single equation was found to adequately describe the relationship between the amount of the deviation and saturation for three soils with different organic carbon contents. Determination of *R* for a nonvolatile organic compound using packed soil columns does not allow for directly distinguishing if the increase in *R* is due to an increase in K_D or an increase in the solid/water ratio upon desaturation. Our data revealed that retardation factors under unsaturated conditions, when normalized to the saturated solid/water ratio, would be very close to the upper limit of solid/water ratio. We could not conclude therefore, that K_D changes as the media is desaturated. For practical purposes, the distinction as to whether the increase is due to changes in K_D or changes in solid/water ratio may not be necessary.

The effect of volatilization on retardation for the case studied is not as significant as the other two factors. Volatilization will have a significant impact on retardation for compounds with higher K_H values and in aquifers with low organic matter content. Further work in this regard is needed. Diffusive transport in the air phase has a significant impact on dispersion. The value of the effective diffusion coefficient in the air phase has been found to be about 2 times lower than the values determined based on previously developed empirical relations.

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CHAPTER 5

SORPTION NONEQUILIBRIUM DURING TRANSPORT OF NONIONIC ORGANIC COMPOUNDS THROUGH SOIL COLUMNS: EFFECT OF SOIL ORGANIC MATTER, PORE-WATER VELOCITY, AND SATURATION

5.1 Introduction

Equilibrium approaches are usually used to model sorption of dissolved nonionic organic compounds (NOCs) in the subsurface. This is consistent with the generally accepted view of the process by which NOCs are sorbed by natural sorbents, i.e. partitioning to sorbent organic matter. While this approach may be adequate under certain conditions, it is usually used to simplify model analysis and to reduce the required computation time. In contrast, kinetic approaches require quantitative treatment of the microscopic transport steps and detailed specification of the geometry of the solid phase. Although such detailed knowledge is impossible for aquifer materials (Valocchi, 1985), an adequate understanding of sorption kinetics is necessary to develop efficient processes to destroy, immobilize, or separate organic pollutants from the soil matrix.

Two general types of models have been developed to simulate sorption kinetics of organic compounds: chemical nonequilibrium models and diffusive mass transfer models. Chemical nonequilibrium models assume that the sorption reaction is the rate-limited process. The two-site chemical nonequilibrium models, for example, assume two parallel sorption domains: sorption on one of the domains is instantaneous, while sorption on the other is kinetically controlled (Cameron and Klute, 1977). The conceptualization upon which the diffusive mass transfer models was developed, however, requires that the rate limiting process is physical rather than chemical. Two types of models have been developed in this regard: intraparticle diffusion (Ball and Roberts, 1991) and intraorganic matter diffusion models. These models assume that the two classes of sites are arranged in series rather than in parallel and that sorption on these sites is always at equilibrium.

Brusseau and Rao (1989) and Brusseau *et al.* (1991b) discussed the appropriateness of using chemical nonequilibrium models for the transport of NOCs. They stated that the assumption of two types of sorption sites with one being rate-limited is not viable, and that the nature of hydrophobic reaction results in hydrophobic sorption being a rapid process. Experimental evidence of physical, not chemical, contribution to nonequilibrium is given by Wu and Gshwend (1986): the lack of temperature dependence was interpreted as evidence that a physical process was being manifested; the dependence of sorption on particle size is consistent with a diffusive mechanism. Moreover, Brusseau *et al.* (1991b) concluded that their experimental results were explained well using the intraorganic matter diffusion model, but could not be explained using the intraparticle diffusion model. Evidence supporting the existence of intraorganic matter diffusion, although indirect, has also been presented by other investigators (Nkedi-Kizza *et al.*, 1989; Bouchard *et al.*, 1988).

It is not surprising, therefore, that soil organic matter (SOM) has evolved as an important parameter that affects sorption nonequilibrium of NOCs. Qualitative assessment of the effect of SOM on the degree of nonequilibrium has been reported (Bouchard *et al.*, 1988). No study has been found that quantitatively compares the extent of sorption nonequilibrium for natural aquifer materials that have different organic matter but the same texture. The rate of approach to equilibrium has been shown to be influenced by the particle size (Wu and Gshwend, 1986; Ball and Roberts, 1991). It is our first objective to quantitatively evaluate changes in the degree of sorption nonequilibrium as the SOM changes. To avoid differences in the extent of nonequilibrium associated with different particle size, aquifer materials selected for this study have similar grain size distributions.

The degree of nonequilibrium is usually quantified by the Damkohler number (Jennings and Kirkner, 1984; Valocchi, 1985; Bahr and Rubin, 1987). The Damkohler number, which is the ratio of hydraulic residence time to characteristic sorption time, is inversely proportional to pore-water velocity. However, the validity of this direct relationship between pore-water velocity and Damkohler number is dependent on the invariance of other parameters that define the Damkohler number with pore-water velocity. Apparent variations of the rate "constant", which is directly related to the Damkohler number, with the time of experiment has been reported (van Genuchten *et al*, 1974; Brusseau *et al*, 1991a; Brusseau, 1992). Dependence of the rate "constant" on the time of the experiment may have significant impact on the appropriateness of the developed criteria that are used to validate local equilibrium assumptions. Hence, it would have an impact on the validity of directly translating lab-determined parameters to field scenarios. An investigation of the potential existence of a functional relationship between pore-water velocity and nonequilibrium parameters including the rate constant is the second objective of this study.

The third objective is to determine the effect of saturation on sorption nonequilibrium of NOCs. Several investigators reported an increase in the extent of nonequilibrium as the porous media is desaturated (van Genuchten and Wierenga, 1976, 1977; Nkedi-Kizza *et al.*, 1983; De Smedt and Wierenga, 1979, 1984, 1986; Bond and Wierenga, 1990, among others). In their studies, nonequilibrium was attributed to slow solute diffusion into and out of immobile water regions. Therefore, nonequilibrium was associated, in their case, with the existence of immobile water regions which affect the transport of both ideal tracers as well as solutes that sorb. No study has been reported regarding the potential impact of saturation on sorption-related nonequilibrium. In Chapter 4 of this study, we reported an increase in retardation of two NOCs upon desaturation. We, indirectly, attributed this increase to an increase in the solid/water ratio when the soil is desaturated and argued that accessibility of the compound to the grains in the emptied large pores occurs through diffusion from the water-filled pores into a stagnant water covering these grains. Hence, there is a possibility of a higher degree of nonequilibrium in the transport of NOCs in unsaturated soils as compared to that when the soil is saturated. To evaluate the effect of saturation on sorption nonequilibrium, we compared between the values of the nonequilibrium parameters determined for two NOCs under both saturated and unsaturated conditions.

5.2 Materials and methods

Three soils were employed in this study. These soils were selected because of their different organic matter contents and similar textures. The organic carbon content of the Oakville A, Pipestone, and Oakville B soils is 2.25, 1.57, and 0.70%, respectively. Other physical properties are shown Table 2.2. Two NOCs were chosen: benzene and dimethylphthalate (DMP). ^{14}C-labeled benzene was analyzed by liquid scintillation counting. DMP was analyzed by high pressure liquid chromatography. The physical properties of the two compounds were described in Table 3.2 and the references cited therein.

