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Field and laboratory investigations of solute transport through soil

by

Francis Xavier McKeon Casey

**A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY**

Co-majors: Soil Science (Soil Physics); Water Resources

Major Professors: Robert Horton and LaDon C. Jones

Iowa State University

Ames, Iowa

2000

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ABSTRACT

Two single tracer methods (basic and variance) and one multiple tracer method were developed to simultaneously estimate soil hydraulic properties and mobile/immobile solute transport parameters *in situ*. In this study, immobile water contents (θ_{im}) and mass exchange coefficients (α) were estimated with the multiple tracer method and the single tracer methods on the same five field sites. The θ_{im} values estimated by the basic single tracer method were consistently lower than the multiple tracer method values. This was attributed to the assumption that $\alpha=0$ for the basic single tracer method. Furthermore, α values estimated by multiple tracer method were more realistic and easier to obtain than the variance single tracer method.

A novel miscible-displacement system with on-line high performance liquid chromatograph (HPLC) was developed to study the fate and transport of volatile organic compounds. This system was capable of low detection limits and simultaneous detection of multiple compounds. This system was automated and capable of running for long time periods (several days to weeks) with minimal flow rate fluctuations and stable chemical detections.

Lastly, zero-valent metals were used to reduce chlorinated solvents in contaminated groundwater by passing it through columns or trenches filled with zero-valent metals. Previous zero-valent metal research included batch or resident concentration column experiments to study degradation processes and to design remediation systems; however, difficulties were associated with these methods such as determination of sorbed concentrations and estimation of effluent concentrations from resident concentrations. In this study miscible-displacement experiments were used as an alternative to study trichloroethylene (TCE) fate and transport through zero-valent metals. Dissolved TCE was passed through columns filled with sand, iron, or copper-plated iron filings (Cu-Fe) at three velocities and effluent breakthrough curves were determined with an on-line HPLC. There was no detectable TCE degradation in the sand column experiments. More TCE was reduced in the presence of Cu-Fe than iron. The reduction of TCE produced ethylene which resulted

in simultaneous breakthrough curves of these compounds. These simultaneous breakthrough curves were described with a two-site partial nonequilibrium sorption model with degradation and production. Based upon the experimental results sorption should be a consideration when designing flow through remediation systems.

CHAPTER 1. GENERAL INTRODUCTION

Introduction

Field Study

In the past eight years, *in situ* methods have been developed to approximate the physical mobility properties of field soil that effect preferential flow solute transport. These methods are based on the mobile/immobile model (Coats and Smith, 1964) and approximate the immobile water content (θ_{im}) and mass exchange coefficient (α). Clothier et al. (1992) did pioneering research in this area and they were the first to develop an innovative method to estimate θ_{im} . This field method used a tension infiltrometer to apply chemical tracer to the soil surface. By applying solute under specific boundary conditions and making assumptions about its transport in the soil, Clothier et al. (1992) developed the following expression to estimate θ_{im} :

$$\theta_{im} = \theta(1 - C/C_o) \quad [1]$$

where θ is the volumetric water content, C is the tracer concentration in the soil extract, and C_o is the input tracer concentration from the infiltrometer reservoir. For the first time, preferential flow and water transfer properties of a field soil could be simultaneously estimated using this method; however, it makes the assumption that α is sufficiently small and can be ignored.

Using the Clothier et al. (1992) method as a basis, Jaynes et al. (1995) extended it to include the estimation of α , thus eliminating the assumption that $\alpha=0$. The Jaynes et al. (1995) technique had similar assumptions and methods to the Clothier et al. (1992) technique; but, instead of applying a single tracer, a series of tracers were applied. The θ_{im} and α are approximated using the following linear expression (Jaynes et al., 1995):

$$\ln(1 - C/C_o) = -t \cdot \alpha/\theta_{im} + \ln(\theta_{im}/\theta) \quad [2]$$

where $t^* = t - \ell/v$ is the time required to reach the depth of sampling (ℓ), t is the tracer application time, and v is the average pore water velocity. Immobile water content is obtained from the intercept of the plot of t^* versus $\ln(1-C/C_0)$ and α is obtained from the slope. Several field studies (Casey et al., 1997, 1998) and a laboratory study (Lee et al., 1999) have shown that Eq. [2] reasonably described tracer concentration profiles and provided accurate approximation of both θ_{im} and α . The plots of $\ln(1-C/C_0)$ versus t^* from the Casey et al. (1997, 1998) and Lee et al. (1999) studies were sufficiently linear which suggested Eq. [2] was a good approximation of the full mobile/immobile model. Nonetheless, Clothier and his colleagues contest the slopes of the plots of t^* versus $\ln(1-C/C_0)$ result from dispersion, probably caused by sampling the tracer front. On the other hand, Casey et al. (1997) and (1998) have found that θ_{im} values approximated from the Clothier et al. (1992) method were consistently lower than the values estimated by the Jaynes et al. (1995) method. The lower θ_{im} values were attributed to the assumption that $\alpha=0$. Clothier and his colleges developed a second field method to estimate α , where the variance of the tracer concentration is monitored through time (Clothier et al., 1995). This dissertation offers, for the first time, a critical experimental comparison between the multiple tracer method and single tracer methods.

Laboratory Studies

Miscible-Displacement System. Miscible-displacement experiments through soil columns provide unique insights into solute transport processes. Using miscible-displacement experiments, we can quantify the transport behavior of compounds as affected by complex chemical, physical, and biological interactions. Problems arise, however, when miscible-displacement techniques developed with conservative tracers such as chloride are used for hydrophobic organic chemicals. Many of these hydrophobic organic compounds are volatile and undergo transformations in the transport process. There exists a need to develop a miscible-displacement system applicable to these hydrophobic and volatile compounds that can simultaneously detect multiple compounds. This study provides detailed description of a novel miscible-displacement system and the operational performance of this system. The design criteria of this system includes the following: 1) closed system, 2) non-sorbing

material construction, 3) accurate aqueous detection of volatile organic compounds at low concentrations, 4) capability of measuring multiple solutes, 5) automation, and 6) safety.

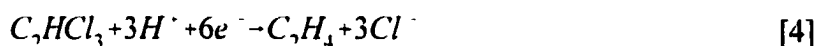
Zero-Valent Metals. The use of zero-valent metals to facilitate the reduction of organic pollutants has drawn much attention as a means to remediate contaminated groundwater. Industrial uses of trichloroethylene (TCE) and other organic solvents have lead to wide spread contamination problems. Trichloroethylene was identified as the most common contaminant at nearly 300,000 to 400,000 hazardous waste sites in the United States, and over the next 30 years approximately \$750 billion could be spent on its remediation (NAS, 1994). Pump and treat and bioremediation are common groundwater remediation methods; however, these methods can be relatively expensive, intensive, have slow reaction rates, and are not effective. More recently, remediation technologies that use zero-valent metals (such as iron (Fe) filings) are promising because they are relatively inexpensive, easy to maintain, and effectively eliminate TCE and other chlorinated solvents.

The use of zero-valent metals to facilitate the reduction of organic compounds was first reported by Sweeny and Fischer (1972) in patent literature and later in Sweeny (1981, 1983). These studies showed that catalyzed metallic iron powder degraded a wide range of halogenated organic compounds. Unfortunately, Sweeney's work was overlooked and never published in refereed journals. Later, applications of zero-valent metals to remediate organics were pioneered by researchers at the Institute for Groundwater Research at the University of Waterloo. This was followed by the full-scale pilot application of this technology at two private industrial facilities, one in Belfast Northern Ireland and one in Mountain View, CA (Focht et al., 1996). Today, full-scale applications of the zero-valent metals to contaminated aquifers can be found at numerous locations including Cape Cod, MA; Coffeyville, KA; Elizabeth City, NC; Lakewood, CO; and New York (Appleton, 1996). The initial success and prospective applications of this technology have spawned much attention and generate entire conferences and businesses dedicated to this subject.

Johnson et al. (1996) reported TCE half life ($t_{1/2}$) values from a collection of batch and column studies that range from 0.67 to 10.8 hr. These values generally increased for the less chlorinated hydrocarbon species. Normalized with respect to the iron surface area per 1 mL

of solution, the $t_{1/2}$ values were 5 to 15 orders of magnitude lower than natural abiotic rates reported in the literature (Gillham and O'Hannesin, 1994). Furthermore, many studies have shown that iron enhanced with nickel, copper, palladium and other metals enhanced degradation and decreased $t_{1/2}$ by one or two orders of magnitude (i.e. Sweeney and Fischer, 1973; Korte, 1995; Gillham et al., 1997; Gavaskar et al., 1998; Fryzek, 1998). Further benefits of the enhanced zero-valence metals were decreased amounts of toxic TCE degradation byproducts such as vinyl chloride and various dichloroethylene isomers.

The reactive chemistry of the dehalogenation process of TCE is unknown but involves the simultaneous oxidative corrosion of reactive iron by both water and chlorinated organic compound (Matheson and Tratnyek, 1994; Orth and Gillham, 1996; Focht et al., 1996). The two half reactions of iron and TCE are:



These are accompanied by hydrolysis of water and formation of hydrogen gas:



In the presence of iron, TCE degrades spontaneously as suggested by Eq. [3]. Also, as the reaction occurs, the pH of the system will naturally increase as indicated by Eq. [5]. In bimetal systems the second metal may have a catalytic effect on the reactivity of the iron. Another probable effect of a bimetal system is that the difference in their electric potentials may form a galvanic couple (i.e., two dissimilar metals are electrically connected in an electrolyte, current flows from the more noble metal (cathode) to the less noble metal (anode)) (Gavaskar et al., 1998). In this proposed process, the anodic metal is preferentially sacrificed or corroded. The increased availability of electrons further drives the reduction reaction to the right (Eq. [3]) and increase the rate of TCE degradation.

The factors that effect the degradation of TCE are (i) surface area, (ii) presence of dissolved iron, (iii) presence of dissolved oxygen, and (iv) pH. Gotpagar et al. (1997) report that degradation rates were independent of initial TCE concentrations in the range of 72-103 mg L⁻¹, initial pH had an insignificant effect on the rate of degradation, and the presence of dissolved oxygen in solution caused no change in TCE degradation rates. Finally, they found the amount of TCE degraded was directly proportional to the amount of dissolved iron in the solution and concluded that the reaction mechanism appears to be direct electrolytic reduction at the metal surface, making it highly dependent on the metal surface area.

The *in situ* applications of zero-valent metals utilize permeable reactive walls or above ground columns through which contaminated groundwater flows. For the reactive walls, trenches are dug — sometimes up to 120 ft deep — normal to the flow of contaminated groundwater and filled with zero-valent metals (Appleton, 1996). Previous research has measured simple first-order degradation rate constants (*k*) for chlorinated hydrocarbons to estimate the width of *in situ* systems needed to completely degrade the organic contaminants and its daughter products (i.e., Orth, 1992; Gillham and O'Hannesin, 1994; Orth and Gillham, 1996; Focht et al., 1996; Gillham et al., 1997; Reihart et al., 1997, Gavaskar et al., 1998). The methods used to measure *k* values were batch or resident concentration column experiments, which did not take into consideration sorbed phase concentrations, advection, and dispersion. Using these methods lead to difficulties when results from these experiments are extended to flowing zero-valent metal systems. In regards to an above ground pilot-scale field column demonstration, Gillham et al. (1997) stated, "the performance did not meet expectations based on the results of the initial laboratory tests". It may be that the "unmet expectations" were caused by the use of batch or resident concentration column experiments and extending the results to flowing remediation system. In this laboratory study the complexities of the fate and transport of TCE flowing through zero-valent metal systems were addressed using miscible-displacement studies. These studies used a novel miscible-displacement system to simultaneously determine TCE and degradation products.

Dissertation Objectives and Organization

A common theme in each study of this dissertation was solute transport. The increased importance of groundwater quality in rural, suburban, and urban areas have drawn particular attention to solute transport studies. Industrial solvents in urban areas (Fussillo et al., 1985), lawn fertilizers and septic tanks in suburban areas (Flipse et al., 1984), and agricultural fertilizers (Pionke and Urban, 1985) and biocides (Rothschild et al., 1982) in rural areas have all degraded the quality of groundwater in these environments.

The objective of the first study, chapter two, was to compare field methods that estimated solute transport parameters and may help identify soils that are susceptible to rapid solute transport to groundwater. This was the first comparison of these methods *in situ* and was published in the *Soil Science Society of America Journal*. The objective of the second study, chapter three, a laboratory study, was to develop and evaluate an automated miscible-displacement system to study solute transport of volatile organic chemicals. This study introduces a novel system which will further the understanding of contaminant fate and transport in subsurface water, and the manuscript was submitted to *Soil Science*. Lastly, the objectives of chapter four were to use miscible-displacement experiments to investigate the fate and transport of TCE flowing through zero-valent metals. This study has implications on remediation of contaminated groundwater and the manuscript will be submitted to *Environmental Science and Technology*. The final chapter of this dissertation provides the general conclusions about the field and laboratory experiments and ideas for future research.

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CHAPTER 2. COMPARING FIELD METHODS THAT ESTIMATE MOBILE/IMMOBILE MODEL PARAMETERS

A paper published in the Soil Science Society of America Journal¹

Francis Casey^{2,3}, Dan Jaynes⁴, Robert Horton², and Sally Logsdon⁴

Abstract

Recent studies have used field techniques that estimate soil hydraulic and solute transport parameters. These methods utilize a tension infiltrometer to infiltrate either a single tracer or a series of tracers to estimate immobile water content (θ_{im}) and mass exchange coefficient (α) of the mobile/immobile solute transport model. The objective of this study was to compare two single tracer methods (basic and variance) with one multiple tracer method for estimating θ_{im} and α from data obtained on the same field soil location. Hydraulic conductivity ($K(h_r)$) was also estimated using these field techniques. Research was done at five interrow sites in a ridge-tilled corn (*Zea mays*) field, and the soil was mapped as a Nicollet series (fine-loamy, mixed, superactive, mesic, Aquic Hapludoll). The values of θ_{im} and α estimated by the multiple tracer method compared well with previously measured values using the same technique on the same field. The θ_{im} values for the multiple tracer technique were larger than values derived from the basic single tracer technique. The basic single tracer technique did not take into consideration a mass exchange between θ_{im} and the mobile water domain (θ_m). The α values were less variable for the multiple tracer method than for the single tracer-variance method. Values of immobile water fraction (θ_{im}/θ) for the multiple and single tracer techniques ranged from 0.30 to 0.52 and from 0.24 to 0.35, respectively. The values of α for the multiple and single tracer-variance techniques ranged

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²Graduate student and Professor, respectively, Agronomy Department, Iowa State University

³Primary researcher and author, and author for correspondence

⁴Scientist at the National Soil Tilth Laboratory, USDA-ARS, Ames, IA.

from 0.06 to 0.9 d⁻¹ and from 0.03 to 60 d⁻¹, respectively. The volumetric water content (θ) changed considerably over the course of the experiment for the estimation of α using the single tracer-variance method; thus, the assumptions of this technique were compromised. The measured $K(h_r)$ values at the five sites ranged from 0.47 to 1.66 $\mu\text{m s}^{-1}$. There was evidence that the basic single tracer method underestimated θ_{im} and overestimated θ_m because this method considers $\alpha = 0$ during the tracer application.

Introduction

Many agricultural problems involve the reactivity and transport of dissolved chemicals in the soil. Chemicals such as fertilizer and pesticide are deliberately added to the soil, but may result in significant contamination of the groundwater (Pye et al., 1983). These chemicals can be managed to maximize their effectiveness within the root zone and minimize their transport below the root zone. Chemicals often move preferentially through soil resulting in a high risk of groundwater contamination. Preferential flow is exemplified by the early breakthrough and long tailing in laboratory column experiments and in field lysimeter experiments (Beven and Germann, 1982; Ressler et al. 1998). The mobile/immobile solute transport model (Coats and Smith, 1964), developed within the field of petroleum engineering, includes preferential flow. This model has been expanded and applied to soil columns (van Genuchten and Wierenga, 1976, 1977; van Genuchten et al., 1977). The mobile/immobile model was also applied to field scale solute transport by Toride and Leij (1996) using a stochastic stream tube model.

The mobile/immobile solute transport model separates θ into θ_m and θ_{im} . The soil solution is stagnant in θ_{im} and advection and dispersion occur in θ_m . For one-dimensional transport of a non-interacting, conservative solute, the mobile/immobile model can be written as follows:

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} = \theta_m D_m \frac{\partial^2 C_m}{\partial x^2} - q \frac{\partial C_m}{\partial x} \quad [1]$$

where C_m and C_{im} are the solute concentrations in the mobile and immobile domains, t is time, D_m is the dispersion coefficient for θ_m , x is distance, and q is Darcy flux. The two domains are connected by a diffusive transfer of chemical at the boundary of θ_{im} and θ_m :

$$\theta_{im} \frac{\partial C_{im}}{\partial t} = \alpha (C_m - C_{im}). \quad [2]$$

The diffusive mass transfer is characterized by α . The mobile/immobile model can account for more rapid solute transport because flow only occurs in a fraction of total θ . It can also account for tailing because of the solute exchange between the domains (Eq. [2]).

Values of θ_{im} and α can be estimated from solute breakthrough curves in laboratory experiments. Matching the observed flux concentrations of tracers in column effluent with concentrations predicted from analytical solutions of the mobile/immobile model results in a set of best-fit solute transport parameters (Parker and van Genuchten, 1984; van Genuchten and Wagenet, 1989; Garminger et al., 1990; Toride et al., 1995). Although the observed and calculated flux concentrations may match closely with this method, the estimated transport parameters may not be a unique set of values. Alternative methods for estimating parameter values are needed so that unique sets of solute transport values may be determined. There also exists a need to estimate these parameters without running extensive column breakthrough experiments. Methods that do not require effluent breakthrough curves to estimate solute transport properties are also useful in estimating these parameters *in situ*.

Tracer techniques have been proposed for estimating θ_{im} and α in the field. These methods give an alternative approach for the estimation of θ_{im} and α without the need for breakthrough curves or solute distribution profiles. These methods are a single tracer method (Clothier et al., 1992, 1995; Angulo-Jaramillo et al., 1996) and a multiple tracer method (Jaynes et al., 1995; Jaynes and Horton, 1998; Casey et al., 1997, 1998; Lee et al., 1996 and 1997). The single and multiple tracer methods have been applied in the field and have received limited validation. The multiple tracer method was field tested by Casey et al. (1997) and further laboratory tested by Lee et al. (1996 and 1997). Lee et al. (1996 and 1997) used both the breakthrough curve method and the multiple tracer method to estimate θ_{im} and

α in the same aggregated soil columns. In those studies a series of tracers were applied, after which the soil columns were sectioned and analyzed for resident tracer concentrations. The multiple tracer method was used with the resident tracer concentrations to estimate θ_{im} and α . Lee et al. (1996 and 1997) were able to use these estimates to accurately predict solute breakthrough curves and resident concentration profiles in soil columns. The single tracer method has been field tested in several studies (Clothier et al., 1992; 1995; Angulo-Jaramillo et al., 1996) but no laboratory validation has been done.

