MONTANA STATE UNIVERSITY

Fate of chlorsulfuron, 2, 4-D, and naphthalene in unsaturated soil
by Richard Harold Veeh

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Crop and Soil Science
Montana State University
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Abstract:

The objectives of this study were to: (i) determine the unsaturated transport characteristics of chlorsulfuron, a sulfonylurea herbicide, in disturbed and undisturbed soil columns and investigate the capability of LEACHM, a computer transport model, for predicting chlorsulfuron transport, (ii) evaluate soil depth and temperature effects on 2,4-D degradation rates, and (iii) investigate the effects of organic cosolvents on degradation, volatilization, and unsaturated transport of naphthalene in soils. Disturbed and undisturbed column experiments were conducted with either of two Montana surface soils under unsaturated flow conditions. Unit gradient was established on all columns by balancing surface water (with or without methanol or acetone cosolvent fractions) input with outflow at the bottom of each column fitted with a stainless steel microporous plate connected to a vacuum source. A nonlinear least-squares computer program (CXTFIT) was employed to analyze fraction-collected effluent breakthrough curves (BTCs) for Br, 14C-chlorsulfuron, 3H2O, and 14 C-naphthalene and derive dispersion coefficients and retardation factors. Observed Br and 3H2O breakthrough curves (BTCs) were adequately described using the local equilibrium assumption (LEA) model. Observed chlorsulfuron and naphthalene BTCs demonstrated significant chemical nonequilibrium during transport. LEACHM-predicted BTCs for chlorsulfuron utilizing independently measured or estimated soil physical parameters as input data did not adequately reflect observed chlorsulfuron BTCs because the model had no capabilities for accepting input parameters relating to nonequilibrium conditions. The experimentally determined chlorsulfuron BTCs confirmed the high mobility of this chemical at neutral soil pH values. Naphthalene sorption decreased in a log-linear relationship as the fraction of cosolvent increased, resulting in an increase in naphthalene transport. Degradation kinetics of 2,4-D were studied in soils from 0-30, 30-60, and 60-120 cm depths of two Montana soils at three different temperatures of 10°C, 17°C, and 24°C. Air-dried and sieved (2 mm) soil samples were placed in reaction flasks and treated with a solution of 14C-2,4-D simulating field rates. A carrier gas (air) was used to continuously evacuate evolved 14CO2 into NaOH traps as a measure of 2,4-D degradation. Quantitative treatment comparisons of soil depth and temperature effects were made by fitting the experimental data to both logistic and first-order kinetic models. Degradation rates of 2,4-D decreased significantly with increasing depth and with decreasing temperature. Naphthalene degradation kinetics were investigated using a similar system with the addition of an activated carbon trap to assess 14C-naphthalene volatilization. Experiments were conducted at 24°C using soil from the 0-30 cm depth of the Amsterdam silt loam. Treatments included 100% water (control) and 25 % methanol and 10% acetone cosolvent fractions. Naphthalene degradation decreased in the methanol and increased in the acetone cosolvent treatment compared to the control. Volatilization increased as the cosolvent fraction increased.

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APPROVAL

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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The author would like to dedicate this thesis to the memory of his loving parents, who both supported and encouraged him throughout his academic career.

VITA

Richard Harold Veeh was born to Harold and Clara Veeh on August 13, 1949 at Santa Ana, California. He attended elementary and secondary school at Tustin, California where he graduated from Tustin High School.

Richard received a Bachelor of Arts degree in Biology with a minor in Philosophy from Humboldt State College, located in Arcata, California, in 1971. After relocating in Clancy, Montana in 1975, he was employed by the U.S. Forest Service until January, 1980 when he entered graduate school at Montana State University under the guidance of Dr. Earl O. Skogley. He received a Master of Science degree in Soils in December, 1981.

Upon receiving his M.S. degree, Richard worked as a consultant for Alpha Laval of Sweden near Riyadh, Saudi Arabia. He was primarily involved with conducting soil surveys and assessing sites for agricultural production potential. Richard then accepted the position of Laboratory Manager for the Saudi Arabian Agriculture and Dairy Company, a company in partnership with Alpha Laval. In this position he was responsible for routine analyses of cattle feeds and water, crop tissue, and soil samples. In August, 1984 Richard accepted a position as Laboratory Aide II with the Laboratory Bureau of Montana State Department of Agriculture and was later promoted to Laboratory Technician II for the Chemistry Station affiliate of Montana State University. During this time he performed routine extractions for pesticide residues and other analyses for a wide variety of sample matrices.

Richard entered graduate school in pursuit of a Ph.D. at Montana State University in September of 1987 as a Research Associate for Dr. William P. Inskeep. The courses in his program focused on subjects pertinent to the area of environmental chemistry. His research program involved the use of soil column and batch reactor systems to study and model the transport and degradation of selected organic contaminants.

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ABSTRACT

The objectives of this study were to: (i) determine the unsaturated transport characteristics of chlorsulfuron, a sulfonylurea herbicide, in disturbed and undisturbed soil columns and investigate the capability of LEACHM, a computer transport model, for predicting chlorsulfuron transport, (ii) evaluate soil depth and temperature effects on 2,4-D degradation rates, and (iii) investigate the effects of organic cosolvents on degradation, volatilization, and unsaturated transport of naphthalene in soils. Disturbed and undisturbed column experiments were conducted with either of two Montana surface soils under unsaturated flow conditions. Unit gradient was established on all columns by balancing surface water (with or without methanol or acetone cosolvent fractions) input with outflow at the bottom of each column fitted with a stainless steel microporous plate connected to a vacuum source. A nonlinear least-squares computer program (CXTFIT) was employed to analyze fraction-collected effluent breakthrough curves (BTCs) for Br^-, ^{14}C-chlorsulfuron, ^3H_2O, and ^{14}C-naphthalene and derive dispersion coefficients and retardation factors. Observed Br^- and ^3H_2O breakthrough curves (BTCs) were adequately described using the local equilibrium assumption (LEA) model. Observed chlorsulfuron and naphthalene BTCs demonstrated significant chemical nonequilibrium during transport. LEACHM-predicted BTCs for chlorsulfuron utilizing independently measured or estimated soil physical parameters as input data did not adequately reflect observed chlorsulfuron BTCs because the model had no capabilities for accepting input parameters relating to nonequilibrium conditions. The experimentally determined chlorsulfuron BTCs confirmed the high mobility of this chemical at neutral soil pH values. Naphthalene sorption decreased in a log-linear relationship as the fraction of cosolvent increased, resulting in an increase in naphthalene transport. Degradation kinetics of 2,4-D were studied in soils from 0-30, 30-60, and 60-120 cm depths of two Montana soils at three different temperatures of 10°C, 17°C, and 24°C. Air-dried and sieved (2 mm) soil samples were placed in reaction flasks and treated with a solution of ^{14}C-2,4-D simulating field rates. A carrier gas (air) was used to continuously evacuate evolved $^{14}CO_2$ into NaOH traps as a measure of 2,4-D degradation. Quantitative treatment comparisons of soil depth and temperature effects were made by fitting the experimental data to both logistic and first-order kinetic models. Degradation rates of 2,4-D decreased significantly with increasing depth and with decreasing temperature. Naphthalene degradation kinetics were investigated using a similar system with the addition of an activated carbon trap to assess ^{14}C-naphthalene volatilization. Experiments were conducted at 24°C using soil from the 0-30 cm depth of the Amsterdam silt loam. Treatments included 100% water (control) and 25% methanol and 10% acetone cosolvent fractions. Naphthalene degradation decreased in the methanol and increased in the acetone cosolvent treatment compared to the control. Volatilization increased as the cosolvent fraction increased.