Pulse-type miscible displacement experiments using 5.45 i.d. x 30.2 cm glass columns under both saturated and unsaturated flow conditions were conducted. For the saturated-flow experiments, three different flow rates were employed. The unsaturated experiments were conducted at four levels of uniform saturation. The two compounds were dissolved in a 0.01 N calcium chloride deionized, deaired water solution. Unless otherwise indicated, the two compounds were injected simultaneously into the column via a syringe pump using glass syringes. Effluent samples were collected using glass syringes attached to the outlet of the column and were analyzed shortly after collection. At the end of the experiment, the columns were displaced by an organic compound-free calcium chloride solution until the effluents were almost free from any amount of NOCs. The experimental conditions applied in this study were exactly the same as the ones reported in Chapter 2.

5.3 Data analysis

Generated BTCs of benzene and DMP were analyzed to determine the optimized parameter values, and their confidence intervals using the nonlinear least squares inversion program CXTFIT of Parker and van Genuchten (1984). The program was slightly modified, as described in Chapter 2, to achieve better accuracy in the numerical integration. The BTCs were analyzed using both equilibrium and nonequilibrium approach.

For a linear sorption reaction, the equilibrium model in a nondimensional, scaled form is given as:

$$R\frac{\partial C}{\partial T}=\frac{1}{P}\frac{\partial^2 C}{\partial Z^2}-\frac{\partial C}{\partial Z} \qquad (5.1)$$

where,

$$C=c/c_0 \qquad (5.2a)$$

$$Z=z/L \qquad (5.2b)$$

$$T=v_0 t/L \qquad (5.2c)$$

$$P=v_0 L/D \qquad (5.2d)$$

$$R=1+\frac{\rho K_D}{\theta} \qquad (5.2e)$$

and where c is solute concentration, c_o is solute concentration in the influent solution, z is distance, L is column length, t is time, T is number of pore volumes, v_o is average pore-water velocity, D is hydrodynamic dispersion coefficient, P is the Peclet number, ρ is bulk density, θ is moisture content, K_D is distribution coefficient, and R is the retardation coefficient. The values of R for benzene and DMP along with the sum of square errors (SSE) are shown in Table 5.1. Input parameter values for v_o, T_o and D used in the simulation are also listed in the table. Values of D used are those determined from tritium BTCs under the same experimental conditions (Table 2.4).

Although significant differences exist between the conceptualization of sorption-related nonequilibrium models, they are mathematically equivalent for the case of linear sorption (Nkedi-Kizza *et al.*, 1989). This mathematical formulation in a normalized form is given as:

$$\beta R\frac{\partial C}{\partial T}+(1-\beta)R\frac{\partial Q_2}{\partial T}=\frac{1}{P}\frac{\partial^2 C}{\partial Z^2}-\frac{\partial C}{\partial Z} \tag{5.3}$$

$$(1-\beta)R\frac{\partial Q_2}{\partial T}=\omega(C-Q_2) \tag{5.4}$$

where,

$$\beta=\frac{\theta+F\rho K_D}{\theta+\rho K_D} \tag{5.5a}$$

$$Q_2=\frac{1}{(1-F)K_D}\frac{q_2}{c_o} \tag{5.5b}$$

$$\omega=\frac{kL}{v_o}(1-\beta)R \tag{5.5c}$$

and where q_2 is sorbed concentration in the rate-limited domain, β and ω are the parameters that specify the degree of nonequilibrium in the system. The values of R, β, and ω for benzene and DMP were determined using the input parameter values listed in Table 5.1. The optimized values along with their 95% confidence limits and the SSE values are listed in Table 5.2.

The nonequilibrium model was also used to analyze the data of DMP under unsaturated conditions. Input parameter values for v_o, T_o and D are listed in Table 5.3. The values of D are those for tritium under the same experimental conditions (Table 2.6). The optimized parameter values for R, β and ω and their confidence intervals are also reported in Table 5.3.

Table 5.1 Results of fitting the AD model to benzene and DMP using independently determined dispersion coefficient

Exp.	Tracer	v_o cm/hr	T_o	D for ^{3}H cm^2/hr	R	SSE
Oakville A						
SA1	Benzene	31.55	1.95	20.88	1.98(±0.05)	0.214
	DMP				2.14(±0.08)	0.635
SA3	Benzene	6.30	1.96	5.37	2.05(±0.07)	0.354
	DMP				2.50(±0.05)	0.980
SA6	Benzene	0.62	1.91	0.222	2.19(±0.08)	0.445
	DMP				2.86(±0.07)	1.405
Pipestone						
SP1	Benzene	33.60	2.08	18.78	2.09(±0.08)	0.185
	DMP				1.95(±0.08)	0.419
SP3	Benzene	6.72	2.09	2.88	2.15(±0.06)	0.432
	DMP				2.14(±0.10)	1.060
SP6	Benzene	0.67	2.05	0.156	2.32(±0.08)	0.377
	DMP				2.55(±0.10)	0.702
Oakville B						
SB1	Benzene	36.47	2.18	18.04	1.36(±0.06)	0.540
	DMP				1.41(±0.04)	0.368
SB3	Benzene	7.29	2.20	3.27	1.43(±0.03)	0.250
	DMP				1.54(±0.05)	0.350
SB6	Benzene	0.73	2.17	0.204	1.44(±0.05)	0.260
	DMP				1.52(±0.04)	0.310

Table 5.2 Results of fitting the nonequilibrium model to the saturated experiments using dispersion coefficient determined from tritium BTCs.

Experiment	Tracer	*R*	β	ω	SSE	*F*	*k*, 1/hr
Oakville A							
SA1	Benzene	2.45(±0.13)	0.787(±0.007)	0.265(±0.051)	0.018	0.64	0.534
	DMP	2.95(±0.16)	0.642(±0.032)	0.528(±0.068)	0.012	0.46	0.526
SA3	Benzene	2.78(±0.84)	0.693(±0.193)	0.204(±0.079)	0.104	0.52	0.050
	DMP	3.28(±0.25)	0.639(±0.033)	0.718(±0.168)	0.048	0.48	0.127
SA6	Benzene	2.73(±0.17)	0.755(±0.038)	0.383(±0.072)	0.03	0.61	0.011
	DMP	4.03(±0.19)	0.583(±0.023)	0.977(±0.117)	0.015	0.45	0.012
Pipestone							
SP1	Benzene	2.76(±0.34)	0.733(±0.083)	0.220(±0.048)	0.027	0.58	0.334
	DMP	2.83(±0.29)	0.640(±0.050)	0.381(±0.064)	0.033	0.44	0.419
SP3	Benzene	2.74(±0.19)	0.750(±0.040)	0.302(±0.056)	0.028	0.61	0.099
	DMP	2.92(±0.21)	0.660(±0.030)	0.610(±0.130)	0.059	0.48	0.138
SP6	Benzene	2.75(±0.14)	0.797(±0.037)	0.342(±0.072)	0.029	0.68	0.014
	DMP	2.77(±0.06)	0.740(±0.020)	1.170(±0.320)	0.022	0.59	0.036
Oakville B							
SB1	Benzene	1.64(±0.02)	0.750(±0.050)	0.130(±0.020)	0.184	0.62	0.544
	DMP	1.85(±0.17)	0.756(±0.034)	0.176(±0.032)	0.049	0.47	0.474
SB3	Benzene	1.61(±0.15)	0.894(±0.079)	0.161(±0.155)	0.164	0.72	0.229
	DMP	1.70(±0.06)	0.820(±0.024)	0.259(±0.045)	0.049	0.56	0.206
SB6	Benzene	1.65(±0.03)	0.708(±0.058)	0.225(±0.037)	0.026	0.67	0.026
	DMP	1.73(±0.04)	0.796(±0.016)	0.570(±0.170)	0.016	0.52	0.039

Table 5.3 Results of fitting the nonequilibrium model to DMP unsaturated experiments using dispersion coefficient determined from tritium BTCs.

