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I am submitting herewith a thesis written by Oren C. Reedy entitled "Quantifying Diffusive Mass Transfer of Nonreactive Solutes in Undisturbed Soil Columns Using Flow Interruption." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Plant and Soil Science.

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QUANTIFYING DIFFUSIVE MASS TRANSFER OF NONREACTIVE SOLUTES IN UNDISTURBED SOIL COLUMNS USING FLOW INTERRUPTION

A Thesis

Presented for the

Master of Science

Degree

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Oren Clyde Reedy

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DEDICATION

This thesis is dedicated to my beloved parents

Mr. Roger Clyde Reedy

and

Mrs. Merab Elizabeth Reedy

who have provided me with unconditional love and support.

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ABSTRACT

Subsurface transport processes of low-level radioactive contaminants at hazardous waste sites are highly complex due to a vast continuum of pore regions in heterogeneous media. Contaminant transport is typified by a multitude of interacting concentration profiles that exist due to the complexity of subsurface media. Two concentration profiles are typically assumed to describe the transport of solutes in heterogeneous subsurface media. These profiles provide a means for subsurface contaminants to move rapidly through preferential flow paths associated with larger pores, or they may move slowly and continuously through smaller pore regions. During transport, however, contaminant mass is continuously transferred between the various sized pore regions via hydraulic and concentration gradients.

The objective of this study was to quantify the diffusive mass transfer of nonreactive solutes between the matrix porosity and the preferential flow paths through a heterogeneous subsurface media. The intent of this study was to provide an improved understanding and predictive capability of contaminant migration for improving remediation strategies at contaminated waste sites.

A large, undisturbed subsurface soil column (17 x 41 cm) of highly weathered fractured shale was acquired from a proposed waste site on the Oak Ridge Reservation in eastern Tennessee. The flow interruption technique was used in

nonreactive tracer experiments involving the transport of Br (a ^{3}H surrogate) under saturated conditions. The technique involved the displacement of the nonreactive tracer into the column, inhibiting tracer flow for a designated time period (interruption), and then reinitiating the tracer flow. Experiments considered tracer infusion and displacement, variations of duration of flow interruption (6, 18, 84, and 166 hours) and variations in flux (4, 41, 216, and 475 cm d^{-1}).

Displacement of Br through the undisturbed media was characterized by asymmetric breakthrough curves (BTC) that were indicative of heterogeneous flow phenomena. The rapid initial breakthrough and exaggerated "tailing" in BTCs are indicative of rapid solute transport through preferential flow zones coupled with slower transport into the soil matrix. When flow interruption was initiated during the infusion of Br, a concentration (C/C_0) decline was encountered upon flow reinitiation, indicating diffusion between the preferential flow zones and the soil matrix during the interruption period. Likewise during displacement, flow interruption resulted in a concentration rise due to Br diffusing from the soil matrix into the preferred flow channels. More pronounced concentration declines were also observed with higher fluxes (216 and 475 cm d^{-1}). A longer interrupt time (166 h) resulted in larger tracer concentration perturbations. Flux and interrupt duration had profound affects on the magnitude of concentration perturbation. A direct relationship for each

was observed with respect to concentration perturbation. In addition, the interrupt duration approached a value at which the percent change in concentration after interruption became constant.

Experimental data were adequately modeled with a two-region flow interrupt model. Observed effluent concentrations were adequately modeled by fitting the transfer coefficient to the experimental BTC. These results suggested that a direct relationship exists between the transfer coefficient and flux. Model simulations also suggest that interrupt duration had a negligible effect on the transfer coefficient for low to moderate fluxes.

The results of these investigations conclusively demonstrated that the flow interruption technique can be used to quantify the diffusion of nonreactive solutes in heterogeneous porous media. Results indicate that preferential flow processes are significantly greater at larger fluxes, and that the molecular diffusion of solutes is a significant transport process over a large range of fluxes. In heterogeneous subsurface systems where traditional pump and treat methods have failed because of slow contaminant diffusion, a modified flow interrupt pump and treat method may enhance the effectiveness and efficiency of contaminant removal.

TABLE OF CONTENTS

CHAPTER		PAGE
I	INTRODUCTION	1
	MODES OF SUBSURFACE MIGRATION	1
	ADVECTION	4
	HYDRODYNAMIC DISPERSION	5
	DIFFUSION	8
	NONEQUILIBRIUM	13
	CHEMICAL NONEQUILIBRIUM	14
	PHYSICAL NONEQUILIBRIUM	16
	MISCIBLE DISPLACEMENT	18
	TAILING	27
	EFFECTS OF FLUX	28
	MODELING TRANSPORT-RELATED NONEQUILIBRIUM	30
	ADVECTIVE-DISPERSIVE MODEL	32
	PHYSICAL DIFFUSION MODELS	34
	PHYSICAL MASS-TRANSFER MODEL	35
	THE FLOW INTERRUPTION TECHNIQUE	36
	METHOD DESCRIPTION	36
	EFFECTS OF FLOW INTERRUPTION DURING MD	36
	FLOW INTERRUPTION EFFECTS ON BTC's	40
	FLOW INTERRUPT APPLICATION	42
	OBJECTIVES	51
II	MATERIALS AND METHODS	55
	SITE CHARACTERIZATION	55
	SOIL COLUMN EXCAVATION	59
	MISCIBLE DISPLACEMENT EXPERIMENTS	62
	CHEMICAL EFFLUENT ANALYSIS	66
	NUMERICAL MODELING	67
	TWO-REGION MODELS	67
	GENERAL FORMULATION	68
III	RESULTS AND DISCUSSION	71
	EFFECTS OF FLUX ON BTC's	71
	EFFECT OF INTERRUPT DURATION	77
	MODEL SIMULATION: STOPFLO	82
IV	CONCLUSIONS	86
	LITERATURE CITED	88
	VITA	96

LIST OF FIGURES

FIGURE		PAGE
I.1.	Mobile-immobile system	2
I.2.	Equilibrium and nonequilibrium breakthrough curves	15
I.3.	Schematic diagram of the multireaction retention model	20
I.4.	Breakthrough curve representing (a) piston flow and (b) longitudinal dispersion	23
I.5.	Breakthrough curve representing (a) effect of chemical reaction, exchange, or precipitation, and (b) extremely wide range in velocity distribution	24
I.6.	Breakthrough curve representing exclusion of solute by solute-solid interaction or velocity distribution with velocities near zero	25
I.7.	Typical BTC obtained using flow interruption technique	38
I.8.	Shape of BTC as influenced by flow interruption at low C/C_0	41
I.9.	BTC of observed and fitted data for displacement of 2,4-D amine through Eustis soil	48
II.1.	Location of soil column collection on proposed SWSA-7	56
II.2.	Excavation pit showing fractured saprolite (light brown) interbedded with clay lens (dark red)	60
II.3.	Isolated soil pedestal encased in paraffin wax containing fractured saprolite and clay lens	61
II.4.	Experimental column system showing	63
III.1.	Experimental (circles) and simulated (line) BTC's for constant interrupt duration of 166 hours with different flux (q)	72

III.2. Observed relative concentration change as a function of flux during bromide . . . 76

III.3. Experimental (circles) and simulated (line) BTC's for constant flux of 41 cm d^{-1} with different interrupt durations 79

III.4. Observed concentration change as a function of interrupt duration for q=41 cm d^{-1} during 80

III.5. BTC's for constant flux, 41 cm d^{-1}, with different interrupt durations 81

III.6. *STOPFLO* transfer coefficients (TR) as function of flux for the 166 h interrupt 84

Chapter I.

INTRODUCTION

Groundwater sources have become increasingly polluted with various contaminants such as low-level radioactive wastes, inorganic chemicals, and volatile and weakly hydrophobic organic compounds. Many of these contaminant sources originate from radiochemical production facilities, leaking underground storage tanks, hazardous chemical waste disposal sites, and accidental chemical spills. Once these contaminants have been introduced into the vadose zone several pathways may be followed before the contaminant ultimately reaches the groundwater supply. For investigation and assessment of groundwater contamination a number of mechanisms such as advection, dispersion, adsorption, and diffusion must be examined. These processes must also be effectively coupled with numerical models for description and prediction of contaminant migration.

MODES OF SUBSURFACE MIGRATION

Traditionally, solute transport through a structured saturated soil is viewed as rapid transport occurring through preferential paths (macropores) coupled with diffusive mass transfer of solutes between the rapid flow region and the stagnant region (micropores), i.e., mobile-immobile concept (van Genuchten, 1981; Seyfried and Rao, 1987; Nkedi-Kizza et al., 1982; Pandey and Gupta, 1984). A representation of the mobile-immobile concept is shown in Fig. I.1. The interaction

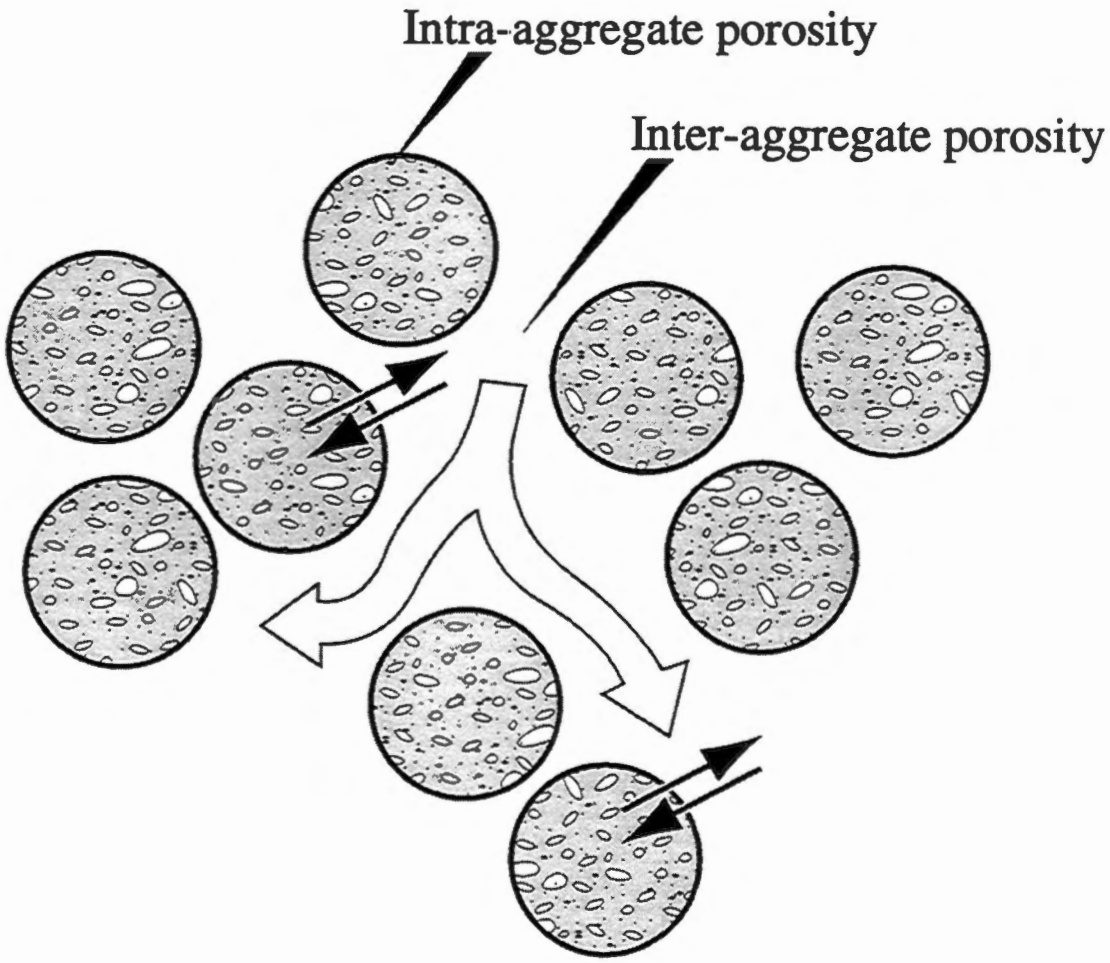


Fig. I.1. Mobile-immobile system. Mobile phase is the inter-aggregate porosity and the immobile phase is the intra-aggregate porosity.

Source: Brusseau M.L., and P.S.C. Rao. 1989*b*. Sorption nonideality during organic contaminant transport in porous media. Crit. Rev. Environ. Control., 19:33-99.

between the mobile and immobile regions is a major process occurring within subsurface media which contributes to solute transport. Several mechanisms are associated with solute transport in saturated porous media: (1) diffusion across the adsorbed water (i.e., film diffusion); (2) advective-dispersive transport from bulk solution to the boundary layer (i.e., adsorbed water surrounding the sorbent); and (3) pore and/or surface diffusion within the immobile region (i.e., intra-aggregate diffusion) (Brusseau and Rao, 1989*b*). The mobile-immobile concept neglects solute movement within the soil matrix and implicitly assumes that physical equilibrium exists between flow regions. However, under variably saturated and unsaturated soil conditions, preferential flow causes physical non-equilibrium, thus establishing hydraulic gradients between the stagnant region and the preferential flow zones. During such conditions, diffusion and convection drive solute mass transfer between the two regions (Jardine et al., 1990).

As previously mentioned, several mechanisms are involved in the solute transport processes which contribute to nonequilibrium by controlling the flux into and out of the elemental volume of a porous media. Any or all of these processes may serve as rate limiting steps in transport of contaminants as they migrate through groundwater systems. It is usually assumed that one of these processes is slow relative to the others. That process may therefore be

designated as the primary rate-limiting step in solute transport (Brusseau and Rao, 1990 *a*, *b*).

ADVECTION

As water flows through the subsurface, solutes may be carried faster (exclusion) or slower (adsorption) than the rate of the average groundwater flow. This process is known as advection (Fetter, 1980). Advective transport is attributed to the average motion of the fluid. In systems involving displacement of miscible fluids in one dimension, with advection the only transporting mechanism, a sharp front is maintained between the initial and displacing fluids. This front moves through the porous system at a velocity equal to the average linear pore water velocity. The average linear pore water velocity, defined macroscopically at a discrete point in the porous medium, is the microscopic solution velocity averaged over a representative elemental volume (REV) about that point (Gillham and Cherry, 1982). The advective solute flux is defined as:

$$\bar{J}_a = \bar{q}C, \tag{1}$$

where J_a is the mass of solute crossing a unit area of porous media oriented normal to the flow direction per unit time [$ML^{-2}T^{-1}$], q is the flux density (Darcy flux) [LT^{-1}], and C is the solute concentration (mass of solute per unit volume of solution) [ML^{-3}] (Gillham and Cherry, 1982).

The advective-flow domain is generally assumed to be well-mixed, thus minimizing the importance of mass-transfer resistances within this region (Brusseau and Rao, 1990*a*). The term convection is often used interchangeably with advection.

HYDRODYNAMIC DISPERSION

The process of hydrodynamic dispersion (i.e., mechanical dispersion) is also of critical importance when discussing contaminant movement and migration. Dispersion in a porous material refers to the mixing of discrete water volumes due to pore water velocity and path length heterogeneities while flowing through the subsurface media. If a spot of dye, for example, is injected into a porous media through which groundwater flow is occurring, it will spread as it is transported down gradient. Since dispersion increases as groundwater flow velocity increases, the dye plume will be larger with more rapid groundwater flow. More specifically, in a three-dimensional Cartesian coordinate system where the average groundwater velocity is parallel to the x axis, a sphere of dye moving horizontally along the x axis will undergo longitudinal spreading or dispersion parallel to the x axis, and transverse dispersion parallel to the y and z axes (Anderson, 1984).

Due to dispersion, a contaminant is spread over a larger volume of aquifer material than would be predicted from the mean groundwater velocity alone. This spreading is of particular importance when toxic or hazardous wastes are

involved. Dispersion is of concern because it causes a particular contaminant of interest to arrive at a discrete point (e.g., discharge point) earlier than anticipated by the average groundwater flow velocity and causes the time for complete displacement to be increased. Dispersion causes some parts of the contaminant plume to migrate faster than others yielding accelerated contaminant arrival (Anderson, 1984).

The dispersion process is most easily viewed as a macroscopic process but it may also be considered a microscopic process as well. On the microscopic scale, dispersion is caused by three mechanisms. The first mechanism is pore water velocity variations caused by the difference in pore sizes. Poiseuille's law for flow through a pipe states that the volume flow rate is proportional to the pressure drop per unit distance and to the fourth power of the tube radius. This describes flow as being laminar at low flow velocities and in narrow tubes. However, at increased flow rates and/or increased tube sizes, the laminar flow changes to turbulent flow. Laminar flow is the rule rather than the exception in most water flow processes taking place in soils due to the narrowness of soil pores (Jury, 1980). A second process occurs in an individual pore because molecules are traveling at various flow velocities at different positions orthogonal to the pore surface due to the restraint on the fluid exerted by the pore surfaces. The velocity of water flowing at the center of the pore is faster than the (immobile) water

molecules fixed adjacent to the walls of the pores. Thirdly, dispersion is related to the branching and tortuosity of the pore channels. Longitudinal dispersion, solute spreading in the direction of bulk flow, and transverse dispersion, solute spreading perpendicular to flow, are directly affected by the tortuous paths characteristic of aggregated media. Normally, longitudinal dispersion is much larger than lateral or transverse dispersion (Freeze and Cherry, 1979) because the solute is being transported more rapidly in the direction of fluid flow rather than perpendicular to its flow. On the microscopic scale, diffusion may also be considered a factor in the dispersion process. Diffusion refers to the migration of solutes from a higher concentration area to an area of lesser concentration due to Brownian movement. The contribution of diffusion on hydrodynamic dispersion is generally considered to be insignificant, especially in the range of velocities typical to many cases of concern (Brusseau and Rao, 1989*b*). However, it is the quantification of diffusive mass transfer of solutes between the mobile and immobile pore regions that drive this series of investigations.