CHAPTER 1

INTRODUCTION

Organic chemical contamination of soils within the unsaturated vadose zone has resulted from agricultural use of pesticides, industrial use of organic solvents, and point source pollution at toxic waste sites and sanitary land fills. It is now of national concern that we attempt to assess the potential for contamination of our groundwater systems by focusing research on understanding the processes which affect movement of organic contaminants in soils. These processes include adsorption, leaching (transport), chemical decomposition, photodecomposition, biological degradation, volatilization, plant root uptake and exudation, runoff, and capillary flow. The objective of the present study was to investigate several of these processes under controlled laboratory conditions for three organic compounds that represent a diversity of potential soil and groundwater contaminants. These organic compounds included two herbicides, chlorsulfuron and 2,4-D, and one common aromatic oil and gasoline constituent, naphthalene.

Chlorsulfuron (Glean) is classified as a sulfonylurea herbicide and is used in Montana for broadleaf weed control in small grains. This compound is characterized by its high herbicidal activity at very low application rates and shows differences in soil persistence and mobility depending upon soil conditions such as pH, moisture content, temperature, organic matter content, and texture. In Montana, residual chlorsulfuron has had detrimental effects on alfalfa grown in fields previously used for small grain crops.

Because of the anionic character of chlorsulfuron at neutral to basic pH conditions typical of Montana soils, there is concern that the potential for groundwater contamination will be high in soils in Montana, especially under high moisture conditions or in areas with shallow water tables.

Risk assessment using predictive models for determination of potential ground water contamination from agricultural herbicide use is now a requirement in many states. Consequently, validation of transport models is a necessary step for predicting herbicide transport under unsaturated flow conditions typical of the vadose zone. Model performance is dependent on our ability to accurately quantify transport parameters that are used as inputs into the model. Thus, the objectives of this first area of thesis research were to: (i) quantify the transport characteristics of chlorsulfuron through soils, and (ii) determine the predictive capability of a transport model, LEACHM (Leaching Estimation And CHemistry Model), developed at Cornell University with regard to transport of chlorsulfuron.

In many transport models such as LEACHM, subroutines within the model are designed with inputs related to degradation kinetics. Accurate assessment of degradation kinetics of organic contaminants in soils is critical to transport model predictions. However, limited data exist on the effects of environmental factors such as temperature on the degradation rate of organic chemicals in soils. Also, populations of microorganisms are known to vary with conditions that change with soil depth.

Of the herbicides used extensively in Montana, 2,4-D is the most commonly used herbicide for broadleaf weed control in cereal grain production. A state-wide groundwater monitoring program in Montana has discovered contamination of a number of wells with 2,4-D; consequently, there is significant concern about the fate and transport of 2,4-D under regional environmental conditions in surface and vadose zone soils. Thus, the second set of objectives of this thesis research involved determination of the effects of soil depth and soil temperature on the degradation rates of 2,4-D in two representative Montana soils.

Another group of organic contaminants found in soils is hydrophobic organic chemicals (HOC), commonly associated with oil and gasoline spills. Naphthalene is a typical HOC in this category, which is characterized by compounds that have very low solubilities in water. However, naphthalene has been found in groundwater and has migrated significant distances in aquifer systems.

In some cases, HOC contaminants in soils are associated with miscible organic cosolvents which may enhance contaminant solubility. Existing data and theories for sorption and transport of HOC in soils have dealt primarily with aqueous solutions. Extrapolation of these data and theories to mixed solvent systems is not appropriate, due to solvent effects on the solubility and subsequent sorption of HOC by the soil organic carbon fraction. Several recent studies on the transport of HOC in the presence of miscible solvents have established that miscible solvents generally reduce the amount of HOC sorption resulting in accelerated transport through porous media like soils. It is probable that organic cosolvents increase transport of HOC by both increasing HOC solubility and the degree of reversible partitioning. An understanding of sorption mechanisms of HOC in the presence of organic solvents is important for predicting the fate and transport of organic contaminants in soils and groundwaters. Previous transport studies have established our ability to quantify the effect of organic cosolvents on HOC transport under saturated conditions. However, the influence of cosolvents on the transport of HOC in the unsaturated vadose zone in soils has received little attention. Losses of HOC due to volatilization and biotic and abiotic reactions have been shown to be significant. Consequently, the third set of objectives of this thesis research included: (i) assessment of transport in a single sorbate (i.e. naphthalene)-mixed solvent (either methanol-water or acetone-water) system using soil columns under slightly unsaturated flow conditions, and (ii) assessment of the relative importance of degradation and volatilization as processes that affect naphthalene transport in the presence of cosolvents.

CHAPTER 2

OBSERVED AND PREDICTED TRANSPORT OF CHLORSULFURON IN SOIL COLUMNS

Introduction

Chlorsulfuron (trade name Glean) is a sulfonylurea herbicide used in Montana for broadleaf weed control in small grains. Chlorsulfuron has high herbicidal activity at application rates as low as 10 g ai ha^{-1} and demonstrates differences in soil persistence and mobility depending upon soil conditions such as pH, moisture content, temperature, organic matter content, and texture. In order to accurately predict the transport of chlorsulfuron through the vadose (unsaturated) zone, the relationship among factors that affect chlorsulfuron movement in soils must be understood.

Chlorsulfuron is a weak acid ($pK_a = 3.6$) with water solubilities ranging from 60 ppm at pH 5 to 7000 ppm at pH 7 (Beyer et al., 1988). In soils with pH values greater than 5, chlorsulfuron exists primarily as an anion, and is only weakly adsorbed (Thirunarayanan et al., 1985). Several studies have shown that the mobility of chlorsulfuron increases with increasing soil pH (Mersie and Foy, 1985; Fredrickson and Shea, 1986). Shea (1986) postulated that the small amount of chlorsulfuron adsorbed is due to H-bonding with soil organic matter and not simple partitioning.