Exp.	*vo* cm/hr	*To*	*S* (%)	$D(^3H)$ cm²/hr	*R*	β	ω	SSE	*F*	*k* 1/hr
USA1	16.51	1.94	95.5	12.16	2.83 ±0.13	0.66 ±0.02	0.60 ±0.09	0.017	0.475	0.344
USA2	7.272	2.08	78.0	10.73	3.38 ±0.18	0.61 ±0.02	0.60 ±0.08	0.009	0.452	0.112
USA3	2.156	1.38	58.5	3.800	5.46 ±0.13	0.45 ±0.01	1.60 ±0.09	0.002	0.330	0.038
USA4	0.806	1.80	52.2	0.757	7.29 ±0.33	0.37 ±0.02	2.24 ±0.24	0.011	0.274	0.013
USP1	17.50	2.12	96.0	11.84	2.64 ±0.25	0.73 ±0.06	0.28 ±0.06	0.033	0.561	0.231
USP2	8.397	2.42	72.0	14.42	3.36 ±0.20	0.69 ±0.04	0.45 ±0.09	0.014	0.559	0.121
USP3	2.562	1.64	55.4	2.797	4.55 ±0.12	0.57 ±0.02	1.91 ±0.28	0.009	0.447	0.084
USP4	1.026	2.30	43.6	0.665	5.86 ±0.12	0.55 ±0.02	2.01 ±0.24	0.006	0.457	0.026
USB1	18.74	2.16	95.6	8.052	1.55 ±0.08	0.84 ±0.08	0.19 ±0.09	0.074	0.564	0.479
USB2	9.180	2.56	71.0	7.853	1.57 ±0.04	0.86 ±0.02	0.24 ±0.09	0.011	0.655	0.309
USB3	2.735	1.69	50.6	2.089	2.21 ±0.09	0.71 ±0.02	0.49 ±0.08	0.016	0.502	0.066
USB4	1.014	2.21	47.8	0.705	2.88 ±0.28	0.67 ±0.06	0.27 ±.0.04	0.022	0.52	0.009

5.4 Results and Discussion

Examples of simulations using the predicted parameter values of Table 5.1 for the equilibrium model and of Table 5.2 for the nonequilibrium model are shown in Figure 5.1. The dashed and solid lines were fitted to the measured points using the equilibrium and nonequilibrium models, respectively. The optimized simulation for the nonequilibrium model closely match the experimental results, while obvious deviations between optimized simulation for the equilibrium model and the data points can been seen. Comparison of the corresponding SSE values listed in Table 5.1 and 5.2 reveals that the nonequilibrium model performed better, in all cases, than the equilibrium approach. The difference in performance appears to increase as the SOM increases, i.e. higher differences in the SSE values for the equilibrium and nonequilibrium model using Oakville A, than for Pipestone, than for Oakville B soil. This is consistent with the findings of Bouchard *et al.* (1988) and of Brusseau *et al.* (1991a) who suggested higher deviations between the equilibrium and nonequilibrium approach as the value of retardation coefficient increases.

Table 5.1 and 5.2 show that the values of R predicted using the nonequilibrium model are higher than those predicted using the equilibrium model. Moreover, the values of R predicted by the equilibrium model appear to increase with the increase in flow rate. Those predicted by the nonequilibrium model do not have the same trend, except for DMP on Oakville A soil. Dependence of R on the flow rate, as discussed by Brusseau *et al.*, (1991a), is generally regarded as an indication of sorption- related nonequilibrium. The use of an equilibrium model, therefore, may not lead to the true value of R.

5.4.1 Impact of SOM on sorption nonequilibrium

BTCs of DMP and benzene on the three selected soils at the lowest conducted flow rate are shown in Figure 5.2. It is noticed in the figure that the retardation of DMP increases, as the BTC is shifted to the right, with the increase in SOM. This is not the case however, for benzene. Although the curves using Pipestone and Oakville A soils are

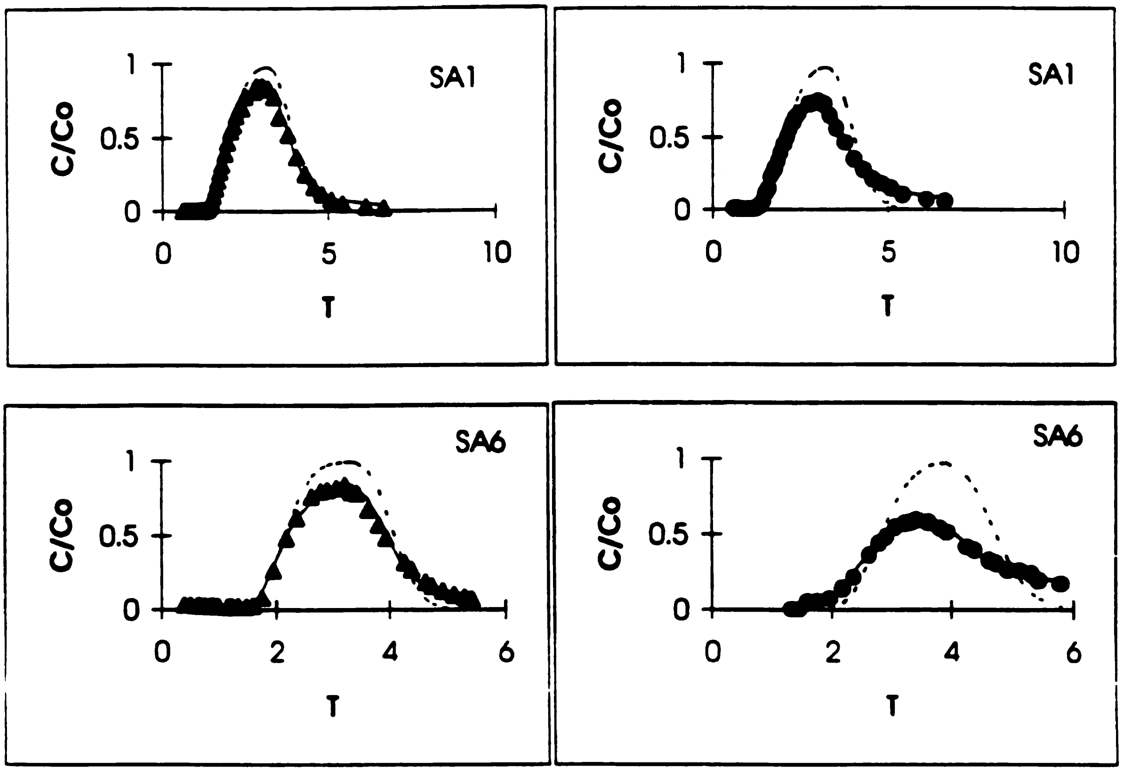

Figure 5.1 Selected BTCs of benzene (triangles) and DMP (circles). Dashed lines are simulations using the equilibrium model and solid lines are simulations using the nonequilibrium model.