Both the multiple and single tracer methods are simplifications of the full mobile/immobile model. There exist two separate single tracer methods: the basic single tracer method to estimate θ_{im} (Clothier et al., 1992), and the single tracer-variance method to estimate α (Clothier et al., 1995). The basic single tracer method used to estimate θ_{im} assumes that $\alpha = 0$ and that there is no significant solute exchange between θ_m and θ_{im} ($C_{im} = 0$) during the course of the experiment. The single tracer-variance method for estimating α does not assume $\alpha = 0$ and that α can be measured over a long period of time. The multiple tracer method simultaneously estimates α and θ_{im} while assuming that α is not negligible. Both single and multiple tracer methods assume that there is piston displacement of tracer within θ_m and that C_m behind the tracer front is approximated by the input tracer concentration. There are advantages with both of these methods. The basic single tracer method is simple to use when estimating θ_{im} and the analytical techniques are not complex; however, the single tracer-variance method is more involved when estimating α . Both techniques are capable of simultaneously determining soil hydraulic properties. To date there has not been a critical comparison of the two methods. The objective of this study is to compare the single and multiple tracer methods for estimating α and θ_{im} of a field soil.

Materials and Methods

Research took place in a ridge-tilled corn (*Zea mays*) field between August 30 and September 14, 1996 at the Agronomy and Agricultural and Biosystems Engineering Research Center west of Ames, IA. The soil was mapped as a Nicollet series derived from glacial till. Five infiltration sites were located in the interrow areas of adjacent corn rows. The infiltration

sites were cleared of corn debris and weeds to ensure suitable hydraulic contact between the infiltrometer disk and the soil surface. Experiments to estimate soil hydraulic properties preceded experiments to estimate the solute transport coefficients, θ_{im} and α .

Near each site a soil core was taken using a beveled brass ring with height 37 mm and diameter 73 mm. These soil cores were used to determine the antecedent θ and bulk density. A large-base diameter (230 mm, Perroux and White, 1988) tension infiltrometer was filled with a 4 mmol L⁻¹ solution of KCl and placed on the flat soil surface. Infiltration began at a pressure head of -30 mm and the early cumulative infiltration (I) volumes were automatically recorded every second for the first 100 seconds. These early I values were later used to calculate sorptivity (S). The infiltrometers were automated with transducers as described by Ankeny et al. (1988). After the first 100 seconds of cumulative infiltration, the automated recording interval was changed to read every 576 seconds for 16 hours. These later I values were used to determine the steady state infiltration rates (i) according to White and Sully (1987).

To estimate S , early stages of I values were used with the following expression (Philip, 1957; White and Sully, 1987 and 1988):

$$I = St^{1/2} \quad [3]$$

where t is the infiltration time. Sorptivity was estimated from the slope of the measured I versus $t^{1/2}$, and coefficients of determination were determined for the regression.

To estimate $K(h_e)$, the White and Sully (1987) method was used. White and Sully (1987) derived the following expression for the matrix flux potential (ϕ):

$$\phi = bS^2/(\Delta\theta) \quad [4]$$

where b is a shape factor between $1/2$ and $\pi/4$ and $\Delta\theta$ is the change in θ during the entire infiltration period. Taking a reasonable approximation for b of 0.55 (Smettem and Clothier, 1989) and substituting Eq. [4] into Wooding's (1968) solution for unconfined steady state infiltration from a disk results in the following expression:

$$K(h_o) = i - (2.2S^2)/(\Delta\theta\pi R) \quad [5]$$

where R is the base radius of the infiltrometer (115 mm) and h_o is the pressure head, -30 mm.

After the 4 mmol L⁻¹ KCl solution had reached steady state infiltration rate, a series of four benzoic acid tracer solutions was applied to each site. The tracer solutions were mixed in the same manner as described by Jaynes et al. (1995) and Casey et al. (1997, 1998). The tracers used were *o*-trifluoromethylbenzoate, 2,6-difluorobenzoate, pentafluorobenzoate, and 2,3,6-trifluorobenzoate. Tracer application order was randomized to minimize any error caused by nonidentical transport, recovery, and analysis. Each tracer solution was applied using a separate infiltrometer; detailed laboratory experiments have shown that infiltration rates quickly return to steady state after brief removal of a tension infiltrometer (Clothier et al., 1992). The final tracer solution was applied for approximately 1 to 2.5 hrs so that the tracer front was well beyond the soil sampling depth of 15 mm. Clothier et al. (1995) determined that infiltrating 25 to 30 mm of tracer was sufficient to sample soil 10 to 15 mm deep while well avoiding the tracer front. We used the same criteria as the Clothier et al. (1995) study for tracer application and sampling depth.

Within seconds after the final tracer application the infiltrometer was removed, and the soil was sampled from the area that had been beneath the tension infiltrometer. The infiltration area was sectioned into four equal parts, and eight cylindrical samples (15 mm deep and 10.6 mm diameter) were taken from one of the quarters (Fig. 1) at approximately the same time. The infiltration area was sectioned into four quarters so that sampling disturbance was localized to a single quarter and minimized at the other quarters. The infiltration sites were then covered with plastic and loose soil was spread over the plastic. This was done to prevent water loss by evaporation and infiltration from precipitation. During the course of the experiment there was no precipitation. Approximately, two days after the start of the tracer application, the soil and plastic sheets were taken off the infiltration sites and eight soil samples were taken from another quarter of the infiltration site. The soil was then covered again with the plastic and loose soil. This procedure was repeated

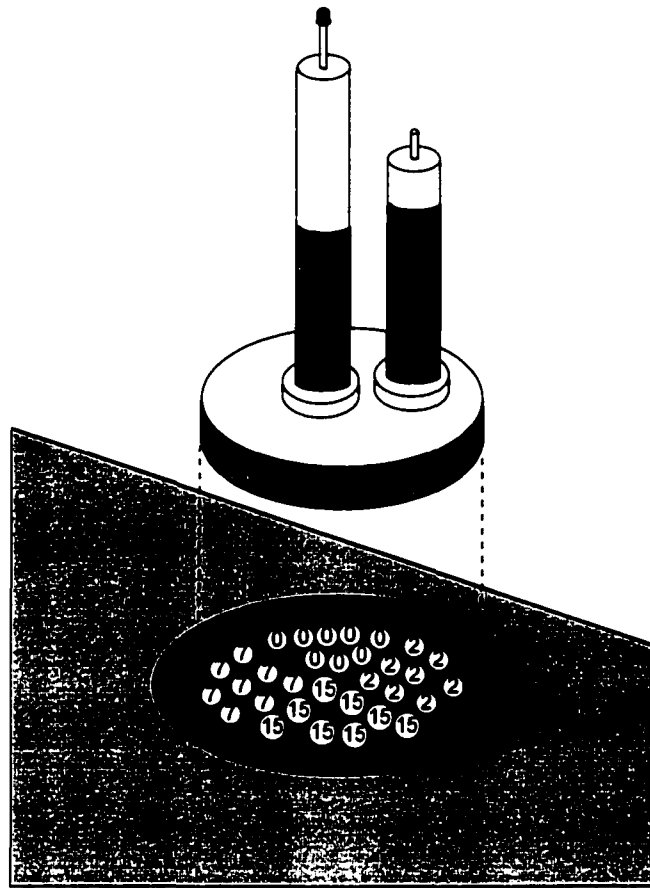


Fig. 1. A diagram of the soil sampling scheme beneath the tension infiltrometer. The soil sampled immediately after the tracer application was used to estimate θ_{im} with the Clothier et al. (1992) method. All sampling dates were used to estimate α with the Clothier et al. (1995) method. The sampling dates immediately after the final tracer application, 2, 7, and 15 d correspond to the numerals 0, 2, 7, and 15 within the white circles, respectively.

approximately at 7 d and 15 d after the start of the tracer application. Figure 1 shows the sampling scheme. All soil samples were weighed and placed in plastic zip-lock bags and refrigerated to prevent any loss of tracer or change in θ .

The soil samples were taken to the laboratory for tracer extraction and θ measurements. Tracer extractions of the soil samples were done in 150 ml Erlenmeyer flasks using approximately 1:1 soil/0.0005 M CaSO_4 solution. The extraction mixture was shaken for 5 min on a wrist shaker and allowed to settle for 5 min. The solution was then decanted through No. 40 filter paper and stored at 2°C until analysis. Approximately 10 ml of filtered solution was needed for tracer solution determination. The remaining decant and soil retained on the filter paper were oven dried at 105°C to compute θ .

Analysis for the fluorobenzoate tracers was done on a Dionex Series 4500i ion chromatograph (West Mont, IL) as described by Bowman and Gibbens (1992). For the fluorobenzoates, a SAX column (Regis Chemical Co., Morton Grove, IL)⁵ was used with 30 mM KH_2PO_4 , adjusted to a pH of 2.65 with H_3PO_4 and 20 mL L^{-1} acetonitrile as the eluting solution. The flow rate was 1 mL min^{-1} and the detection wavelength was set to 205 nm.

Extracted tracer concentrations from the soil sampled immediately after the tracer application were used to estimate θ_{im} and α with the modified Jaynes et al. (1995) method (Jaynes and Horton, 1998; Casey et al., 1997):

$$\ln(1 - C/C_o) = -\alpha t/\theta_{\text{im}} + \ln(\theta_{\text{im}}/\theta) + \ell\alpha\theta_{\text{m}}/(\theta_{\text{im}}q) \quad [6]$$

where C is the measured tracer concentration from the extract, C_o is the tracer concentration from the input tracer solution, t is tracer application time, and ℓ is the soil sampling depth. It is assumed that $C_o = C_m$ when the soil is sampled. Plotting $\ln(1 - C/C_o)$ as a function of t should result in a straight line with the intercept of $[\ln(\theta_{\text{im}}/\theta) + \ell\alpha\theta_{\text{m}}/(\theta_{\text{im}}q)]$ and the slope $-\alpha/\theta_{\text{im}}$ (Fig. 2). Since θ_{im} is in both the intercept and slope, a least-squares optimization has to be done to estimate α and θ_{im} .

⁵Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may be suitable.

Extracted tracer concentrations from the soil sampled immediately after the tracer application were also used to estimate θ_{im} with the basic single tracer method (Clothier et al., 1992):

$$\theta_{im} = \theta(1 - C/C_o). \quad [7]$$

Equation [7] is identical to Eq. [6] if α is zero. Extracted tracer concentrations that were used to estimate θ_{im} from Eq. [7] were of the longest applied tracer in the series. The basic single tracer method assumed $\alpha = 0$ for the entire tracer experiment, so it should not matter which tracer we chose. However, to diminish concern that the assumption that $C_m = C_o$ was not being violated we chose to use the final tracer in the series. The longer the tracer was applied the higher the probability that $C_m = C_o$ was true.

Clothier et al. (1995) proposed a single tracer-variance method to estimate α by measuring the variance of tracer concentration over time. First, Clothier et al. (1995) analytically expressed the decrease of C_m over time:

$$C_m(t) = C^* [1 + ((\theta - \theta_m)/\theta_m) \exp[-\alpha(\theta_{im}/\theta_m)\theta t]] \quad [8]$$

and the simultaneous increase of C_{im} over time:

$$C_{im}(t) = C^* [1 - \exp[-\alpha(\theta_{im}/\theta_m)\theta t]] \quad [9]$$

where C^* is the equilibrium tracer concentration when $C^* = C_m = C_{im} = C_o(1 - \theta_{im}/\theta)$ as t approaches infinity. Finally, Clothier et al. (1995) developed the following expression to predict the normalized variance in tracer concentration under the infiltrometer over time:

$$s^2(t)/s_o^2 = \frac{(\theta_m/\theta)[C_m(t) - C^*]^2 + (\theta_{im}/\theta)[C(t)_{im} - C^*]^2}{C^*(C_o - C^*)} \quad [10]$$

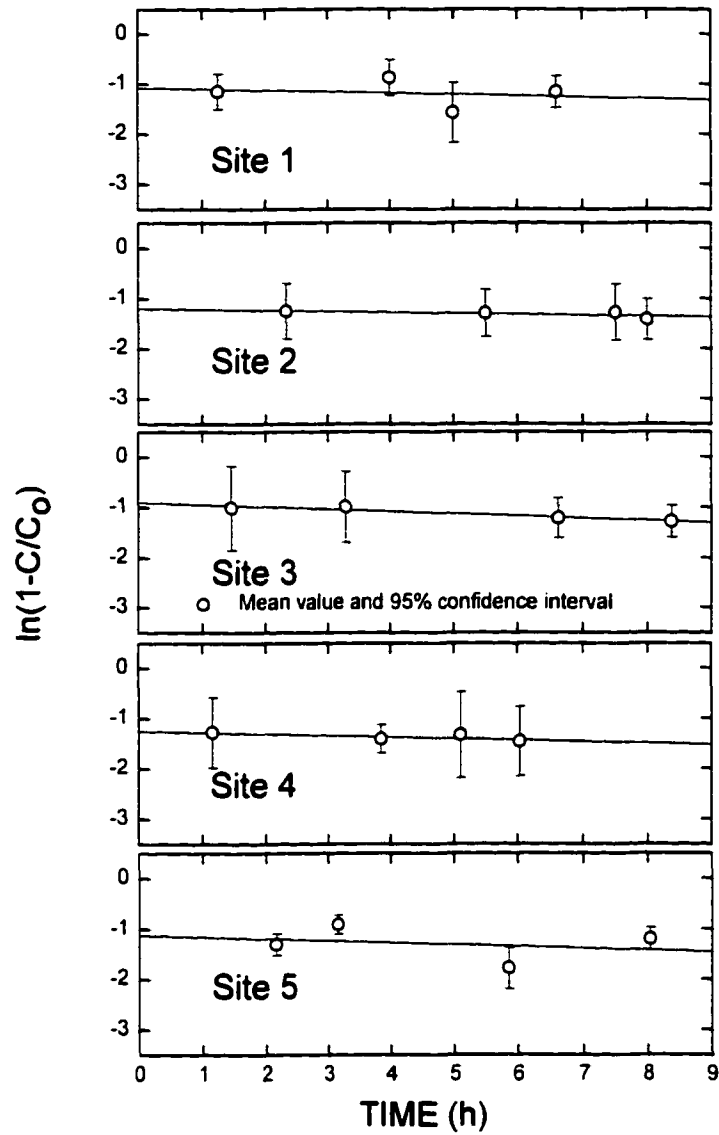


Fig. 2. Regressions of $\ln(1-C/C_0)$ vs. time used by the Jaynes et al. (1995) method to estimate θ_{im} and α at each site. The slope gives $-\alpha/\theta_{im}$ and the intercept gives $\ln(\theta_{im}/\theta) + \alpha \theta_m/(\theta_{im}q)$.

where $s^2(t)/s_0^2$ is the predicted normalized variance in the soil samples over time. The temporal decline in $[C_m(t)-C^*]$ and $[C_{im}(t)-C^*]$ can be found using the analytical expressions of Eq. [8] and Eq. [9]. At the time the soil was first sampled it is assumed that the values of $C_{im} = 0$ and of $C_m = C_0$. Also, the values for θ_m and θ_{im} that were used in Eq. [8], [9], and [10] came from Eq. [7].

The variance of each of the tracer concentrations from each application site was determined at approximately 0, 2, 7, and 15 d after the start of the tracer infiltration. The time at 0 d was the time the first tracer was applied, and the first sampling occurred at the completion of the last tracer infiltration. The following expression was used to determine the sample variance (s^2) of the tracer concentrations (Steel and Torrie, 1980):

$$s^2 = \sum_{i=1}^n \frac{(C - \bar{C})^2}{n-1} \quad [11]$$

where n is the number of the soil samples ($n=8$), and \bar{C} is the mean value of the n samples. The sample variance values from Eq. [11] were normalized by dividing through by the initial sample variance, s_0^2 , calculated from all of the tracers. This approach for estimating α assumed that the soil samples that were taken from the infiltration site were either sampled from θ_m or θ_{im} (Clothier et al., 1995).

All four tracers were used in estimating the measured $s^2(t)/s_0^2$ values. The tracers were assumed to move through the soil identically, and the tracers were applied at different times. Each tracer was used to estimate a $s^2(t)/s_0^2$ value. Figure 3 shows the observed $s^2(t)/s_0^2$ values (Eq. [11]) from all four tracers and corresponding model curves that were calculated from Eq. [10]. To calculate Eq. [10] it was necessary to calculate $C_m(t)$ and $C_{im}(t)$ values which were calculated using Eq. [8] and Eq. [9], respectively. The different calculated $s^2(t)/s_0^2$ values from Eq. [10] were obtained by using various α values, which are reported in Fig. 3.

To evaluate the basic single tracer method's assumption that $\alpha \approx 0$, calculations were made with the α values from Eq. [6] to estimate the amount of solute accumulation in θ_{im} over the time of the experiment. The program CXTFIT 2.0 (Toride et al., 1995) was used to calculate the accumulation of tracer in θ_{im} with time.

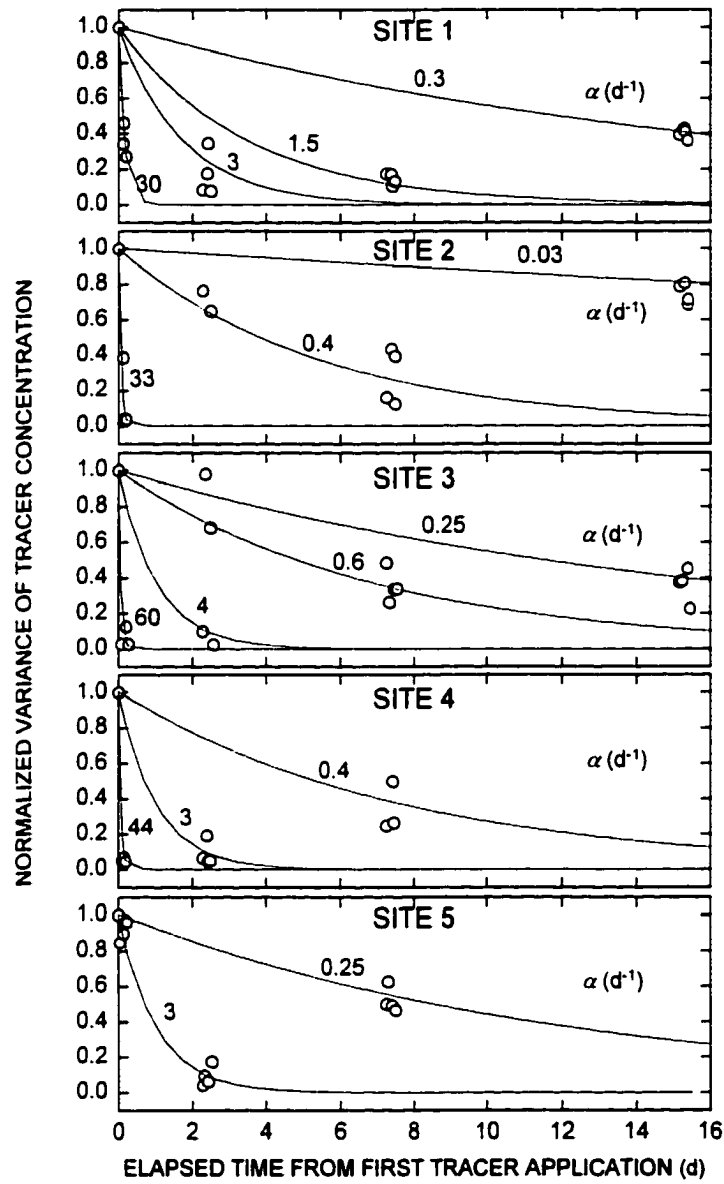


Fig. 3. The predicted and measured values of the normalized sample variance ($s^2(t)/s^2_o$) as a function of time elapsed from the start of the tracer application for each site. Here the predicted $s^2(t)/s^2_o$ curves were derived from Eq.[10] using the α values indicated on the graph. Note, that the measured $s^2(t)/s^2_o$ values that were >1 were excluded from site 2 on second sampling date and from site 4 and 5 on the last sampling date.