The slow rate of chlorsulfuron degradation coupled with its high potential mobility in soils suggests a high potential for transport below the root zone with subsequent

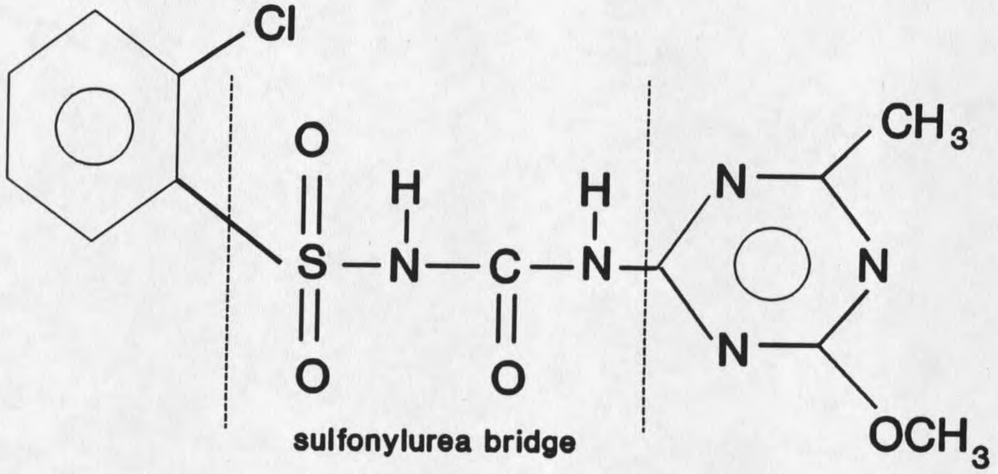


Figure 1. Molecular structure of chlorsulfuron.

movement into groundwaters, especially in soils with shallow groundwater tables. Chlorsulfuron half-lives were found to range from 1.9 weeks at pH 5.6 to 10 weeks at pH 7.5 (Fredrickson and Shea, 1986). Shorter half-lives at pH values < 7 are primarily a result of chemical hydrolysis where higher H^+ concentrations accelerate the rate of cleavage of the sulfonylurea bridge of the chlorsulfuron molecule (Figure 1).

Many states are requiring risk assessment via predictive models of potential ground water contamination from agricultural herbicide use. Consequently, validation of transport models such as LEACHM (Wagenet and Hutson, 1986) is a necessary step for predicting herbicide transport under unsaturated flow conditions typical of the vadose zone. Model performance is dependent on our ability to accurately quantify transport parameters such as soil hydraulic conductivity and the dispersion coefficient and retardation factor of the convection-dispersion equation (Biggar and Nielsen, 1976):

$$R\frac{\partial c_r}{\partial t} = D\frac{\partial^2 c_r}{\partial x^2} - v\frac{\partial c_r}{\partial x} - \mu c_r + \gamma \qquad (1)$$

where R = the retardation factor, D = the apparent dispersion coefficient, v = pore water velocity, c_r = the volume-averaged resident concentration of the solute in the soil liquid phase, t = time, x = a positive distance from the inlet boundary, μ = the combined soil liquid and solid phase rate constant for first-order decay, and γ = the combined soil liquid and solid phase rate constant for zero-order production (the zero-order production term assumes the source of a particular solute within the defined system boundaries to be independent of the concentration of that solute). Least-squares computer methods are among the most accurate and convenient ways to fit D and R values to experimental data. These computer methods can be based on different analytical solutions for solute concentration (c_r in Equation 1) according to the definition of inlet and outlet boundary conditions. Thus, computer methods applied to the same experimental data will often yield different values for D and R. However, for Peclet numbers ($P = vL\ D^{-1}$; where v is pore water velocity and L is column length) greater than about 20, the estimated value of D has been shown to be fairly independent of the analytical solution to Equation 1 (van Genuchten and Wierenga, 1986). Because of the relatively narrow range of practical $v\ D^{-1}$ ratios, in practice this means that experiments should be carried out using columns of at least 10 to 15 cm in length for homogeneous soils with relatively narrow pore-size distributions.

The existence of immobile regions of soil water and potential nonequilibrium processes also complicates efforts to model solute transport (De Smedt et al.,1986;

Jaynes et al., 1988; Gvirtzman and Magaritz, 1986). The immobile water fraction has been shown to vary with flow velocity and aggregate size (van Genuchten and Wierenga, 1977; Nkedi-Kizza et al., 1983; Smettem, 1984). Intraparticle diffusion in the immobile water fraction has been shown to control sorption kinetics (Wu and Gschwend, 1986). Transport models must make assumptions about the equilibrium of physical and chemical processes of diffusion between and within mobile and immobile soil water regions (van Genuchten and Wierenga, 1976; van Genuchten et al., 1977; Rao et al., 1979; Brusseau et al., 1989; Brusseau and Rao, 1989).

The primary objectives of the present study were to: (i) quantify the transport characteristics of chlorsulfuron through soils, and (ii) determine the predictive capability of transport model, LEACHM, with regard to transport of chlorsulfuron. The choice of LEACHM reflected the need for flexibility to deal with both controlled laboratory experiments as in the present study, and field experiments currently in progress.

Materials and Methods

Soils

Soil samples were taken from two sites in Montana from the 0-30 cm depth. One of the soils sampled was an Amsterdam silt loam (fine-silty mixed Typic Haploboroll) at a site near Bozeman, MT, and the other was a Haverson silty clay loam (fine-loamy mixed (calcareous) Mesic Ustic Torrifluvent) located at Huntley, MT (Table 1). The pipette method of particle-size analysis (Day, 1965) was performed on each soil. Each soil was also analyzed for total organic C (Snyder and Trofymow, 1984), cation exchange capacity (Chapman, 1965), and soil pH using a 1:1 soil-water ratio.

Table 1. Characteristics of soils used in column experiments.

Soil Series	Classification	Clay	Silt	Sand	Organic Carbon	Soil pH	CEC
		——(g kg^{-1})——				(1:1)	mmol charge g^{-1}
Amsterdam silt loam	Typic Haploboroll Cryoboroll	231	606	163	10.6	6.9	0.21
Haverson silty clay loam	Mesic Ustic Torrifluvent	404	414	182	10.1	7.1	0.24

Column Experiments

Disturbed soil columns were constructed using homogeneous air-dried and sieved (2 mm) soil uniformly packed in 5.1 cm diameter by 30 cm long plexiglass columns (Soil Measurement Systems; Tucson, AZ.). Undisturbed soil columns were extracted as field core samples using 51 mm PVC pipe adapted to fit a Giddings hydraulic probe. Both disturbed and undisturbed columns were fitted with stainless steel porous plates to seal the bottom of the columns and with tensiometer ports near the top and bottom of the column to monitor water potential (Figure 2).