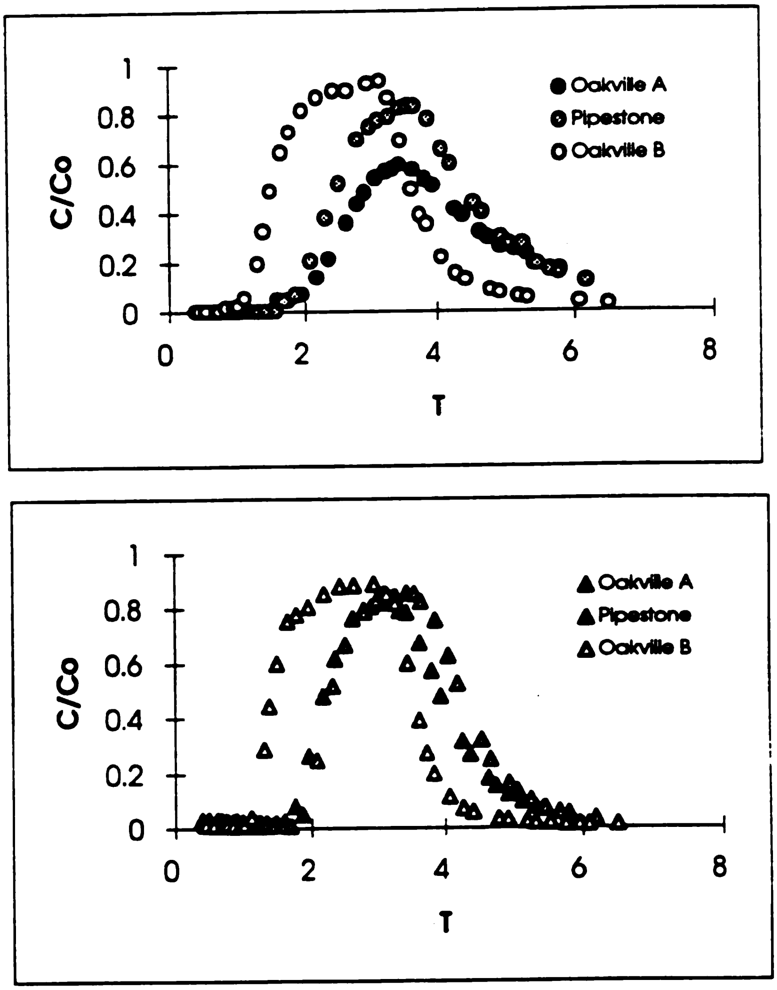

Figure 5.2 Effect of SOM on transport of benzene (triangles) and DMP (circles).

shifted to the right of that using Oakville B, it is surprising to see that Pipestone causes retardation to benzene as much or even a little more than with the Oakville A soil. Batch sorption coefficients of the two compounds (see Table 2.3) follow a consistent trend with SOM (i.e. the coefficient increases with the increase in SOM). The physical properties (ρ and θ) of the packed columns of Pipestone and Oakville A are not significantly different from each other to cause an impact on the values of retardation of benzene in the column. We investigated the behavior of the two compounds when injected simultaneously and separately into the soil columns. There was no evidence of sorption competition as can be seen clearly in Figure 5.3. It is possible that there was not enough time for benzene to diffuse into the interior portion of the SOM on Oakville A. DMP, however, showed increased retardation with the increase in SOM. This should not contradict the above possible explanation offered for benzene if one adopted the possibility of another sorption mechanism for DMP such that the inaccessibility of DMP to partition on the interior layers of the SOM on Oakville A did not significantly alter the retardation factor as was the case with benzene.

The values of β listed in Table 5.2 are dependent on the SOM. The average value of β for benzene on Oakville A, Pipestone, and Oakville B soils is 0.745, 0.76, and 0.87, respectively, and that for DMP is 0.62, 0.68, and 0.79, respectively. Table 5.2 also shows that at a certain flow rate, the value of β for benzene is higher than that for DMP. Since β is defined as the fraction of retardation caused by instantaneous sorption, a compound with a higher value of β means that the compound is easier to access or faster to react with the sorption sites.

If nonequilibrium is caused by diffusion rather than slow reaction, then one would expect an increase in the extent of nonequilibrium for a compound with low diffusion coefficient and with the increase in the thickness of the organic coating on the mineral surface. The above findings agree with this picture. If nonequilibrium, however, is caused by slow reaction with SOM, then one has to assume that SOM is stratified in a manner that the reaction on the sorption sites closer to the exterior surface is faster than that on

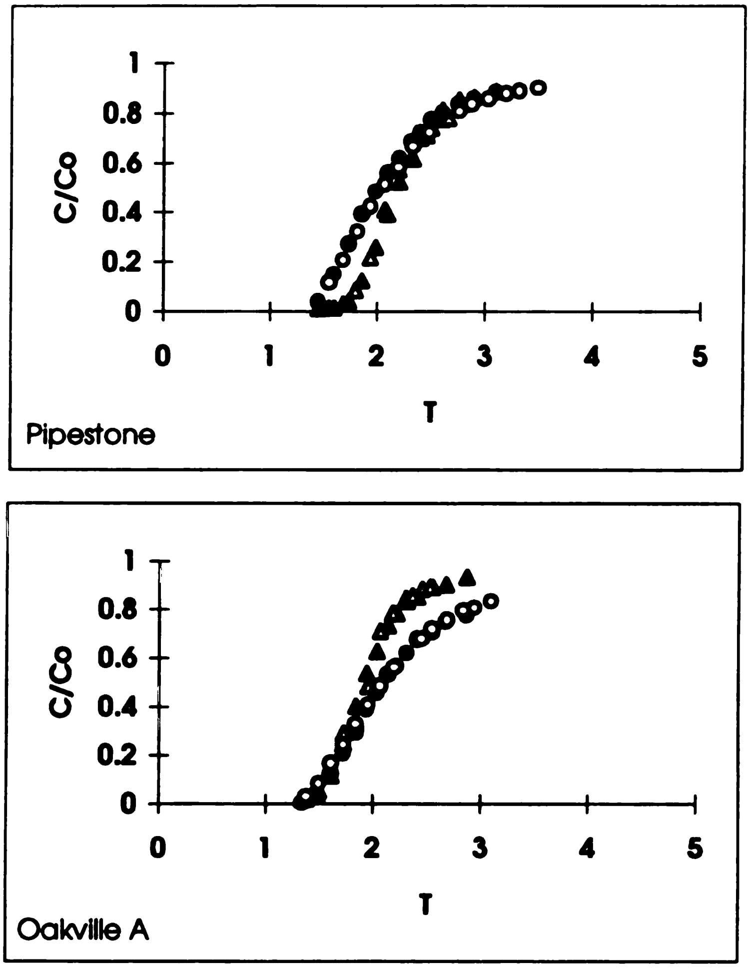

Figure 5.3 BTCs of benzene (triangles) and DMP (circles) as single (open symbols)- and dual (closed symbols)-injected into the soil columns.