On a macroscopic scale, dispersion is caused by the presence of large-scale heterogeneities present in the subsurface. Skibitzkie and Robinson (1963) demonstrated that lenses of high permeability material within a matrix of lower permeability cause the spreading of dye streams as water and

dye travel through a tank filled with sand. It is now generally recognized that macroscopic heterogeneities in the subsurface, rather than microscopic dispersion alone, are responsible for the spreading of contaminants. Such evidence is documented in a number of field studies (e.g., Anderson, 1979).

Physical nonequilibrium is the result of flow regions with distinctly different flow velocities. Therefore, under such conditions, solute spreading is a result of the combined effects of hydrodynamic dispersion and diffusion. The relative importance of these dispersion mechanisms depends on the conditions eliciting their effect. Under low fluxes, hydrodynamic dispersion will be the dominant process of solute spreading in fine-grained, poorly aggregated media (Brusseau and Rao, 1989*b*). Diffusion will be dominant under extremely low fluxes and in the presence of sizeable concentration gradients.

DIFFUSION

As previously discussed regarding hydrodynamic dispersion, diffusion also serves as a process for contaminants to eventually reach groundwater supply systems. In aqueous solutions, the process of diffusion is defined whereby solutes migrate under the influence of their Brownian motion. This random movement of molecules results in a net flux in the direction of their concentration gradient (Freeze and Cherry, 1979). As solutes are transported primarily by

advection in the more permeable heterogeneities, migration into lesser permeable heterogeneities is controlled by diffusion. This thereby reduces the concentration in the more conductive zones and increases it in the less conductive zones (Gillham and Cherry, 1982). Diffusion also occurs in the absence of any bulk fluid flow or hydraulic movement. The process halts only when a concentration gradient becomes nonexistent.

The diffusion coefficient is a numerical term used to describe the ability at which a particular ion will diffuse in a porous medium. Diffusion coefficients for many ions in aqueous solutions are very well known. Among these, Na^{+}, K^{+}, Ca^{2+}, Cl^{-}, HCO^{3-}, and SO^{4-} are ions primarily found in groundwater systems. These ions have a range of diffusion coefficients that tend to be on the order of 1×10^{-9} to 2×10^{-9} m^2 s^{-1} at 25°C (in pure water) (Robinson and Stokes, 1965). In porous media the diffusion coefficients for these ions are much smaller than in pure water. This is because ions follow longer paths of diffusion determined by pores in the matrix and because of adsorption onto solid particles (Freeze and Cherry, 1979). The effective diffusion coefficient for nonadsorbed species in porous media, D*, is represented by the relation

$$D^{*}=\omega D \qquad (2)$$

where ω, which is less than 1, is an empirical coefficient

that takes into account the effect the solid phase imposes on the porous medium by diffusion (tortuosity), and D is the diffusion coefficient [L^2T^{-1}].

The mass of diffusing substance passing through a given cross sectional area is proportional to the concentration gradient. This is known as Fick's first law which can be expressed as

$$F=-D\frac{dC}{dx} \tag{3}$$

where F is the mass of solute per unit area per unit time [$ML^{-2}T^{-1}$]; D is the diffusion coefficient [LT^{-1}]; C is the solute concentration [ML^{-3}]; and dC/dx is the concentration gradient, which is a negative quantity in the direction of diffusion.

There have been many attempts to describe diffusion under a variety of conditions through the use of numerical and analytical models. Nielsen and Biggar (1962) present a descriptive equation for solute transport by diffusion and advection through porous media. A dispersion coefficient, D_s, for a given porosity and an average flow velocity, v, were used in a unidirectional model

$$\frac{\partial C}{\partial t}=D_s\frac{\partial^2 C}{\partial x^2}-v\frac{\partial C}{\partial x}. \tag{4}$$

The solution of equation (4) subject to the conditions

$$C = C_0 \qquad X = 0 \qquad t > 0$$

$$C = 0 \qquad X > 0 \qquad t = 0$$

$$C = 0 \qquad X \rightarrow \infty \qquad t \geq 0$$

may be found as

$$C/C_0 = 1/2\left[erfc\left(\frac{x-vt}{\sqrt{4Dt}}\right) + \exp\frac{vx}{D}\, erfc\left(\frac{x+vt}{\sqrt{4Dt}}\right)\right] \qquad (5)$$

where C/C_0 is the reduced solute concentration, *erfc* is the complementary error function, D is the diffusion coefficient, t is time, v is flux, and x is distance.

For this model, the concentration across any cross-section of the column must remain constant. However, in reality the invading fluid displaces the original fluid in an irregular manner owing to the wide range in microscopic pore water velocities. This creates a region of higher concentration many times greater than that of the water-filled cross-sectional area of the column through which diffusion may occur. Thus, the faster the displacement (i.e., higher flux), the greater the dispersion coefficient that will be calculated from equation (5). This is a direct consequence of using a constant average velocity for the fluid in equation (4) as an approximation to its unknown average velocity distribution between soil pores (Nielsen and Biggar, 1962). In the use of this model no chemical or physical interaction between solute, liquid, and porous material is assumed.

Miscible displacement experiments by Kirda et al. (1973) under saturated conditions used $CaCl_2$ labeled with ^{36}Ca to assess the effect of flux on the dispersion coefficient. For column experiments using fluxes above 14.4 cm d^{-1} the dispersion coefficient decreased with decreasing values of flux. However, in experiments where the flux monotonically decreased below 14.4 cm d^{-1}, the dispersion coefficient was no longer dependent upon flux. One particular experiment described the determination of a dispersion coefficient under decreasing flux values over a duration of 75 hours. This dispersion coefficient was constant for fluxes less than 14.4 cm d^{-1} suggesting that dispersion contributed significantly to the mixing process (Kirda et al., 1973). The results from these studies indicated that diffusion alone cannot be responsible for the spreading of a solute in a soil column or under natural field conditions when flux is large.

The physical characteristics of the porous media, such as soil structure, obviously control nonideality for transport of nonsorbing solutes and water. It is suggested that the primary factors contributing to nonideal transport for organic solutes are chemical and physical soil properties and chemical and physical nonequilibrium (Brusseau and Rao, 1989a). From this rationale, formulated assumptions and experimental data confirm transport nonideality of inorganic nonreactive solutes are highly influenced by sorption as well as transport (chemical and physical) related nonequilibrium.

NONEQUILIBRIUM

The local equilibrium assumption (LEA) is a major component of the conventional solute-transport equation (Brusseau and Rao, 1989*b*). For the LEA to be valid, the sorption rate must be fast relative to the other processes affecting solute concentration (e.g., hydrodynamic dispersion, advection). Such conditions must prevail for the establishment of chemical equilibrium between the sorbent and the pore fluid. It was initially thought that because subsurface water movement is so slow, chemical equilibrium conditions would prevail, thus rendering the LEA valid. However, results from numerous laboratory and field-scale investigations provide data whereby the validity of the LEA is challenged and often refuted.

Breakthrough curves (BTC's) provide a means of describing solute transport in porous media by which the reduced solute concentration(effluent divided by influent concentration, C/C_0) is plotted against cumulative outflow volume (pore volume or reduced time). If LEA is valid, relative solute BTC's obtained from miscible displacement experiments using packed columns will be symmetrical. However, if LEA is invalid, reactive solute BTC's show asymmetry with early solute breakthrough and increased "tailing" (i.e., delayed approach to $C/C_0 = 1$). Data from many laboratory and field studies exhibit breakthrough curve asymmetry (Rao et al., 1979; Seyfried and Rao, 1987; Sudicky et al., 1985; Rao et

al., 1980). Fig. I.2 represents BTC's exhibiting chemical equilibrium and nonequilibrium. As nonequilibrium increases, ω decreases (ω is a dimensionless mass-transfer coefficient for physical mass-transfer model), the BTC shifts to the left and both early breakthrough and tailing increase (Brusseau and Rao, 1989*b*). The processes of nonequilibrium may be grouped into two general categories: chemical and physical. Each process is briefly discussed below.

CHEMICAL NONEQUILIBRIUM

Chemical nonequilibrium (CNE) may result from both sorption nonequilibrium and intrasorbent diffusion. Sorption nonequilibrium results from kinetic interactions between the solute and specific sorption sites of the sorbent. Sorption of low-polarity HOC's, because of their non-site-specific nature, are generally not affected by sorption nonequilibrium (Brusseau et al., 1989). Conversely, hydrophilic organic chemicals and inorganic solutes may be influenced by sorption nonequilibrium. Chemical nonequilibrium resulting from intrasorbent diffusion involves the diffusive mass transfer of sorbate within the sorbent matrix. Given that organic matter and mineral components are generally the two major sorbents, intrasorbent diffusion may involve either intraorganic matter diffusion or intramineral diffusion. Solute transport, as described by breakthrough curves, in such systems is characterized by early initial breakthrough resulting from rapid transport in the advective flow domain and by tailing.

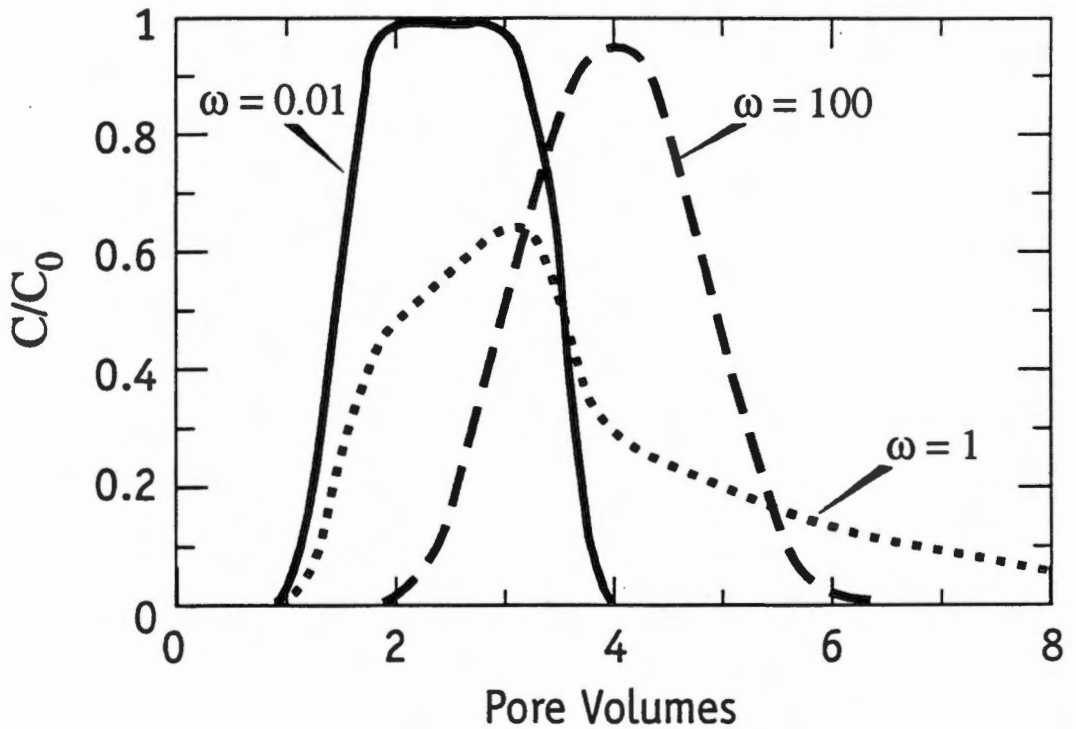


Fig. I.2. Equilibrium and nonequilibrium breakthrough curves. Nonequilibrium increases with decreasing ω.

Source: Brusseau M.L., and P.S.C. Rao. 1989*b*. Sorption nonideality during organic contaminant transport in porous media. Crit. Rev. Environ. Control, 19:33-99.

Tailing is a result of rate-limited mass transfer between the advective and nonadvective flow domains. Such behavior is observed in aggregated, macroporous, heterogeneous, and fractured porous media (Brusseau et al., 1989).

PHYSICAL NONEQUILIBRIUM

Physical nonequilibrium (PNE), results from the existence of regions within the porous medium consisting of distinctly different flow velocities. Inter-region diffusive mass transfer of solute between nonadvective flow (or immobile) regions and advective flow (mobile) regions results in the former behaving as a distributed source/sink component. Although inter-region diffusion and intra-region diffusion involve a mass transfer mechanism, they are considered to be different because inter-region diffusion is predominantly a free-water diffusion process, while intra-region diffusion is a fixed-water diffusion process. Solute transport influenced by PNE may be similar to that exhibited by CNE systems, whereby breakthrough curves display early solute breakthrough and tailing. However, unlike CNE, PNE may result in bi- or tri-modal breakthrough curves. BTC's exhibiting CNE or PNE may also display a delayed solute breakthrough coupled with increased tailing.

Breakthrough curves obtained under saturated conditions exhibit a relatively large amount of dispersion. Under unsaturated conditions, some fraction of pores no longer readily conduct solution and this dispersion should decrease

(Brusseau and Rao, 1990). However, during storm flow, meso- and micropore flow converge into macropore flow channels, thus initiating macropore flow even under unsaturated conditions (Wilson et al., 1991*a*; Radulovich et al., 1992). Once flow is occurring in the macropores, unsaturated aggregates containing meso- and micropores are by-passed at deeper depths due to the relatively high flux in the macropore region. This variably saturated preferential flow scenario explicitly means that hydraulic nonequilibrium (HNE) conditions exist within the soil (Wilson et al., 1994). After soil water pressure falls below field capacity, flow occurs only through micropores. de Marsily (1986) stated that the water thickness adjacent to the particle surface must be >1 μm to be freely mobile due to viscous drag forces acting upon water molecules near the particle surfaces. Therefore, micropore flow may be negligible, however, micropores may still serve as a source/sink of solutes as well as a source for biological uptake (Wilson et al., 1994). BTC's obtained under variably saturated preferential flow conditions exhibit a greater degree of dispersion and may be shifted leftward (lower pore volume) in comparison to BTC's for saturated conditions. The skewness in the breakthrough curve is due to the impact that immobile domains elicit upon the entire soil matrix (Brusseau and Rao, 1990).

The occurrence of CNE, PNE, and HNE may have a significant impact upon many facets of groundwater

contamination and remediation. For example, efforts to address potential groundwater contamination problems and to assist aquifer restoration activities have become much more involved such that LEA based models are not valid (Brusseau et al., 1989). Chemical and physical nonequilibrium may result in the breakthrough of a contaminant at a point of interest (observation well) earlier than predicted by LEA model. Therefore, the magnitude of the contaminant plume and its rate of migration may be much more extensive than initially anticipated. The time required for renovation of a contaminated aquifer can be greatly increased because of nonequilibrium-induced tailing especially when "pump and treat" techniques are implemented (Brusseau et al., 1989).

MISCIBLE DISPLACEMENT

Solute transport under saturated conditions is an extensively studied topic in hydrogeology and soil physics. Previous investigations have lead to the assumption that local equilibrium conditions exist during solute transport under field and natural conditions. However, recent experimental and theoretical work has cast doubt on the validity of this assumption (Brusseau et al., 1989). Numerous investigators demonstrated the absence of local equilibrium conditions under naturally encountered gradients (Roberts et al., 1986; Goltz and Roberts, 1986; Brusseau and Rao, 1989a) and through investigations using laboratory soil columns (Lee et al., 1988; Angley et al., 1992; Brusseau et al., 1990; Nkedi-Kizza

et al., 1989; Seyfried and Rao, 1987).

Due to CNE, the LEA adsorption isotherm models are often replaced with kinetic adsorption models. The simplest kinetic models are the single-site irreversible first and second order adsorption models. A more common and more powerful model is the first-order kinetic reversible model that was incorporated into solute transport equations by Lapidus and Amundson (1952). By far, the most advanced kinetic model is the multi-reaction model (MRM) developed by Selim and colleagues (Selim et al., 1986, 1990, Selim and Amacher, 1988, and Amacher et al., 1988). The MRM illustrated in Fig. I.3 by Selim et al., 1990, is the most rigorous approach currently available. It includes an irreversible site, S_{irr}, an equilibrium adsorption site, S_e, included, forward kinetic adsorption rates (k_1 & k_3) for two kinetic sites (S_1 and S_2, respectively) which are separated from the respective backward kinetic desorption rates (k_2 & k_4), along with a concurrent reversible (k_5 & k_6) kinetic adsorption site-3 for solute that is strongly retained by soil due to slow reversible reactions with site-2. Selim et al. (1990) applied the MRM to the transport of heavy metals through several soils common to Louisiana. They demonstrated methods of estimating these forward and backward kinetic coefficients and found that the MRM greatly improved the capabilities to predict heavy metal transport.

Laboratory column experiments for investigating chemical/physical nonequilibrium involve the miscible

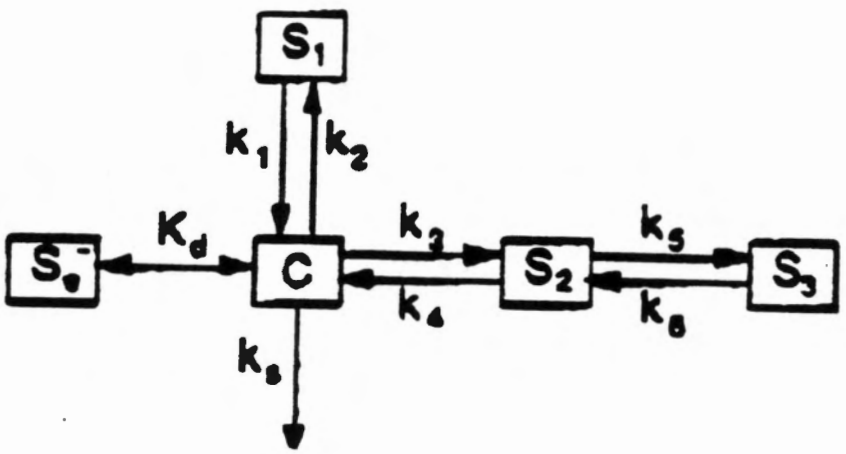


Fig. I.3. Schematic diagram of the multireaction retention model.