Values of θ_{im}/θ and α from this study were compared with the Casey et al. (1997) study using a one-way ANOVA at a 5% level (Steel and Torrie, 1980).

Results and Discussion

Soil Hydraulic Properties

The first objective of this study was to estimate the hydraulic properties of the soil at -30 mm pressure head, these values are presented in Table 1 for the five measurement sites. The coefficients of determination for the estimation of S using the early time infiltration data ranged from 0.77 to 0.99 with a mean of 0.87. Estimations of $K(h_e)$ from the long time steady state infiltration data using the White and Sully (1987) method were reasonable and fell within the ranges that others have found in soils near this research area (Logsdon and Jaynes, 1996; Logsdon, 1993). Under similar tillage systems and time of the season, Logsdon and Jaynes (1996) found the mean $K(h_e)$ values at $h_e = -30$ mm to be $4.52 \mu\text{m s}^{-1}$ with a plus or minus one standard deviation range of 1.81 to $10.70 \mu\text{m s}^{-1}$. These values are slightly higher than the values reported in this study. Also, Logsdon (1993) found $K(h_e)$ values in similar soils to range from 0.67 to $2.2 \mu\text{m s}^{-1}$, which were similar to our values (Table 1).

Soil Transport Properties

Multiple Tracer Method. Figure 2 shows the graphs of $\ln(1-C/C_e)$ versus t from the first sampling, where only the mean $\ln(1-C/C_e)$ values and 95% confidence intervals of the

TABLE 1 — Physical and hydraulic properties of the five measurement sites. Hydraulic conductivity was calculated by the White and Sully (1987) method.

Site	i	$K(h_e)$	S	Antecedent θ	Final θ	Bulk Density
	($\mu\text{m s}^{-1}$)	($\mu\text{m s}^{-1}$)	($\text{m}^3 \text{s}^{-1/2}$)	($\text{m}^3 \text{m}^{-3}$)	($\text{m}^3 \text{m}^{-3}$)	(Mg m^{-3})
1	2.27	1.66	73.98	0.25	0.31	1.11
2	0.49	0.47	20.32	0.28	0.43	1.09
3	2.16	1.02	23.95	0.23	0.34	1.13
4	1.05	1.55	107.80	0.33	0.41	1.20
5	1.45	1.46	0.39	0.21	0.32	1.02

eight samples were plotted to avoid clutter. As plotted, the slopes and intercepts of the regression from the eight soil samples at the five sites were quite similar. The estimated median values of θ_{im} for sites 1, 2, 3, 4, and 5 were 0.17, 0.29, 0.16, 0.19, and 0.10 $\text{m}^3 \text{m}^{-3}$ respectively, from the multiple tracer method. The variances in θ_{im} values were relatively low for all sites, ranging from $5.0 \times 10^{-4} \text{m}^6 \text{m}^{-6}$ at site 1 to $3 \times 10^{-3} \text{m}^6 \text{m}^{-6}$ at site 5. The corresponding θ_{im}/θ values were 0.52, 0.48, 0.44, 0.44, and 0.30 for respective sites 1, 2, 3, 4, and 5. An ANOVA comparison with the Casey et al. (1997) study showed that θ_{im}/θ values in this study were not statistically different at a 5% level. The Casey et al. (1997) study was conducted two years earlier on the same research field, using the same pressure head.

The median α values for sites 1, 2, 3, 4, and 5 were 0.6, 0.9, 0.3, 0.7, and 0.1 d^{-1} respectively. The variances of α values were low, ranging from $2.5 \times 10^{-5} \text{d}^{-2}$ at site 5 to 0.4 d^{-2} at site 2. The α values from this study were not significantly different from the Casey et al. (1997) study at a 5% level.

Single Tracer Methods. The estimates of θ_{im} using the basic single tracer method for sites 1, 2, 3, 4, and 5 were 0.10, 0.15, 0.10, 0.14, and 0.10 $\text{m}^3 \text{m}^{-3}$ respectively. The variances of θ_{im} values ranged from $1.0 \times 10^{-4} \text{m}^6 \text{m}^{-6}$ at site 1 to $2.1 \times 10^{-5} \text{m}^6 \text{m}^{-6}$ at site 2, which was lower than the values estimated by the multiple tracer method. The θ_{im}/θ values estimated by the basic single tracer technique were 0.24, 0.35, 0.26, 0.33, and 0.24 for the respective sites 1, 2, 3, 4, and 5.

Although the exact same soil samples were used, the estimates of θ_{im} and θ_{im}/θ from the single tracer method were lower than the estimates from the multiple tracer method. The single tracer method assumes that the tracer enters the soil surface and moves through θ_m exclusively. This technique assumes that $\alpha = 0$, therefore there is no mass exchange between θ_{im} and θ_m and no accumulation of tracer in θ_{im} . If $\alpha = 0$ then the concentration of the tracer should not change over time, which is contrary to the negative slopes shown for the $\ln(1-C/C_0)$ vs. t function (Fig. 2) Clothier et al. (1995) expressed concern that some of their samples did not reach final concentration due to dispersion. As a result Clothier et al. (1995) recommended that a tracer should infiltrate to depths of 25 to 30 mm for soil samples taken to the 10 to 15 mm depth. These sampling criterion were exceeded in this study. Since the

Clothier et al. (1995) sampling recommendations were exceeded, it is less likely the change in tracer concentrations changed with time due to dispersion rather than α . The Clothier et al. (1995) recommendations are supported by several studies showing that dispersion approaches zero close to the solute application source at the soil surface (Yates, 1992; Gimmi, 1994). Our soil samples were taken at a shallow depth so that the effect of dispersion approached zero. A likely explanation of the increase in tracer concentration over time in Fig. 2 (i.e., decrease of $\ln(1-C/C_0)$ vs. t) was diffusion of tracer into θ_{im} .

Assuming $\alpha = 0$ does not appear realistic. For instance, using α of 0.5 d^{-1} as estimated by Clothier et al. (1995), a measurable diffusion of solute into θ_{im} occurs within a few hours (Jaynes and Horton, 1998). Ignoring this diffusion with the basic single tracer method leads to an underestimation of θ_{im}/θ . As a demonstration, C_{im} was calculated using CXTFIT 2.0 (Toride et al., 1995) with α values from the multiple tracer method (Eq. [6]). Figure 4 shows the relative C_{im} as a function of time, and indicates appreciable accumulation of tracer in the immobile domain at the time of the first soil sampling. This gives further evidence for the underestimation of θ_{im} with the basic single tracer method.

The normalized variance calculated from the measured tracer concentrations with time did not fit the single tracer model (Eq.[10]) very well (Fig. 3). For each of the sampling dates a separate α value could be estimated using this method, so there was not a single α value that characterized the decrease in $s^2(t)/s^2_0$ with time for any of the sites. Also, at any one site the estimated α values ranged from two to three orders of magnitude. The range of α values for all the sites was 0.03 to 60 d^{-1} .

The calculated $s^2(t)/s^2_0$ values did not decrease with time as the assumptions of this method predict. Furthermore, the spread of $s^2(t)/s^2_0$ values between the tracers at each sampling date did not diminish with time (Fig. 3). Values of $s^2(t)/s^2_0$ even went above 1 for site 2 on the second day of sampling and again at sites 4 and 5 on the last day of sampling. The $s^2(t)/s^2_0$ values that were greater than one were excluded when creating Fig. 3.

The single tracer-variance method requires constant θ over the course of the experiment to estimate α (Clothier et al., 1995). Although the infiltration areas were covered by plastic and loose soil between each of the sampling periods, θ values decreased, either

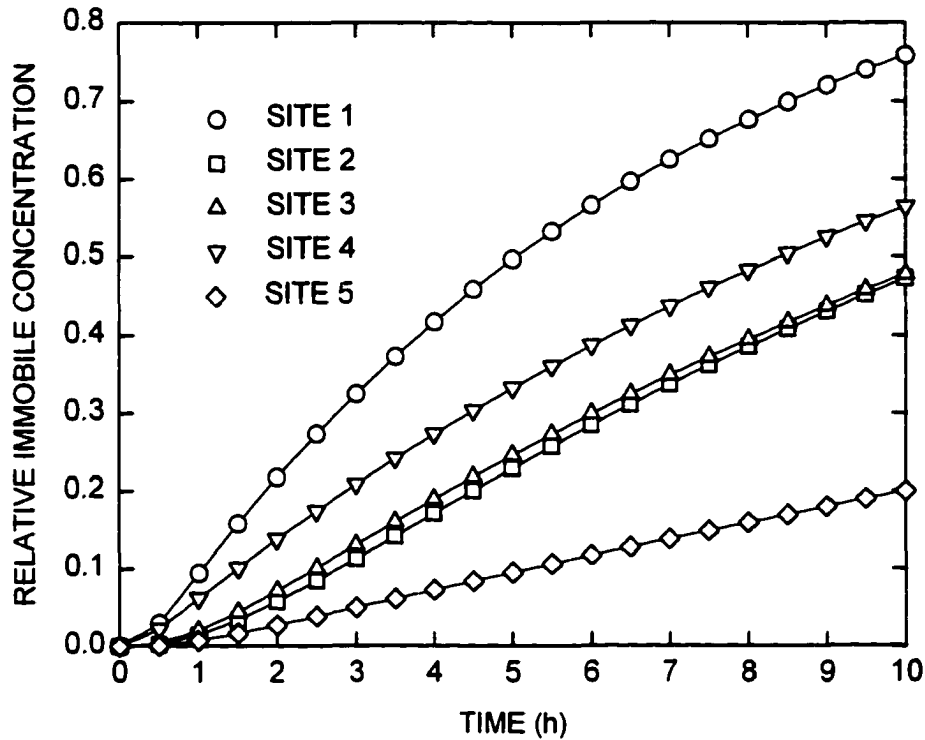


Fig. 4. The calculated relative tracer concentration in the immobile domain as a function of time. Relative immobile tracer concentrations were calculated using CXTFIT 2.0 (Toride et al., 1995) and α values obtained from the multiple tracer method .

from lateral distribution, drainage, condensation on the plastic, or transpiration during the experiment (Fig. 5). An increase in tracer concentration over time at some of the sites was measured and was consistent with the occurrence of transpiration. Corn plants may have drawn soil water from the experimental volume and concentrated the tracer. The large decrease in θ over the 15 d period compromised the single tracer-variance method and probably added variability in the tracer concentration with time. During the first two sampling dates the mean θ values changed the least, 20%; but, there was no consistent decrease in $s^2(t)/s^2_0$ values with time during the first two days. We speculate that the variation in θ for the first two sampling dates was caused by the wetting properties of the soil as affected by the interface with the infiltrometer base, not by the exchange of tracer between θ_m and θ_{im} . Clothier et al. (1995) showed the same disagreement between the single tracer-

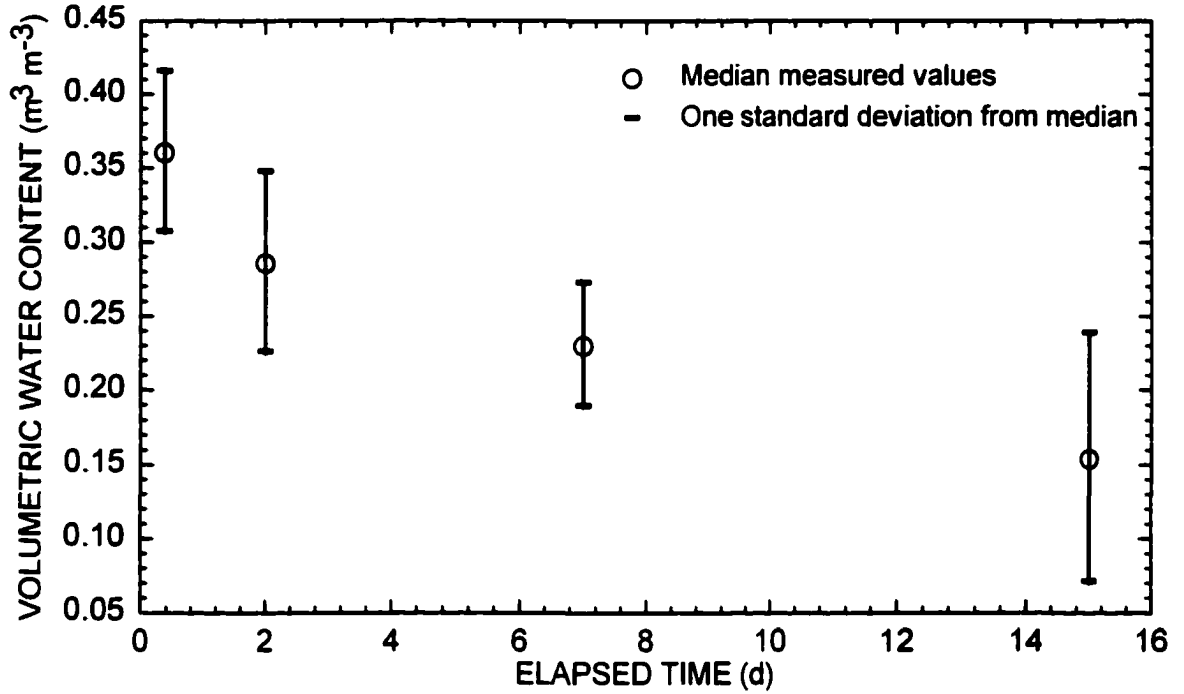


Fig. 5. Soil volumetric water content as a function of time.

variance model and their measured $s^2(t)/s^2_0$ values but attributed the disagreement to advective transport. As a rule, the multiple tracer method fit the C data better than the single tracer method.

Also, the single tracer method for estimating α assumes that soil samples taken from the infiltration site are either sampled from θ_m or θ_{im} . This macroscopic interpretation of θ_m and θ_{im} is a fundamental difference between the two tracer methods. The multiple tracer method assumes that the domains of solute transport are on a small scale and not found in large pockets of the soil. The single tracer method assumes that the solute transport domains are on a large scale and can be sampled individually.

Conclusion

Two single tracer (basic, variance) methods and a multiple tracer method have been proposed for the estimation of the mobile/immobile model transport parameters α and θ_{im} but have not been used on the same site. By using these methods at one site, we estimated the hydraulic parameters along with the solute transport parameters. The multiple tracer method consistently gave θ_{im} values that were larger than those given by the basic single tracer method, and we attributed this result to an invalid assumption of $\alpha = 0$ used in the basic single tracer method. The single tracer-variance method for estimating α was less practical than the multiple tracer method because it took a long time and was less consistent with the measured data. The single tracer-variance method gave biased estimates of α because of decreasing soil water during the test period.

Acknowledgments

This material is based upon work supported by the CSREES-USDA under agreement # 94-37102-01906.

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CHAPTER 3. AUTOMATED SYSTEM FOR MISCIBLE-DISPLACEMENT THROUGH SOIL OF MULTIPLE VOLATILE ORGANIC COMPOUNDS

A manuscript submitted to Soil Science Journal

Francis X. M. Casey^{1,2}, Robert P. Ewing², and Robert Horton^{2,3}

Abstract

A novel, automated, miscible-displacement system has been developed to study the fate and transport of volatile chemicals within soil. This system presents advantages over existing systems that utilize fraction collection, head space analysis, or single flow-through UV detectors; because there is no volatilization, there is high chemical resolution, and there is simultaneous detection of multiple chemicals. This study presents the design of the system and demonstrates its capabilities. The system's flow rate and chemical concentration detection stability were tested through time; in addition to its ability to detect multiple compounds. For a chemical detection stability test of 2.7 d, the pump was able to supply 10 mg L⁻¹ of toluene and measure its absorbency every 10 min. A coefficient of variation (CV) of 1.55 % for the measured values suggested a very stable measurement with time. The CV of pumping rate was less than 1 % for continuous flow over a 9 d period of time. A toluene breakthrough curve through an Ottawa sand resulted in 99.99% mass recovery of toluene, indicating no volatilization or irreversible sorption to the equipment. Lastly, the system's ability to measure multiple compounds was demonstrated with simultaneous breakthrough curves of three chlorinated hydrocarbons through sand. This system makes possible a wide variety of experiments that previously could not be performed on volatile organic compounds with acceptable precision.

¹Primary researcher and author

²Graduate student, postdoctoral appointee, and professor, respectively, Department of Agronomy, Iowa State University

³Author for correspondence

Introduction

Contamination of the vadose zone and groundwater by pesticides, petroleum products, and organic solvents compels us to better understand the transport and fate of organic chemicals. Miscible-displacement experiments allow us to quantify the transport behavior of these compounds as affected by complex chemical, physical, and biological interactions (Brusseau et al., 1990; Wu and Gschwend, 1986; Lee et al., 1988). Problems arise, however, when miscible-displacement techniques developed with conservative tracers such as chloride are used for hydrophobic organic chemicals (HOCs). First, many HOCs sorb to equipment as well as to soil components. To minimize sorption artifacts, only inert materials such as stainless steel and glass should come in contact with the solution. Second, HOCs have low solubilities, and concentrations within a dissolved plume are generally well below solubility. To avoid introducing behaviors specific to unrealistically high concentrations, experiments should be conducted at representative concentrations, and so the equipment must be capable of resolving low concentrations (e.g., below 10 mg L^{-1}). Third, solubility levels of HOCs are sensitive to temperature, so the dissolved HOC reservoir should be kept at constant temperature, and have either excess free-phase HOC or a reliable dilution method. One reliable dilute method is to contain the HOC solution in collapsible reservoirs such as Teflon[®] bags with no head space (Gillham and O'Hannesin, 1994).