Column displacement experiments were performed under unsaturated flow conditions as described by van Genuchten and Wierenga (1986). A timer-controlled syringe pump was used to apply an intermittent pulse of solution to the top of the column. A vacuum chamber with a vacuum of 75 mm Hg connected to the bottom of the respective columns was used to control the soil matric potential at approximately 30 mbars throughout the soil column. A fraction collector (Isco, Inc.; Lincoln, NE.) placed

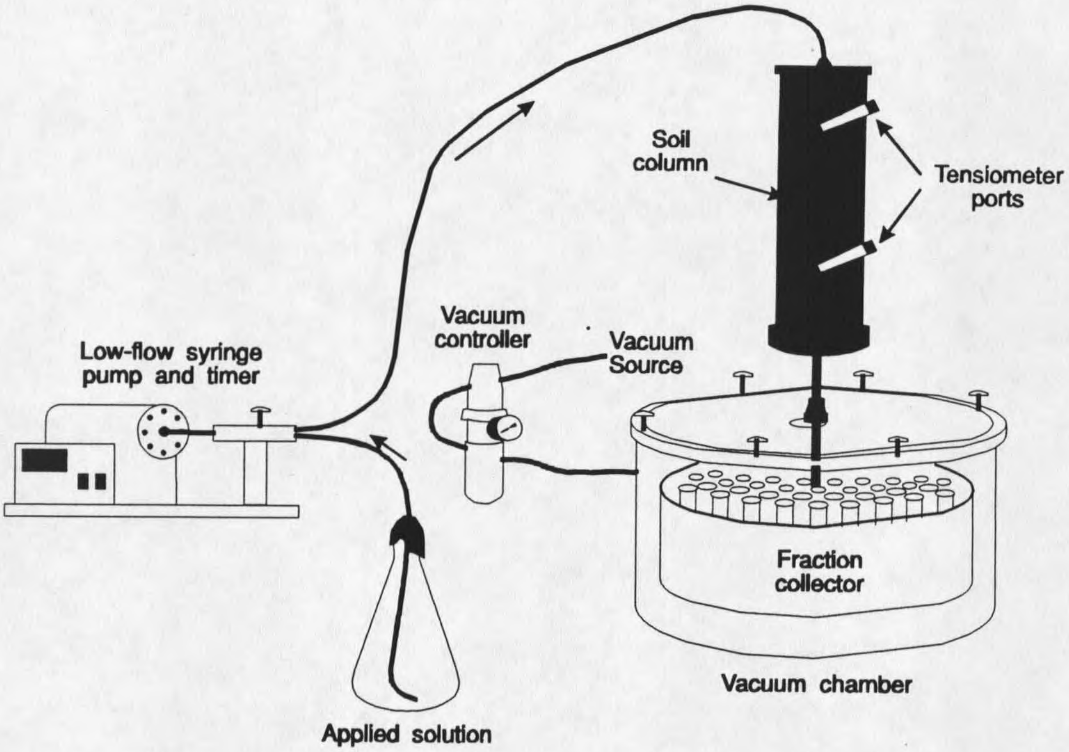


Figure 2. Soil column apparatus used in chlorsulfuron transport experiments.

inside the vacuum chamber was used to collect column effluent at intervals of 3.5 or 4 hours.

Disturbed columns for each soil were prepared in duplicate with replicate runs for each column. A total of four undisturbed columns of the Amsterdam silt loam were run in duplicate. Soil columns were initially conditioned with at least 2 pore volumes of 3 mM $CaCl_2$, which was also used as a constant background ionic strength solution for the duration of each experiment. The solution was applied at a rate of approximately 4 ml/hr with the syringe pump set at 10 cycles/hr. A pulse of ^{14}C-labeled chlorsulfuron (specific activity of 15.2 uCi mg^{-1} (5.62×10^{-5} Bq mg^{-1}); DuPont Corp.; Wilmington, DE.) with a conservative Br^- tracer (50 ppm) was applied for approximately 26 hours at the above rate. ^{14}C-labeled chlorsulfuron was applied at a concentration of 73 ppb (corresponding to a field rate of 40 g ha^{-1} and a solution activity of 4.10 Bq L^{-1}). An applied chlorsulfuron concentration (365 ppb) corresponding to a 5x field rate was also used in subsequent experiments on several of the same columns. Dissolved humic acid (K & K Laboratories, Inc.; Hollywood, CA.) at 2m$\underline{M}$ C was also included in the pulse solution on two replicates of the Amsterdam silt loam undisturbed columns to assess the influence of soluble C on transport rates of chlorsulfuron. Humic acid C content was determined using a C analyzer (Dohrmann CD-80; Santa Clara, CA.).

After the pulse application, fraction collection of the column effluent proceeded for 5-6 d to establish breakthrough curves for both Br^- and ^{14}C-labeled chlorsulfuron. At the end of each experiment, test tubes in the fraction collector were capped and weighed to establish an average volumetric flow rate. Subsamples were analyzed for Br^- using ion chromatography (Dionex Corp.; Sunnyvale, CA.) and for ^{14}C using liquid scintillation analysis. Six mL of ScintiVerse E scintillation cocktail was added to each 1 mL effluent subsample and counted on a Packard 2200CA Tri-Carb Liquid Scintillation Analyzer (Meriden, CT.). Subsamples of the applied solution were also analyzed for Br^- and ^{14}C-labeled chlorsulfuron to establish initial concentration levels. Selected samples (6-7) from each experiment were analyzed for possible formation of metabolites. A 1 mL subsample was added to 100 uL 100 ppm unlabeled chlorsulfuron standard solution in 3 m$\underline{M}$ $CaCl_2$. A 100 uL subsample of this solution was injected into a Dionex HPLC system using a Hibar 250 mm LiChrosorb RP-18 (5 um) column and UV detector set at

238 nm. Effluent collected under the chlorsulfuron peak was counted as previously described for ^{14}C, and the results (corrected for dilution) were compared to counts of a 100 uL subsample dissolved directly in scintillation cocktail. No metabolites were detected in any of the column experiments using this method.

CXTFIT

The computer program CXTFIT (Parker and van Genuchten, 1984b) was used to provide a nonlinear least-squares solution of the one-dimensional homogeneous system convection-dispersion equation (Equation 1). The deterministic linear equilibrium adsorption (local equilibrium assumption, LEA) and two-site/two-region (i.e. bicontinuum model) modes for pulse injection with first-order decay and zero-order production (both assumed to be zero due to nonapplicability and long chlorsulfuron half-life, respectively) for flux-averaged concentrations (Parker and van Genuchten, 1984a) were used to interpret the Br^- and chlorsulfuron breakthrough curves (BTCs) as reduced concentration versus time. Time values at the end of the collection period were used primarily, but the effect of using mean time values was also evaluated. Equations describing the linear equilibrium adsorption (or LEA) model and the bicontinuum model are given in Parker and van Genuchten (1984a) and are not repeated here. The primary parameters estimated using the LEA model include the dispersion coefficient, D, and the retardation factor, R. Under equilibrium conditions the following equation defines R:

$$R = 1 + \rho K_d / \theta \qquad (2)$$

where ρ = soil bulk density, K_d = the equilibrium partition coefficient, and θ = total volumetric water content. The additional parameters estimated using the bicontinuum model include β and ω, which are evaluated based on conditions of either chemical or physical nonequilibrium. In the case of chemical nonequilibrium the following equations define β and ω:

$$\beta = \frac{\theta + F\rho K_d}{\theta + \rho K_d} \qquad and \qquad \omega = \alpha(1-\beta)RL/v \tag{3}$$

where F = fraction of total adsorption sites which react instantaneously with the solute, L = an arbitrary positive distance from the origin, v = pore water velocity, and α = first-order rate constant for the adsorption of solute on time-dependent adsorption sites. Interpreted in terms of physical nonequilibrium processes β and ω become:

$$\beta = \frac{\theta_m + F\rho K_d}{\theta + \rho K_d} \qquad and \qquad \omega = \alpha^{*}L/q \tag{4}$$

where F = fraction of total adsorption sites that equilibrate with the mobile liquid phase, θ_m = mobile volumetric water content, α^* = rate constant for solute exchange between mobile and immobile soil water, and q = volumetric liquid phase flow rate (i.e. vθ).