Source: Selim, H.M., Amacher, M.C., and I.K. Iskandar. 1990. Modeling transport of heavy metals in soils. Monograph 90-2. U.S. Corps of Engineers, Cold Regions Research and Engineering Laboratory. Hanover, N.H. 03755.

displacement technique (MD) which is used primarily to study transport dynamics under saturated conditions. The technique incorporates the use of reactive and non-reactive tracers to simulate contaminant transport. Some non-reactive solutes frequently used in miscible displacement studies are Cl^-, tritiated water (^3H), and Br^-. The miscible displacement technique is widely used in chemical and petroleum engineering and soil science to investigate various aspects of solute transport in porous media (Brusseau et al., 1990). Use of the MD technique to investigate nonequilibrium sorption (or sorption kinetics) of organic solutes was initiated by soil scientists seeking to evaluate the behavior of pesticides in soils. Miscible displacement studies have become important tools in soil physics, particularly for predicting the movement of nitrates, heavy metals, pesticides, low-level radioactive wastes, as well as other solutes traveling through subsurface media. These studies can provide valuable information about both the behavior of a chemical in a porous medium and about the medium itself (pore size distribution, aggregation) (van Genuchten and Wierenga, 1976).

The MD technique employs the elution of a known concentration of tracer solution through a natural or artificial porous medium commonly packed in a column. The solute is passed through the column at a predetermined flux (q) for a specified period of time or until a particular effluent concentration is reached. The column effluent is

collected in discrete volume fractions for concentration analysis. Typical BTC's obtained during various miscible displacement experiments are shown in Fig. I.4-I.6. For Fig. I.4 (*A* and *B*), it is assumed that the solute spreads as a result of advection, dispersion, and diffusion, i.e., there is no interaction between the solute and solid. Physically, this means that the original fluid occupies exactly one pore volume or that the quantity of solute within the column that eventually reaches chemical equilibrium with the influent and effluent is C_0V_0 (Nielsen and Biggar, 1962). Fig I.5 displays BTC's affected by chemical reactions, exchanges, precipitation, and the effects of velocity distributions.

Fig. I.4*A* exhibits the flow phenomena known as piston flow which rarely if ever occurs in natural soils or artificially packed laboratory columns. There exists for a single capillary tube of constant radius, only a narrow range of fluxes at which this type of flow is approached. In this case, flow is strictly occurring within macropores by advection only, i.e., no porous microstructure present. Because subsurface media does not contain a constant pore sequence, the probability of piston flow observation is negligible (Nielsen and Biggar, 1962). The influence of local longitudinal dispersion on solute transport is exhibited in the breakthrough curve of Fig. I.4*B*. Sudicky et al. (1985) concluded from their numerical model predictions that local longitudinal dispersion is only of secondary importance as a

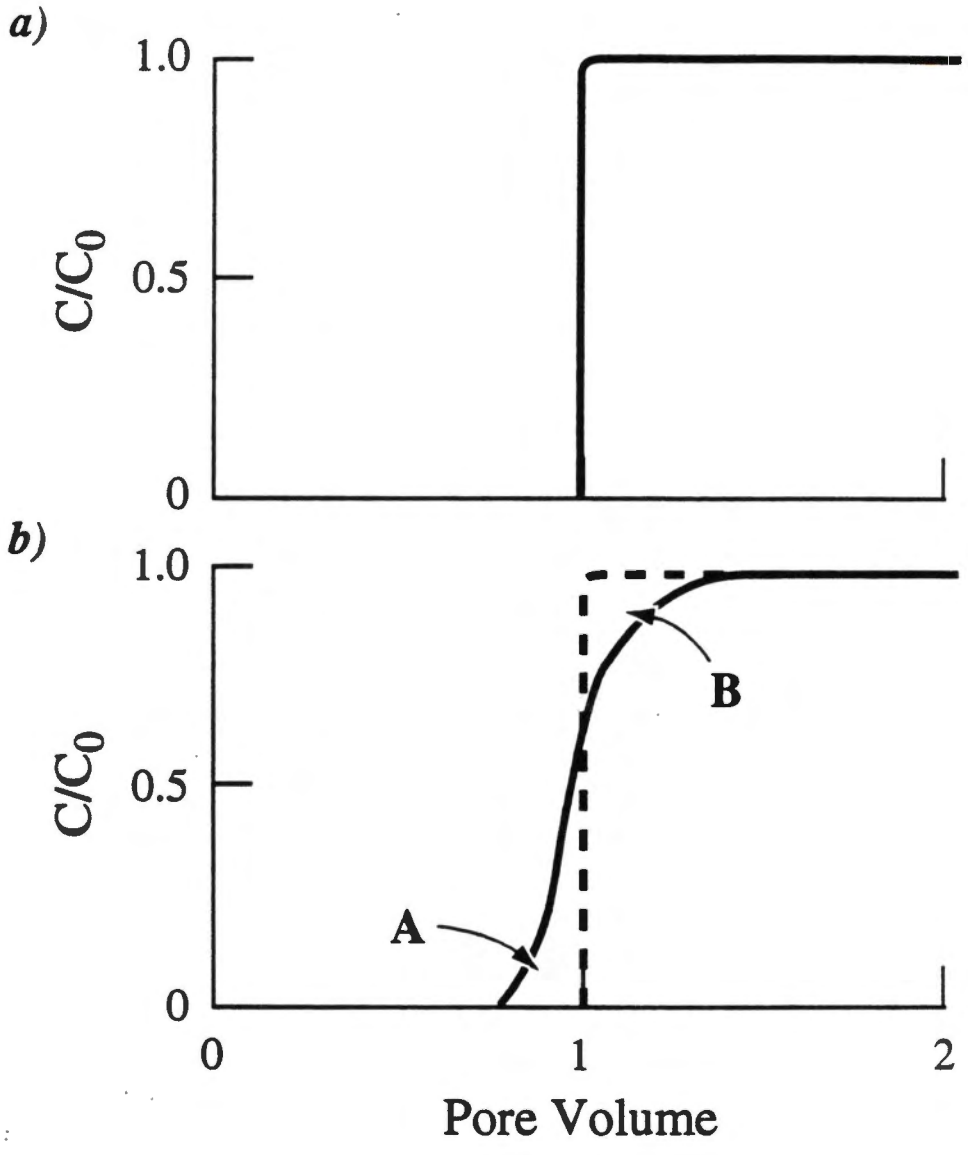


Fig. I.4. Breakthrough curve representing (a) piston flow and (b) longitudinal dispersion.

Source: Biggar, J.W., and D.R. Nielsen. 1962. Some comments on molecular diffusion and hydrodynamic dispersion in porous media. J. Geophys. Res., 67:3636-3637.

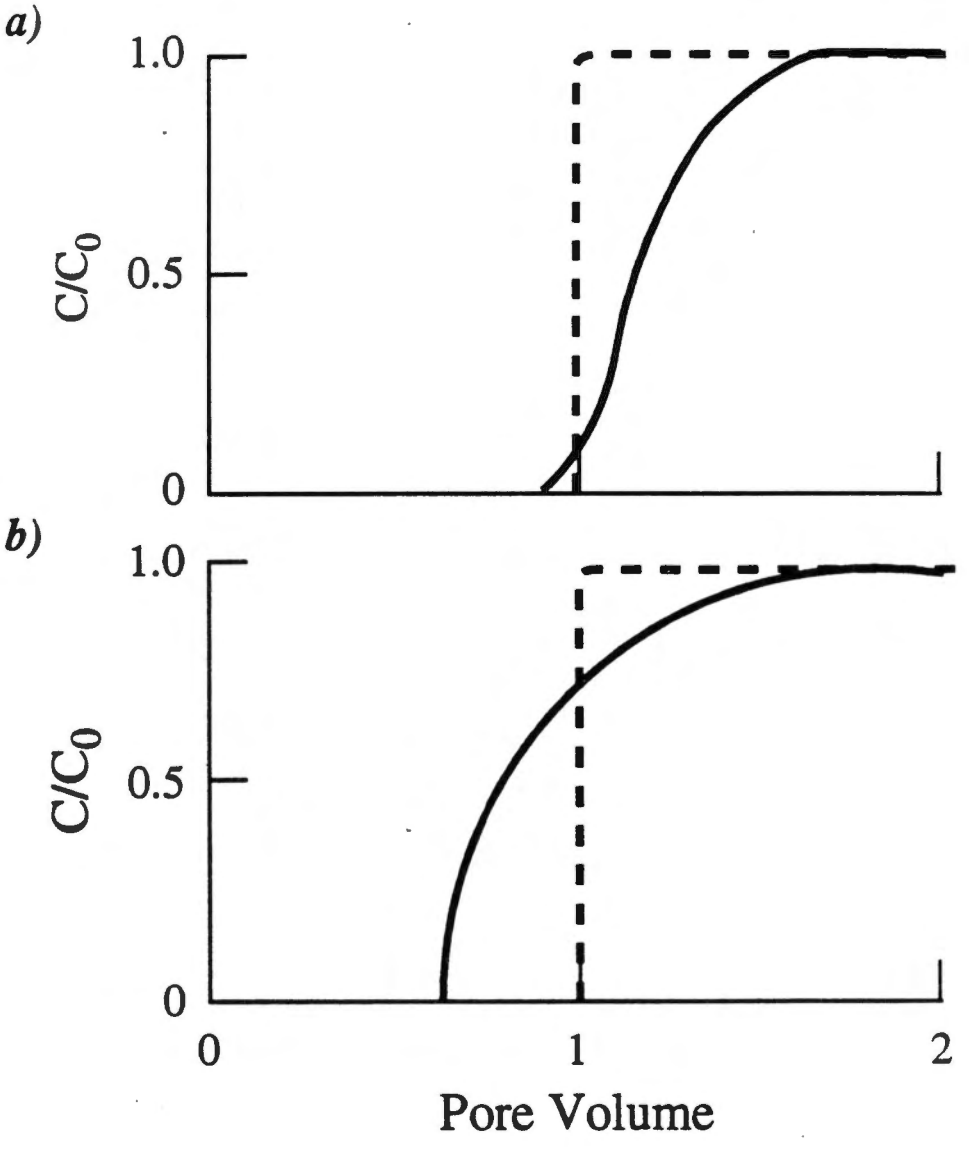


Fig. I.5. Breakthrough curve representing (a) effect of chemical reaction, exchange, or precipitation, and (b) extremely wide range in velocity distribution.

Source: Biggar, J.W., and D.R. Nielsen. 1962. Some comments on molecular diffusion and hydrodynamic dispersion in porous media. J. Geophys. Res., 67:3636-3637.

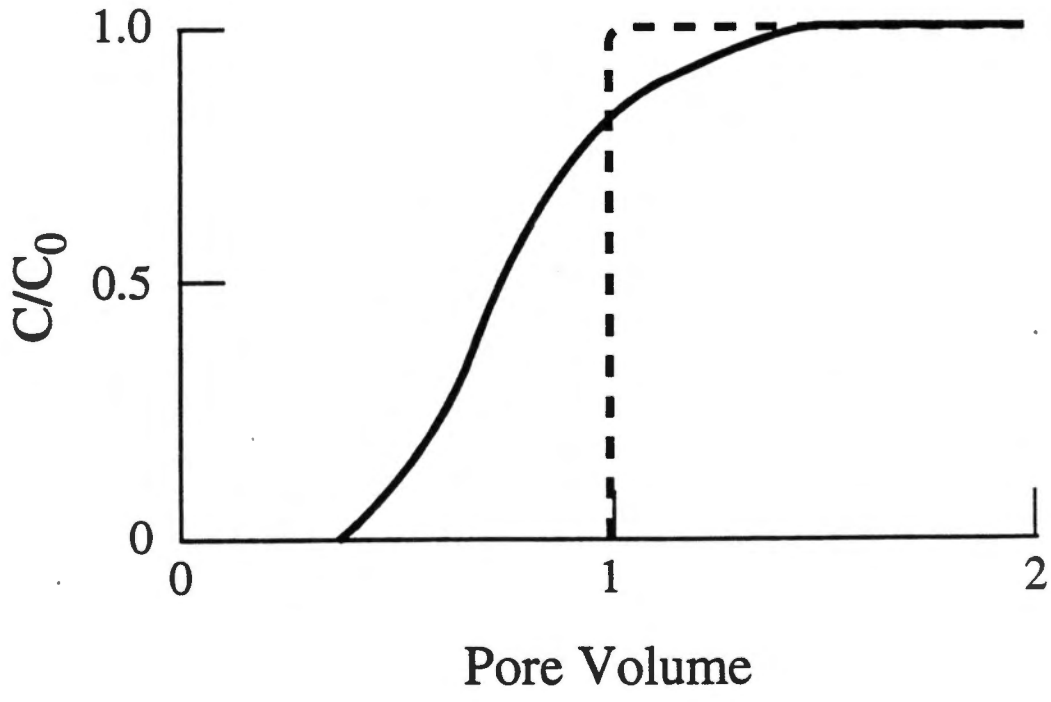


Fig. II.6. Breakthrough curve representing exclusion of solute by solute-solid interaction or velocity distribution with velocities near zero.

Source: Biggar, J.W., and D.R. Nielsen. 1962. Some comments on molecular diffusion and hydrodynamic dispersion in porous media. J. Geophys. Res., 67:3636-3637.

spreading process in random porous media. For their model, the strong longitudinal dispersion exhibited by the experimental BTC is principally the result of a diffusive exchange between sand and silt layers of the column used during the miscible displacement of Cl^-. Strong indicators of longitudinal dispersion are: 1) observed rates of increase in concentration with pore volume being noticeably skewed, and 2) the shape of the breakthrough curve being flattened (Sudicky et al., 1985).

Chemical or physical processes occurring within the soil column may result in retention of the displacing fluid or its solutes. As a result of such processes the experimental breakthrough curve will be translated to the right as shown in Fig. I.5*A*. A soil containing equal-sized aggregates with no smaller or larger particles possesses an extremely wide range in pore water velocity distribution which is bimodal at saturation. This characteristic will cause a left-hand shift in the BTC as represented by Fig. I.5*B* (Nielsen and Biggar, 1962).

Any process within the soil causing an increase of solute concentration due to incomplete mixing (dispersion) throughout the entire soil will yield a BTC translated to the left as shown in Fig. I.6. In the case of anion solution displacement through a porous media, the anions will experience a repulsion away from negatively charged clay surfaces, causing a left-handed shift (early breakthrough) in the observed breakthrough

curve. The same would occur if solute mixing were not complete due to essentially stagnant pores. Solutions of slightly soluble salts already present in the soil will also translate the curve to the left.

The processes responsible for and the results of asymmetric breakthrough curves previously discussed are indicative of solute transport nonequilibrium during solute transport through soil columns. However, the breakthrough curve characteristic known as "tailing", which is also associated with chemical and physical nonequilibrium, has not been adequately discussed. Tailing refers to the delayed total breakthrough (i.e. delayed attainment of $C/C_0 = 1$ during solute injection, and $C/C_0 = 0$ during solute displacement) of a solute passing through a porous material.

TAILING

Tailing may be observed in MD experiments under saturated or unsaturated flow conditions in aggregated media and at different fluxes (Hutzler et al., 1986; Brusseau et al., 1991; Angley et al., 1992; Brusseau et al., 1990; Nkedi-Kizza et al., 1989; Lee et al., 1988; Nkedi-Kizza et al., 1982; Rao et al., 1980). Nielsen and Biggar (1961) reported considerable tailing with decreasing water content at approximately the same flux. It is argued that under unsaturated conditions the large pores are eliminated for transport and that the portion of water which does not readily move within the soil is increased (van Genuchten and Wierenga, 1976). This water is

referred to as stagnant or immobile water. A decrease in this fraction of water increases the fraction of air-filled macropores. These air-filled "voids" create dead end pores which can only attain equilibrium with the displacing solution by diffusion if flow is steady state (Gupta et al., 1973). Under these conditions it requires more solute displacement, which creates extensive breakthrough curve tailing.

Porous media may be composed of a series of different sized aggregates which produce rapidly and slowly conducting pore sequences. Convection and dispersion are the dominant transport processes occurring between aggregates, leaving diffusive processes to transport solute within the aggregate (Fig. I.1). This results in a slow and incomplete solute mixing process, thus inducing BTC tailing. Within larger aggregates the amount of immobile water increases while the diffusive pathway from the mobile to immobile domain becomes longer, resulting in breakthrough curves with more and more exaggerated tailing (Biggar and Nielsen, 1962; Green et al., 1972; McMahon and Thomas, 1974).

EFFECTS OF FLUX

Experimentation implementing variations in flux between experiments (van Genuchten and Wierenga, 1977) demonstrated the amount of immobile water generally increased with decreasing flux. The decreased flux results in a longer diffusive pathlength for a chemical within the mobile liquid to migrate to the center of the immobile liquid, thus

increasing equilibration time (i.e., increasing tailing). This phenomena occurs because the thickness of the slipping plane increases due to the frictional forces exerted between the particle surface and the eluting solute. Thus, the diffusional pathlength is increased. Similar effects of flux are documented by Bennet and Goodridge (1970); Coats and Smith (1964); and by Nielsen and Biggar (1962). Akratankul et al. (1983) also demonstrated the effect of flux on the rate of adsorption under nonequilibrium conditions. These authors investigated the adsorption of CdI_2 using the miscible displacement technique in saturated soil columns. Their study indicated that the rate of adsorption increased with increasing flux. It was postulated that higher fluxes yield shorter residence times for the ions in solution passing through the soil, thus producing a case of slower adsorption. However, their studies showed that higher fluxes introduced a greater mass of ions during a fixed time span. This maintains a higher ionic concentration in the bulk solution which introduces more ions to surfaces of soil particles. Their studies also included the effect of flux on the boundary layer existing near soil particles where solution is immobile. Ions in solution must migrate across this region (i.e., adhesive layer) via molecular diffusion. Akratankul et al. (1983) concluded that the thickness of this boundary layer is a function of flux, where higher fluxes reduce the thickness of the stagnant layer, thereby decreasing the diffusive

pathlength. The soil-water electrolyte composition (types of solutes and their respective concentrations) also strongly effects diffusion. These findings indeed demonstrated that diffusion may be a rate limiting process for adsorption, and flux is directly correlated with the magnitude of tailing. This is very important, especially when the adsorption is far from equilibrium.