When the pollutants are volatile organic compounds (VOCs), further potential pitfalls arise. Miscible-displacement studies commonly collect fractions of the soil column effluent. Fraction collection suffers from potential volatilization losses during the collection, storage and analysis of the fractions, and while these can be minimized, they still introduce experimental error. Brusseau et al. (1990) developed a flow-through method that uses an in-line UV detector to measure VOCs without the problems typically associated with fraction collecting. This technique eliminates volatilization losses, but unless it is modified, it only can measure a single solute compound. Furthermore, flow-through UV detectors cannot detect VOCs at concentrations typical of contaminant plumes, meaning that either data has low resolution, or concentrations are unrealistically high. Additionally, safety is a concern. Release of VOCs to the environment can be reduced by using a completely closed system.

Finally, many miscible-displacement and batch experiments do not use direct aqueous measurements of effluent solution. Rather these techniques use gas chromatography with either direct aqueous injection, or indirect measurement of aqueous concentrations via head space analysis. Head space analysis depends on the Henry's law constant, which can vary in accuracy according to the compound being used. More importantly, both techniques are sensitive to temperature fluctuations and interactions of two or more compounds. This can introduce additional error into the analysis.

The goal of this study is to develop a miscible-displacement system applicable to VOCs. Criteria included in the system's design are 1) closed system, 2) non-sorbing material construction, 3) accurate aqueous detection of VOC at low concentrations, 4) capability of measuring multiple solutes, 5) automation, and 6) safety.

We note that individual investigators have successfully addressed two or three of these criteria but to our knowledge none have integrated all these criteria into one system. Some experimenters have addressed individual concerns such as fraction collection and volatilization (e.g., Brusseau et al., 1990) but have not addressed analytical resolution or simultaneous multiple breakthrough curves, while others have addressed simultaneous detection of multiple chemicals but have neglected to use non-sorbing material (Gillham and O'Hannesin, 1994; Conklin et al., 1995) or to minimize volatilization (Gillham and O'Hannesin, 1994). Most investigators have neglected problems associated with automation, especially when long term studies are needed.

Experimental System

A schematic of the miscible-displacement system is shown in Fig. 1. The system is composed of a transport portion with a pump and soil column, and an analysis portion consisting of a high performance liquid chromatograph (HPLC). The two portions are joined together by an electronically controlled valve with a sampling loop.

A Beckman 128 (*Disclaimer: Names of all products or brands are provided solely for the reader's information and do not imply endorsement of individual brands, nor criticism of similar suitable products not used by Iowa State University*) binary pump is used to deliver

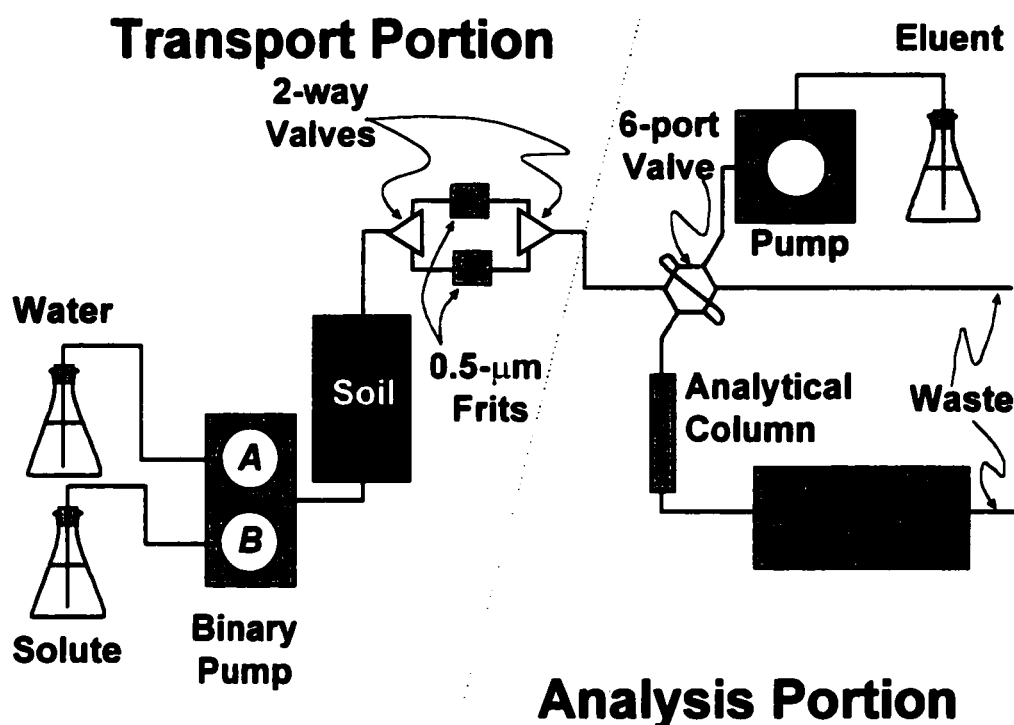


Fig. 1. Diagram of the miscible-displacement system.

water and/or solvent to the soil column. The binary pump has two separate pumps, referred to as *A* and *B*. Pump *A* draws from a reservoir containing water or a weak buffer solution; pump *B* draws from a separate reservoir that has a constant concentration of VOC. Pump *B*'s reservoir VOC concentration is kept constant either at saturation levels by the presence of free product in the reservoir, or below the saturation level if a collapsible Teflon[®] bag reservoir is used (Gillham and O'Hannesin, 1994). The concentration delivered to the soil column is set by the percent pump *B* is programmed to deliver. Pumps *A* and *B* of the binary pump are individually capable of flow rates from 0.001 to 10 mL min⁻¹, and at any chosen flow rate, the pump delivery ratio between *A* and *B* can be programmed. The range of ratios between the delivery of pump *A* and *B* is from 0:1 to 1:0 with a resolution of 0.01%. The wetted surfaces of the binary pump consist of stainless steel, Teflon[®], Peek[®], sapphire, ruby, and glass.

The mixed solution is then pumped at a constant rate through the soil column, in our case a stainless steel column. Each end of the column has a distribution plate, a wire mesh, and a 2 μm frit, all made of stainless steel. The plates and wire mesh assure flow uniformity through the column, and the frit prevents large particles from leaving the column.

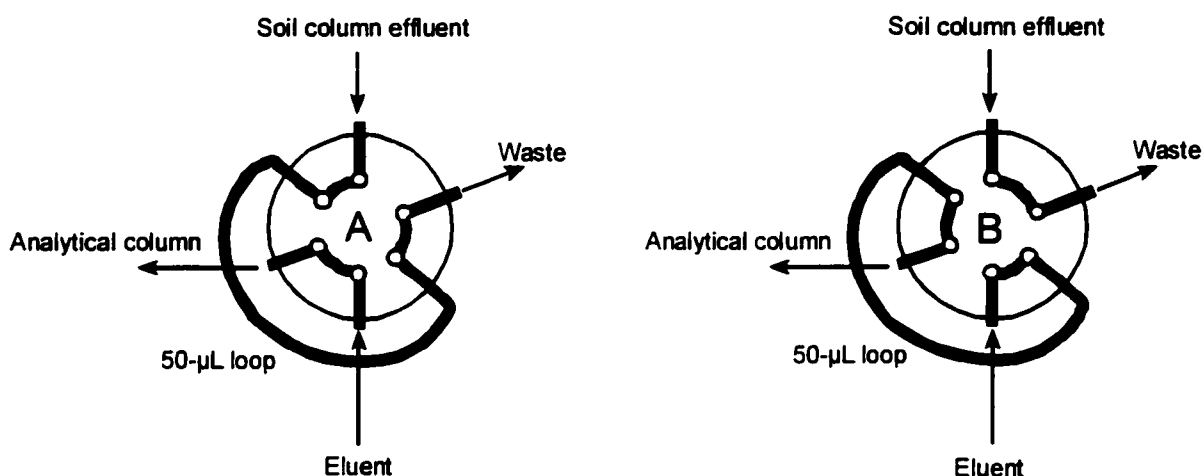


Fig. 2. Diagram of the six-port, two-way valve in its two positions. Notice that the sample loop is filled in one direction and flushed in the opposite direction.

After the soil column, the effluent passes through a manual three-port valve, a 0.5 μm frit, and another three-port valve. If the 0.5 μm frit clogs, the two three-port valves can divert flow through a second 0.5 μm frit while the clogged frit is being replaced. The frits protect the sampling valve and analytical column from particles in the effluent. Effluent then flows through a Valco two-position six-port valve with a 50 μL sampling loop (Fig. 2). When the six-port valve is in position *A* (Fig. 2), effluent is flowing through the 50 μL loop. A 50 μL effluent sample from the loop is passed into the analysis portion of the system when the six-port valve is in position *B* (Fig. 2). Minimum duration between effluent samples points depend on the elution and reequilibration times of the HPLC. The analysis portion consists of a second Beckman pump, an analytical column, and a diode array UV/VIS HPLC detector. Our particular setup uses an isocratic pump and a C18 analytical column, but other HPLC components may be substituted as the analysis demands.

To reduce temperature-dependent concentration fluctuations of the VOC in the reservoir, the entire system is located in a constant-temperature room. For safety reasons, all waste streams are collected in a fume hood. The entire system is controlled by a computer running Beckman “Gold Nouveau” software that controls the two pumps, the sampling valve and the UV detector, and also integrates the peaks of the chromatogram. A comparison between this system and other miscible-displacement systems is given in Table 1.

TABLE 1 — Comparisons between miscible-displacement methods

Comparison Criterion	Flow-through UV detection	Fraction Collection	Flow-through with HPLC
Monitoring	continuous	point	point
Resolution	low	high	high
Risk of volatilization losses/Safety	low/good	medium/poor	low/good
Adaptable for multiple samples	somewhat	yes	yes
Automation and convenience	high	medium	high

Experimental System Performance

System Linearity

An HPLC detector gives results in absorbance units which should be linearly related to absolute concentrations. To test system linearity, the soil column was bypassed so the results would reflect system performance. Pump *A*'s reservoir was pure water, and Pump *B*'s reservoir was water saturated with toluene. The aqueous solubility of toluene was calculated to be 495 mg L⁻¹ at 24 °C using Antoine's equation (American Petroleum Institute, 1964). In three separate 400 minute runs, the system was set to deliver 1.01%, 2.02%, and 4.04% *B* (toluene-saturated water), giving concentrations of 5, 10, and 20 mg L⁻¹, respectively, at a flow rate of 1 mL min⁻¹. Samples were analyzed via the sampling loop every 10 min. The eluent was 70:30 acetonitrile:water at a flow rate of 1 mL min⁻¹, and toluene was detected at 215 nm. A calibration curve was created from the peak absorbency values.

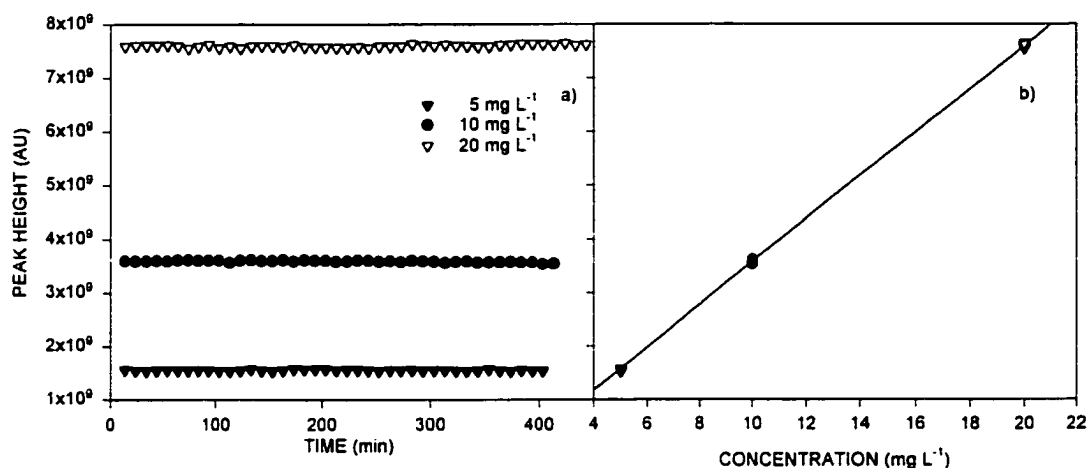


Fig. 3. (a) Three separate system stability tests where constant concentrations of toluene were pumped from the binary pump at 1 mL min^{-1} and the effluent was measured every 10 min. (b) Toluene calibration curve created from the values obtained from the three system stability tests in Fig. 3a.

The system's ability to supply and measure constant concentrations is indicated by the stability of each set of 40 measurements (Fig. 3a). The resulting calibration curve (Fig. 3b) has a coefficient of determination (r^2) of 0.9999, indicating that pump and detector performance are linear and stable over time. Further calibration curves have been made using dilute trichloroethylene supplied by a zero head space Teflon[®] bag reservoir. By using dilute concentrations of VOC, lower application concentrations can be achieved and a wider range of concentrations can be used to create calibration curves. Using the Teflon[®] reservoir, we developed a calibration curve with r^2 value of 0.98 that covered concentrations ranging from 0.94 mg L^{-1} to 49.0 mg L^{-1} .

System Stability

Organic pollutants can exhibit "slow sorption" (Pignatello and Xing, 1996), a secondary sorption period in which dissolved VOCs sorb to the solid phase over a period of weeks or months. A system must have stable pumping rates and detection behavior over a similar time period if it is to be useful in measuring such behavior. A system stability test was performed using a flow rate of 1 mL min^{-1} and a toluene concentration of 10 mg L^{-1} (2.02%

B). Samples were taken every 10 min, and the stability run lasted approximately 4000 min (2.7 d). Detector drift was minimized by automatically re-zeroing the detector between each sample. This test resulted in 380 measurements with a CV of 1.55% for the measurement values. This low CV indicates reliably stable pump and detector performance over an extended time period.

Over long periods of time, particles leaching off soil columns can lead to frits clogging and pressures increasing within the system. This leads to concerns about changing flow rates, so a second stability test was done monitoring the flow rate independently. This stability experiment was performed on a Clarion soil (fine-loamy, mixed, superactive, mesic Typic Hapludoll) with 2.3% organic matter, over a 9 d period where the effluent was collected and pressure was monitored. The mass of the effluent was automatically recorded on a digital scale through time. Figure 4 shows the results of this experiment where the CV of 3,218 flow rate measurements was 0.78 %, a very low number given that pressure more than doubled during the experiment.

Example Flow-Through Experiment

A toluene breakthrough curve experiment (Fig. 5) was performed on an Ottawa sand to demonstrate the system's ability to run a pulse input miscible-displacement experiment. A stainless steel column (diameter = 21.65 mm, length = 124.5 mm) was packed with sand to a bulk density of 1.63 Mg m^{-3} . The sand was saturated to a volumetric water content of 0.384 by slowly wetting the column from the bottom under vacuum, then pressurizing the column to 8 MPa and flushing with de-gassed water to purge any remaining bubbles. The binary pump was programmed to displace one pore volume every 30 min, which translated to a flow rate of $0.587 \text{ mL min}^{-1}$ or a pore water velocity of $0.415 \text{ cm min}^{-1}$. A step-input solute pulse was introduced into the column at a concentration of 16 mg L^{-1} for approximately 6 pore volumes or 180 minutes. One $50 \text{ }\mu\text{L}$ effluent sample was collected every 10 min and analyzed over the course of the 15 pore volume experiment.

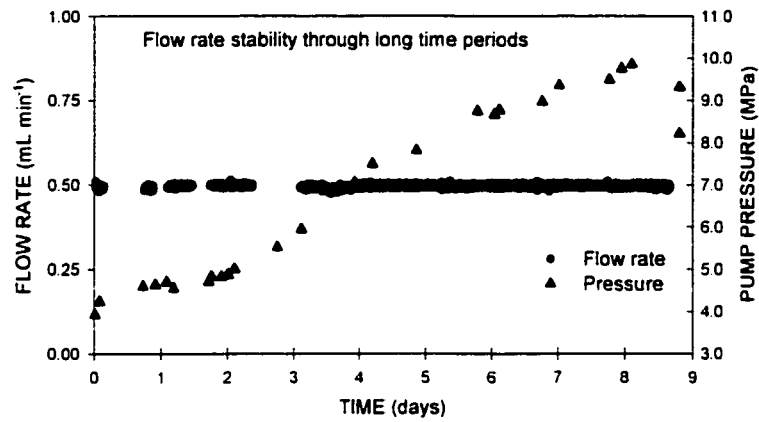


Fig. 4. Flow rate stability test indicating the flow remained very stable even though the frits clogged and increased the pressure inside the setup.

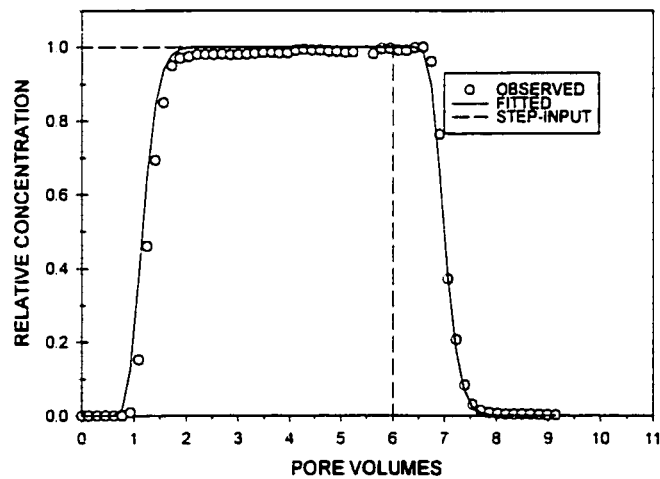


Fig. 5. Toluene breakthrough curve through Ottawa sand, measured by the miscible-displacement system.

The mass recovery of toluene for the solute breakthrough curve (Fig. 5) was 99.99% as calculated via Riemann sums. The program CXTFIT 2.0 (Toride et al., 1995) was used to obtain the retardation and dispersion coefficients by fitting the analytical solution of the one-dimensional, deterministic, equilibrium, advective-dispersive equation to the measured data. Slight retardation ($R = 1.11$) was observed, and the breakthrough curve followed a typical advective-dispersive type behavior. The dispersion coefficient for the breakthrough curve was $0.122 \text{ cm}^2 \text{ min}^{-1}$.