CXTFIT was used to fit BTCs for Br$^-$ and chlorsulfuron using several different scenarios. First, apparent dispersion coefficients (D) and retardation factors (R) for the Br$^-$ BTCs were estimated with the linear equilibrium adsorption (i.e. local equilibrium assumption or LEA) model using the measured value of pore water velocity (v) as an input. Secondly, a comparative analysis for Br^- was performed where R was assumed to be 1 for a conservative non-adsorbing solute, and D and v were derived. Thirdly, BTCs for chlorsulfuron were fit with the LEA model using the measured v, where D and R values were allowed to float. Finally, BTCs for chlorsulfuron were fit with both the LEA model and the bicontinuum model using the D value optimized from the Br^- BTCs. Collectively, this series of CXTFIT analyses were performed to (i) optimize the fit of the nonadsorbing tracer dispersion coefficient and (ii) determine the extent of physical or chemical nonequilibrium occurring during transport.

LEACHM

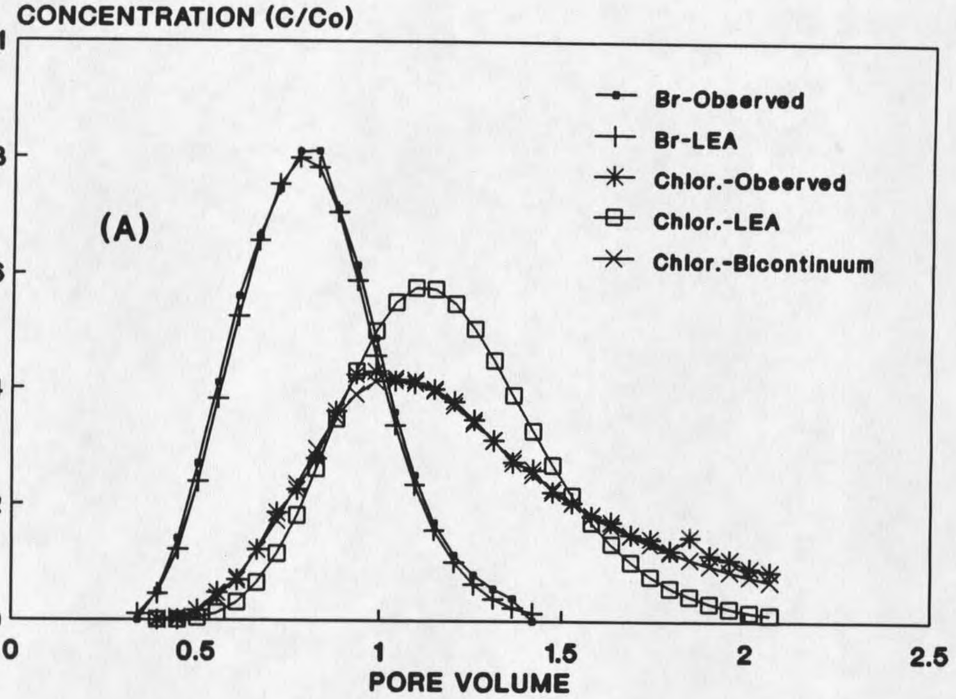
Selected column experimental and CXTFIT-derived BTCs were compared with respective BTCs generated by the computer model LEACHM utilizing the LEACHP routine (Wagenet and Hutson, 1989). Because LEACHM includes input parameters that are only applicable to field experiments (e.g. pan evaporation and rooting depth), only LEACHM inputs pertinent to the column experiments were included to generate predicted chlorsulfuron BTCs. The following variables were established as input parameters to the model: starting and ending dates, solute application pulse length (either 1.1 or 1.2 days), profile depth (column length), soil bulk density (measured), exponent in Campbell's equation and air-entry value (both estimated from soil retentivity data from Rawls and Brakensiek, 1989), saturated hydraulic conductivity (obtained using estimated Campbell's exponent and measured volumetric water content and hydraulic conductivity), dispersivity (obtained using CXTFIT), volumetric water content (measured), partition coefficient (K_{oc}), rate of solution application (equals macroscopic water flux), and application concentration of chlorsulfuron. Input parameters that remained constant over all column experiments included: temperature (23°C), molecular diffusion coefficients in air (4.93E+5 $mm^2 d^{-1}$) (Fuller et al., 1966) and water (39.63 $mm^2 d^{-1}$) (Hayduk and Laudie, 1974; Reid et al., 1977), constants a (.001) and b (10) in Bresler's equation (Kemper and Van Shaik, 1966; Olsen and Kemper, 1968), chlorsulfuron solubility (7000 mg dm^{-3}) and vapor density (4.43E-11 mg dm^{-3}) (Beyer et al., 1988). Input data for plant uptake, temperature flux, first-order rate constants, and pan evaporation were not included since these subroutines were not executed in the program under our experimental conditions.

Saturated hydraulic conductivity (K_s) was calculated from the measured volumetric flow rate and the relationship defined in Campbell's equation (Campbell, 1974). For comparison, K_s was determined experimentally for the Bozeman soil using a disturbed soil column not employed in the transport experiments. In addition, K_s was determined utilizing an empirically derived equation based on soil retentivity data (Rawls and Brakensiek, 1989). Values for dispersivity (λ) and partition coefficients were calculated from CXTFIT derived D and R values using (i) the LEA model for chlorsulfuron where D and R were allowed to float, and (ii) the bicontinuum model for chlorsulfuron where D was fixed from the Br^- BTC R value, while β and ω were allowed to float. Column K_d values were converted to K_{oc} values ($K_{oc} = K_d OC^{-1}$; where OC is the soil organic C fraction). A batch experiment was conducted to establish an independent partition coefficient (K_{oc}) for both soils. Two g of soil and 10 mL of a 3m$\underline{M}$ $CaCl_2$ solution plus an amount of ^{14}C-labeled chlorsulfuron corresponding to 0x, 1x, 5x, 10x, 50x, or 100x chlorsulfuron application rates were added to 40 mL centrifuge tubes in triplicate. The field rate treatment (1x rate) was .0041 ug ^{14}C-labeled chlorsulfuron per 10 ml solution. The centrifuge tubes were placed on a mechanical shaker for 16 hours, after which the tubes were centrifuged for 20 minutes at 10,000 rpm. Subsamples of the supernatant liquid were analyzed for ^{14}C-labeled chlorsulfuron and pH.