These flow characteristics cause the breakthrough curve to exhibit nonsigmodial and asymmetric forms which are indicative of sorption nonideality. Due to the importance of sorption nonequilibrium, there is a need to investigate the occurrence of, and the processes responsible for, these phenomena. Unfortunately, current techniques are not always capable of identifying the causative mechanisms controlling sorption nonideality. Current transport analysis frequently involves curve-fitting to experimental data obtained under steady-state solute flow through disturbed soil columns with various models and selecting the model exhibiting the best fit to experimental data.

MODELING TRANSPORT-RELATED NONEQUILIBRIUM

Definitive experimental results encountered in the literature demonstrate that prediction of solute migration in natural hydrogeologic systems is not adequately understood. Formulation of the transport processes into mathematical expressions therefore provides a means of predictive description of solute migration. The equation most commonly

used to describe solute transport in natural hydrogeologic media is the advective-dispersion (AD) equation. It is defined by Gillham and Cherry (1982) for a homogeneous medium as

$$\frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2} - \bar{V} \frac{\partial C}{\partial x} . \qquad (6)$$

Equation (6) is similar to equation (4) with the exception of the D_L component. This term is defined as the dispersion coefficient. Others re-define the D term in equation (4) to include the effects of diffusion, as well as hydrodynamic dispersion. This lumped parameter replaces the D_L term in (4) to accommodate a wider variety of experimental conditions. The general form of equation (4) is frequently applied to contaminant migration scenarios, however, it is subject to many assumptions and limitations including the following:

1) The contaminants are soluble in water.
2) The fluid properties (viscosity and density) are independent of solute concentration.
3) The fluid is incompressible.
4) The coefficients of molecular diffusion and mechanical mixing are additive.
5) The solute is nonreactive (i.e., the ionic species of interest is not complexed with the media).

For modeling purposes, the objective of this study is to effectively model the physical nonequilibrium existing between

the mobile and immobile regions in an undisturbed saturated soil column. Solute transfer between the mobile and immobile regions may be accounted for in the following ways:

1) Explicitly, with the use of Fick's law to describe the physical mechanism of diffusive transfer.
2) Implicitly, with the use of an effective or lumped dispersion coefficient (as discussed above).
3) Explicitly, with the use of an empirical first-order mass-transfer expression, in place of the mechanistic expression of (2), to approximate solute transfer (Brusseau and Rao, 1989*b*, 1990).

ADVECTIVE-DISPERSIVE MODEL

As briefly described above, this type of nonequilibrium model employs a lumped or "effective" dispersion parameter in the conventional advective-dispersive (A-D) transport model. This effective dispersion coefficient implicitly accounts for any diffusive mass transfer occurring between the mobile and immobile domains (Brusseau and Rao, 1990). Approaching conditions of near-equilibrium, BTC symmetry will increase to a point where asymmetry is difficult to ascertain. Increased dispersion will then be the only evidence of nonequilibrium. The advective-dispersion model will fit experimental data especially well under this condition (Brusseau and Rao, 1990).

These models are useful and necessary; however, they may not provide an adequate means for establishing the validity of the actual phenomena occurring during subsurface transport.

This is especially true when the mathematical equations associated with a conceptual model are non-unique (Brusseau et al., 1989). The two-region transport model used to represent physical nonequilibrium is said to be equivalent to the two-site sorption model used to represent chemical nonequilibrium for the case of the linear sorption isotherm (van Genuchten, 1981; Nkedi-Kizza et al., 1984; Brusseau and Rao, 1989b). The two-site sorption model may also be used to represent IOMD (intraorganic matter diffusion) (Lee et al., 1988; Brusseau and Rao, 1989a). There is an obvious need for experimental techniques and mathematical models that can differentiate between the various nonequilibrium processes .

Under certain conditions, such as using a high flux in a short column, sorption nonequilibrium cannot be readily perceived when analyzing data obtained with the typical continuous flow column experiment (Brusseau et al., 1989). Therefore, a more sensitive technique must be implemented for the detection and quantification of such a process. One technique is known as "flow interruption" where the steady-state flow process is stopped for a designated period of time to allow a new chemical equilibrium state to be approached.

PHYSICAL DIFFUSION MODELS

These types of models assume film-transfer resistance to be negligible. If this is not the case, incorporation of a film transfer parameter may prove beneficial for enhanced model prediction. Solute transfer from mobile to immobile

regions is described by a two-step series; diffusion through a boundary layer surrounding the particle (i.e., film transfer), followed by diffusion within the aggregate (i.e., intra-aggregate diffusion) (Brusseau and Rao, 1990).

Early variations of diffusion-based models were developed assuming a spherical aggregate geometry which, for many cases, is not totally applicable under many experimental conditions. Thus, the physical diffusion model was extended for application of more general conditions involving aggregates with non-spherical geometries through the use of a geometry-dependent shape factor (Rasmuson, 1985). However, this transformation does not render the physical diffusion model totally functional for experimental evaluation under field conditions. Incorporation of an aggregate size distribution (ASD) parameter also must be defined within the model to account for variation in aggregate sizes within a porous media (Rao et al., 1981). Combining the shape transformations of Rasmunson (1985) with the aggregate size-distribution transformation of Rao et al. (1981), a porous medium consisting of different sizes of aggregates having various non-spherical shapes can be transformed into a representative medium consisting of an equivalent, spherical aggregate of an equivalent uniform size. In this manner, the physical diffusion model may be extended to some nonideal field situations (Brusseau and Rao, 1989*b*, 1990).

PHYSICAL MASS-TRANSFER MODEL

Early development of the two-region models occurred in the field of petroleum engineering, where models for non-sorbing solutes are presented by various authors. van Genuchten and Wierenga (1976) extend this approach for the incorporation of sorbing solutes. In essence, the physical mass-transfer model is the linear driving force approximation employed by chemical engineers to simplify the problem of diffusion into spherical particles. Due to the uncertainty surrounding pore geometry analysis, the diffusion model is simplified by replacing the mechanistic description of diffusive transfer with a kinetic first-order mass-transfer coefficient. The actual description of the porous medium's structure is then no longer needed. Solute transfer between regions is described by a mass-transfer coefficient and is assumed to be a function of the solute concentration difference between the mobile and immobile regions. An average immobile-region concentration is also assumed to represent a perfectly mixed region (Brusseau and Rao, 1989*b*, 1990).

THE FLOW INTERRUPTION TECHNIQUE

METHOD DESCRIPTION

This method is based upon the "interruption test" which is employed in chemical engineering to distinguish between systems that are controlled by intra-particle diffusion vs. film diffusion (Kunin and Myers, 1947; Kressman and Kitchener,

1949). Interrupting flow provides a means to differentiate between purely advective and purely diffusive transport processes in a column experiment (Koch and Flühler, 1993). The technique involves the injection of a tracer solution into a physically or chemically heterogeneous column of porous media, inhibiting flow for a period of time (the interruption period), and then reinitiating solution flow. If inter-region diffusion is the rate-controlling process, the tracer will continue to diffuse between the matrix microporosity and the fracture during the interruption period in response to concentration gradients between the mobile and immobile pore regions. As a result, interruption during tracer injection, the effluent concentration will be less upon flow reinitiation than prior to flow interruption. However, if film diffusion is the rate-controlling process, the flow interruption will have no observable effect on solute diffusion into the matrix (Brusseau et al., 1989).

EFFECTS OF FLOW INTERRUPTION DURING MD

Before flow interruption (during tracer injection only), solution in macropores (inter-aggregate pores) is more concentrated than that in micropores (intra-aggregate pores). This is evidenced due to the advection process occurring mainly in macropores. Diffusive transport into the micropores is slow compared to advection, thus the solute concentration in the immobile region lags behind that of the mobile region (Koch and Flühler, 1993). When flow ceases the difference in

concentration between the micro- and macropores will proceed towards equilibration by diffusion. This results in a lower concentration in the macropore region when flow is reinitiated. Under these physical nonequilibrium conditions, the concentration decline will be obvious in breakthrough curves for a non-reactive solute upon flow reinitiation. These results are strong evidence for diffusive mass transfer between macro- and micropore regions (Koch and Flühler, 1993). A typical example, using simulated data, of a BTC exhibiting a concentration drop after a flow interruption is represented in Fig. I.7. Points *A* and *B* in Fig. I.7 correspond to the pre- and post-interruption reduced concentrations, respectively. The dip in the BTC was a result of sorption being a rate-limited rather than an instantaneous process. The sorption process continued to proceed during the no-flow "incubation" period, thus reducing the aqueous-phase solute concentration. The *I* position on the BTC in Fig. I.7 was due to the elution of the interrupt-period resident solution. The ensuing portion of the BTC, *II*, exhibited an increase in slope which was indicative of the breakthrough front of the solute pulse injected upon flow reinitiation (Brusseau et al., 1989). This portion of the BTC is usually allowed to approach a C/C_0 of 1.0, after which the eluting tracer solution is then switched to a tracer-free solution inducing tracer solution displacement (flush).

There may not be any detectable change in outflow

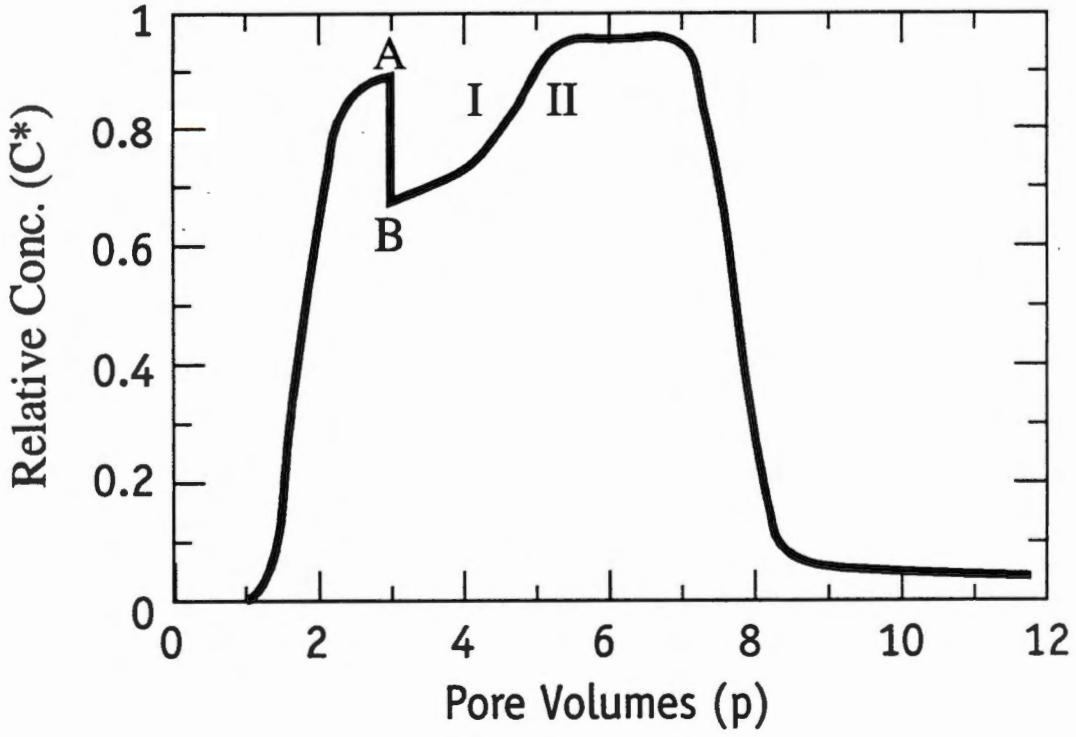


Fig. I.7. Typical BTC obtained using flow interruption technique.

Source: Brusseau, M.L., P.S.C. Rao, R.E. Jessup, and J.M. Davidson, 1989. Flow interruption: A method for investigating sorption nonequilibrium. J. Contam. Hydro., 4:223-240.

concentration despite diffusive transport into micropores. This phenomena is encountered when a tracer pulse is eluted through a column at a significantly slow enough flux such that convection and diffusion are occurring at approximately the same rate. Intra-region diffusion depends upon the concentration gradients in the direction of flow along the column while inter-region diffusion depends upon the gradients between the two pore regions. If advection and diffusion are occurring at the same rate there will not be an inter-region concentration gradient.

Generally, for greatest effluent concentration drop in the BTC, the interruption should occur within a discrete range of reduced concentration, C/C_0 . This optimum range is dependent upon the sorptive and diffusive character of the eluting chemical (tracer) as well as the sorptive nature of the sorbent. Diffusion of the solute between pore regions will occur during the interrupt period if concentration gradients along the column are established (Brusseau and Rao, 1989*a*).

An increase in solute spreading resulting from diffusion during no flow conditions was demonstrated by Biggar and Nielsen (1962) and Fukui and Katsurayama (1975). The magnitude of the concentration drop may be masked by the effects of solute redistribution on rate-limited sorption. At lower C/C_0 values, the intra-column concentration gradient and the resultant solute redistribution become greater.

Therefore, to minimize the effects of diffusion, the flow interruption period should be initiated at large enough C/C_0 values such that the in situ solution concentration gradient is small (Brusseau et al., 1989).

FLOW INTERRUPTION EFFECTS ON BTC's

Fig. I.8 demonstrates the effect of interrupting flow of a sorbing solute at a low C/C_0 value on the adsorption limb of the BTC. All parameter values are identical to those for Fig. I.7, except for the time at which flow interruption was initiated. For this BTC, the magnitude of concentration decrease is negligible in comparison to the drop in the previous figure. At lower C/C_0 values, the solution concentration decline resulting from continued sorption, is negated by an increase in concentration from the occurrence of diffusion during the interrupt period. Due to diffusion at low C/C_0 values, the magnitude of concentration decline may not be readily distinguished from the scatter typical of experimental data (Brusseau et al., 1989).

Flow interruption at higher C/C_0 values (i.e., $C/C_0 \approx 1$) on the injection limb, however, may not yield a detectable concentration decrease when near-equilibrium conditions exist. Therefore, interruption must be initiated at a slightly lower C/C_0 value (0.90-0.95) to maximize conditions for elucidation of a concentration perturbation. Therefore, the opposing effects of diffusion and degree of nonequilibrium must be considered in the appraisal of an optimal C/C_0 value for flow

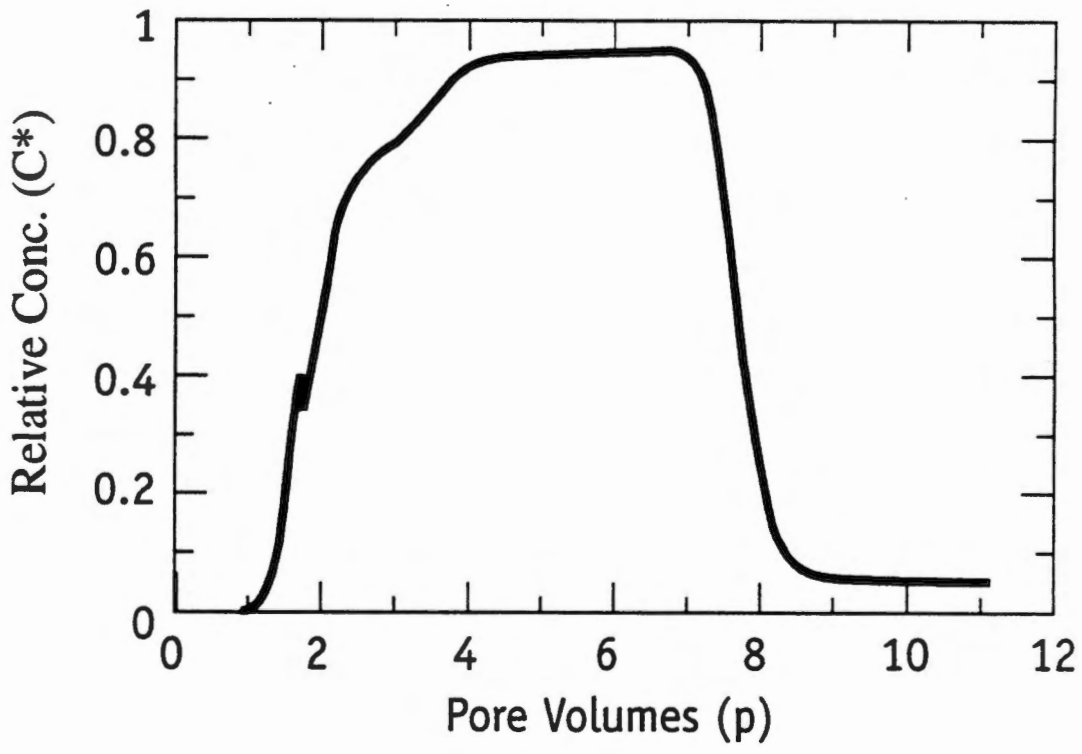


Fig. I.8. Shape of BTC as influenced by flow interruption at low C/C_0.

Source: Brusseau, M.L., P.S.C. Rao, R.E. Jessup, and J.M. Davidson, 1989. Flow interruption: A method for investigating sorption nonequilibrium. J. Contam. Hydro., 4:223-240.

interruption.