Multiple Solutes

Multiple solutes can be applied to a soil column and detected separately in the effluent using the diode array UV detector. This aspect of the system was tested by simultaneously passing trichloroethylene (TCE) and two common metabolites (*cis*-1,2-dichloroethylene or *cis*-DCE, and *trans*-1,2-dichloroethylene or *trans*-DCE) through an Ottawa sand column. Calibration curves were first developed for each compound present in the effluent solution, and satisfactory separation of the various compounds was achieved. One pore volume of water saturated with TCE, *cis*-DCE, and *trans*-DCE was introduced to the soil column over the course of 40 min, giving a flow rate of 0.44 mL min^{-1} and a pore water velocity of $0.311 \text{ cm min}^{-1}$. The resulting breakthrough curves (Fig. 6) showed similar results for the three compounds and resulted in mass balance of 99.82% for TCE, 98.43% for *cis*-DCE, and 98.36% for *trans*-DCE. As expected, the three curves are nearly identical, which demonstrates the system's ability to discriminate and accurately measure similar compounds.

Soils with high organic matter content may have dissolved organic matter leach off the column, perhaps leading to interference with peak separation in the chromatograph. In this case, modifications of the HPLC analytical methods would be made to minimize the interference from the organic matter. The modifications may include one or a combination of the following: eluent modification, using a different wavelength, changing the analytical column, or changing from an isocratic pump to a gradient pump.

The ability to measure multiple compounds simultaneously makes this system unique, and is important in studies where an initial compound is transformed into other species during transport (i.e., chemical reduction of TCE). Additionally, multiple chemicals can be introduced into a soil and analyzed simultaneously in the effluent, either as a time-saving measure or as a means of analyzing their differences and/or interactions.

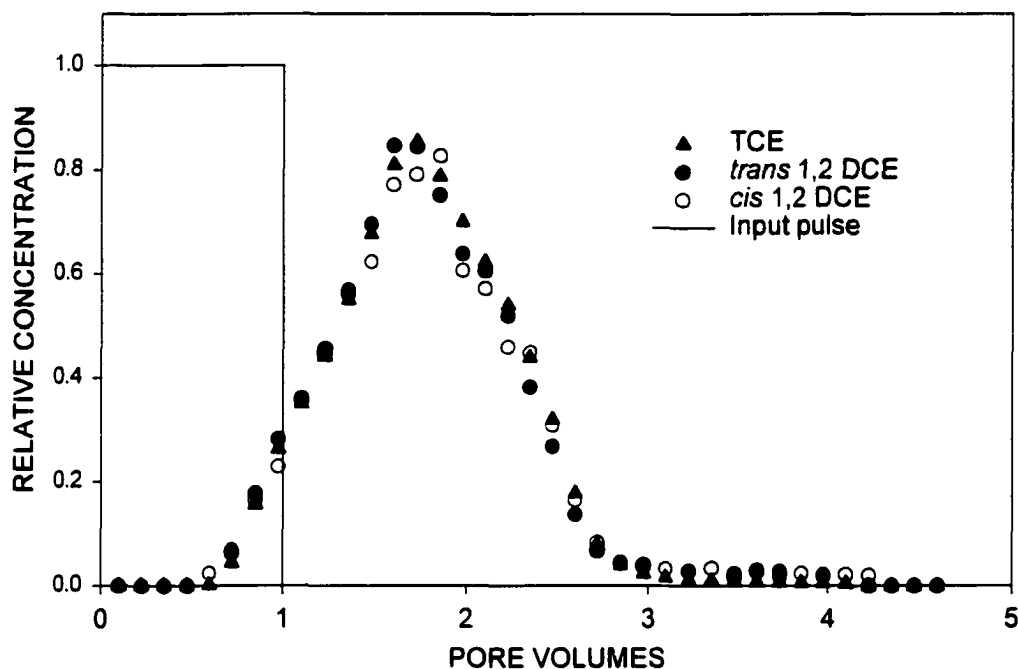


Fig. 6. Breakthrough curve for TCE, *cis*-DCE, and *trans*-DCE through Ottawa sand.

System Induced Dispersion

Dead volume of the system can lead to induced dispersion. The calculated dead volume before and after the column was 0.48 mL and 0.49 mL, respectively. James and Rubin (1972) reported a 40% overestimation of dispersion coefficient due to dispersion introduced by their miscible-displacement apparatus. To measure the significance of system induced dispersion, a nonsorbing tracer (Cl^-) breakthrough curve from the current system (Fig. 1) was compared to a Cl^- breakthrough curve from a conventional fraction collecting

method. For both breakthrough curves, the same sand filled column was used. End cap assemblies were removed for the conventional breakthrough curve so that they would not contribute any dispersion (James and Rubin, 1972). Chloride concentrations were determined with a Haache Buchler Digital Chloridometer. The analytical solution of the advective dispersive equation (Toride et al., 1995) was then fit to the Cl^- breakthrough curves to determine the column dispersivity (λ). For a single soil column, λ should be the same regardless of the velocity and it is generally less than 0.01 m for repacked or highly homogeneous soils (van Genuchten and Wierenga, 1986). We found the λ values obtained from the system breakthrough curve (0.00346 m) compared well with the λ from the conventional method (0.00347 m). Since the λ values were nearly identical we have confidence that the system's dead volume does not cause detectable dispersion; however, it should be accounted for when calculating the tracer travel time through the system.

Acknowledgments

The authors acknowledge assistance from Kevin Patt and Jim Mott in designing the laboratory setup described in this paper, and helpful discussions with Mark L. Brusseau. This work was funded by a grant from the Raymond and Mary Baker Trust.

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CHAPTER 4. DEGRADATION AND TRANSFORMATION OF TRICHLOROETHYLENE IN MISCIBLE-DISPLACEMENT EXPERIMENTS THROUGH ZERO-VALENT METALS

A manuscript to be submitted to Environmental Science and Technology Journal

Francis X. M. Casey^{1,2}, Say Kee Ong³, and Robert Horton^{2,4}

Abstract

Fate and transport of chlorinated solvents flowing through reactive barriers containing zero-valent metals are influenced by advection, dispersion, adsorption, and transformation reactions. Batch experiments or resident concentration column experiments have been used extensively to study reactions of zero-valent metals and for the design of *in situ* flow-through reactive barriers. However, extending results from batch or resident concentration column experiments to zero-valent metal flow-through systems may be challenging because sorption and degradation are indistinguishable, and nonequilibrium adsorption-desorption may occur. In this study, miscible-displacement experiments were used to understand the fate and transport of trichloroethylene (TCE) flowing through zero-valent metal systems. Pulses of dissolved TCE were introduced, at three different flow rates, into columns filled with sand, iron filings, or copper-plated iron filings (Cu-Fe). Column effluent was directed through a high performance liquid chromatography (HPLC) diode-array detector that determined concentrations of TCE and its degradation daughter products. Trichloroethylene did not degrade in the presence of sand. Slightly less TCE was observed with the Cu-Fe breakthrough curve than for the iron breakthrough curve. The reduction of TCE produced

¹Primary researcher and author

²Graduate student and professor, respectively, Department of Agronomy, Iowa State University

³Assistant professor Civil and Constructional Engineering, Iowa State University

⁴Author for correspondence

ethylene, which resulted in simultaneous breakthrough curves of these compounds. The simultaneous breakthrough curves were described with an equilibrium sorption/degradation model and a two-site partial nonequilibrium sorption model with degradation and production of daughter products. Results of the experiments indicate that sorption may have to be considered in the design of zero-valent reactive barrier systems.

Introduction

Chlorinated solvents were the most commonly identified contaminants at nearly 300,000 to 400,000 hazardous waste sites in the United States as of 1994 and \$750 billion could be spent on their remediation over the next 30 years (NAS, 1994). Remediation methods using zero-valent metal for the degradation of chlorinated solvents were pioneered by researchers at the Institute for Groundwater Research, University of Waterloo, Canada. Today, full-scale applications of zero-valent metals for the remediation of contaminated aquifers can be found at numerous locations including Belfast, Northern Ireland; Mountain View, CA; Cape Cod, MA; Coffeyville, KA; Elizabeth City, NC; Lakewood, CO; and New York (Focht et al., 1996; Appleton, 1996). Remediation systems with zero-valent metals have shown promise because they are relatively inexpensive, easy to maintain, and effectively eliminate TCE and other chlorinated solvents.

The *in situ* applications of zero-valent metals utilize permeable reactive walls or above ground columns through which contaminated groundwater flows. Flow through remediation systems are designed to completely degrade chlorinated solvents and their daughter products as they pass out of the system. However, batch and resident concentration column experiments have been used extensively to study the reactions of zero-valent metals and to design remediation systems. These simple laboratory methods measure first-order degradation rate constants (k) and usually do not take adsorption or the dynamics of a flowing system (i.e., advection and dispersion) into consideration (Burris et al., 1995). Resident concentration column experiments continuously introduce dissolved organic contaminant into columns filled with zero-valent metal and resident concentrations are monitored at various sampling ports throughout the length of the column (Orth, 1992; Gillham and O'Hannesin,

1994; Orth and Gillham, 1996; Focht et al., 1996; Gillham et al., 1997; Reihart et al., 1997, Gavaskar et al., 1998). Resident concentration is the mass of solute per unit volume of fluid contained in an elementary volume of fluid at a given instant. To our knowledge, effluent concentrations have not been observed in any previously reported zero-valent metal column studies. For modeling purposes, if proper boundary conditions are not described, difficulties may arise when resident concentrations are used to predict effluent concentrations — this may compromise the design of flow-through remediation systems (Barry and Sposito, 1988). Furthermore, if the zero-valent material is not homogeneous there may be increased difficulties in predicting effluent concentrations from resident concentrations. With regards to an above ground pilot-scale field column demonstration, Gillham et al. (1997) stated that “the performance did not meet expectations based on the results of the initial laboratory tests”. It may be that the “unmet expectations” resulted from the use of batch and resident concentration column experiments which may be associated with difficulties when extending the results to zero-valent metal flow-through remediation systems.

The objective of this research was to use miscible-displacement breakthrough curves, in conjunction with mathematical model description, to study the fate and transport of TCE flowing through zero-valent metals. Influent pulses of TCE were passed through three different porous medium (sand, iron, or iron-plated copper (Cu-Fe)) at three different steady-state flow rates. Breakthrough curves were described with convective-dispersive models to identify the processes that govern the fate and transport of TCE flowing through zero-valent metals.

Materials and Methods

Miscible-Displacement System

A schematic of the system used for the miscible-displacement experiments is presented in Fig. 1. The system was comprised of two portions, 1) a column transport portion and 2) an analytical portion. Casey et al. (2000) and Ewing et al. (1998) provided in depth description and evaluation of this system. This system was unique because it was fully

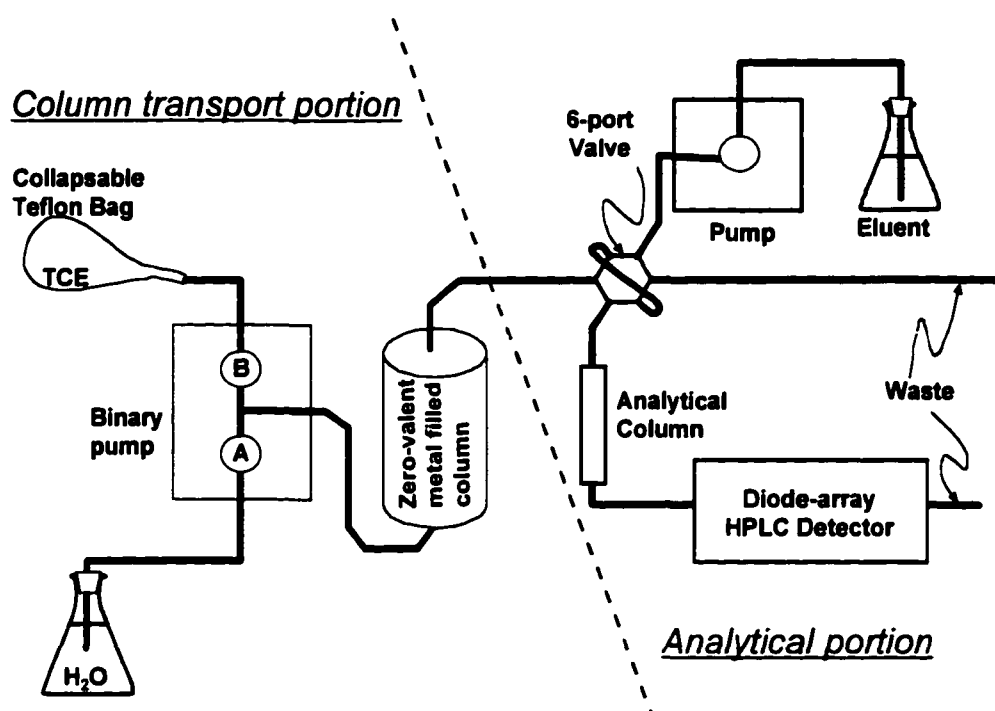


Fig. 1 Schematic of system used for miscible-displacement experiments. The system consists of two portions, a transport portion and an analytical portion.

enclosed and constructed of nonsorbing material with minimum chemical loss from the system. Also, this system could simultaneously detect multiple chemicals present in the column effluent. The column transport portion consisted of a fully programmable binary pump with one reservoir supplied by a Teflon[®] bag (Gillham and O'Hannesin, 1994) filled with 92 mg L⁻¹ TCE, and the other reservoir supplied by de-gassed nanopure water. Gas was purged from the nanopure water by boiling and placing the boiled water under vacuum as it cooled. The flow rate and the supply ratio from each pump's reservoir was programmed, so that concentrations up to 96 mg L⁻¹ could be achieved. The column transport portion was connected to the analytical portion by a six-port, two-way, automated valve with a 50 µL sampling loop. The analytical portion of the system was a basic HPLC set-up. A 50 µL effluent sample could be diverted to the analytical portion of the system when the six-port

valve was switched. A direct injection port was also used to determine known solution concentrations and developing chemical calibrations.

For the calibration curves, standards for TCE and probable daughter products such as 1,1-dichloroethylene; 1,2-cis-dichloroethylene; 1,2-trans-dichloroethylene; vinyl chloride; and ethylene were prepared. Separation of TCE and its daughter products was achieved using an eluent of 88% acetonitrile and 12% water and a flow rate of 1 mL min⁻¹. An Alltech C-18 analytical column was used and the peak detection wavelength was 212 nm.

Effluent samples were fraction collected in 10 mL glass syringes with a Swage-lok[®] fitting for copper (Cu) analysis. The fitting was connected to the effluent tubing that bypassed the HPLC, avoiding acetonitrile contamination. Analysis for free Cu⁺² was done using a Cu⁺²-ISE (Orion 94-29), a reference electrode (Orion 900200), and a pH/ion meter (Corning 135). The crystal membrane of the Cu electrode was polished with a polishing strip and equilibrated in 7.87×10^{-4} M Cu solution for at least 30 min before use. The volume of the samples collected were small and had to be combined so that a sufficient volume of the solution could be used for analysis. Furthermore, at the end of each run, the pH of the column effluent and the influent water was measured using a pH/ion meter (Corning 135).

Column Packing Materials

Three stainless steel columns (21.4 mm diameter and 124 mm length) were packed with Ottawa sand, 40 mesh iron filings (Fisher Scientific), or 40 mesh Fisher iron filings plated with 1.78 % Cu. Placed at each column end were distribution plates, wire mesh, and a 2 µm frit, all made of stainless steel. Stainless steel was used because it is relatively inert and does not reduce TCE (Gillham and O'Hannesin, 1992). The distribution plates and wire mesh assured flow uniformity and distribution through the column, while the frits prevented large particles from leaving the column.

The sand was washed with deionized water and dried before it was packed into the column. The column bulk density (ρ_b) was 1.40 Mg m⁻³. Assuming a particle density (ρ_s) of 2.63 Mg m⁻³ the column porosity was calculated to be 0.47.

De-gassed nanopure water was then used to slowly saturate (flow rate= 0.2 mL min⁻¹) the column from the bottom up while vacuum was applied to the top. Once water appeared at

the top of the column, it was capped while water was still pumped into the bottom of the column. The water pumped into the bottom pressurized the column above 1.03×10^7 Pa and forced any entrapped gas into the water. The column pressure was then released and flushed with more de-gassed water. This was repeated until nearly 100 ± 0.2 % saturation was achieved.

Before the iron filings were packed into the column, they were acid washed by soaking in a 5% by volume solution of sulfuric acid in nanopure water for 15 min. Aliquots of ethanol and nanopure water were then used to rinse the iron and then the iron was oven dried at 35-40 °C overnight. Specific surface measurements were obtained from two ± 10 g samples using BET nitrogen sorption isotherms (Brunauer et al., 1938). The mean specific surface for the two samples was $5.76 \text{ m}^2 \text{ g}^{-1}$. The ρ_s was 6.04 Mg m^{-3} measured with a bath pycnometer. The column was packed so that the surface area concentration (Johnson et al., 1996) was $21,147 \text{ m}^2 \text{ L}^{-1}$. Using the previously described method to saturate the sand column, nearly $100 \pm 0.7\%$ saturation was achieved with the iron column.

Copper was plated onto the iron filings by a cold electrodeless method, where the substrate metal acts as a reducing agent to displace copper ions from solution and coat the surface (Fryzek, 1998). Iron was added to a solution of copper sulfate. The mean specific surface obtained from the BET nitrogen sorption isotherms for two ± 10 g Cu-Fe samples was $3.73 \text{ m}^2 \text{ g}^{-1}$, the pycnometer measured value of ρ_s was 6.36 Mg m^{-3} , and the packed column surface area concentration was $22,417 \text{ m}^2 \text{ L}^{-1}$. The previously described saturation technique was used to achieve nearly $100 \pm 0.5\%$ saturation for the Cu-Fe column.

Transport Experiments

A series of three different steady-state flow miscible-displacement experiments were done on each porous media. The three different flow rates that were used, resulted in respective pore water velocities (v) of 12.4, 6.2, or 3.1 mm min^{-1} , so that one pore volume was displaced each 10, 20, or 40 min. The column retention times were varied while the sorption sites remained constant. Varying the retention times and using the same column was done to distinguish between degradation and adsorption. For each experiment a pulse of 46 mg L^{-1} TCE was introduced into the column for one pore volume and then flushed out.

Column effluent was sampled every 5 min for analysis with the on-line HPLC, and the effluent was monitored for at least 10 pore volumes. The order in which the column experiments were done was fast, intermediate, then slow flow rate; after which, a replicate of the first fast flow rate was done for the iron and Cu-Fe columns. The columns were flushed with at least 40 pore volumes of nanopure water between each experiment.

A non-sorbing anionic tracer, Cl^- , was used to determine whether the zero-valent metal columns displayed physical nonequilibrium (Skopp et al., 1981). A uniform background solution of 0.0025 M of KCl was applied to the columns and then one pore volume of 0.1 M KCl was applied. Water was passed through these columns so that one pore volume was displaced every 26 min. Effluent was fraction collected and analyzed with a Haache Buchler Digital Chloridometer.