the interior sites of the matrix of organic matter. In fact, the opposite has been proposed by Bouchard *et al.*, (1988) to explain the increase in the degree of sorption nonequilibrium as the soil organic matter increases. They suggested that the more polar soil organic carbon moieties are oriented toward the aqueous phase, leaving more hydrophobic regions less accessible to organic solutes within the matrix of organic carbon. Therefore, one may conclude that nonequilibrium, for the case presented here, is caused by slow diffusion. Unfortunately, the values of β cannot assist in differentiating whether this slow diffusion of tracer is within the matrix of SOM or within the intraparticle pores.

The values of F calculated from the values of β using Eq. (5.5a) are also listed in Table 5.2. One might assume that observations made regarding β would apply to F, as well. This is, indeed, true; the average value of F for benzene on Oakville A, Pipestone and Oakville B soil is 0.59, 0.62, and 0.67, respectively, while that for DMP is 0.46, 0.50, and 0.51, respectively. This variation in F, however, among the different soils is not as significant as the variation in the amount of SOM itself. For example, a 3-fold increase in soil organic matter between Oakville B and Oakville A soils caused less than a 15% reduction in the value of F. This raises a question regarding the arrangement of SOM on the mineral surfaces. If the soil carbon was uniformly spread over the sand surface, it would form a film that varies linearly in its thickness with variation in the amount of carbon available, assuming that the density of the organic matter remains the same for the three soils. Based on this type of arrangement of organic carbon, higher variations in F are expected using the aquifer materials utilized in this study. Since this is not the case, the above picture regarding the arrangement of soil organic matter may not be valid. Electron microscopic examination of the arrangement of SOM revealed that SOM exists as patches or porous blobs (Schnitzer, 1978). If one were to adopt this picture, then the number of organic matter "blobs" associated with the soil that has the high organic matter content will be higher. The fraction of accessible sorption sites, however, remains almost constant, Inspection of Table 5.2 also reveals that the value of k, for the same flow rate, does not change with changes in SOM. This supports the above argument regarding the arrangement of SOM on the solid surface. To see this, diffusion into SOM is usually expressed as (Brusseau *et al.*, 1991b):

$$k = \frac{c\,D_p}{(1-F)\,l^2} \tag{5.6}$$

where c is the shape factor, D_p is the diffusion coefficient into polymers, l is the characteristic diffusion length. If one were to assume that the three aquifer materials have the same c, and that D_p for a given compound is constant, then one would expect k to be function of F and l. Variations in F among the soils utilized in this study, as shown before, are very slight. Therefore, similar k values are an indication of similar diffusion path lengths. Hence, the SOM on the three aquifers would have similar thicknesses, but more organic matter "blobs" are associated with the soil that has higher organic matter.

5.4.2 Impact of pore-water velocity on sorption nonequilibrium

BTCs of benzene and DMP for different pore-water velocities are presented in Figure 5.4. The BTCs do not seem to be influenced by flow rate, except for DMP on Oakville A soil. A shift to right with the reduction in flow rate for DMP on Oakville A has resulted, as discussed in Chapter 4, in variations in the value of retardation coefficient. We attributed the velocity dependence observed in R to the possibility of the existence of an additional sorption process that is observable when relatively slow velocities are used. The impact of pore-water velocity on the nonequilibrium parameters β and ω is the subject of the remainder of this section.

Table 5.2 shows that the values of β are independent of pore-water velocity. Hence, the value of F should be independent of velocity. Table 5.2 shows, in fact, that there is no functional relationship between F and pore-water velocity for the two compounds using the three soils. The F factor would likely be a function of velocity for a