Flow interruption may also be initiated on the desorption limb of the BTC. For this case, a rise in solute concentration rather than a drop will occur. This is due to solute diffusion from the micropore region into the macropore region as a result of the concentration gradient created during the exit of the tracer solution from the column. For optimization of concentration increase, flow interruption should be initiated at low C/C_0 values (i.e., 0.10-0.02).

FLOW INTERRUPT APPLICATION

Zogorski et al. (1976) employed this method to investigate sorption kinetics of 2,4-dichlorophenol on granular activated carbon. In their experiments, two initial concentrations (54 and 310 mg L^{-1}) of 2,4-D were used to define the nature of the rate-limiting step in the adsorption of phenols. Continuous flow experiments were also conducted under the same experimental conditions. The rate of adsorption of 2,4-D at the lower initial concentration appears to be limited by interparticle transport. This is evidenced by: 1) the lack of influence that flow interruption had on the concentration profile; and 2) the similarity of results for the continuous and interrupted tests. This is evidence that adsorbate redistribution does not occur within the pores of the adsorbent during flow interruption. Data from experiments using the higher initial concentration yield significantly different results than those of the lower concentration

experiment. A very marked increase in the cumulative removal of 2,4-D after interruption was encountered with the 130 mg L^{-1} initial concentration. Coupled with results from the continuous experiment, which demonstrated a three fold time increase for the same amount of removal to occur, the data provide evidence that external transport was not a rate-limiting step in the adsorption at the higher concentration. Cumulative uptake data from both experiments suggested that intraparticle diffusion is of equal or possibly greater importance than diffusion in determining the overall rate of adsorbate transfer to the adsorption sites (Zogorski et al., 1975). Zogorski et al. (1975) did not apply a numerical model simulation to their experimental data. Weber and Morris (1963) also used the interruption method to confirm diffusion as the rate-determining step for the sorption of a series of benzenesulfonates on granular activated carbon.

The flow interruption method was also implemented by Koch and Flühler (1993) to measure the breakthrough curves of a mobile dye tracer through columns packed with geometrically well-defined porous glass beads. They reported experimental results which were well described with a bicontinuum spherical diffusion model using parameters determined in independent measurements. Hence, the assumption of diffusion in micropores appears to be adequate for transport through such porous media (Koch and Flühler, 1993). In the experiments of Koch and Flühler (1993), the tracer flow was interrupted when

the outflow concentration reached three quarters of the inflow concentration. After a period of flow interruption, the flow was re-established. Interrupting the flow induced a slight decline in concentration in one specific experiment and a very slight but detectable decrease in another. Before flow interruption, the solute concentration in the macropores was greater than that in the micropores (intra-aggregate pores), due to the process of advection which occurs exclusively in the macropores (Koch and Flühler, 1993). Because diffusive transport into the micropores was slow, the concentration of the solute lagged behind that of the mobile region inducing a slight concentration decline. These results offer evidence for diffusive mass exchange between macro- and micropores (Koch and Flühler, 1993). Further examination of their data suggests that the interruption of tracer flow caused little to no concentration drop due to the slow flux in which the tracer was injected into the column. It appears that the bulk fluid flow rate used by the authors was slow enough so that diffusion and advection were proceeding at approximately the same rate, thus yielding little if any apparent change in outflow concentration following interruption.

Murali and Aylmore (1980) implemented the flow interruption technique by eluting solutions of phosphate, selenite, and sulfate ions, and a tritiated water solution through a finely ground soil. The breakthrough curves for the phosphate and selenite solutions demonstrated a concentration

decline upon flow interruption (24 hour). However, this perturbation is not attributed to intra-aggregate diffusion. This is verified by the absence of measurable BTC depressions in the case of sulfate, despite the measurable adsorption of this ion, and for the effectively non-adsorbed tritium ion. It is therefore clear that the adsorption dynamics can be particularly important in controlling ionic transport. The significant difference in the shapes of the BTC's for sulphate and tritium, despite the absence of no-flow depressions for both, clearly demonstrated that adsorption kinetics form only part of the total adsorption dynamics influencing ionic transport. The experimental BTC data were adequately predicted by computer simulation using a numerical method for non-instantaneous equilibration involving a range of different adsorption and release rates (k_1 and k_2, respectively, for each ion) (Murali and Aylmore, 1980).

Ma and Selim (1993, unpublished data) employed the flow interruption technique for the investigation of atrizine transport in saturated and unsaturated packed soil columns. Water saturated columns were used for the miscible displacement of atrizine and tritium through a very fine nonacidic soil to study the effect of 4, 8, 15, and 16 day flow interruption periods. Interruption periods of 15 and 16 days resulted in a few of the large pores emptying during unsaturated experiments. The breakthrough curves for the experiments conducted under saturated conditions (interrupt

periods of 4 and 8 days), as well as those for unsaturated conditions, demonstrated sharp concentration declines after flow interruption. The dip in atrizine concentration is good evidence that the retention mechanism was highly kinetic in nature. However, this phenomenon was not observed in the tritium breakthrough results with the 15 day interruption. The tritium results suggest that there was no obvious evidence of chemical or physical nonequilibrium governing tritium transport in the particular soil of study (Ma and Selim, 1993). In contrast, the dip in atrizine concentration suggests a chemical nonequilibrium component was present in the system studied.

A second-order two-site model (SOTS) was evaluated for the description of atrizine transport. The SOTS model successfully described the effluent concentration dip and adequately predicted atrizine transport under unsaturated conditions with an interrupt duration of 4 days. The sharp concentration dip was also well defined by the SOTS model for the 8 and 16 day interrupt periods (Ma and Selim, 1993).

Experiments by Brusseau et al. (1989) assessed the applicability of the flow interruption method as a technique for investigating sorption nonequilibrium using a nonadsorbed solute (^3H) and an adsorbed solute (2,4-D amine) for a range of fluxes (0.59-37.3 cm h^{-1}). The displacement of tritiated water was interrupted at a $C/C_0 = 0.75$. Upon flow reinitiation there was no observable decrease in solute effluent

concentration which suggested the absence of physical nonequilibrium. The absence of mobile-immobile regions was expected for this system (sandy soil, grain size less than 1 mm, saturated conditions). However, the BTC for the displacement of 2,4-D amine did exhibit a significant decrease after flow interruption. The combination of no BTC drop for the ^{3}H and a significant drop in the BTC for 2,4-D amine suggested that a chemical-related nonequilibrium process exists. Upon further experimentation involving treatment of the soil with H_2O_2, Brusseau et al. (1989) concluded that a chemical nonequilibrium mechanism was associated with the sorbent organic matter. The BTC's simulated by the two-site sorption model, using values for the kinetic parameters obtained by non-linear least squares optimization, are presented with the experimental data during displacement of 2,4-D amine through the sandy soil (Eustis sand) in Fig. I.9. The fit obtained with the *R* value (retardation factor) optimized is essentially identical to that obtained with *R* from independent data. This supports the validity of using independently determined K_f (sorption partition coefficient) values for simulating column BTC data (Brusseau et al., 1989). These results have also been determined by others (Lee et al., 1988).

Biggar and Nielsen (1962) employed the interruption technique under experimental conditions identical to those described by Bear (1961). A BTC for a 30 cm sand packed

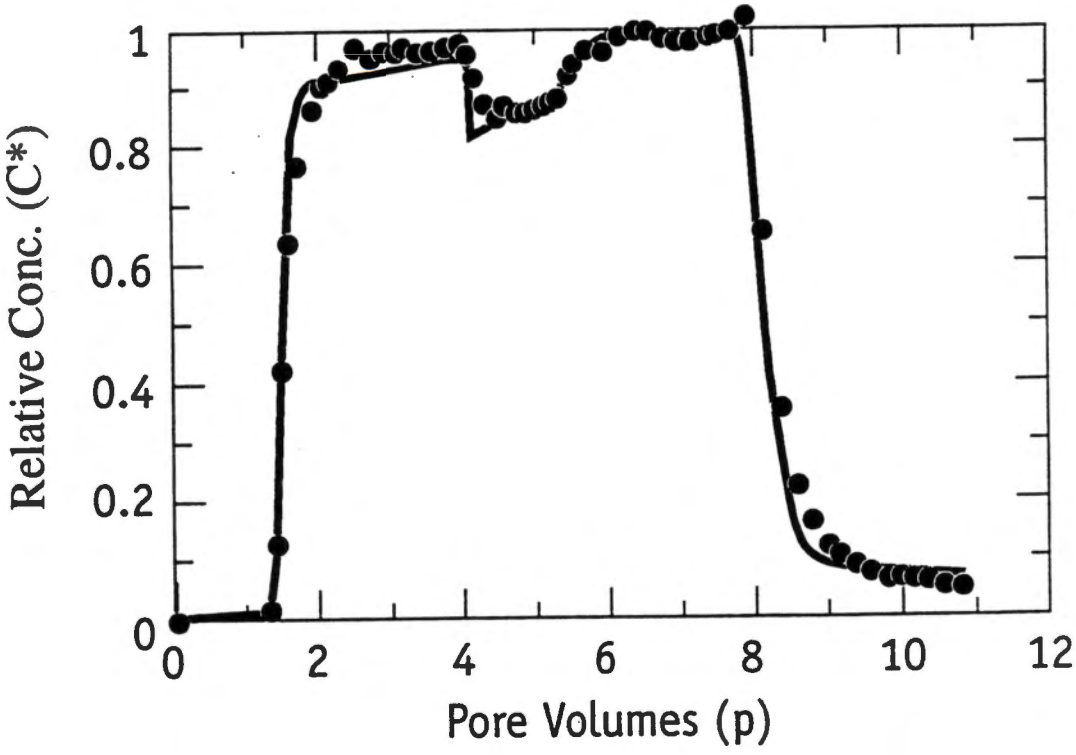


Fig. I.9. BTC of observed and fitted data for displacement of 2,4-D amine through Eustis soil.

Source: Brusseau, M.L., P.S.C. Rao, R.E. Jessup, and J.M. Davidson, 1989. Flow interruption: A method for investigating sorption nonequilibrium. J. Contam. Hydro., 4:223-240.

column constantly eluted with NaCl solution was obtained at a flux of 87.0 cm h^{-1}. In the same column under identical conditions, a second BTC was obtained by allowing the Cl^- front to penetrate only one-half the length of the column at the same flux. Flow was interrupted for 7 days, after which the flow was allowed to continue at the same flux. The variations between the two curves were attributed to molecular diffusion occurring during the interrupt period. Biggar and Nielsen (1962) concluded from the above experiment that molecular diffusion's true contribution to mixing during displacement cannot be ascertained by such a procedure. The magnitude of mixing depends upon the time-dependent coupling between diffusion and the microscopic pore water velocity distribution (Biggar and Nielsen, 1960). No numerical modeling techniques accompany this study.

Intra-aggregate diffusion was also examined by gas chromatography, employing the same theoretical flow interruption rationale. This procedure is commonly known as "arrested-flow" gas chromatography. Knox and McLaren (1964) were the first to describe arrested-flow chromatography for the measurement of intra-aggregate diffusion coefficients in packed and open columns. In arrested-flow chromatography the flow of a band of tracer gas in a carrier gas is stopped when the band reaches the mid-region of the column (Park et al., 1987). The band spreads by diffusion during the arrested-flow period. Elution is then continued by resuming flow. Park et

al. (1987) evaluated the arrested-flow technique for determination of effective diffusivities in chromatography columns packed with either porous or nonporous media. Each arrested-flow experiment was performed at the same flux and constant temperature and atmospheric pressure with helium tracer in a nitrogen carrier gas. Four different numerical models were used for estimation of intraparticle diffusion coefficients. Modified as well as unmodified models produced coefficients that were nearly the same in magnitude, yielding fairly good estimates for composite diffusion for packed beds of porous material. Experimental results demonstrated that the band-broadening process was dominated by diffusion within the void spaces. From the information reported above, it was concluded that the arrested-flow chromatography procedure is particularly useful for large-pore and large-porosity particles, for which other methods might be less satisfactory due to intra-aggregate flow (Park et al., 1987).

Fukui and Katsurayama (1975) investigated the effects of average axial velocity of flow, size and shape of porous media, and flow length on the dispersion coefficient. They also considered the applicability of applying diffusion type equations to dispersive phenomena. Experimental work was conducted with glass beads and a standard sand. Lucite columns (2 cm i.d.) were carefully packed with sample for miscible displacement experiments using tritiated water as the tracer solution. The average fluxes for the experiments

ranged from 2.2×10^{-3} to 1.9×10^{-2} cm s^{-1}. During the transition between tracer and tracer free solution, flow was stopped for 2, 7, and 30 days to examine the effect of diffusion. BTC's obtained under the above conditions failed to demonstrate any significant concentration decline upon flow interruption. This absence in concentration decrease may be attributed to the extremely slow flux which allows for significant diffusion and convection to occur simultaneously. These two processes cannot be readily discerned from BTC data at such slow fluxes. The dispersion coefficient was found to be dependent upon the variance of pore-water velocities suggesting that it is not essential to adopt the diffusion type equation to examine the dispersion process (Fukui and Katsurayma, 1975).

OBJECTIVES

Subsurface contaminant transport issues are highly complex due to multi-pore region flow characteristics in heterogeneous media. Contaminant transport is typified by numerous interacting concentration profiles that exist due to the complex continuum of pores in bulk soil. Two concentration profiles are typically assumed to describe transport of solutes in heterogeneous subsurface media; one in which solute moves slowly and continuously through micropores, and the second, where solute moves rapidly and discretely through preferred paths (Wilson et al., 1993). These processes are well conceptualized; however, quantification of

such processes are not well documented.

At the Oak Ridge Reservation (ORR) in Oak Ridge, TN remediation strategies at the Solid Waste Storage Area 5 (SWSA-5) are severely limited due to poorly defined source terms within shallow low-level radioactive burial sites. Transport of tritium, the most commonly encountered contaminant in SWSA-5, is constantly being monitored and evidence suggests that the mechanism of contaminant flow is complicated by matrix storage and preferential flow patterns. Since the source of the tritium is ill-defined, quantifying the long term implications of the secondary matrix source becomes increasingly difficult. Thus, environmental remediation is presented with a series of problems due to the complex transport mechanisms existing within the subsurface media and the absence of a well defined contaminant source.

A means of better understanding the implications of tritium transport is through the injection of a surrogate tracer into the groundwater, coupled with extensive spatial and temporal monitoring of the tracer plume. An ideal tracer would be bromide since it does not react with the subsurface media and exhibits no adverse toxicity effects on aquatic or terrestrial ecosystems. Because the bromide source will be well-defined, quantification of the solute advective and diffusive fluxes within the media can be determined. Experimental methods to simulate the above strategy in the

laboratory can provide data to support field-scale prediction of transport processes. Improved knowledge of the advective flow rates and mass transfer rates into, and from secondary source regions will significantly benefit remediation efforts at solid waste storage areas and other waste storage sites on ORR. The information provided in this study should enable engineers to develop remediation strategies for restoration of SWSA-5 and related storage areas. The objectives of this study are: (1) to quantify the diffusive mass transfer of Br between the matrix porosity and the mobile fracture flow using undisturbed subsurface columns and the flow interruption technique, and (2) to provide an improved understanding and predictive capability of ^{3}H mobility from the Oak Ridge National Laboratory (ORNL) burial grounds. Improved predictability will be drawn from data obtained during miscible displacement experiments involving flow interruption coupled with data generated from a mobile-immobile multi-region transport model.

By eliminating HNE, we hypothesized that solute mobility into the matrix of the subsurface media is by diffusion.

This study is driven by the following hypothesis:

1) Two flow velocities exist: a) fracture (mobile), and b) matrix (immobile).
2) Concentration gradients develop between pore regions due to the 2 velocities.
3) Diffusion will occur due to these concentration

gradients when flow is interrupted.

4) Concentrations within preferred flow paths and the soil matrix will become increasingly dissimilar at larger fluxes.

5) The rate of solute diffusion into the soil matrix will be similar to diffusion out of the soil matrix (no hysteresis).

6) Concentrations within preferred flow paths and the soil matrix will become increasingly dissimilar at longer interrupt durations.

The experimental and numerical aspects of this study will address each of these hypotheses.

Chapter II.

MATERIALS AND METHODS

A column of saprolite was acquired from a non-contaminated site on the ORR which possesses essentially the same physical and chemical properties as burial ground soils currently in use. Miscible displacement experiments were conducted under steady-state saturated flow to quantify diffusive mass transfer of nonreactive solutes between flow regions, i.e., fractures and saprolite matrix. Experimental data were also simulated with a two-region flow interrupt model developed by Selim et al., 1992 to quantify solute exchange between pore regions.

SITE CHARACTERIZATION

The site from which the saprolite column was excavated (SWSA-7) is located on the eastern portion of the Melton Branch Watershed (MBW) on the ORR approximately 10 km southwest of Oak Ridge, TN (Fig. II.1). The soils at the site are developed from the Conasauga Group and are generally very thin (<1 m deep, Cr horizon). The primary soil at the MBW is the Montevallo variant series (loamy skeletal, mixed, thermic, shallow Typic Dystrochrept) on the upslope, where it transcends into the Shelocta series (Aquic Hapludults: fine loamy over clayey, mixed, thermic) on the downslope (Lietzke, 1983 unpublished data; Wilson et al., 1989). The Montevallo is characterized by a shallow (10-30 cm) partially weathered layer above a zone of saprolite interbedded with clay lenses.