Mathematical Models

The program CXTFIT ver 2.0 (Toride et al., 1997) was used to estimate the dispersion (D) coefficients for the Cl^- breakthrough curves of the zero-valent metal columns and for the TCE breakthrough curves of the sand column. The measured breakthrough curve data was fitted with the analytical solution to the one-dimensional, discrete, advective-dispersion equation using least-squares parameter optimization. The optimized D values from the column breakthrough curves were used to estimate column dispersivity ($\lambda = D/\nu$) (Bear, 1972).

The model HYDRUS-1D (Šimůnek et al., 1998) was used to describe the zero-valent metal breakthrough curve experiments. This model was used in the forward mode with specified model parameters to predict the breakthrough curves with model solutions. It was also used to fit measured breakthrough curves by optimizing parameters so that the model curve-fit the measured data. A subroutine within HYDRUS-1D numerically solved advective-dispersive transport of the solutes involved in the sequential decay and production reactions for up to four chain members. However, HYDRUS-1D could only be used to fit the first chemical in the series when optimizing parameters. The following set of coupled differential equations shows the one-dimensional, advective-dispersive transport of the four chain members under steady-state flow and linear equilibrium transport conditions (van Genuchten, 1985):

$$R_1 \frac{\partial C_1}{\partial t} = D \frac{\partial^2 C_1}{\partial x^2} - v \frac{\partial C_1}{\partial x} - k_{s,1} R_1 C_1, \quad [1a]$$

$$R_i \frac{\partial C_i}{\partial t} = D \frac{\partial^2 C_i}{\partial x^2} - v \frac{\partial C_i}{\partial x} + k_{s,i-1} R_{i-1} C_{i-1} - k_{s,i} R_i C_i \quad [1b]$$

($i=2,3,4$),

where C_i are solute concentrations, x is the distance, t is the time, $k_{s,i}$ are first-order degradation rate constants, and the retardation factors (R_i) are given by

$$R_i = 1 + \frac{\rho_b K_{d,i}}{\theta} \quad [2]$$

where $K_{d,i}$ are empirical distribution coefficients and θ is the volumetric water content; the subscript i denotes the i^{th} chain member. Equations [1a-1b, 2] is the equilibrium sorption with first-order degradation rate model.

The concept of two-site sorption nonequilibrium adsorption-desorption reactions (Selim et al., 1977; van Genuchten and Wagenet. 1989) was also considered for the zero-valent metal breakthrough curves and it was implemented in HYDRUS-1D. Sorption on labile exchange sites or Type-1 sites (S_1) was assumed to be instantaneous while on remaining resistant exchange sites or Type-2 sites (S_2) the sorption was considered kinetic (Fig. 2). The degradation was considered to be a surface process and the equation that governs mass transport for the system as a whole under steady-state flow and in a uniform system follows:

$$\left(1 + \frac{\rho_b f K_{d,1}}{\theta}\right) \frac{\partial C_1}{\partial t} = D \frac{\partial^2 C_1}{\partial x^2} - v \frac{\partial C_1}{\partial x} - \frac{\alpha_1 \rho_b}{\theta} [(1-f) K_{d,1} C_1 - S_{2,1}] - \frac{f \rho_b K_{d,1} k_{s,1} C_1}{\theta} \quad [3a]$$

$$\begin{aligned}
\left(1 + \frac{\rho_b f K_{d,i}}{\theta}\right) \frac{\partial C_i}{\partial t} = D \frac{\partial^2 C_i}{\partial x^2} - v \frac{\partial C_i}{\partial x} + \frac{\alpha_{i-1} \rho_b}{\theta} [(1-f) K_{d,i-1} C_{i-1} - S_{2,i-1}] + \\
\frac{f \rho_b K_{d,i-1} k_{S,i-1} C_{i-1}}{\theta} - \frac{\alpha_i \rho_b}{\theta} [(1-f) K_{d,i} C_i - S_{2,i}] - \frac{f \rho_b K_{d,i} k_{S,i} C_i}{\theta}
\end{aligned} \quad [3b]$$

(i=2,3,4)

where f is the fraction of exchange sites assumed to be at equilibrium, $k_{S,i}$ are rate constants for first-order degradation rate of the sorbed phase, and α_i are first-order kinetic rate sorption constants.

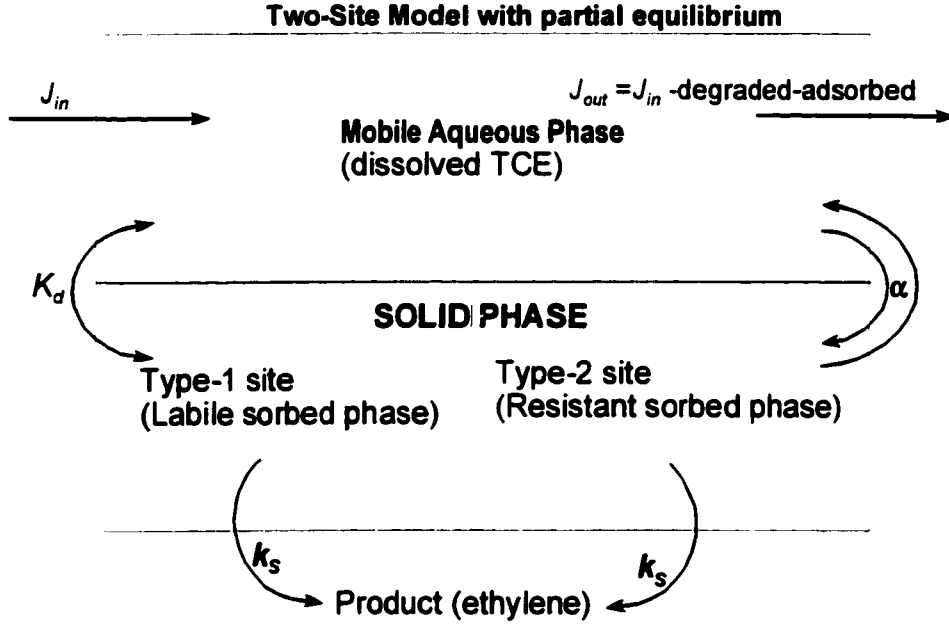


Fig. 2. Schematic of two-site advective-dispersive model with partial equilibrium and partial kinetic sorption and degradation (adapted from van Genuchten and Wagenet, 1989). Where J is the solute flux density, K_d is partitioning coefficient, and α is the first-order adsorption rate coefficient. Double-headed arrows link compartments that reach equilibrium instantaneously

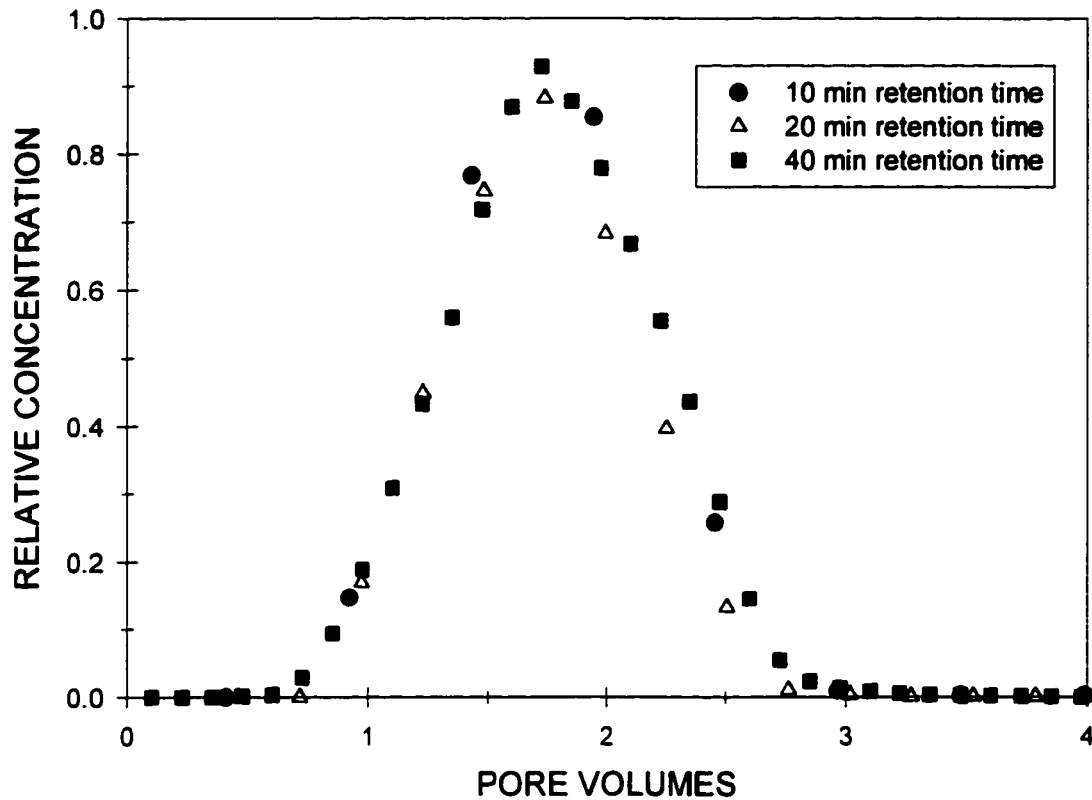


Fig. 3. Trichloroethylene breakthrough curves through sand column. The input pulse was one pore volume for each experiment.

Results and Discussion

TCE Transport in Sand Column

Only TCE was detected in the effluent breakthrough curves for the sand columns (Fig. 3) and no degradation daughter products were measured. The mass of the TCE applied to the system relative to the mass of TCE recovered in the effluent ranged from 98% to 102%. These results suggest that there was no degradation of TCE in the presence of sand or stainless steel. Similarly, Gillham and O'Hannesin (1992) found no detectable degradation of TCE in the presence of stainless steel. The mass balance calculations were subjected to numerical and detection errors which may have caused TCE mass recovery values slightly greater or less than 100%.

TCE Transport in Zero-Valent Metal Columns

Ethylene and TCE were the only compounds detected in the effluent of all iron column (Fig. 4a-4c) and Cu-Fe column (Fig. 5a-5c) breakthrough curves. For the iron column, 74%, 87%, and 95% of the TCE were reduced for the flow rate series of fast, intermediate, and slow, respectively. For the Cu-Fe column, 79 %, 89%, and 98% of the TCE were reduced, respectively, for this flow rate series. These results suggested that the Cu-Fe column slightly reduced more TCE at each flow rate than did the iron column. Several studies have noted that the presence of a second metal increased the reduction rates of the zero-valent iron (i.e. Sweeney and Fischer, 1973; Korte, 1995; Gillham et al., 1997; Gavaskar et al., 1998; Fryzek, 1998). Although a secondary metal such as nickel and Cu enhance TCE degradation and decrease the amount of reduction daughter products, there remains a danger of producing metal plumes in the groundwater (Appleton, 1996). However, no Cu was detected in the Cu-Fe column effluent, which supported using Cu-Fe as a remediation media. For the series of flow rates, the mass of carbon present in the effluent (in the form of TCE and ethylene) relative to the mass of carbon introduced into the column (in the form of TCE) was 96%, 97%, and 94% for the iron column and 100%, 89%, and 82% for the Cu-Fe column. The lower carbon mass balance for the Cu-Fe column may reflect the reduction of ethylene to other aliphatic compounds such as ethane and butene which were not analyzed by the HPLC. This may explain why the carbon mass balance decreased as column retention times within the Cu-Fe column increased. For both iron or Cu-Fe columns, the last replicate breakthrough curve was very similar to the first breakthrough curve (Fig. 4a and 5a). The similarity of these breakthrough curves indicated that there was no significant change in degradation capacity of the iron column or Cu-Fe column between each experiment.

Gillham and O'Hannesin (1994), Orth and Gillham (1996), and Gotpagar et al. (1997) suggested that TCE reduction was a surface process where the TCE molecule does not leave the iron surface until sufficient electrons have been transferred for complete dechlorination. This may explain why there were no degradation daughter products detected in the column effluent for all experiments. The attachment of TCE to the iron surface may reflect its hydrophobicity or a covalent bonding induced by the transfer of the first electron in the

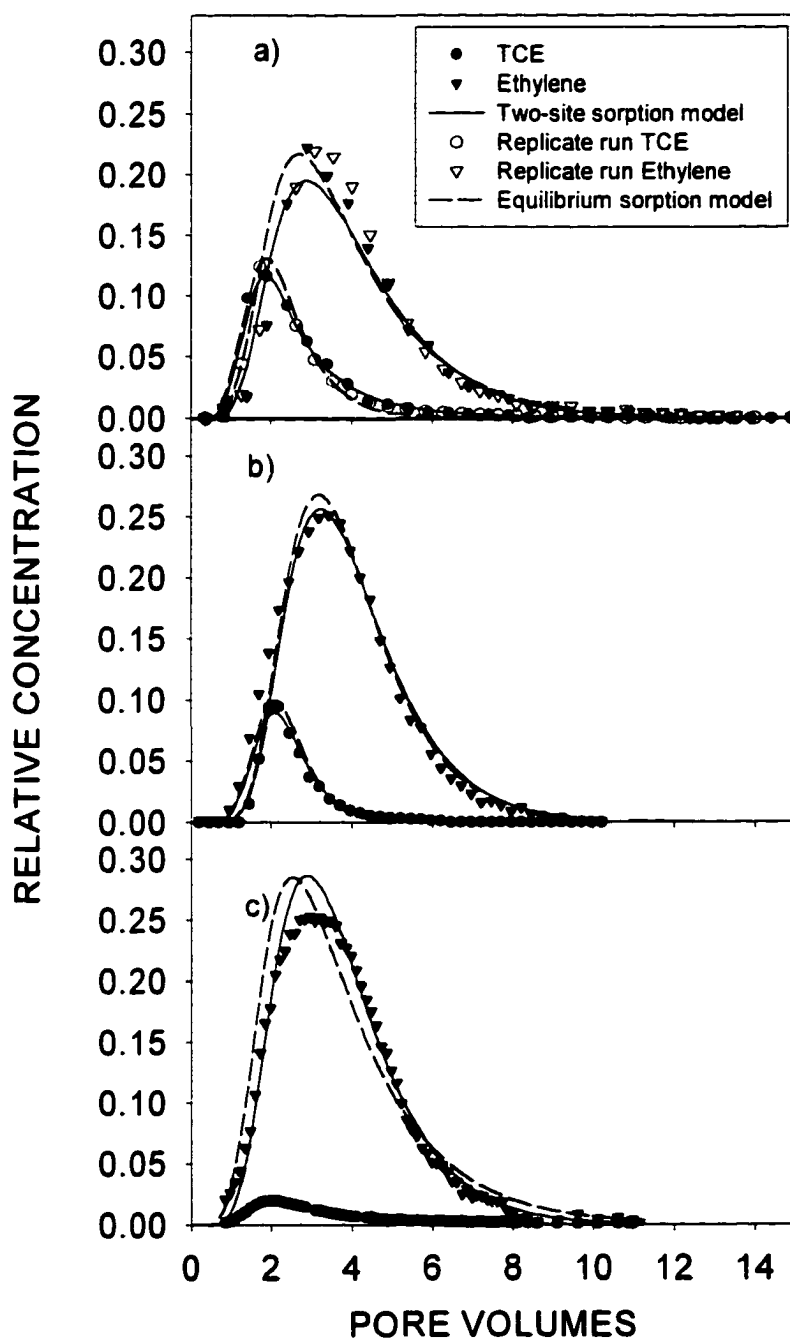


Fig. 4. Iron column TCE breakthrough curves for (a) fast, (b) intermediate, and (c) slow flow rates. The input pulse was one pore volume for each experiment. The equilibrium and two-site sorption models were fitted to the first replicate of TCE breakthrough curves.

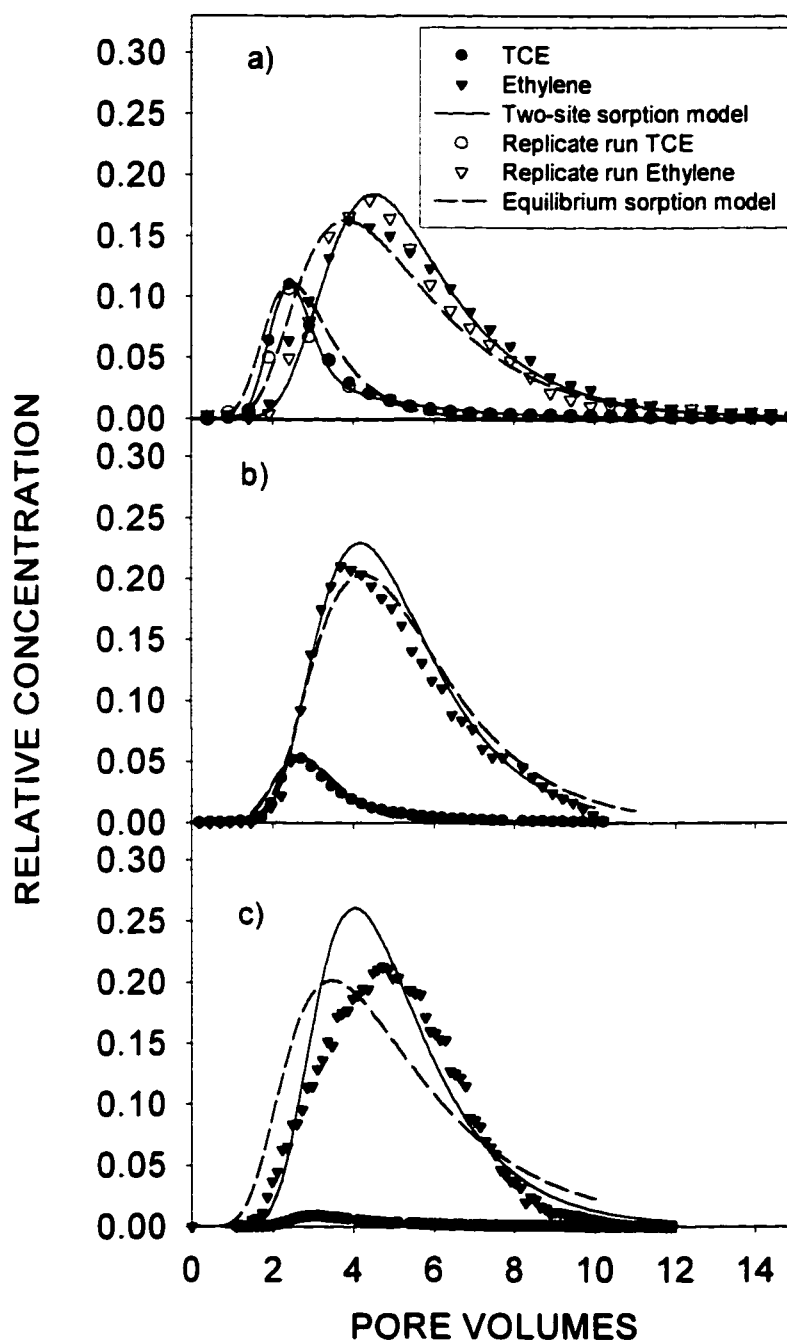


Fig. 5. Copper-iron column TCE breakthrough curves for (a) fast, (b) intermediate, and (c) slow flow rates. The input pulse was one pore volume for each experiment. The equilibrium and two-site sorption models were fitted to the first replicate of TCE breakthrough curves.

reduction process (Orth and Gillham, 1996). The TCE dechlorination product, ethylene, would have to dissociate from the surface site before that site was available for further reaction with the reactant solute molecules, TCE (Burris et al., 1995). As a result individual molecules of TCE would bypass reactive sorption sites that were occupied and they would exit the column intact. This was further indicated by the increased mass of TCE degraded and increased production of ethylene when the retention times within the column increased (Fig. 4a-4c and 5a-5c).