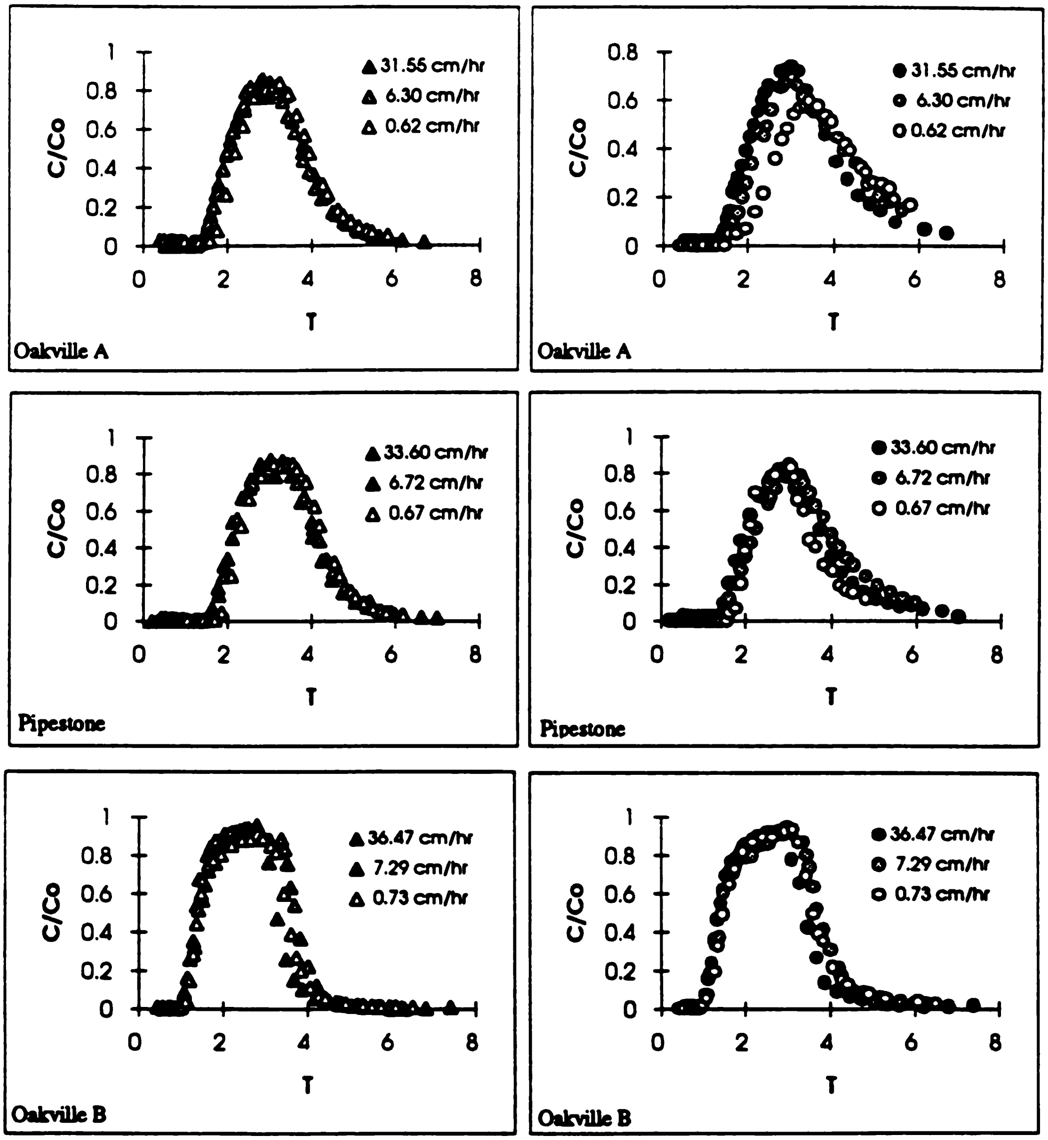

Figure 5.4 Effect of pore velocity on transport of benzene (triangles) and DMP (circles).

chemical nonequilibrium process involving a continuous distribution of reaction times (Schwarzenbach and Westall, 1981). On the contrary, *F* should be fairly independent of velocity for nonequilibrium caused by slow diffusion (Brusseau *et al.*, 1991a). Therefore, the independence of *F* on velocity is suggestive that sorption nonequilibrium is due to slow diffusion. Again, the *F* factor does not allow distinguishing if slow diffusion is within the matrix of SOM or within intraparticle pores.

Values of ω, as indicated by Eq. (5.5c), are expected to be velocity dependent. The values of *k*, the mass transfer coefficient, are not expected to be, however. The values of *k* for the two compounds using the three aquifer materials are presented in Figure 5.5 as a function of pore-water velocity. The figure shows dependence of *k* on pore-water velocity. This is inconsistent with a constant mass transfer coefficient of the compound that would describe all the experiments on the same soil. van Genuchten *et al.* (1974) noticed dependence of the first-order reaction constant of picloram on flow velocity. van Genuchten *et al.* (1974) hypothesized that at high flow velocity the residence time of the herbicide in the column is too short to allow diffusion to all sorption sites. They argued that not all the sorption sites actively participate in sorption at high flow rate. Brusseau *et al.* (1991a) also noticed a time-scale effect on *k*. Brusseau *et al.* (1991a) compared their *k* values with those of Ball and Roberts (1991), Roberts *et al.* (1989) and Lee *et al.* (1988) and noticed that smaller "rate constants" are associated with longer experimental times. The dependence of *k* on pore-water velocity in the above studies was attributed to changes in K_D. The same reason can be used here to explain variation of *k* with velocity for DMP on Oakville A, since K_D , in this case, changes with velocity. However, for all the other sorbate-sorbent combinations there was no dependence of K_D (or *R*) on pore-water velocity. Therefore, a different explanation should be offered for the noticed functionality.

The dependence of *k* on pore-water velocity could be a result of a time-scale effect, where the value of the "rate constant" is dependent on the length of time of the experiment but the actual sorption process is not altered. Therefore, the dependence of *k*, not K_D, on pore-water velocity is a result of the mass transfer coefficient being a time-

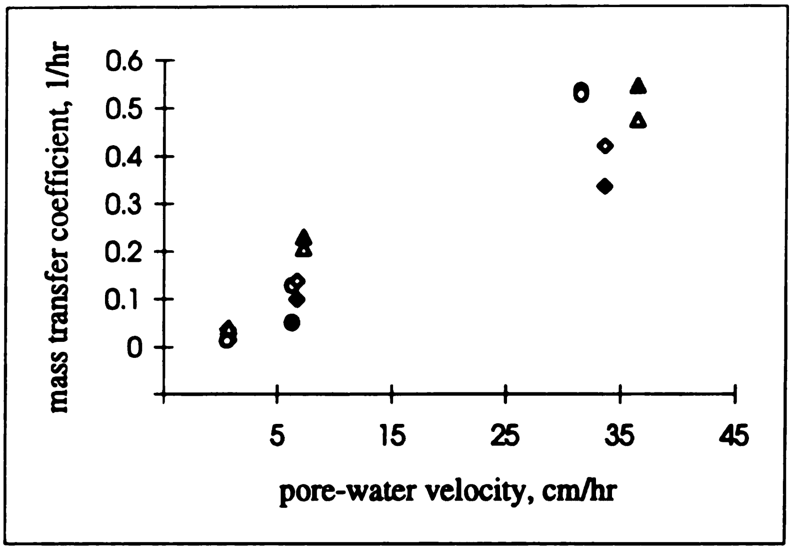

Figure 5.5 Relationship between mass transfer coefficient and pore-water velocity, circles for Oakville A, diamonds for Pipestone and triangles for Oakville B soil, open symbols for DMP and closed ones for benzene.

averaged parameter. Brusseau (1992) noticed similar dependence of *k* on pore-water velocity. The author argued that the dependence of *k* on pore-water velocity could be a result of variation of the diffusion coefficient or the characteristic diffusion length or both with the time of experiment. Schwarzenbach and Westall (1981) proposed using a continuous distribution, not a single value, of *k* to be able to describe the effect of flow velocity on transport of chemicals affected by sorption nonequilibrium. As indicated by Schwarzenbach and Westall (1981), the different *k* values would correspond to different diffusion path length. Hutzler *et al.* (1986), indeed, used different values of *l* to describe BTCs generated at different flow rates.

5.4.3 Impact of saturation on sorption nonequilibrium

Parameters values for all the unsaturated experiments are reported in Table 5.3. Values for *F* and *k* are estimated using Eqs. (5.5a) and (5.5c), respectively, along with the values of *R* and v_o listed in the table. An example of the simulations produced by the nonequilibrium model at two levels of saturation using Oakville A soil is shown in Figure 5.6. The figure shows that the nonequilibrium model was able to provide a good description of the generated BTCs. Changes in *R* with the decrease in saturation, as noticed in Table 5.3, have been discussed in Chapter 4 and were attributed to changes in the solid/water ratio upon desaturation. The following discussion will focus on the values of the nonequilibrium parameters β and ω of Table 5.3.