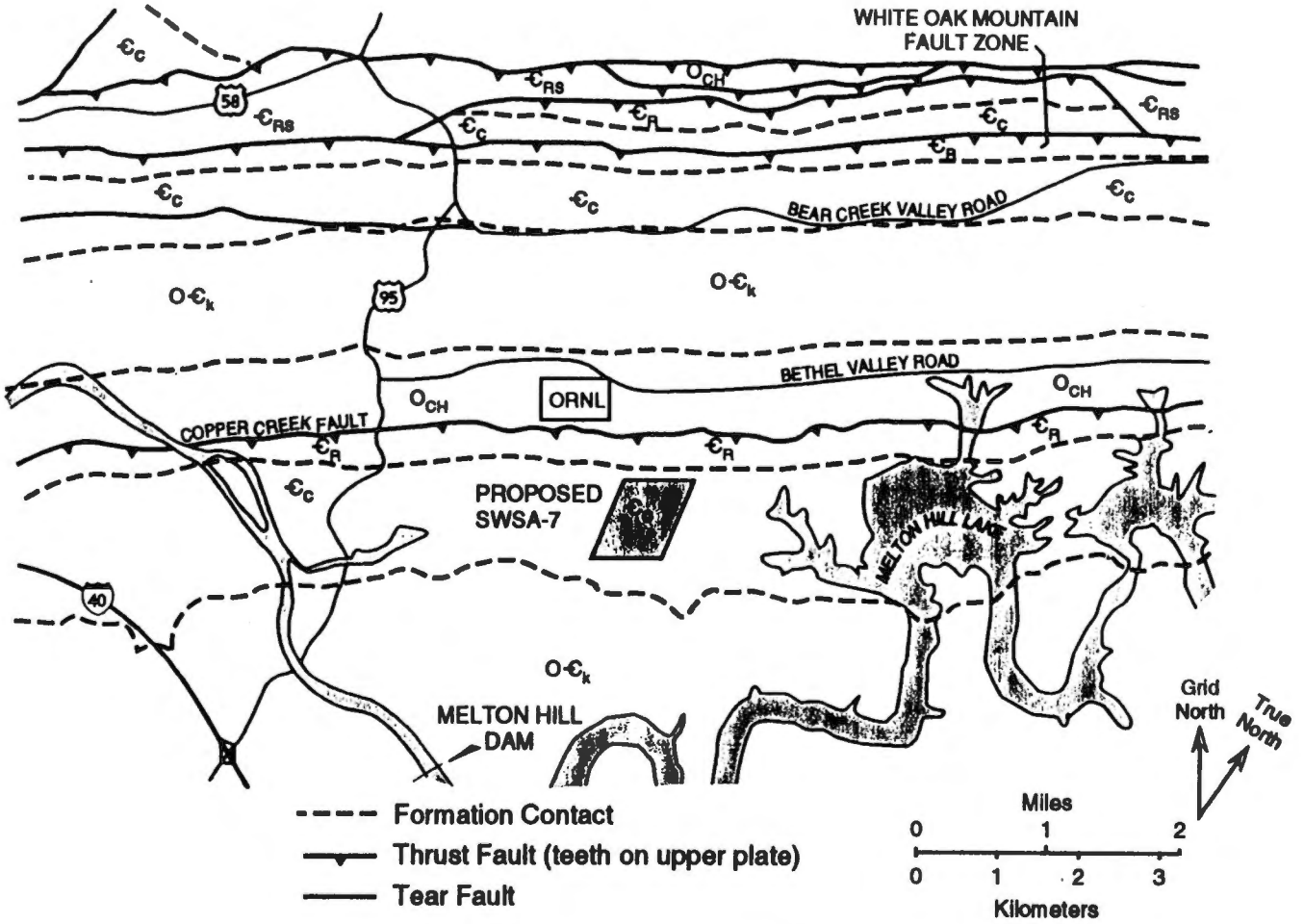


Fig. II.1. Location of soil column collection on proposed SWSA-7.

Source: Rothschild, E.R., D.D. Huff, B.P. Spalding, S.Y. Lee, R.B. Clapp, D.A. Lietzke, R.G. Stansfield, N.D. Farrow, C.D. Farmer, and I.L. Munro. 1984. Characterization of soils at proposed solid waste storage area (SWSA) 7. Oak Ridge National Lab. ORNL/TM-9326, pp 9-15.

The saprolite is highly fractured with fracture densities up to 200 fractures m^{-1} (Drier et al., 1987) and highly conducive to preferential flow. Large fractures, with mm sized apertures separate units of saprolite. Secondary μm size fractures also exist within saprolite units. These are coated with Mn and Fe oxides and contain translocated clay that has plated out, indicating that they also serve as preferred paths for oxygenated water (Wilson et al., 1993).

The proposed solid waste storage area 7 (SWSA-7) has been intensively characterized to assess the spatial variability of physical and chemical soil properties. For the surface layer, a mean hydraulic conductivity of 9.56 X 10^{-5} m s^{-1} was found by Wilson and Luxmoore, 1988. For the subsurface, Wilson et al., 1989 found a mean hydraulic conductivity value of 0.76 X 10^{-5} m s^{-1}. The shallow profile (0.5 to 3.0 m) of the MBW contains soils with pH and CEC values of 4 to 6 and 20 $cmol_c$ kg^{-1}, respectively. Select chemical, physical, and mineralogical properties were reported (Table II.1) by Jardine et al., 1989. The major clay mineral components of the soils are inherited from the parent rocks (Conasauga Group). These minerals have been transformed to other minerals in varying degrees, depending on the stability of the minerals and intensity of environmental factors during pedogenic processes (Rothschild et al., 1984).

The major minerals of the clay sized fraction found in the sampling interval were illite, hydroxy-interlayered

Table II.1. Selected physical, chemical, and mineralogical properties of the Melton Branch Watershed.

Particle Size Analysis			Organic matter content	DCB extractable Fe (g kg^{-1})	Mineralogy of < 2 μm fraction
Sand	Silt	Clay			
----------%					
31	50	19	0.6	28.71	I IS V K VC F M

Kaolinite; V = vermiculite; VC = chloritized vermiculite; I = illite;
IS = interstratified 2:1; Q = quartz; F = feldspar; M = montmorillonite.

Source: Jardine, P.M., N.L. Weber, and J.F. McCarthy. 1989. Mechanisms of dissolved organic carbon adsorption on soil. Soil Sci. Soc. Am. J., 53:1378-1385.

vermiculite, and kaolinite (Reedy, 1994 unpublished data). Quartz is the dominant mineral present in the silt sized fraction with predominantly shaly fragments composed of micaceous minerals dominating in the sand fraction (Rothschild et at., 1984).

SOIL COLUMN EXCAVATION

An undisturbed soil column was isolated from the C-horizon parallel to the fractured bedding planes. Fig. II.2 represents the heterogeneity encountered at SWSA-7 from which the soil column was acquired. This was accomplished by isolating a large (50 x 22 x 100 cm) soil pedestal (Fig. II.3) and carefully shaping it into a columnar form. A layer of paraffin wax was applied to the soil pedestal to maintain the integrity of the soil structure during shaping of the column. The column was excavated at approximately a 50° angle allowing the fractured bedding planes to be oriented longitudinally within the column. A number of wax-and-cut series occurred before the final cylindrical dimensions (17 cm diameter x 41 cm length) were obtained. After the desired columnar shape was obtained, a precut PVC pipe with a diameter slightly larger than the soil column was placed over the soil/wax monolith. The space existing between the column and the PVC pipe was then filled in with an epoxy resin. After the epoxy had hardened, the column was extracted from the pit and transported back to the laboratory. In the laboratory, each end of the column was fitted with a coarse fritted glass



Fig. II.2. Excavation pit showing fractured saprolite (light brown) interbedded with clay lens (dark red).



Fig. II.3. Isolated soil pedestal encased in paraffin wax containing fractured saprolite and clay lens.

plate using paraffin wax and epoxy resin. Contact between the fritted glass and the soil was assured by using a small quantity of fine quartz sand to fill the voids of the irregularly shaped column ends. The fritted glass end plates serve dual purposes: (1) to allow for the uniform distribution of Br through the column during tracer injection, and (2) to serve as ports for both influent injection and effluent collection. The fritted glass plates had a bubbling pressure head of -20 cm.

MISCIBLE DISPLACEMENT EXPERIMENTS

The column was inverted and leached very slowly with a steady flow of 0.005 M $CaCl_2$, via a medical infusion pump, from the bottom up for removal of entrapped air. After complete saturation, $CaCl_2$ was continuously eluted through the column at a slow (4.12 cm d^{-1}) flux until tracer experiments were initiated. After a steady flux of $CaCl_2$ had been achieved, a 0.005 M $CaBr_2$, i.e., 800 mg L^{-1} $CaBr_2$, solution was injected into the column for a predetermined pulse duration (≈16,800 mLs). During tracer experiments, sequential effluent volume fractions (50 mLs) were collected for Br analysis. The experimental laboratory set-up is shown in Fig. II.4.

Bromide injection continued until the effluent tracer concentration approached $C/C_0 = 0.93$ (pore volume = 4.1). The Br pulse was then "interrupted" and the column ends sealed to

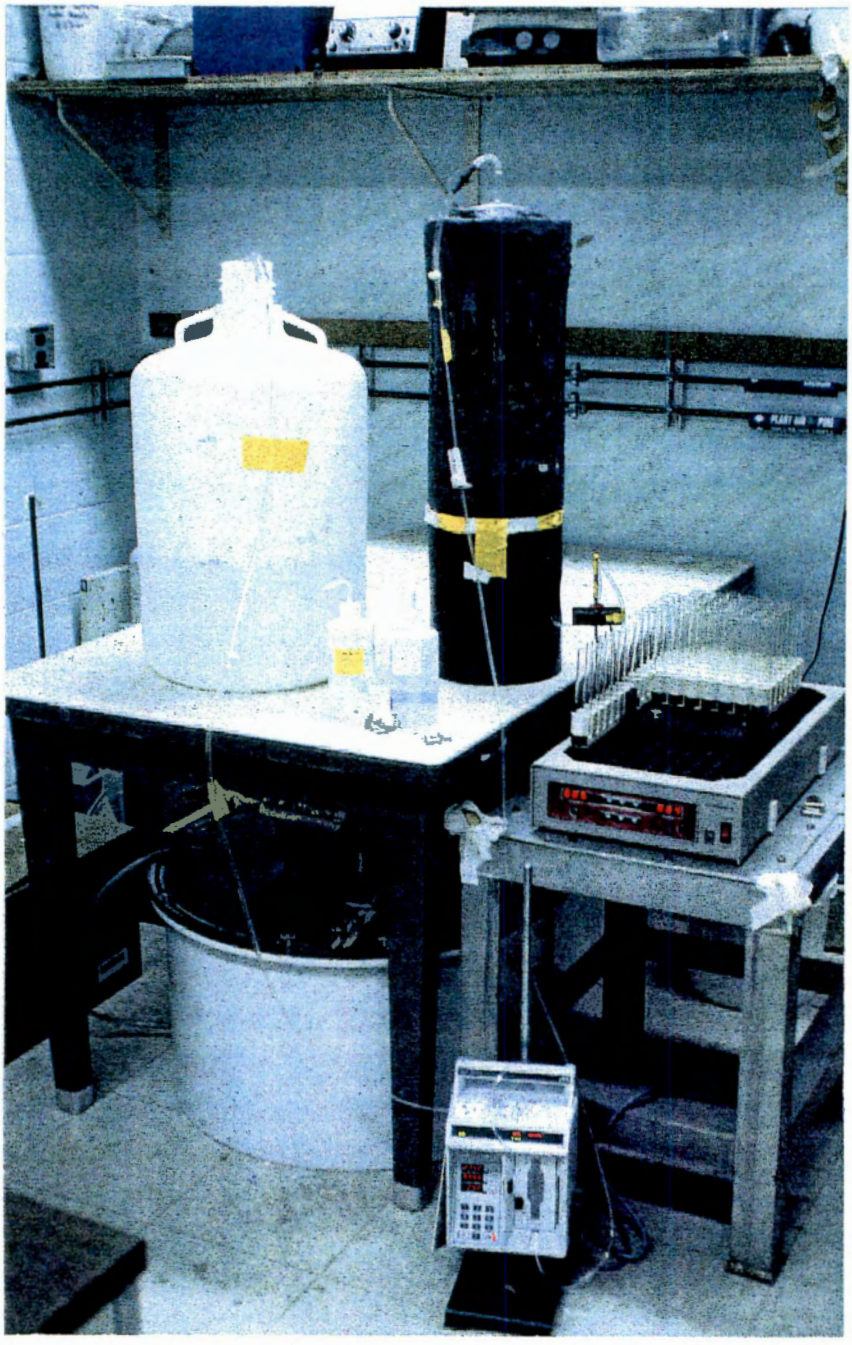


Fig. II.4. Experimental column system showing: A) influent solution, B) infusion pump, C) undisturbed soil column, and D) effluent fraction collector.

prevent drainage, i.e., no flow. This was done in order to allow for solute diffusion between the mobile and immobile pore regions between and within the saprolite matrix, respectively. Flow interrupt durations ranging from 6 to 166 hours, as described in Table II.2, were employed. Following interruption, the Br pulse was reinitiated and allowed to leach through the column until $C/C_0 = 1.0$. After $C/C_0 = 1.0$, a solution of 0.005 M $CaCl_2$ (800 mg L^{-1}) was reintroduced into the column to displace the tracer solution. In order to observe solute diffusion from the micropores back into the macropores, the flow interruption technique was repeated during the displacement period (when $C/C_0 = 0.07$). The conditions that determine the C/C_0 at which to interrupt flow and the duration of interrupt were similar to those described earlier and also by Brusseau et al., 1989. Four different fluxes and interrupt durations were used for the experiments in this study (Table II.2). The fluxes chosen for this study are based on flow rates observed previously at the site of column excavation (Wilson et al., 1992) whereby flux, q, is defined as:

$$q = v \cdot \theta^m \tag{7}$$

where

$$v = r/\pi\ r_d^2\ \theta^m \tag{8}$$

where v is velocity [LT^{-1}], θ^m is mobile region water content [L^3L^{-3}], r is the rate of infusion [LT^{-1}], and r_d^2 is the column radius [L^2]. The highest flux of 475 cm d^{-1} is still 2

Table II.2. Experimental (q and I) and physical (ρ_b, τ, and F) input parameters used for model simulations with *STOPFLO*:

Exp. #	q cm d^{-1}	I h	ρ_b g cm^{-3}	τ	F
E-1	4	166	1.56	0.60	0.45
E-2	475	166	1.56	0.60	0.45
E-3	41	166	1.56	0.60	0.45
E-4	41	6	1.56	0.60	0.45
E-5	41	18	1.56	0.60	0.45
E-6	41	84	1.56	0.60	0.45
E-7	216	166	1.56	0.60	0.45

Flux (q), interrupt duration (I), bulk density (ρ_b), tortuosity (τ), and fraction of mobile water (F).
† Column porosity (f) = 0.11

orders of magnitude lower than the rate of 560 m d^{-1} estimated by Wilson et al. (1992) for solute transport under natural rainfall events.

CHEMICAL EFFLUENT ANALYSIS

Effluent fractions (≈ 50 mLs) collected during miscible displacement experiments were analyzed for Br potentiometrically via ion specific Br electrodes. The instrumentation used for detection of Br was calibrated using an 800 mg L^{-1} standard prepared in deionized water, for Br detection at higher concentrations (C > 25 mg L^{-1}), and a 10 mg L^{-1} standard prepared in 0.005 M $CaCl_2$ for lower concentration detection (C < 25 mg L^{-1}). The lower concentration standard was prepared in a 0.005 M $CaCl_2$ solution to correct for chloride interference for samples containing a lower Br concentration. Samples containing minimal Br concentrations may yield false positives due to the presence of chloride which has a valance state very similar to bromide.

Analyses were conducted by mixing 5 mLs of effluent solution with 0.1 mL of ionic strength adjustor (ISA). The purpose of the ISA is to normalize the ionic strength of the sample to the ionic strength of the standards which in essence provides a "comparative" concentration result.

NUMERICAL MODELING

TWO-REGION MODELS

A number of experimental studies demonstrated early breakthrough results and tailing with nonsymmetrical

concentration distributions of BTCs. Discrepancies from symmetrical or ideal behavior for several solutes led to the concept of solute transfer between mobile and immobile waters. It was postulated that tailing under unsaturated conditions was perhaps due to the fact that larger pores are eliminated for transport and the proportion of the water that does not readily move within the soil increased. This fraction of water was referred to as stagnant or immobile water. A decrease in water content increases the fraction of air-filled macropores resulting in the creation of additional dead end pores which depend on diffusion processes to attain equilibrium with a displacing solution. However, the conceptual approach of mobile-immobile or two-region behavior is perhaps more intuitively applicable for well-structured or aggregated soils under either saturated or unsaturated flow. Here one can assume that within soil aggregates, where micropores are dominant, diffusion is the primary process contributing to solute transport. In contrast, convection and dispersion are the dominant processes in the macro (or inter-aggregate) pore space which occur between large aggregates or structural units (Coats and Smith, 1964, and van Genuchten and Wierenga, 1976).

GENERAL FORMULATION

The equations describing the movement for a nonreactive solute through a porous media having mobile and immobile water fractions are:

$$\Theta^m \frac{\partial C^m}{\partial t} = \Theta^m D_{LH} \frac{\partial^2 C^m}{\partial x^2} - \nu^m \Theta^m \frac{\partial C^m}{\partial x} - \alpha (C^m - C^{im}) \qquad (9)$$

and:

$$\Theta^{im} \frac{\partial C^{im}}{\partial t} = \alpha (C^m - C^{im}) \qquad (10)$$

where D_{LH} is the hydrodynamic dispersion coefficient in the mobile water region ($cm^2\ h^{-1}$), θ^m and θ^{im} are mobile and immobile water fractions, respectively ($cm^3\ cm^{-3}$), C^m and C^{im} are the concentrations in the mobile and immobile water ($\mu g\ cm^{-3}$), and v^m is the average pore-water velocity in the mobile region ($cm\ h^{-1}$). Also x is depth (cm) and t is time (h). We also assume that the immobile water (θ^{im}) is located inside aggregate pores (inter-aggregate) where the solute transfer occurs by diffusion only. In eq. (9) α is a mass transfer coefficient (h^{-1}) which governs the transfer of solutes between the mobile- and immobile-water phases in an analogous manner to a diffusion process.