Miscible Displacement Model Description

Gotpater et al. (1997) suggested the slow down of TCE degradation with time in batch experiments was possibly caused by mass transfer limitation resulting from corrosion and precipitate build-up on iron surfaces. Furthermore, Cumming et al. (1998) had demonstrated that iron corrosion and surface precipitates caused physical nonequilibrium transport of bromide in zero-valent metal column experiments. However, Cl^- breakthrough curves (Fig. 6) from the iron and Cu-Fe columns done after the TCE reduction experiments,

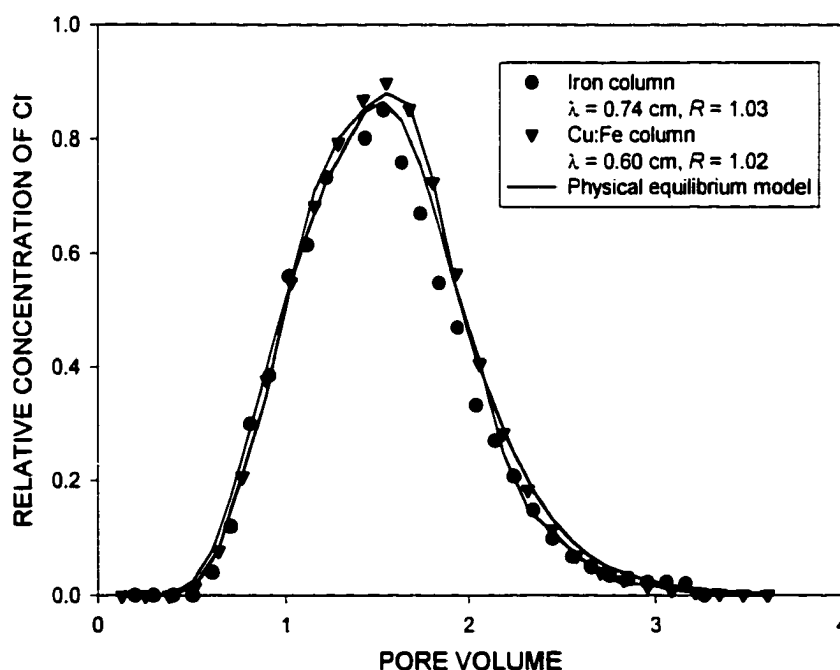


Fig. 6. Iron and Cu-Fe column chloride breakthrough curves through sand. The Cl^- input pulse was one pore volume for each experiment, and the physical equilibrium advective-dispersive equation was fitted to the curves.

did not display physical nonequilibrium. The physical equilibrium advective-dispersive equation fitted the breakthrough curves well with coefficients of determination (r^2 ; Snedecor and Cochran, 1967) ranging from 0.99 to 0.98. The high r^2 values suggested that there was not a need to consider physical nonequilibrium. Additionally, the largest change in pH was 6.7 to 7.2 which was insufficient to cause carbonate precipitates to build up.

The iron and Cu-Fe column TCE breakthrough data were fitted with the equilibrium sorption model (Eq. [1a-1b]) and resulted in good matches between observed and modeled data. The best fit equilibrium sorption model parameters are presented in Table 1. The r^2 values ranged from 0.95 to 0.98 for the iron column and 0.84 to 0.95 for the Cu-Fe column. The optimized k_s values were used as production coefficients to predict the ethylene breakthrough curves, resulting in r^2 values ranging from 0.92 to 0.97 for the iron column and 0.69 to 0.97 for the Cu-Fe column. The equilibrium sorption model (Eq. [1a-1b]) did a good job of fitting the data and produced k_s values similar to earlier reported values (Fig. 7a and Table 1). The column λ values were not significantly different through the range of velocities at a 95% confidence interval, and over a range of v for a single column λ is expected to be constant (Bear, 1972). In general the K_d values were not significantly different except at the lower velocities. The most significant difference was the apparent increase of k_s with an increase in velocity. This may reflect a rate limiting sorption/diffusion process at the iron surface. Additionally, the data were fitted with an equilibrium sorption model (Eq. [1a-1b]) while holding λ constant for each column. The fixed λ values came from the Cl⁻ breakthrough curves (Fig. 7), but good model fits to the data could not be achieved.

The equilibrium sorption model (Eq. [1a-1b]) was capable of describing the TCE breakthrough curve data; however, there may have been more complicated sorption. Burris et al. (1995) reported Langmuir sorption isotherms of TCE in the presence of iron from batch experiments in addition to sorption onto reactive and nonreactive sorption sites. A two-site sorption model (Eq. [3a-3b], Fig. 2) was used to describe the breakthrough curve data, but a linear sorption isotherm was considered instead of Langmuir. The fitted two-site sorption model (Eq. [3a-3b]) parameters are presented in Table 1 with their 95% confidence intervals. To increase the uniqueness of the model solution the column λ and K_d values were held

TABLE 1 — Values of equilibrium sorption model (Eq. [1a-1b]) and two-site sorption model (Eq. [3a-3b]) parameters with 95% confidence interval for the fitted parameters[†].

Equilibrium Sorption Model					
flow rate/column	λ	K_d	$k_{s,sa}$		
	(cm)	(L Kg ⁻¹)	(Lh ⁻¹ m ⁻²)×10 ⁻⁵		
Fast/iron	0.97 (±1.11)	0.40 (±0.44)	19 (±11.0)		
Inter./iron	1.03 (±0.18)	0.40 (±0.04)	21 (±1.5)		
Slow/iron	3.00 (±1.97)	1.36 (±0.75)	8.9 (±2.0)		
Fast/Cu-Fe	1.61 (±0.62)	0.46 (±0.07)	18 (±1.8)		
Inter./Cu-Fe	1.08 (±0.43)	0.498 (±0.08)	14 (±1.3)		
Slow/Cu-Fe	3.75 (±2.50)	1.77 (±0.94)	6 (±0.79)		
Two-site Sorption Model					
flow rate/column	λ	K_d	f	α	$k_{s,sa}$
	(cm)	(L Kg ⁻¹)		(h ⁻¹)	(Lh ⁻¹ m ⁻²)×10 ⁻⁵
Fast/iron	0.74	1.45 (±5.96)	0.30 (±0.18)	1.2 (±4.1)	6 (±6)
Inter./iron	0.74	1.45 (±5.29)	0.37 (±11.51)	0.9 (±3.75)	14 (±117)
Slow/iron	0.74	1.45 (±8.75)	0.32 (±0.88)	3.2 (±1.70)	15 (±3.1)
Fast/Cu-Fe	0.60	2.50 (±0.78)	0.17 (±0.05)	0.6 (±0.19)	7 (±0.8)
Inter./Cu-Fe	0.60	2.50 (±0.54)	0.12 (±0.01)	0.3 (±0.05)	3.7 (±4.5)
Slow/Cu-Fe	0.60	2.50 (±0.20)	0.13 (±0.06)	1.3 (±0.31)	10 (±2.6)

[†] λ = dispersivity; K_d = distribution coefficient; f = fraction of Type-1 sites; α = first-order kinetic rate sorption constants; $k_{s,sa}$ = normalized sorbed reaction rate constant

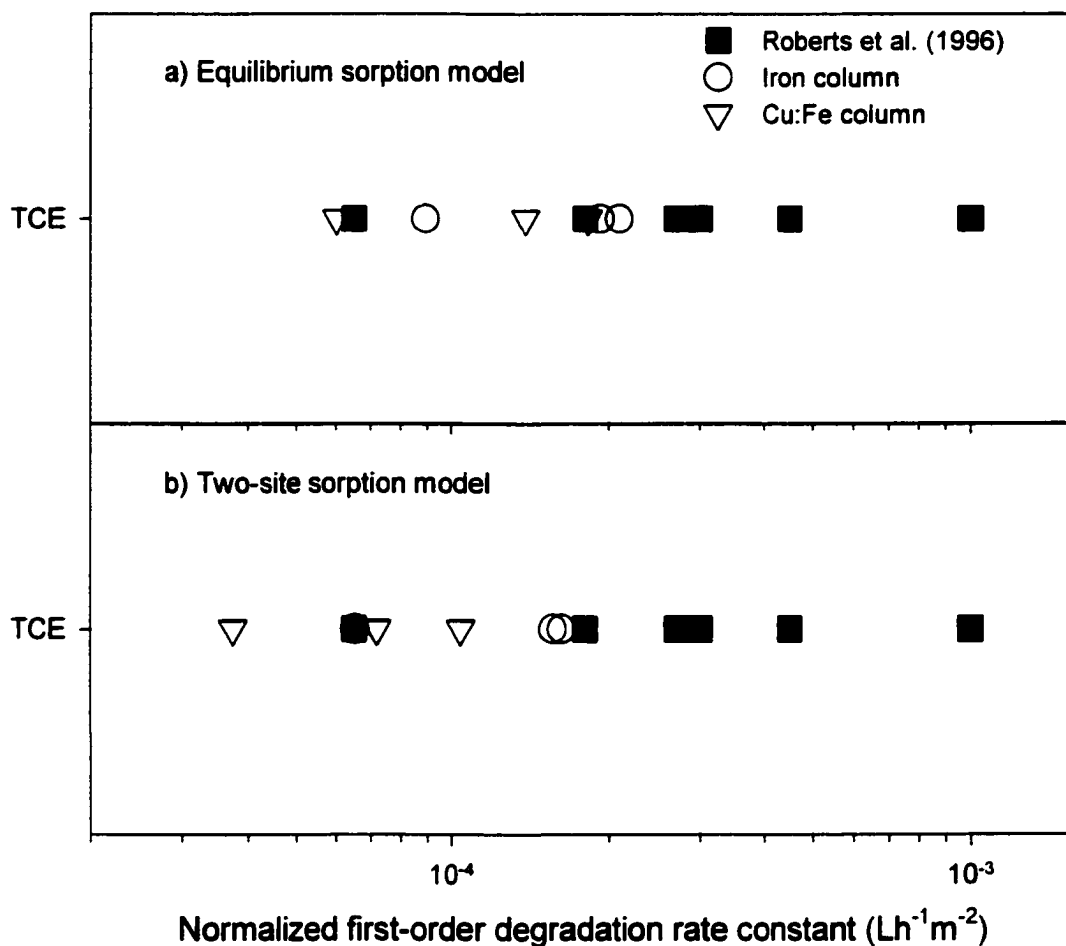


Fig. 7. Figure adapted from Roberts et al. (1996) comparing normalized degradation rates for the iron and Cu-Fe column of this study to previous studies. The normalized degradation rates obtained from curve fits using (a) the equilibrium sorption model (Eq. [1a-1b]) and (b) the two-site sorption model (Eq. [3a-3b]).

constant. The fixed λ values came from the Cl^- breakthrough curve experiments (Fig. 6; $\lambda = 0.74$ cm for the iron column and $\lambda = 0.60$ cm for the Cu-Fe column). Also, the column K_d values were expected to be constant and were fixed to the best fitted value from all the TCE breakthrough curves. The iron/TCE Langmuir sorption isotherm from the Burris et al. (1995) study was linearized and the K_d value was calculated (1.47 L Kg^{-1}) and found to be very

similar to the fitted K_d value from the two-site sorption model (1.45 L Kg^{-1} , Table 1). The two-site sorption model offered good description of the breakthrough data and a realistic interpretation of the macroscopic phenomena associated with the breakthrough curves. The TCE breakthrough curve r^2 values ranged from 0.94 to 0.99 for the iron column and 0.97 to 0.98 for the Cu-Fe column. The two-site sorption model predicted the ethylene breakthrough curves better than the equilibrium sorption model (Fig. 4 - Fig. 5), with r^2 values ranging from 0.97 to 0.99 for the iron column and 0.91 to 0.99 for the Cu-Fe column. The higher r^2 values for the ethylene curves may represent a better physical/chemical description by the two-site sorption model than the equilibrium sorption model; albeit, when more fitting parameters are used then the model fits are generally better.

The iron and Cu-Fe column f' values did not significantly differ at a 95% confidence interval (CI) throughout the range of flow rates. This was expected since the same columns were used for each experiment and the same amount of Type-1 sorption sites should be present for each flow rate. The α values were not significantly different at a 95 % CI constant with the exception of the Cu-Fe column where it was highest for the highest v . Correlations of α to v have been noted by other chemical nonequilibrium investigations (Gamerding et al., 1990; Brusseau, 1992). The increase of α with v may have reflected some rate limiting step in the transformation of TCE as it desorbed from reactive sites. This rate limiting step in the transformation of chlorinated ethylene has been suggested by Burris et al. (1998) who speculated that it was caused by the desorption of the solute off of reactive iron sites.

First-order degradation rates normalized to surface area concentration for the two zero-valent metal systems were not significantly different from each other (Fig. 7b, Table 1). Nonetheless lower concentrations of TCE were eluted in the effluent of the Cu-Fe column than the iron column. It has been suggested that higher k_s values associated with multiple metal systems result from galvanic couples; where one metal preferentially sacrifices electrons or corrodes, further driving the reduction reaction and increasing the rate of TCE degradation (Gavaskar et al., 1998). It appeared that this was not the case for the miscible-displacement studies because the k_s values for the iron and Cu-Fe were not significantly different. Rather it may be that more TCE was removed because there was higher partitioning

of TCE into the sorbed phase. Based on the two-site sorption model, the Cu-Fe K_d values were generally higher but significantly different than the iron column values (Table 1).

The normalized first-order degradation rate coefficients for both iron and Cu-Fe were within the range of values measured by previous investigators (Fig. 7b) but on the lower end. Previous investigators used batch or resident concentration column experiments to estimate their degradation rates. The degradation rates for the two-site sorption model would be smaller because partitioning of TCE from the aqueous solution and nonequilibrium adsorption-desorption were considered. Although, previous investigators were able to describe the degradation of TCE as a first-order process using batch or resident concentration column experiments, the sorbed concentrations or nonequilibrium adsorption-desorption were usually not measured. Naturally, the degradation rates would be higher for the batch or resident concentration column experiments since adsorption and degradation are lumped together resulting in an apparent and overestimated first-order degradation rate. Similarly the degradation rates from the equilibrium sorption model (Eq. [1a-1b]) may be overestimated if rate-limited sorption was present. In fact, k_s values of the equilibrium sorption model were more similar to the earlier reported degradation rates from batch and resident concentration column experiments (Fig. 7a) than were the two-site sorption model k_s values. The simpler equilibrium models can describe TCE degradation but they may be limited because they may not considered other significant processes. This would be especially important when predicting the tailing or late arrival of TCE leaching from a column.

Conclusion

This study presents the first reported miscible-displacement experiments of chlorinated solvents flowing through zero-valent metals. The result was the first reported simultaneous breakthrough curves of TCE and its reduction daughter product, ethylene. Equilibrium sorption and two-site sorption models with degradation and production were used to described the transport of TCE flowing through zero-valent metals. Although the equilibrium sorption model fit the data, it may not accurately model the real sorption processes. The two-site sorption model fit the data well and provided satisfactory parameter

estimation. Miscible-displacement experiments can be used to gain better understanding of design parameters for zero-valent metal treatment systems for chlorinated solvents and sorption is a very important factor that needs to be considered for the fate and transport of chlorinate solvents flowing through zero-valent metals.

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CHAPTER 5. GENERAL CONCLUSION

General Discussion

Field Study

This field study presented the first experimental comparison of the two field methods to determine immobile water content (θ_{im}) and mass exchange coefficient (α) at a single site. It was found that the multiple tracer method consistently estimated larger θ_{im} values than the basic single tracer method. The smaller θ_{im} values obtained from the basic single tracer method may be caused by the assumption that $\alpha=0$; however, it can still be disputed that the multiple tracer method was effected by dispersion. A more realistic value of θ_{im} would probably be an average value from the two methods (which would also provide a compromise between the two sides). The variance single tracer method for estimating α was less practical than the multiple tracer method because it took a long time and did not describe the measured data well. Also, the single tracer method for estimating α assumes that soil samples taken from the infiltration site were either sampled from mobile water or θ_{im} . This macroscopic interpretation of mobile/immobile model was a fundamental difference between these two methods. The multiple tracer method assumes the scale of the domains of solute transport were much smaller than that of the single tracer method.

Future work should include detailed laboratory studies using these field methods on model soil with known mobile/immobile model parameters. Calculations should be made to see whether the single tracer θ_{im} values can be reproduced from α values obtained from the multiple tracer method. Additionally, the variance single tracer method experiment should be repeated over a shorter period of time, controlling the advective transport and evaporative loss of water. One way of controlling the water loss and advection is to harvest the entire soil block.

Laboratory Studies

Miscible-Displacement System. The miscible-displacement system that was developed fulfilled all the design criteria. It was capable of maintaining constant flow rate and detection over long periods of time. The automation of the system was convenient and

may lessen human error. The system had little or no loss of chemical due to volatilization or adsorption to the system. Furthermore, the simultaneous detection of multiple chemicals at low concentration was demonstrated. This system makes it possible to do miscible-displacement experiments where there is degradation and production (i.e., trichloroethylene (TCE) undergoing reduction while flowing through zero-valent metals). Furthermore, the amount and types of experiments that were not possible or difficult to do in the past, are now possible and easily done using this system.

Future work should include an accurate account of dead space volume by sending through pulses of solute with the soil column removed and measuring the travel time. Better ways to introduce low concentration of dissolved volatile organic chemicals need to be devised. The Teflon[®] bag was undesirable and excess nonaqueous phase liquid delivers too high concentrations.

Zero-Valent Metals. Batch and resident concentration column experiments have been used extensively to study the degradation of chlorinated solvents in the presence of zero-valent metals. These methods have helped identify important chemical reactions but they are limited by difficulties when extending their results to flowing systems. When designing flow-through remediation systems, miscible-displacement experiments should be used. There was evidence from the series of miscible-displacement experiments that there was nonequilibrium adsorption-desorption of TCE to zero-valent metals sorption sites.