Saturation and pore-water velocity are coupled. Therefore, to assess the impact of saturation on sorption nonequilibrium, the effect of pore-water velocity should be isolated. To do so, a comparison between nonequilibrium parameter values determined under saturated conditions with those determined when the soil is partially saturated will be performed. Table 5.3 shows that the values of β decrease as saturation is reduced. As indicated earlier, this should not be due to a decrease in velocity, since we accepted the fact that nonequilibrium is due to a diffusion limitations rather than slow chemical reaction. Therefore, changes in β could be due to changes in saturation. However, changes

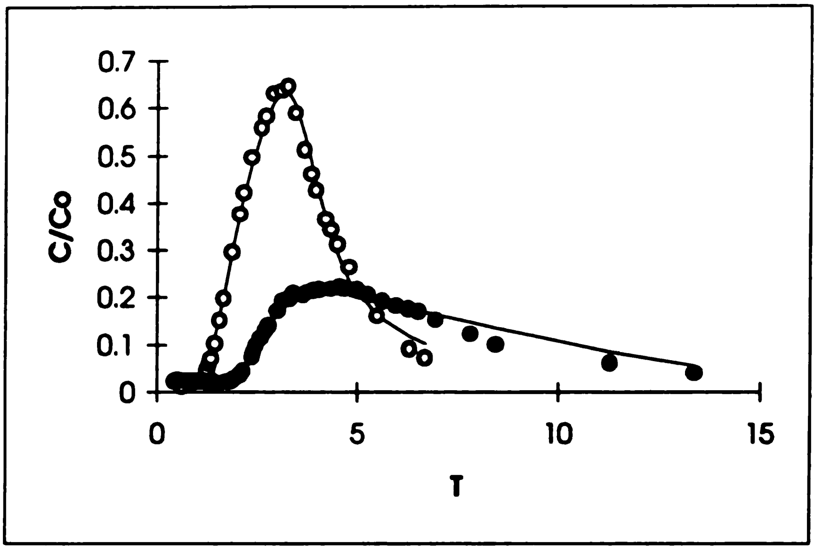

Figure 5.6 Selected BTCs of DMP under unsaturated conditions.Open and closed circles are data of experiment USA2 and USA4 with saturation of 78 and 52%, respectivley. Lines are simulations using the nonequilibrium model.

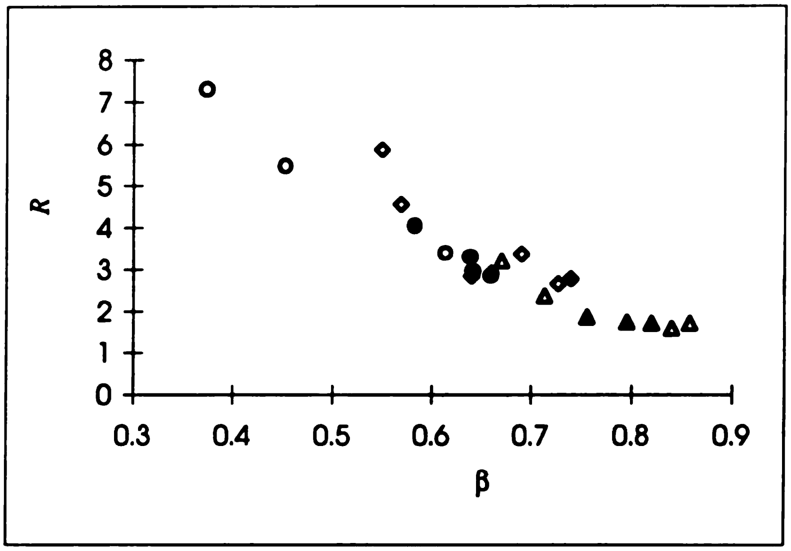

Figure 5.7 Relationship between normalized fraction of instantanuous sorption sites and retardation coefficient, circles for Oakville A, diamond for Pipestone and triangles for Oakville B soil, open symbols are for unsaturated experiments and closed ones for saturated experiments

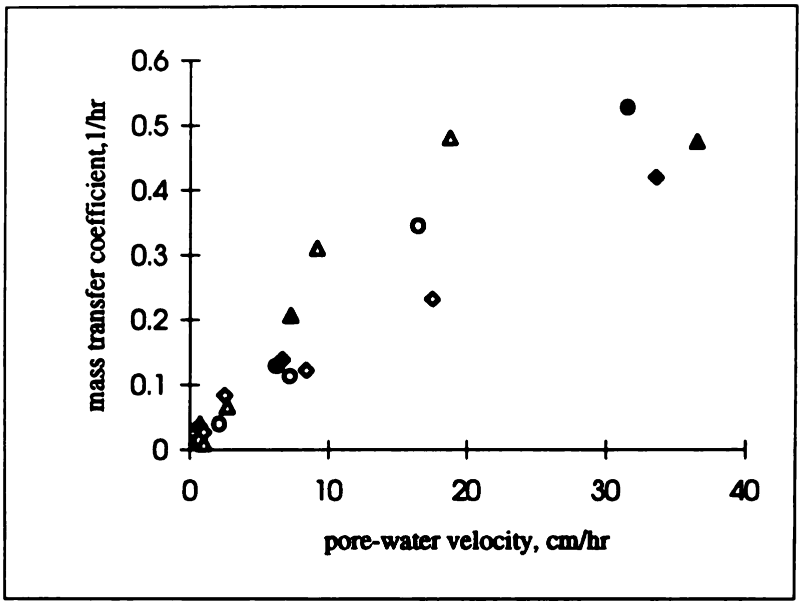

Figure 5.8 Relationship between mass transfer coefficient and pore-water velocity, circles for Oakville A, diamond for Pipestone and triangles for Oakville B soil, open symbols are for unsaturated experiments and closed ones for saturated experiments

in β are also associated, as shown in Table 5.3, with an increase in *R*. In order to determine if changes in β are due to changes in *R* or changes in saturation, the values of β for the unsaturated experiments are compared to those for the saturated ones. This is presented in Figure 5.7. The figure shows that the values of β for the saturated experiments are not different from those for the unsaturated experiments at comparable retardation coefficients. Hence, the variations in β are indeed due to variations in *R* and the decrease in saturation did not directly affect the fraction of instantaneous sorption sites. Similar conclusions can be reached if one compares the values of *F* with pore-water velocity.

For the saturated-flow experiments, the mass transfer coefficient, *k*, was found to be dependent on pore-water velocity. Therefore, the values of *k* determined under unsaturated-flow conditions are expected to vary with velocity (saturation).The impact of saturation on *k* was investigated by comparing the values of *k* for both saturated and unsaturated experiments at the same pore-water velocity. The values plotted in Figure 5.8 show that the values of *k* under unsaturated conditions compare well with those determined when the soil is saturated. Therefore, there is no evidence of change in *k* with changes in saturation.

5.5 Summary and conclusions

Values of transport nonequilibrium parameters determined from analysis of BTCs of two NOCs were utilized to assess the impact of SOM, pore-water velocity and level of saturation on the extent of sorption nonequilibrium. Three aquifer materials with relatively high organic carbon content were used in this study.

The assumption of local equilibrium during transport of NOCs was not valid even at low pore-water velocity. The two NOCs exhibit sorption nonequilibrium which appears to be of diffusive nature rather than a result of slow reaction rates. Our results do not allow one to conclude whether slow diffusion occurs within the matrix of organic matter or within the intraparticle pores.

A 3-fold increase in SOM was accompanied only by a slight increase in the extent of sorption nonequilibrium. This is suggestive that SOM is not uniformly distributed over the mineral surfaces, and is consistent with electron microscopic observations reported by others.

Diffusion mass transfer coefficients vary proportionally with pore-water velocity. Hence, established criteria for the validation of the local equilibrium approach, which is built on the assumption of a constant diffusion mass transfer coefficient, need to be evaluated. The use of previously developed criteria may be problematic in extrapolating lab-obtained parameters to field scenarios when modeling transport of organic chemicals in the subsurface.