Results and Discussion

CXTFIT Analysis of Breakthrough Curves

Breakthrough curves for the nonadsorbing tracer, Br^-, were predominantly symmetrical with little evidence of tailing in both soils and in both disturbed and undisturbed soil columns (Figures 3 and 4). Using the local equilibrium assumption (LEA), dispersion coefficients (D) and retardation factors (R) were optimized utilizing CXTFIT and the measured pore water velocity (v) as an input parameter. The LEA model provided excellent fit to the Br^- BTCs for all columns (Table 2), where r^2 values typically ranged from 0.96 to 0.99. The lack of significant physical nonequilibrium during Br^- transport was also corroborated by fitting the Br^- data to the bicontinuum (two-site/two-region) model. These runs resulted in ω values averaging 1444 (n=11) and 963 (n=8) in disturbed and undisturbed columns, respectively. Values of ω greater than 100 are indicative of a lack of physical non-equilibrium (Bahr and Rubin, 1987; Brusseau et al., 1989). Furthermore, fitted D and R values using the bicontinuum model were essentially identical to those fitted with the LEA model. For the Amsterdam silt loam, average values of D obtained with the LEA model were 0.31 ± 0.07 $cm^2\ hr^{-1}$ and 0.26 ± 0.06 $cm^2\ hr^{-1}$ for disturbed and undisturbed columns, respectively. For disturbed



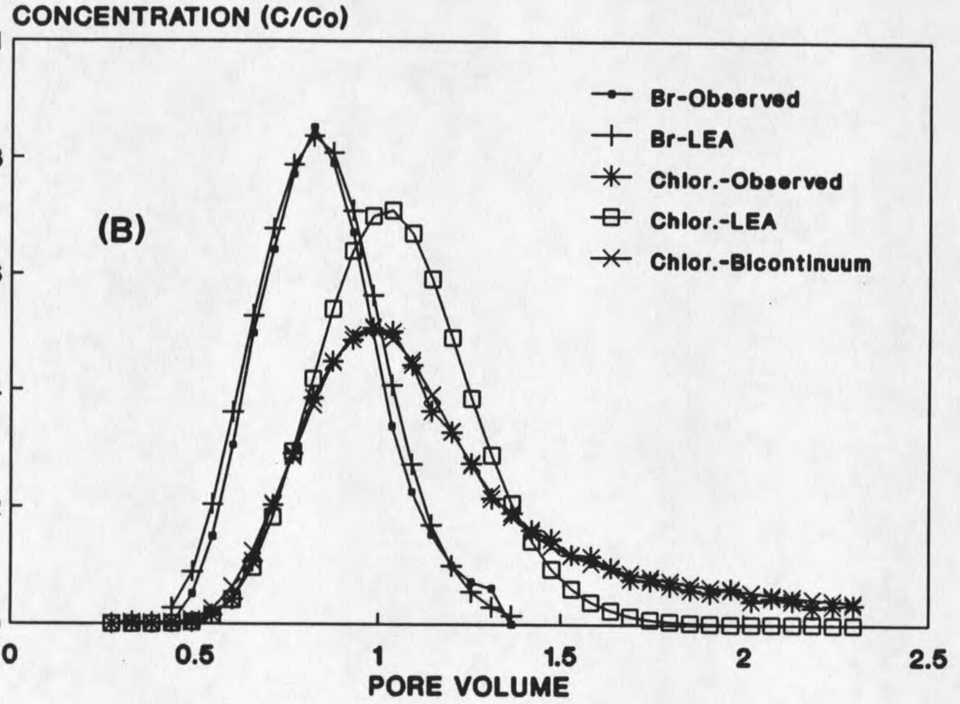


Figure 3. Breakthrough curves for Br^- and chlorsulfuron in disturbed columns of the (A) Amsterdam silt loam (Column 1, Rep. 1) and (B) Haverson silty clay loam (Column 5).

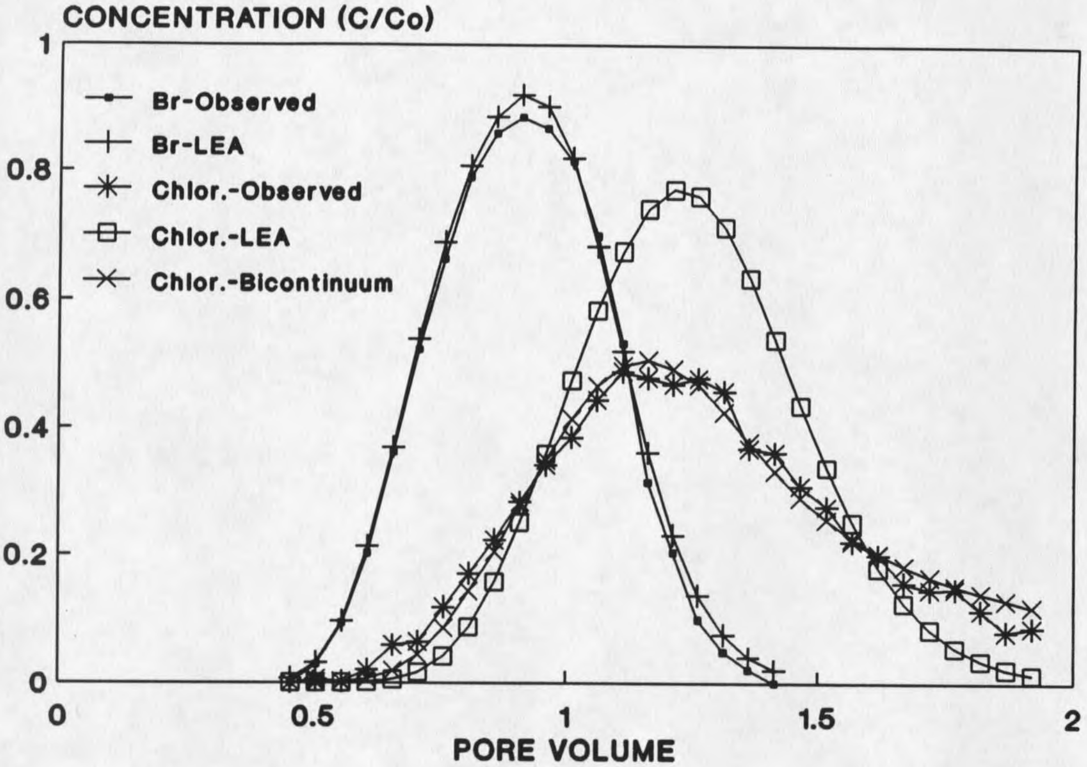


Figure 4. Breakthrough curves for Br^- and chlorsulfuron in an undisturbed soil column of Amsterdam silt loam (Column 3).

columns of the Haverson silty clay loam, D values obtained with the LEA model averaged 0.28 ± 0.08 cm^2 hr^{-1} over all columns (Table 2).