The convective-dispersive equations associated with the above mobile-immobile model formulations were subject to the following initial and boundary conditions.

$$C^m = C^{im} = 0 \qquad t=0, \quad 0<x<L_e \qquad (11)$$

$$\nu^m C_o = - \theta^m D_{LH} \frac{\partial C^m}{\partial x} + \nu^m C^m \qquad x=0, \quad t<t_p \tag{12}$$

$$0 = -\theta^m D_{LH} \frac{\partial C^m}{\partial x} + \nu^m C^m \qquad x=0, \quad t>t_p \tag{13}$$

$$\frac{\partial C^m}{\partial x} = 0 \qquad x=L_e \quad t>0 \tag{14}$$

where t_p is the duration of an applied solute pulse, C_o is input concentration in the applied pulse, and L_e is the solute transport length. The CDEs [9] and [13] subject to the above conditions were solved numerically using the implicit-explicit finite difference (Crank-Nicholson) method, where a mass balance was maintained as a check on the numerical calculations (Selim et al., 1976).

The mobile-immobile is commonly referred to as the two-region model and is regarded as a mechanistic approach where physical nonequilibrium is the controlling mechanism. One method of identifying the extent of physical nonequilibrium is by the use of the method of flow interruption when nonreactive solute tracers are used. Flow interruption can be accounted for in the above formulation by simply assuming $\nu=0$ and $D_{LH}=D_o$ (molecular diffusion coefficient) during interruption. As a result eq. (9) is reduced to the commonly known diffusion equation,

$$\Theta^m \frac{\partial C^m}{\partial t} = \Theta^m D_o \frac{\partial^2 C^m}{\partial x^2} - \alpha (C^m - C^{im}) \qquad (15)$$

Therefore, during flow interruption, we assumed that transport of nonreactive solutes can be described based on molecular diffusion within the mobile water phase. In addition, the exchange between the solute present in mobile and immobile phases were assumed to follow the simple mass transfer in eq. (10) above.

Input parameters (Table II.2) used for model simulations were based on experimental data previously obtained during field-scale tracer experiments (Barone et al., 1990; Barone et al., 1992; and Jardine et al., 1993). During model simulations, physical parameters were held constant and the transfer coefficient (TR or α) was allowed to vary in order to obtain a BTC which best fit the experimental data.

Chapter III.

RESULTS AND DISCUSSION

EFFECTS OF FLUX ON BTC's

The miscible displacement of a nonreactive tracer, Br, was investigated under saturated conditions for a variety of fluxes (q) being subjected to periodic flow interruptions for varying durations. Simulated TR (transfer coefficient) values obtained from the two-region flow and transport model *STOPFLO* are also shown with the BTC's (Ma and Selim, 1994). A constant volume of tracer solution was injected before interrupting flow, ≈4.1 pore volumes, and was interrupted a second time during the displacement stage when $C/C_0 = 0.07$. The solute breakthrough, C/C_0, is plotted as a function of reduced time, i.e., pore volumes. However, it is rational to note that while these BTC's appear as a continuous function of time, the interrupt period is a distinct discontinuity. This discontinuity in the time which allows solute concentration between pore regions to equilibrate by diffusion, appears to be continuous only because it is expressed as pore volumes. For the 166 hour interruption period, Fig. III.1, a perturbation in concentration was observed after each interruption for fluxes greater than 4.1 cm d^{-1}. These observations are indicative of a bypassing of the less mobile pores within the saprolite. This concentration gradient exist between pore domains resulting in diffusive mass transfer between the regions. Concentration perturbations observed in

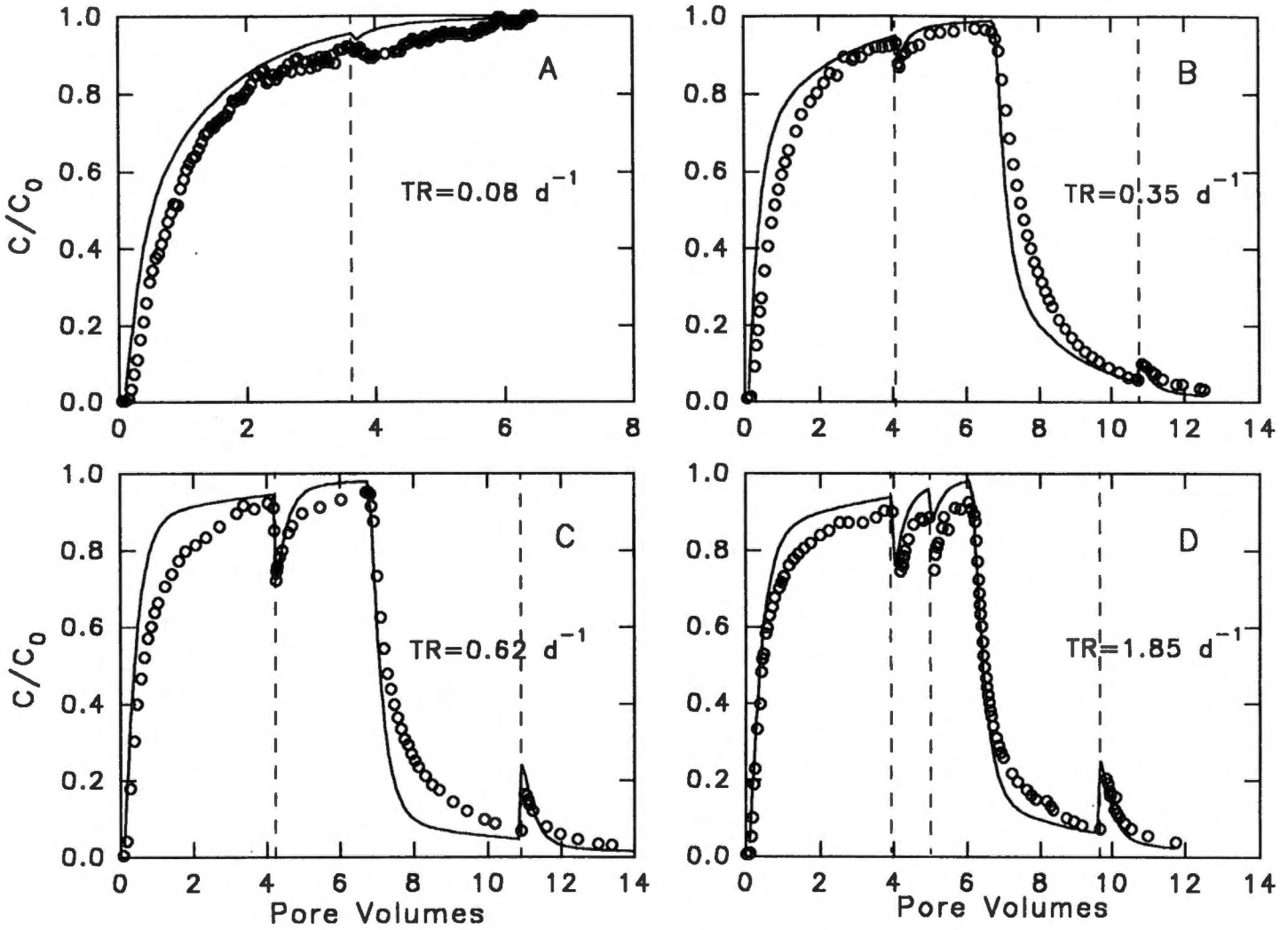


Fig. III.1. Experimental (circles) and simulated (line) BTC's for constant interrupt duration of 166 hours with different flux (q): (A) 4.1, (B) 41, (C) 216, and (D) 475 cm d^{-1}. Broken lines indicate point of flow interruption.

Fig. III.1 were driven by solute gradients established between convective velocities. The relative concentration decrease during tracer injection indicates solute diffusion occurring from larger more conductive pores into smaller pores. The relative concentration increase during interruption of tracer displacement indicates solute diffusion from smaller pore regions back into larger pore regions. The presence of concentration perturbations on each portion of the BTC's not only confirm the occurrence of solute diffusion, but also the presence of a physical nonequilibrium mechanism. This phenomena has also observed by Brusseau et al., 1989; Koch and Flühler, 1993; Ma and Selim, 1993; and Hutzler et al., 1986. As expected, the slower the flux, the smaller the perturbation in solute concentration.

Varying *q* between experiments was intended to examine the effects elevated fluxes impose on the rate of solute diffusion between different sized pore regions. Results shown in Fig. III.1 suggest that a greater concentration disparity between pore regions is created at higher fluxes. This is evidenced by the magnitude of concentration perturbations observed after flow interruption on both the injection and displacement portions of the BTC's (Fig. III.1).

For Fig. III.1A, only the injection of Br was examined. After flow interruption, a very slight concentration perturbation was observed. This is attributed to the extremely slow flux at which the experiment was conducted (4.1

cm d^{-1}). Due to the slow flux, the advective and diffusive processes were essentially occurring at the same rates. Thus, the concentration decrease was very small but detectable. This has also been observed by Koch and Flühler (1993).

For the 41 cm d^{-1} flux, Fig. III.1*B*, 7.0 and 4.1% relative concentration perturbations were observed with flow interruption during tracer injection and displacement, respectively. Thus, confirming the occurrence of solute diffusive mass transfer between pore regions due to concentration gradients established by convective preferential flow. The BTC of Fig. III.1*C*, q=216 cm d^{-1}, exhibits larger relative concentration perturbations of 19 and 9.6% with flow interruption during injection and displacement, respectively. For Fig. III.1*D*, q=475 cm d^{-1}, the flow of tracer injection was interrupted twice to determine whether the previous interruption caused an observable effect in the percent relative concentration decrease of the second interruption. Each interruption during tracer injection illustrated in Fig. III.1*D* resulted in a 21% relative concentration decrease suggesting that the former interruption had no observable effect on the latter interruption. A 17% increase was observed after flow interruption during Br displacement. Comparing these BTC's for the 166 hour interrupt duration, the magnitude of relative concentration perturbation during tracer injection and displacement increased as q values increased (Fig. III.2). However, this relationship is not linear. The

% concentration perturbation asymptotically approaches a constant as q increases. The same results were found by van Genuchten and Wierenga (1977), Nkedi-Kizza et al. (1983), and Brusseau et al. (1989).

BTC's also exhibited asymmetry with increasing values of q. Tailing of the BTC's became less significant at larger pore volumes due to decreasing participation of the larger pores involved in solute transport (Fig. III.1*A* and *B*). Jardine et al. (1993) also observed this phenomena for BTC's through undisturbed soil columns conducted under conditions of decreasing saturation. The rapid transport of Br through the larger pore regions with increased flux is evident in the breakthrough time (i.e., center of mass). The breakthrough times, i.e., pore volume when $C/C_0 = 0.5$, were 0.83, 0.82, 0.60, and 0.45 pore volumes for fluxes of 4.1, 41, 216, and 475 cm d^{-1}, respectively. As q increased, the significance of diffusive mass transfer contributing to initial solute breakthrough decreased (O'Brien and Jardine, 1995). Due to this phenomena, a larger volume of tracer solution must be infused before the eluting tracer solution approaches equilibration, i.e., $C/C_0 = 1.0$, with the soil matrix.

After switching from Br tracer solution to a 0.005 M $CaCl_2$ tracer-free solution, displacement with 0.90 pore volumes were required to decrease C/C_0 to 0.5 for q=41 cm d^{-1}. For q=216 and 475 cm d^{-1}, 0.53 and 0.39 pore volumes of $CaCl_2$ were required for C/C_0 to be reduced to 0.5, respectively.

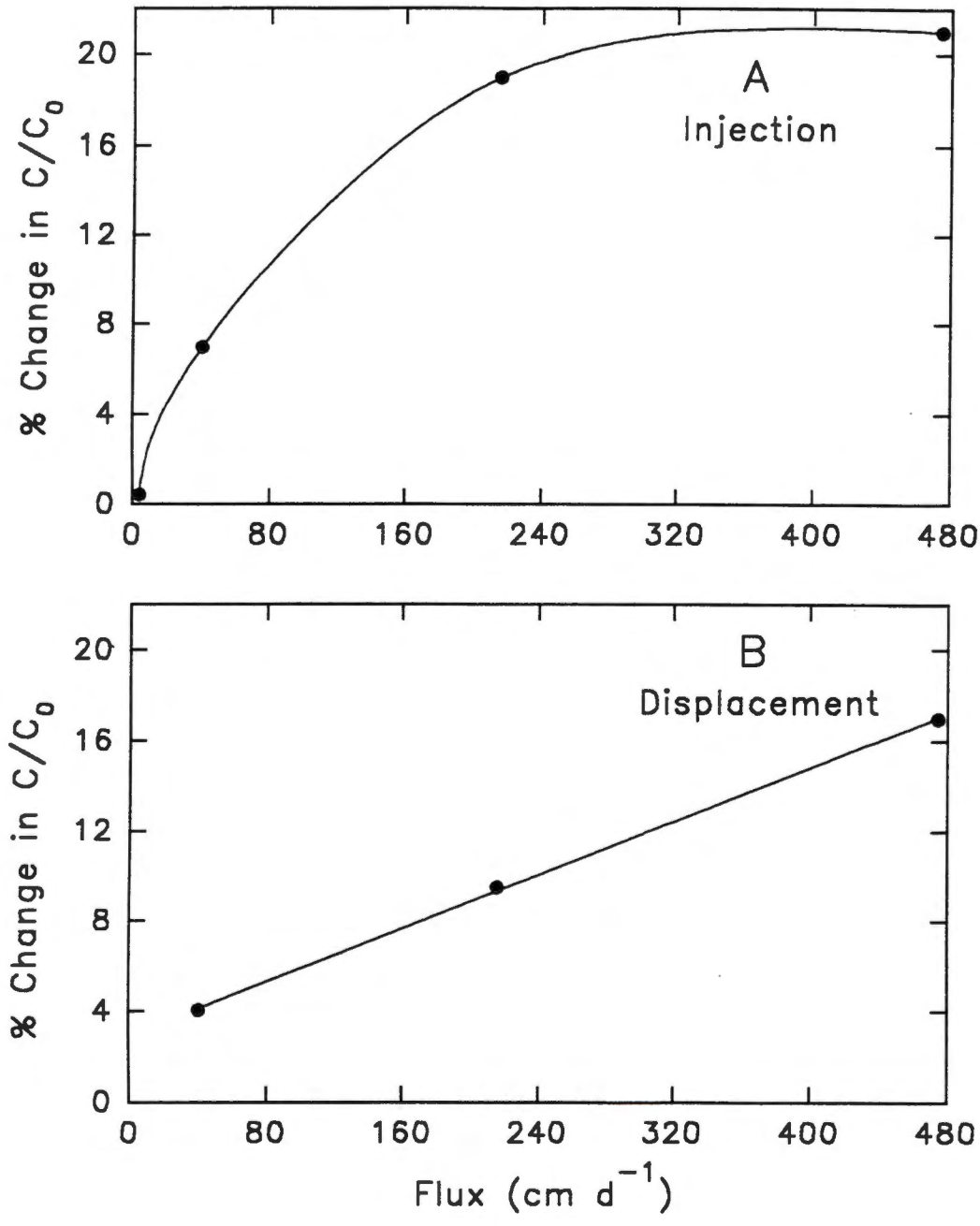


Fig. III.2. Observed relative concentration change as a function of flux during bromide: (A) injection and (B) displacement.

These results are indicative of Br being removed very rapidly form preferential flow paths with increasing q during tracer displacement. These results also suggest that after Br is immobilized in small pore regions, complete Br removal would require a large volume of tracer free solution. This is due in part to the smaller contribution of diffusion during tracer displacement at elevated q values. If, however, flow during displacement was interrupted again, macropore concentrations would increase due to diffusion from micropores. After flow reinitiation a larger concentration of Br would be removed compared to conventional continuous displacement with no interruption. Therefore, multiple interruptions during displacement would increase the effectiveness of tracer removal.

EFFECT OF INTERRUPT DURATION

A series of experiments were also conducted to examine how diffusive mass transfer is affected by interrupt duration. Koch and Flühler (1993) conducted several model simulations in an attempt to describe this relationship but experimental data was not obtained. Each miscible displacement experiment was conducted at the same q (41 cm d^{-1}), but interrupt periods of 166 h, 18 h, and 6 h were employed. As previously mentioned, the BTC for the 166 h interrupt with a flux of 41 cm d^{-1}, (Fig. III.1*B*) exhibited 7 and 4.1% relative concentration perturbations during injection and displacement, respectively. The BTC in Fig. III.3*A* experienced perturbations of 4.0 and

2.1% during injection and displacement, respectively, for the 18 h interrupt. Whereas, concentration perturbations of 1.6 and 0.11% for injection and displacement, respectively, were observed in Fig. III.3*B* for the 6 h interrupt. The results in Fig. III.3 suggest that the diffusive process is very far removed from equilibrium after short interrupt period durations. Thus, more time is required for the eluting solution to equilibrate with the porous media. The results in Fig. III.4 suggest that, at a specific flux, the interrupt duration asymptotically approaches a value beyond which the duration of interrupt has a negligible effect. This may be attributed to the "slow" flux at which the experiments were conduced (41 cm d^{-1}). Had the experiments been conducted at a higher flux, 216 cm d^{-1}, this constant interrupt duration value would probably increase proportionally. This constant interrupt duration value for q=41 cm d^{-1} is estimated to be 48 hours.