Future work with zero-valent metal miscible-displacement studies should include flow-interruption to help distinguish between degradation and adsorption reactions. Different coating percentages of copper on the iron should be used to identify whether galvanic couples or higher partitioning causes more TCE to degrade. The zero-valent metals should be tested to see how sustainable they are and whether they can be regenerated. Different compounds should be used such as nitrate-nitrogen or atrazine to test the applications of zero-valent metals to agricultural systems. Also different material may be considered, such as metal impregnated zeolites, that increase the retention times within a flow-through system.

APPENDIX. RAW DATA

Field Study

-----Tracer application time -----							
----- (h) -----							
	6.60	4.25	4.77	1.25			
	TFMBA	PFBA	DFBA	TFBA	θ_v	α	θ_m/θ
Site-sample	-----ln(1-C/C ₀)-----				(m ³ m ⁻³)	(h ⁻¹)	
1-1	-1.54	-1.16	-1.42	-0.88	0.30	0.11	0.49
1-2	-1.55	-1.13	-1.41	-0.90	0.32	0.11	0.48
1-3	-1.65	-1.07	-1.43	-0.94	0.36	0.13	0.49
1-4	-1.45	-1.12	-1.33	-0.73	0.32	0.10	0.57
1-5	-1.25	-0.80	-1.03	-0.41	0.26	0.04	0.82
1-6	-2.11	-1.33	-2.01	-0.85	0.24	0.08	0.59
1-7	-1.46	-1.04	-1.41	-0.70	0.29	0.09	0.60
1-8	-1.59	-1.11	-1.42	-0.86	0.36	0.12	0.52

-----Tracer application time -----							
----- (h) -----							
	7.71	5.50	7.51	2.33			
	TFMBA	PFBA	DFBA	TFBA	θ_v	α	θ_m/θ
Site-sample	-----ln(1-C/C ₀)-----				(m ³ m ⁻³)	(h ⁻¹)	
2-1	-1.75	-1.42	-1.69	-1.04	0.41	0.14	0.48
2-2	-1.76	-1.42	-1.64	-1.01	0.42	0.15	0.49
2-3	-1.84	-1.24	-1.74	-0.80	0.43	0.10	0.73
2-4	-1.74	-0.98	-1.75	-0.63	0.42	0.01	0.97
2-5	-1.66	-1.16	-1.68	-0.70	0.43	0.08	0.79
2-6	-1.75	-1.37	-1.69	-0.86	0.45	0.13	0.62
2-7	-1.69	-1.05	-1.71	-0.57	0.43	0.00	1.00
2-8	-1.56	-1.31	-1.50	-0.98	0.43	0.15	0.48

-----Tracer application time -----							
----- (h) -----							
	8.38	6.62	3.29	1.45			
	TFMBA	PFBA	DFBA	TFBA	θ_v	α	θ_m/θ
Site-sample	-----ln(1-C/C ₀)-----				(m ³ m ⁻³)	(h ⁻¹)	
3-1	-1.46	-1.10	-1.45	-0.72	0.34	0.13	0.43
3-2	-1.59	-1.12	-1.58	-0.71	0.35	0.13	0.42
3-3	-1.55	-1.01	-1.43	-0.59	0.33	0.12	0.49
3-4	-1.48	-1.11	-1.42	-1.11	0.38	0.14	0.32
3-5	-1.46	-1.00	-1.39	-0.99	0.35	0.13	0.35
3-6	-1.36	-0.84	-1.32	-0.42	0.31	0.10	0.56
3-7	-1.37	-0.98	-1.40	-0.27	0.34	0.10	0.61
3-8	-1.24	-0.69	-1.19	-0.22	0.33	0.09	0.68

-----Tracer application time -----							
----- (h) -----							
	6.03	5.10	3.85	1.15			
	TFMBA	PFBA	DFBA	TFBA	θ_v	α	θ_m/θ
Site-sample	-----ln(1-C/C ₀)-----				(m ³ m ⁻³)	(h ⁻¹)	
4-1	-1.62	-1.32	-1.60	-1.24	0.39	0.14	0.30
4-2	-1.84	-1.58	-1.92	-1.37	0.35	0.12	0.26
4-3	-1.81	-1.45	-1.71	-0.84	0.40	0.14	0.49
4-4	-1.76	-1.43	-1.79	-0.86	0.39	0.14	0.45
4-5	-1.67	-1.36	-1.73	-0.57	0.42	0.12	0.62
4-6	-1.55	-1.32	-1.56	-1.20	0.43	0.15	0.31
4-7	-1.61	-1.26	-1.58	-0.66	0.42	0.14	0.56
4-8	-1.49	-1.22	-1.50	-0.75	0.47	0.16	0.50

-----Tracer application time -----							
----- (h) -----							
	8.03	5.85	3.15	2.15			
	TFMBA	PFBA	DFBA	TFBA	θ_v	α	θ_m/θ
Site-sample	-----ln(1-C/C ₀)-----				(m ³ m ⁻³)	(h ⁻¹)	
5-1	-1.42	-1.20	-1.38	-1.15	0.32	0.12	0.31
5-2	-1.52	-1.25	-1.44	-1.21	0.31	0.11	0.30
5-3	-1.56	-1.25	-1.51	-1.23	0.29	0.11	0.29
5-4	-1.34	-1.08	-1.29	-1.07	0.31	0.11	0.34
5-5	-0.99	-0.84	-1.02	-0.78	0.32	0.12	0.44
5-6	-2.00	-1.59	-2.00	-1.52	0.33	0.11	0.20
5-7	-1.44	-1.21	-1.40	-1.17	0.34	0.12	0.31
5-8	-1.35	-1.11	-1.37	-1.09	0.33	0.12	0.32

Laboratory Studies

Fast flow rate iron column			Replicate fast flow rate iron column		
Pore Volume	TCE C/C	Ethylene C/C	Pore Volume	TCE C/C	Ethylene C/C
0.40	0.00000	0.00000	0.36	0.00000	0.00027
0.90	0.01421	0.00730	0.82	0.00142	0.00825
1.40	0.09819	0.01810	1.27	0.04385	0.01921
1.90	0.11661	0.07637	1.73	0.12420	0.07266
2.40	0.09238	0.17630	2.64	0.07565	0.18970
2.90	0.06278	0.22265	3.09	0.04756	0.21955
3.40	0.04403	0.19963	3.55	0.03013	0.21480
3.90	0.02802	0.17684	4.00	0.02002	0.19028
4.40	0.01426	0.14007	4.45	0.01359	0.15071
4.90	0.01175	0.10966	4.91	0.00971	0.11083
5.40	0.00833	0.07182	5.36	0.00724	0.07727
5.90	0.00447	0.05948	5.82	0.00526	0.05394
6.40	0.00420	0.03673	6.27	0.00412	0.03952
6.90	0.00311	0.02567	6.73	0.00328	0.02874
7.40	0.00298	0.02037	7.18	0.00253	0.02192
7.90	0.00210	0.01594	7.64	0.00219	0.01825
8.40	0.00022	0.01112	8.09	0.00188	0.01108
8.90	0.00066	0.00902	8.55	0.00151	0.00971
9.40	0.00201	0.00611	9.00	0.00124	0.00987
9.90	0.00197	0.00553	9.45	0.00114	0.00933
10.40	0.00140	0.00470	9.91	0.00091	0.00506
10.90	0.00105	0.00485	10.36	0.00078	0.00522
11.40	0.00192	0.00170	10.82	0.00000	0.00645
11.90	0.00000	0.00071	11.27	0.00054	0.00398
12.40	0.00000	0.00000	11.73	0.00060	0.00410
12.90	0.00000	0.00000	12.18	0.00000	0.00342
13.40	0.00000	0.00000	12.64	0.00000	0.00159
13.90	0.00000	0.00000	13.09	0.00000	0.00176
14.40	0.00000	0.00000	13.55	0.00000	0.00106
14.90	0.00000	0.00000	14.00	0.00000	---
15.40	0.00000	0.00000	14.91	0.00000	0.00022

Intermediate flow rate iron column			Slow flow rate iron column		
Pore Volume	TCE C/C	Ethylene C/C	Pore Volume	TCE C/C	Ethylene C/C
0.20	0.00000	0.00144	0.85	0.00164	0.02084
0.45	0.00000	0.00165	0.98	0.00297	0.02605
0.70	0.00000	0.00144	1.10	0.00499	0.03491
0.95	0.00000	0.01031	1.23	0.00759	0.04423
1.20	0.00000	0.02954	1.35	0.01049	0.06299
1.45	0.01517	0.06899	1.48	0.01388	0.07700
1.70	0.05158	0.10511	1.60	0.01635	0.10688
1.95	0.09388	0.13830	1.73	0.01824	0.14126
2.20	0.09469	0.17369	1.85	0.01923	0.16557
2.45	0.07294	0.19683	1.98	0.01970	0.17817
2.70	0.05669	0.22187	2.10	0.01984	0.20510
2.95	0.03695	0.23846	2.23	0.01905	0.21763
3.20	0.02937	0.24956	2.35	0.01810	0.22493
3.45	0.01923	0.25169	2.48	0.01757	0.23892
3.70	0.01384	0.24464	2.60	0.01635	0.23941
3.95	0.00959	0.22225	2.73	0.01537	0.25007
4.20	0.00751	0.20033	2.85	0.01452	0.25089
4.45	0.00557	0.18238	2.98	---	0.25283
4.70	0.00458	0.14885	3.10	0.01197	0.24922
4.95	0.00405	0.12669	3.23	0.01140	0.25207
5.20	0.00287	0.10141	3.35	0.01066	0.24888
5.45	0.00261	0.08359	3.48	0.00956	0.24961
5.70	0.00234	0.07712	3.60	0.00897	0.24544
5.95	0.00140	0.05566	3.73	0.00812	0.23133
6.20	0.00100	0.04426	3.85	0.00733	0.22744
6.45	0.00000	0.03563	3.98	0.00693	0.22066
6.70	0.00000	0.02965	4.10	0.00660	0.20884
6.95	0.00000	0.02295	4.23	---	0.19627
7.20	0.00000	0.01590	4.35	0.00588	0.18522
7.45	0.00000	0.01712	4.48	0.00668	0.17592
7.70	0.00000	0.01353	4.60	0.00505	0.16414
7.95	0.00000	0.00870	4.73	0.00465	0.14677
8.20	0.00000	0.01162	4.85	0.00450	0.14185
8.45	0.00000	0.00522	5.10	0.00415	0.11648
8.70	0.00000	0.00365	5.23	0.00383	0.09953
9.20	0.00000	0.00353	5.35	0.00337	0.08600
9.45	0.00000	0.00079	5.48	0.00337	0.07814
9.70	0.00000	0.00004	5.60	0.00332	0.07237
9.95	0.00000	0.00079	5.73	0.00289	0.06277
10.20	0.00000	0.00004	5.85	0.00277	0.05826
			5.98	0.00260	0.05108
			6.10	0.00303	0.05024
			6.23	0.00265	0.04851
			6.35	0.00237	0.04277
			6.48	0.00259	0.03543
			6.60	0.00229	0.03484
			6.73	0.00227	0.02476
			6.85	0.00188	0.02877
			6.98	0.00212	0.02230
			7.10	0.00209	0.02427
			7.23	0.00217	0.02321
			7.35	0.00188	0.02038
			7.48	0.00193	0.01875
			7.60	0.00179	0.01928
			7.73	0.00206	0.01848
			7.85	0.00187	0.01119
			7.98	0.00168	0.00843
			8.10	0.00143	0.00470
			8.35	0.00148	0.00576
			8.60	0.00101	0.00201
			9.10	0.00101	0.00357
			9.60	0.00101	0.00843
			10.10	0.00101	0.00470
			10.60	0.00101	0.00576
			10.85	0.00101	0.00201
			10.98	0.00101	0.00357

Fast flow rate Cu-Fe column			Replicate fast flow Cu-Fe iron column		
Pore Volume	TCE C/C	Ethylene C/C	Pore Volume	TCE C/C	Ethylene C/C
0.40	0.00035	0.00000	0.40	0.00000	0.00311
0.90	0.00031	0.00196	0.90	0.00512	0.01334
1.40	0.00778	0.00348	1.40	0.00593	0.02452
1.90	0.06441	0.01233	1.90	0.02400	0.07017
2.40	0.11083	0.06440	2.40	0.10668	0.09514
2.90	0.07670	0.09705	2.90	0.06752	0.13049
3.40	0.04728	0.13231	3.40	0.04845	0.17225
3.90	0.03021	0.16337	3.90	0.02657	0.16646
4.40	0.02061	0.15755	4.40	0.02132	0.15765
4.90	0.01479	0.15056	4.90	0.01539	0.15189
5.40	0.01107	0.13682	5.40	0.00996	0.13448
5.90	0.00875	0.12356	5.90	0.00687	0.10284
6.40	0.00684	0.10698	6.40	0.00600	0.08886
6.90	0.00553	0.08793	6.90	0.00471	0.07503
7.40	0.00463	0.07379	7.40	0.00395	0.06135
7.90	0.00392	0.06006	7.90	0.00366	0.04786
8.40	0.00332	0.04869	8.40	0.00332	0.03460
8.90	0.00296	0.03438	8.90	0.00305	0.02167
9.40	0.00255	0.02817	9.40	0.00277	0.01618
9.90	0.00222	0.02436	9.90	0.00265	0.01050
10.40	0.00203	0.01460	10.40	0.00248	0.00971
10.90	0.00175	0.01371	10.90	0.00248	0.00990
11.40	0.00159	0.01035	11.40	0.00181	0.01133
11.90	0.00147	0.00739	11.90	0.00183	0.00841
12.40	0.00138	0.00590	12.40	0.00184	0.00855
12.90	0.00115	0.00573	12.90	0.00149	0.00770
13.40	0.00117	0.00365	13.40	0.00153	0.00526
13.90	0.00103	0.00059	13.90	0.00158	0.00550
14.40	0.00097	0.00000	14.40	0.00119	0.00446
14.90	0.00092	0.00122	14.90	0.00175	0.00205
15.40	0.00086	0.00000	15.40	0.00111	0.00299
16.40	0.00000	0.00000	15.90	0.00100	0.00387
			16.40	0.00092	0.00111

Intermediate flow rate Cu-Fe column			Slow flow rate Cu-Fe column		
Pore Volume	TCE C/C	Ethylene C/C	Pore Volume	TCE C/C	Ethylene C/C
0.20	0.00041	0.00000	1.10	0.00000	0.00000
0.45	0.00086	0.00000	1.23	0.00000	0.00036
0.70	0.00047	0.00000	1.35	0.00000	0.00088
0.95	0.00092	0.00028	1.48	0.00000	0.00556
1.20	0.00140	0.00028	1.60	0.00000	0.00692
1.45	0.00177	0.00028	1.73	0.00000	0.01085
1.70	0.00472	0.00491	1.85	0.00060	0.02414
1.95	0.01630	0.01310	1.98	0.00114	0.03696
2.20	0.03708	0.02209	2.10	0.00200	0.04475
2.45	0.05202	0.05079	2.23	0.00315	0.06263
2.70	0.05282	0.09253	2.35	0.00447	0.06523
2.95	0.04643	0.13846	2.48	0.00606	0.08381
3.20	0.03792	0.17556	2.60	0.00723	0.08433
3.45	0.03047	0.19409	2.73	0.00814	0.09555
3.70	0.02430	0.21066	2.85	0.00862	0.11415
3.95	0.01932	0.20750	2.98	0.00885	0.11484
4.20	0.01556	0.20389	3.10	0.00892	0.12894
4.45	0.01279	0.19456	3.23	0.00853	0.13656
4.70	0.01072	0.18433	3.35	0.00808	0.15170
4.95	0.00897	0.17649	3.48	0.00782	0.14799
5.20	0.00782	0.16139	3.60	0.00723	0.17201
5.45	0.00652	0.14062	3.73	0.00676	0.17506
5.70	0.00571	0.13077	3.85	0.00636	0.17730
5.95	0.00490	0.11625	3.98	0.00000	0.18685
6.20	0.00429	0.11025	4.10	0.00516	0.18993
6.45	0.00380	0.08854	4.23	0.00489	0.19469
6.70	0.00347	0.08362	4.35	0.00455	0.19478
6.95	0.00313	0.07699	4.48	0.00404	0.20823
7.20	0.00278	0.06049	4.60	0.00378	0.21121
7.45	0.00248	0.05386	4.73	0.00339	0.21310
7.70	0.00238	0.05372	4.85	0.00303	0.21107
8.20	0.00197	0.04567	4.98	0.00285	0.20368
8.45	0.00176	0.03767	5.10	0.00271	0.20348
8.95	0.00154	0.02432	5.53	0.00274	0.19090
9.20	0.00153	0.02043	5.65	0.00202	0.18993
9.45	0.00148	0.01683	5.78	0.00185	0.17128
9.70	0.00135	0.01159	5.90	0.00179	0.16003
9.95	0.00138	0.00655	6.03	0.00159	0.15784
10.20	0.00124	0.00206	6.15	0.00164	0.15284
			6.28	0.00150	0.15283
			6.40	0.00131	0.12734
			6.53	0.00131	0.12503
			6.65	0.00128	0.12140
			6.78	0.00110	0.11507
			6.90	0.00106	0.08888
			7.03	0.00099	0.08646
			7.15	0.00116	0.08172
			7.28	0.00101	0.06999
			7.40	0.00089	0.06488
			7.53	0.00098	0.05912
			7.65	0.00086	0.04653
			7.78	0.00085	0.04286
			7.90	0.00069	0.03778
			8.03	0.00079	0.03630
			8.15	0.00078	0.03211
			8.28	0.00081	0.02008
			8.40	0.00069	0.02427
			8.53	0.00071	0.02173
			8.65	0.00066	0.01614
			8.78	0.00076	0.01480
			8.90	0.00069	0.01061
			9.03	0.00062	0.01202
			9.15	0.00052	0.01137
			9.28	0.00053	0.01073
			9.40	0.00052	0.01011
			9.53	0.00035	0.00951
			9.78	0.00000	0.00749
			9.90	0.00000	0.00656

ACKNOWLEDGMENTS

I would like to thank the people who have helped me develop and grow as a scientist, without them I would not have accomplished anything. I am very grateful for the support, resources, and advice from Dan Jaynes, Sally Logsdon, Greg Gwiasda, and Gavin Simmons from the National Soil Tilth Laboratory USDA-ARS. I would like to thank Say Kee Ong and LaDon Jones from the department of Civil and Constructional Engineering and Toby Ewing for their advice, interaction, and cooperative research. I am also thankful to my advisor Robert Horton for helping me develop as a scientist and an individual, encouraging me intellectually and spiritually. I am also grateful to the following individuals and colleagues who have help me through conversation, advice, and support: Brent Clothier, Jaehoon Lee, Mingan Shao, Dan Ressler, Fulin Shen, Salem Aljabri, Tyson Ochsner, Jan Ilsemann, Jill Smart, and my wife Sally. Lastly, I would like to thank the Baker Trust fund for their generous financial contributions to our research.