The retardation factor, R, was not fixed to 1.0 during optimization of D using the LEA model for the nonsorbing tracer. The primary reasons for allowing R to float were (i) the observation that apexes of the Br^- BTCs were significantly less than one pore volume, and (ii) recognition that anion exclusion may cause R values to be significantly less than 1. Retardation factors for Br^- averaged 0.78 ± 0.12 and 0.65 ± 0.01 for disturbed columns of the Amsterdam silt loam and Haverson silty clay loam, respectively, and 0.70 ± 0.02 for undisturbed columns of the Amsterdam silt loam.

Table 2. Dispersion coefficients (D, cm^2 hr^{-1}), retardation factors (R), β and ω values (standard error coefficients in parentheses), and r^2 values from CXTFIT analyses of Br$^-$ breakthrough curves.

Soil	Column	Linear Adsorption Model (Local Equilibrium Assumption)			Bicontinuum Model				
		D	R	r^2	D	R	β	ω	r^2
Amsterdam silt loam	1, Disturbed-Rep. 1	0.37(0.02)	0.62(0.003)	0.99	0.37(0.02)	0.62(.003)	0.78(0.03)	97(10)	0.99
	1, Disturbed-Rep. 2	0.29(0.02)	0.91(0.01)	0.98	0.30(0.01)	0.92(0.01)	0.78(0.005)	2826(398)	0.99
	1, Disturbed*	0.36(0.03)	0.86(0.01)	0.96	0.38(0.01)	0.85(0.01)	0.65(0.01)	4025(174)	0.95
	2, Disturbed*	0.36(0.02)	0.86(0.005)	0.99	0.36(0.03)	0.86(0.004)	0.72(0.01)	646(11)	0.99
	3, Undisturbed	0.20(0.01)	0.71(0.003)	0.99	0.20(0.01)	0.71(0.003)	0.64(0.005)	740(36)	0.99
	3, Undisturbed+	0.19(0.03)	0.70(0.007)	0.96	0.19(0.02)	0.70(0.01)	0.90(0.05)	340(40)	0.97
Haverson silty clay loam	4, Disturbed	0.25(0.02)	0.65(0.003)	0.99	0.24(0.02)	0.65(0.005)	0.71(0.05)	138(8)	0.99
	4, Disturbed*	0.40(0.04)	0.63(0.01)	0.96	0.43(0.02)	0.63(0.01)	0.69(0.01)	1463(35)	0.96
	5, Disturbed	0.25(0.02)	0.66(0.005)	0.98	0.24(0.02)	0.66(0.006)	0.64(0.03)	392(13)	0.98

* chlorsulfuron at 5X field rate
+ 2mM C as humic acid

Retardation factors for Br^- and other anions such as Cl^- are often found to be less than 1, and it is often assumed that anion exclusion is responsible for this observed negative adsorption (i.e. $K_d < 0$) (Gvirtzman et al., 1986; van Genuchten and Wierenga, 1977). In the present study, approximate anion exclusion volumes for the Amsterdam silt loam and Haverson silty clay loam were estimated to be 4.3% and 7.4%, respectively, of the total pore volume. These calculations were made using an average bulk density value of 1.20 g cm^{-3} and known clay contents (23.1% and 40.4%, respectively). Charge exclusion was assumed to be primarily due to the clay fraction. An average value of 1.5 x 10^5 m^2 kg^{-1} was used for clay surface area and an average double layer thickness of 0.5 nm was also assumed (van Olphen, 1977). These estimates of anion exclusion volume are consistent with the lower average R value obtained for the Haverson soil compared to the Amsterdam soil. Elprince and Day (1977) reported a specific anion exclusion volume of 0.3 cm^3 per gram of clay based on the assumption that exclusion was entirely due to negative adsorption of Cl^-. Our calculations (above) resulted in a smaller specific anion exclusion volume of 0.08 cm^3 per gram of clay and, therefore, underestimated anion exclusion volume by a factor of 4 if compared to the Elprince and Day findings. Although these estimates of anion exclusion volume are subject to some uncertainty, it is possible that additional mechanisms may be responsible for R values as low as 0.62 (Table 2). Such mechanisms may be associated with immobile water in the soil column which would not contribute to solute transport.

One approach for estimating the amount of immobile water involves interpretation of β obtained from the fit of Br^- BTCs to the bicontinuum model (Eqn. 4). For nonadsorbing solutes with K_d values approaching zero β reduces to θ_m/θ, where θ_m is the mobile volumetric water content and θ is the total volumetric water content. Values of β averaged 0.71 (n = 11) and 0.61 (n = 8) for disturbed and undisturbed columns, respectively, suggesting that approximately 30-40 percent of the volumetric water was immobile. Given these estimates of immobile water, the lack of physical nonequilibrium for Br^- transport is reflected in the large values of ω indicating that, although immobile water existed in the columns, the rate of solute exchange between mobile and immobile regions (i.e. the α^* term in Eqn. 4) was high enough to preclude physical nonequilibrium.

A second approach for evaluating immobile water involves fitting Br^- BTCs using the LEA model by fixing R = 1, and optimizing v. Fitted and measured pore water velocities (v) can be used to calculate θ using $v = q/\theta$ where q is the experimentally measured water flux. Fitted values of v yield an estimate of the mobile volumetric water content, θ_m, which can be compared to the total volumetric water content for an estimate of immobile water. Estimated percentages of immobile water ranged primarily from 30-38% for undisturbed and disturbed columns (Table 3) and were consistent with values obtained using β from the bicontinuum model. The immobile water fractions may represent contributions from both stagnant soil water and anion exclusion. Based on the estimates presented for anion exclusion volume (see above) and the calculated immobile water fraction for both soils, we feel that a significant fraction of the soil water did not participate in transport and made significant contributions to R values less than 1. These estimates of the immobile water fraction are somewhat lower than those reported by

Table 3. Derivation of immobile water fraction from measured and fitted Br$^-$ pore water velocities.

		Pore Water Velocity		Volumetric Water Fraction		Percent Immobile water
Soil	Column	Measured	Fitted	Total	Mobile	
		-------- cm hr^{-1} --------		------ cm^3 cm^{-3} ------		
Amsterdam silt loam	1, Disturbed-Rep. 1	0.40	0.64	0.43	0.27	38
	1, Disturbed-Rep. 2	0.41	0.45	0.44	0.40	9
	1, Disturbed*	0.41	0.48	0.44	0.38	14
	2, Disturbed*	0.45	0.53	0.40	0.35	14
	3, Undisturbed	0.44	0.62	0.43	0.30	30
	3, Undisturbed+	0.43	0.61	0.43	0.30	30
Haverson silty clay loam	4, Disturbed	0.42	0.65	0.43	0.28	35
	4, Disturbed*	0.41	0.65	0.44	0.28	37
	5, Disturbed	0.40	0.61	0.44	0.29	34

* chlorsulfuron at 5X field rate
+ 2m$\underline{M}$ C as humic acid

Singh and Kanwar (1991) (49-56%), which is consistent with the fact that their columns contained numerous macropores and that the experiments were conducted under saturated flow conditions.