The effect of interrupt duration on solute breakthrough (Fig. III.5) was also examined. For this determination, BTC's were obtained under the same flux (41 cm d-1) but different interrupt durations (166, 84, 18, and 6 hours). In Fig. III.5, only the injection portions of the BTC's prior to flow interruption were examined. Results from Fig. III.5 demonstrate slight discrepancies in solute breakthrough exists for BTC's obtained under the above conditions. It is believed that these discrepancies are evident due to changes

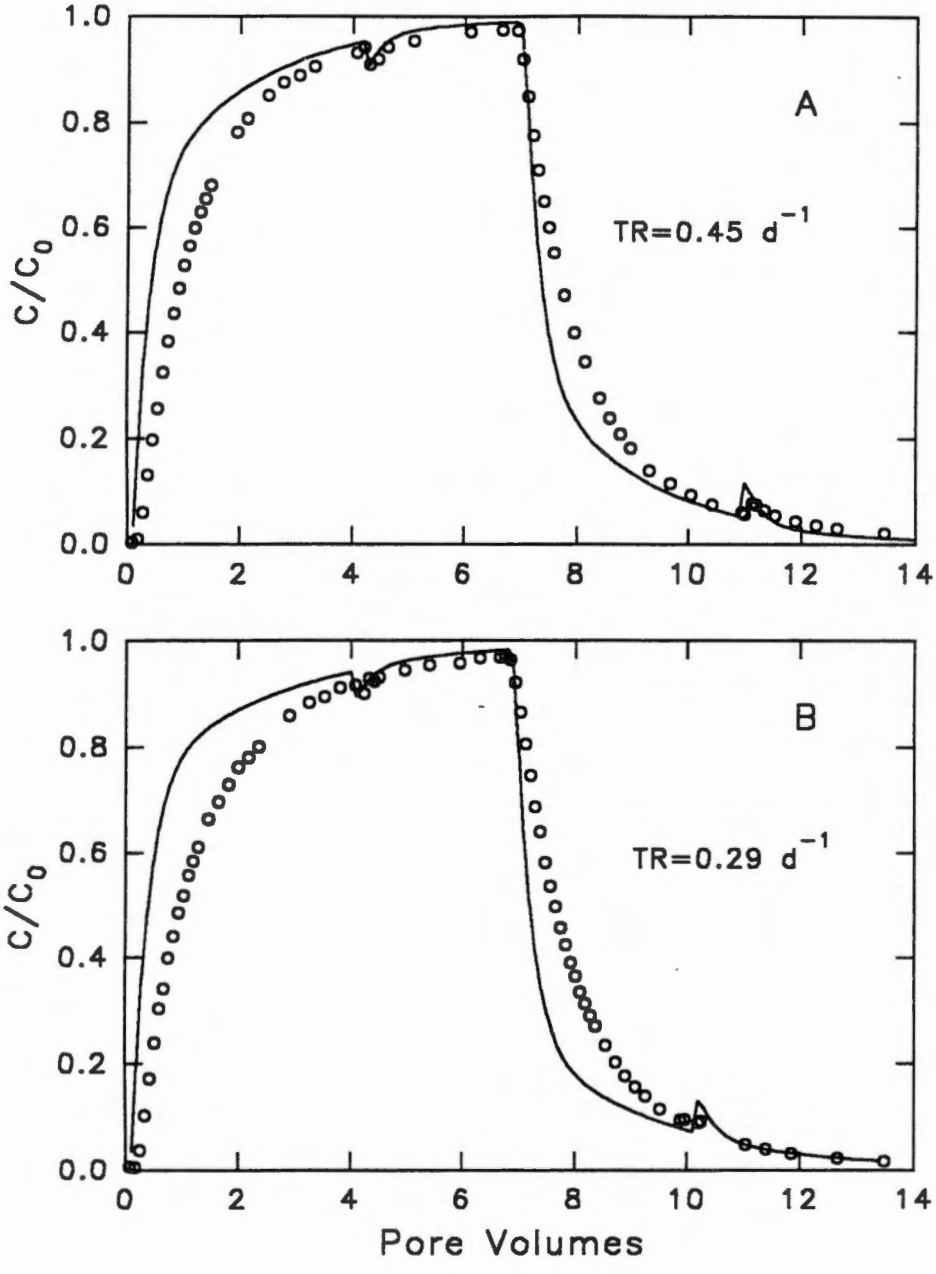


Fig. III.3. Experimental (circles) and simulated (line) BTC's for constant flux of 41 cm d^{-1} with different interrupt durations: (A) 18 and (B) 6 hours.

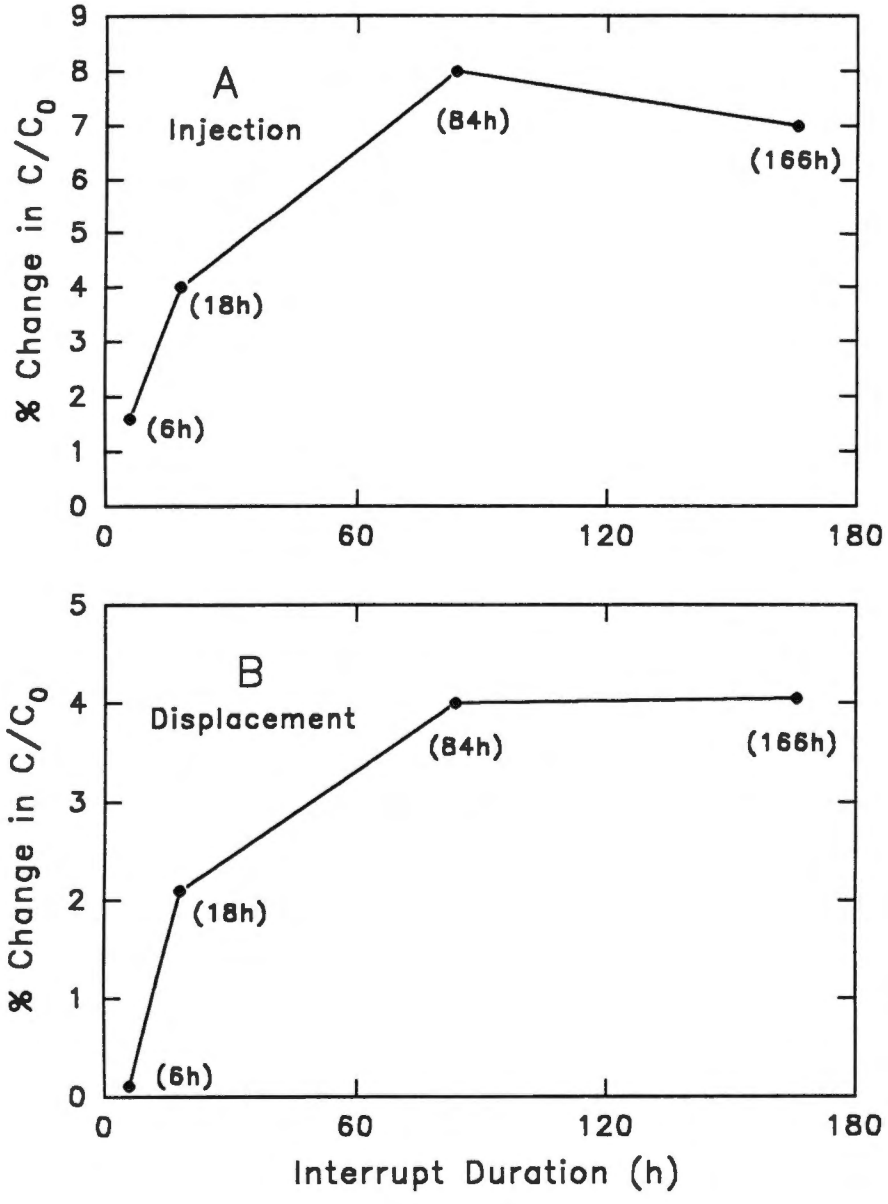


Fig. III.4. Observed concentration change as a function of interrupt duration for q=41 cm d^{-1} during: (A) injection and (B) displacement stages.

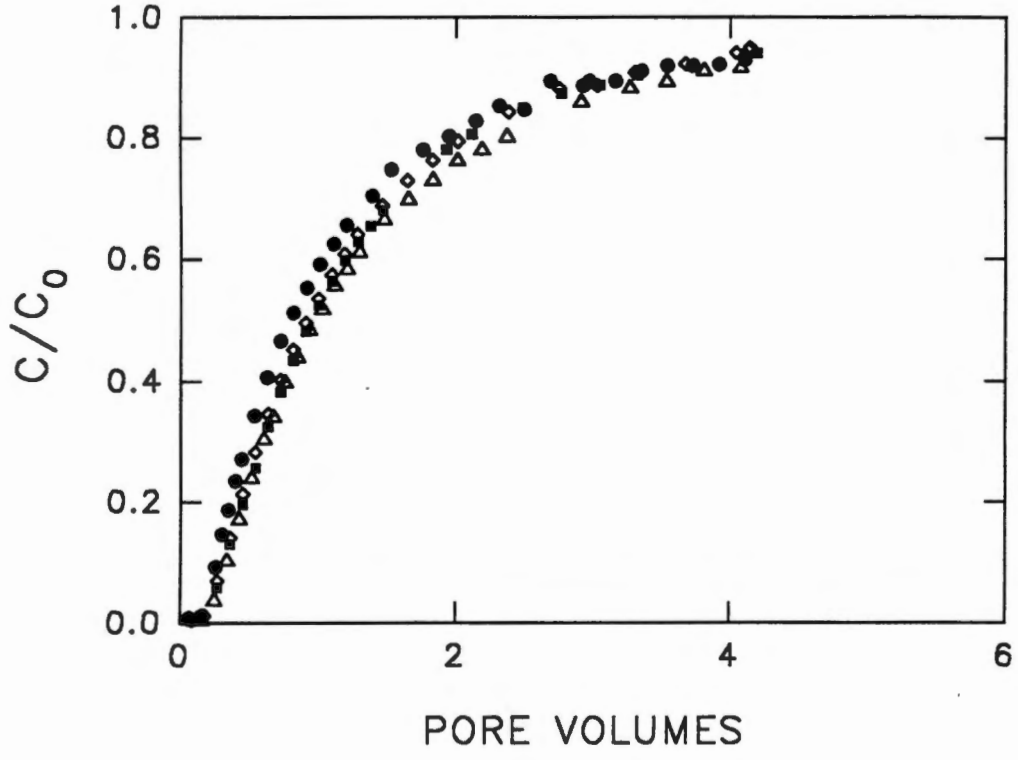


Fig. III.5. BTC's for constant flux, 41 cm d^{-1}, with different interrupt durations: triangles (6 h), squares (18 h), diamonds (84 h), and circles (166 h).

experienced within the soil column between experiments and not the duration of flow interruption.

MODEL SIMULATION: STOPFLO

Experimental BTC's in Fig. III.1 and III.3 are shown with simulations obtained from the two-region flow interrupt model *STOPFLO*. Best fit simulations were obtained using the soil column's physical properties determined after all miscible displacement experiments were conducted. For each simulation, physical parameters were held constant but the transfer coefficient (TR) was "adjusted" to find the best fit. Transfer coefficients for each experiment are shown in Table III.1 with their corresponding values of P and D. Simulated BTC's in Fig. III.1 and III.3 exhibit the general behavior of the experimental data. Flow interruption imposes an added constraint on the modeling of experimental data. There exists, for each experimental data set, a discrete set of parameters which accurately describe the overall shape of the BTC but will not describe the interrupt and vice versa. Therefore, only a very small range of TR values provide good interrupt and curve fits.

TR was found to increase with increasing q (Fig. III.6) for the 166 h interrupt experiments. This relationship exists because the concentration gradients created are larger and established more rapidly at higher fluxes. Results from varying the interrupt duration, Fig. III.4, suggest an inverse relationship should exist between interrupt duration and TR.

Table III.1. Input parameters used during model simulations using *STOPFLO*:

Exp. #	D $cm^2\ d^{-1}$	P	TR d^{-1}
E-1	384.26	1.0	0.08
E-2	44337.40	1.0	1.85
E-3	3842.55	1.0	0.35
E-4	3842.55	1.0	0.29
E-5	3842.55	1.0	0.45
E-6	3842.55	1.0	0.27
E-7	20099.84	1.0	0.62

Dispersion coefficient (D), Peclet number (P), and transfer coefficient (TR).

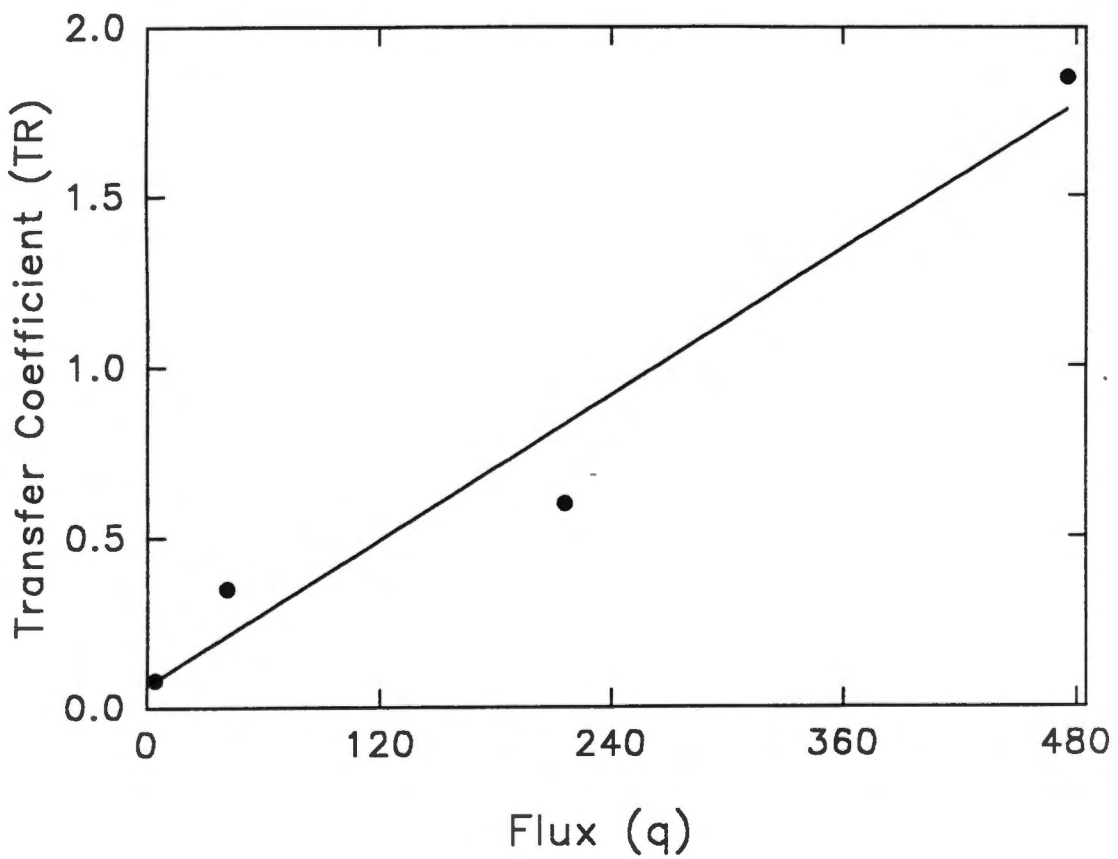


Fig. III.6. *STOPFLO* transfer coefficients (TR) as function of flux for the 166 h interrupt.

However, TR values did not exhibit a correlation with interrupt duration. This may be due to: 1) the relatively "small" concentration perturbations observed for the 41 cm d^{-1} flux (Fig. III.3), or 2) the model sensitivity may be inadequate for accurate determination of TR. We expect that if variation in flow interrupt durations had been conducted at the higher fluxes (475 cm d^{-1}), a relation to interrupt duration would be observed.

TR values can also be obtained at the field as well as the laboratory scale. A study is currently in progress on ORR which involves the constant injection of a non-reactive tracer ($MgBr_2$) into fractured media having similar chemical and physical characteristics of the soil column used in this study. Data obtained from rigorous spatial and temporal monitoring of the tracer plume coupled with a multi-region transport model should provide a quantitative determination of solute transfer occurring between various pore regions.

Chapter IV.

CONCLUSIONS

This study has provided an improved understanding of solute diffusive mass transfer between pore regions in saturated, heterogeneous subsurface media. Using the flow interruption technique with a two-region nonreactive transport model, it was possible to segregate the diffusive and convective components and quantify the diffusive exchange of bromide between pore regions. The flow interruption technique has been implemented in the past, however, we are not aware of any study that has used it to quantify the diffusive mass transfer of a nonreactive solute in undisturbed media. Results reported in this study have provided additional insight for the prediction of contaminant migration in aquifer systems on the Oak Ridge Reservation.

In the saturated fractured media used in this study, a significant process contributing to solute transport was preferential convection. Preferential flow processes were also shown to be significantly greater at larger fluxes. When flow was interrupted, diffusive transfer became important to transport by acting to equilibrate the flow regions. Flux and interrupt duration had profound affects on the magnitude of concentration perturbation. A direct relationship for each was observed with respect to concentration perturbation. In addition, the interrupt duration approached a value at which the percent change in concentration after interruption became

constant. Observed effluent concentrations were adequately modeled with *STOPFLO* by fitting the TR to the experimental BTC. These results suggested that a direct relationship exists between TR and q. Model simulations also suggest that interrupt duration has a negligible effect on TR for low to moderate fluxes.

These studies have shown for the first time that a flow interruption technique can be used to quantify the exchange of a nonreactive solute between pore regions in undisturbed heterogeneous porous media. Through the use of this technique, the removal of contaminants from heterogeneous subsurface media, where the contaminant resides within the soil matrix, may be greatly enhanced. Remediation techniques currently in use which would benefit from this strategy are: 1) the pump and treat technique (commonly used in aquifer remediation), and 2) soil-venting, a practice currently used to remove volatile compounds. This study suggests that, pumping/venting should be routinely interrupted for approximately two days to improve efficiency of contaminant removal.

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