It has been reported by other investigators that physical nonequilibrium, created by the existence of slow solute diffusion into an out of immobile water regions, may develop during transport of solutes in partially saturated soils. Previous work using the same aquifer materials concluded that physical nonequilibrium does not exist. This work also showed that there was no impact of saturation on sorption nonequilibrium.

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CHAPTER 6

DISSERTATION SUMMARY AND RECOMMENDATIONS

6.1 Dissertation summary

The overall objective of this study was to gain a better understanding of the transport of dissolved VOCs in the unsaturated zone. This study focused on transport mechanisms that affect the mean velocity of contaminant movement and the extent of spreading from the mean. An in-depth review of the literature related to these mechanisms has been presented in Chapter 1. The four chapters that follow contain the results of the experimental and analytical investigations. Each of these chapters can stand alone and are currently in the process of being published. This section is a general summary of Chapter 2 through Chapter 5. However, readers interested in a more detailed summary of a particular chapter are directed to the summary section at the end of that chapter.

Three nonaggregated sandy soil samples were utilized in this study. The soils varied in their organic carbon content but had similar grain size distribution. Three tracers, i.e. tritium, benzene and dimethylphthalate were used. The use of tritium served as an ideal tracer, that of dimethyphthalate as a nonvolatile organic compound, and that of benzene as a volatile organic compound. Soil columns were designed to operate in either a saturated or an unsaturated modes. The columns were also designed to eliminate air advection when the soil was partially saturated. Saturated flow experiments were conducted at three different pore-water velocities. Unsaturated experiments were performed under a unit hydraulic gradient to assure uniform water distribution along the depth of the column. Aqueous effluent samples were collected using glass syringes in a manner that avoided losses by volatilization. The samples were analyzed for tracer concentration shortly after collection.

Several studies have been conducted to examine the dispersive behavior of unsaturated media. In reviewing these studies, two unsettled issues were identified: the first is whether there is transport nonequilibrium created by slow solute diffusion into relatively stagnant water regions, and the second relates to changes in the dispersivity of the media when desaturated. The existence of transport nonequilibrium developed as a result of desaturation, enhances solute spreading. Hence, its impact, if not properly isolated, appears as increased dispersion. The objective of Chapter 2 was to investigate the impact of saturation on the dispersivity of natural, nonaggregated porous media. Results of this phase indicated that there was no physical nonequilibrium during transport of tritium through the porous media utilized. Results also showed that the dispersivity under unsaturated conditions was higher than the value determined for the saturated experiments. These results suggest that a model which accounts for intersection of capillary tubes could be more appropriate to represent the geometry of the unsaturated pore volume than the simple bundle-of-capillary tubes model.

Chapter 3 and 4 of this study were directed towards quantifying the average velocity of dissolved organic contaminants relative to that of water. Retardation of dissolved (in water) VOCs in the subsurface occurs due to partitioning into other phases. Under saturated conditions, sorption into the soil matrix will be the cause of retardation. In the unsaturated zone, both sorption and volatilization will influence the average speed of dissolved VOCs. In Chapter 3 a comparison was made between values of retardation coefficients determined by two commonly used techniques: batch and saturated column experiments. Results of this phase showed that batch-determined retardation coefficients are higher than their column-determined counterparts. Several factors have been previously reported to cause discrepancy between the results of the two techniques. These factors are either sorption-related (i.e. nonequilibrium, nonlinearity, nonsingularity) or sorption-nonrelated. Our results showed that the extent of deviation in the values of retardation between the two techniques was independent of the amount of soil organic matter. Hence, sorption-related factors were probably not the cause of this disparity. Although not proven experimentally, mixing differences between the two techniques becomes a potential explanation.

Chapter 4 was the first to report the effect of saturation on retardation of a volatile and a nonvolatile organic compounds under dynamic conditions. Previous work, in this regard, was limited to static (batch) type experiments and for saturation that does not contribute to aqueous flow. Retardation coefficients determined under unsaturated flow conditions were compared to those when the soil was fully saturated. This phase showed that retardation coefficients for unsaturated soils are higher than the values determined when the soil is saturated, and that the deviations in retardation are generally higher as the saturation is reduced. It was also found that there was no functional relationship between the extent of deviations in the values of retardation coefficient and the amount of soil organic matter. The impact of volatilization on retardation of benzene under unsaturated conditions was not significant. This phase demonstrated through theoretical considerations, however, that the impact of volatilization on retardation for VOCs with high volatility and for aquifers with low carbon content is significant.

Besides volatilization, two factors may cause an increase in retardation under unsaturated conditions as compared to when the soil is saturated. The first is an increase in the value of sorption distribution coefficient and the second is an increase in the solid/water ratio. Our data revealed that retardation factors under unsaturated conditions, when normalized to the saturated solid/water ratio, would be very similar. We were not able to conclude that the distribution coefficient changes as the media is desaturated. For practical purposes, a distinction whether the increase in retardation is due to changes in distribution coefficient or changes in solid/water ratio may not be necessary. A distinction is important, however, from a mechanistic standpoint.

Investigation of the impact of soil organic matter, pore-water velocity and level of saturation on the extent of sorption nonequilibrium was the main focus of Chapter 5. Results in this chapter showed that the assumption of local equilibrium during transport of organic chemicals through packed soil columns was not valid even at low pore-water velocity. In addition, sorption nonequilibrium of the utilized nonionic organic compounds appeared to be of a diffusive nature rather than a chemical kinetic limitation. However, the extent of sorption nonequilibrium was not significantly enhanced by increasing the amount of soil organic matter. This suggests that soil organic matter is not uniformly distributed over the mineral surfaces, which is consistent with electron microscopic observations reported by others.

The results of Chapter 5 also showed that the diffusion mass transfer coefficient varies proportionally with pore-water velocity, and that the common assumption of a constant mass transfer coefficient is questionable. This may have serious implications on the validity of previously established criteria for validation of local equilibrium approaches, and may have implications on extrapolating lab-obtained parameters to field scenarios. By comparing the values of the nonequilibrium parameters determined under unsaturated conditions with those determined for the saturated case, it was found that desaturation does not have an impact on sorption nonequilibrium of the employed organic compounds.

6.2 Recommendations

The following includes directions for future research based on the present study:-

- Investigate the dispersive behavior of saturated-unsaturated soil for different column lengths using the same tracer and same technique of sampling.
- Provide a data base to verify the derived stochastic models that characterize dispersion in porous media.
- Design and conduct laboratory experiments to investigate the effect of mixing differences and particle spacing on sorption in a batch and column systems.

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- Experimentally investigate the impact of volatilization on retardation for VOCs with different Henry's constants using low carbon aquifer materials
- Establish relationship(s) for better prediction of effective diffusion coefficients in the air phase.
- Elucidate the reason for the dependence of nonequilibrium mass transfer coefficient on average pore-water velocity.
- Determine whether sorption nonequilibrium of nonionic organic compounds is due to intrasorbent or intraparticle diffusion limitations.