Chlorsulfuron Breakthrough Curves

Observed breakthrough curves for chlorsulfuron were asymmetrical and exhibited significant tailing compared to BTCs for the nonsorbing solute, Br^- (Figures 3 and 4). Attempts to fit chlorsulfuron BTCs to the LEA model fixing D obtained from the Br^- BTCs resulted in poor fit (Figures 3 and 4) with r^2 values as low as 0.14 (Table 4). Allowing D to float in the LEA model resulted in better fit; however, this simply causes D to become an adjustable parameter which effectively compensates for nonequilibrium behavior of chlorsulfuron. Given that Br^- BTCs exhibited no significant physical nonequilibrium it is appropriate to utilize D optimized from the results of Br^- BTCs (Table 2) for fitting chlorsulfuron BTCs (Brusseau and Rao, 1989). Furthermore, any nonequilibrium behavior exhibited by chlorsulfuron is predominantly chemical in nature and should be adequately described by a bicontinuum model were the β and ω terms now reflect chemical nonequilibrium (Parker and Van Genuchten, 1984; Brusseau et al., 1989; Brusseau and Rao, 1989). Results of fitting the chlorsulfuron BTCs to the bicontinuum model where D was fixed show excellent fit to the observed data (Figures 3 and 4) with r^2 values ranging from 0.97-0.99. Comparison of the LEA vs. the bicontinuum model BTC fits for chlorsulfuron demonstrates the importance of considering chemical nonequilibrium for chlorsulfuron transport (Figures 3 and 4). Batch determined K_d values for chlorsulfuron were 0.068 (± 0.066) and 0.006 (± .001) L kg $soil^{-1}$ for the

Table 4. Dispersion coefficients (D, cm^2 hr^{-1}), retardation factors (R), β and ϖ values (standard error coefficients in parentheses), and r^2 values from CXTFIT analyses of chlorsulfuron breakthrough curves.

Soil	Column	Linear Adsorption Model (Local Equilibrium Assumption					Bicontinuum Model			
		D optimized from Br$^-$ BTC		D Fitted			D optimized from Br$^-$ BTC			
		R	r^2	D	R	r^2	R	β	ϖ	r^2
Amsterdam silt loam	1, Disturbed-Rep. 1	1.00(0.02)	0.57	0.90(0.04)	1.07(0.01)	0.97	1.12(0.01)	0.74(0.01)	1.04(0.03)	0.99
	1, Disturbed-Rep. 2	1.25(0.03)	0.14	1.00(0.09)	1.42(0.03)	0.86	1.72(0.03)	0.64(0.10)	0.86(0.04)	0.98
	1, Disturbed*	1.07(0.02)	0.54	0.94(0.06)	1.17(0.02)	0.94	1.35(0.01)	0.70(0.01)	0.71(0.03)	0.99
	2, Disturbed*	1.15(0.02)	0.58	0.98(0.05)	1.26(0.02)	0.95	1.39(0.01)	0.73(0.01)	0.78(0.04)	0.99
	3, Undisturbed	1.04(0.02)	0.30	0.73(0.05)	1.10(0.02)	0.95	1.27(0.03)	0.72(0.01)	0.85(0.07)	0.98
	3, Undisturbed+	1.15(0.02)	0.62	0.49(0.04)	1.20(0.02)	0.90	1.54(0.05)	0.71(0.02)	0.48(0.03)	0.99
Haverson silty clay loam	4, Disturbed	0.87(0.02)	0.73	0.67(0.05)	0.92(0.01)	0.96	1.03(0.01)	0.77(0.01)	0.61(0.04)	0.99
	4, Disturbed*	0.87(0.02)	0.69	0.68(0.05)	0.93(0.01)	0.94	1.10(0.01)	0.73(0.01)	0.55(0.02)	0.99
	5, Disturbed	0.92(0.01)	0.95	0.55(0.03)	0.94(0.01)	0.98	1.01(0.03)	0.87(0.02	0.23(0.05)	0.99

* chlorsulfuron at 5X field rate
\+ 2mM C as humic acid

Amsterdam and Haverson soils, respectively. Although it would be appropriate to fix R based on these batch K_d values in the bicontinuum model (Brusseau et al., 1989; Brusseau et al., 1991), we allowed R to float for the following reasons: chlorsulfuron is very weakly adsorbed and it is difficult to experimentally measure accurate batch K_d values in this range, and comparison of batch K_d values with K_d values generated from the bicontinuum model were within experimental error of the batch K_d values.

It is difficult from our data to partition the observed chemical nonequilibrium for chlorsulfuron into rate-limiting sorption-desorption processes or intraparticle diffusion (Brusseau et al., 1989). However, given the fact that the observed and fitted K_d for chlorsulfuron in these soils is very low, it is unreasonable to expect that a significant fraction of chlorsulfuron would actually be affected by rate limiting adsorption-desorption processes. Conversely, chlorsulfuron may be influenced by intraparticle diffusive mass transfer to a greater extent than would Br^- due to differences in chemical structure and molecular weight. Additional work would be necessary to evaluate the exact mechanisms responsible for the chemical nonequilibrium observed for chlorsulfuron transport. However, it is clear from the ω values obtained with the bicontinuum model (ranging from .2 to 1) for both soils (Table 4) that chlorsulfuron exhibited significant departure from the LEA model (also see Figures 3 and 4).

Complexation of organic compounds with dissolved or suspended organic solids has been shown to affect the transport of certain solutes (Lafrance et al., 1989a; Lafrance et al., 1989b). Two undisturbed soil column replicates included addition of 2 mM C as humic acid to the usual pulse solution of Br^-, chlorsulfuron, and 3 mM $CaCl_2$. The observed BTCs did not appear significantly different with respect to D or R values for either the Br^- or chlorsulfuron data (Tables 2 and 4). Since chlorsulfuron is already extremely water soluble at pH 7, soluble organic C did not play an important role in accelerating chlorsulfuron transport.

LEACHM Predictions

Breakthrough curves for chlorsulfuron were predicted using LEACHM with two sets of K_{oc} and dispersivity (λ) values generated from CXTFIT: (i) those obtained using the LEA model where R and D were allowed to float, and (ii) those obtained from the bicontinuum model where D was fixed from the Br^- BTC and R was optimized (Figure 5). Predicted results using inputs from the LEA model were closer to the observed data, whereas predicted BTCs using inputs from the bicontinuum model demonstrated a significant right-handed displacement relative to observed BTCs (Figure 5). A right-handed displacement of predicted chlorsulfuron BTCs from LEACHM using inputs from the bicontinuum model can be explained by the larger R and smaller D values compared to those generated using the LEA model where both R and D were fitted (Table 4). We previously showed (Table 4) that both the LEA (R and D floating) and the bicontinuum model resulted in adequate chlorsulfuron BTC fit using CXTFIT. However, LEACHM does not accept inputs related to nonequilibrium transport (β and ω); therefore, using D and R values from the bicontinuum model only provides LEACHM a partial explanation of the chlorsulfuron BTCs. Although the LEA model (where R and D are both floated) may not provide an accurate mechanistic interpretation of the chlorsulfuron BTCs, inputs from this CXTFIT solution of the BTCs provides LEACHM apparent values of D and

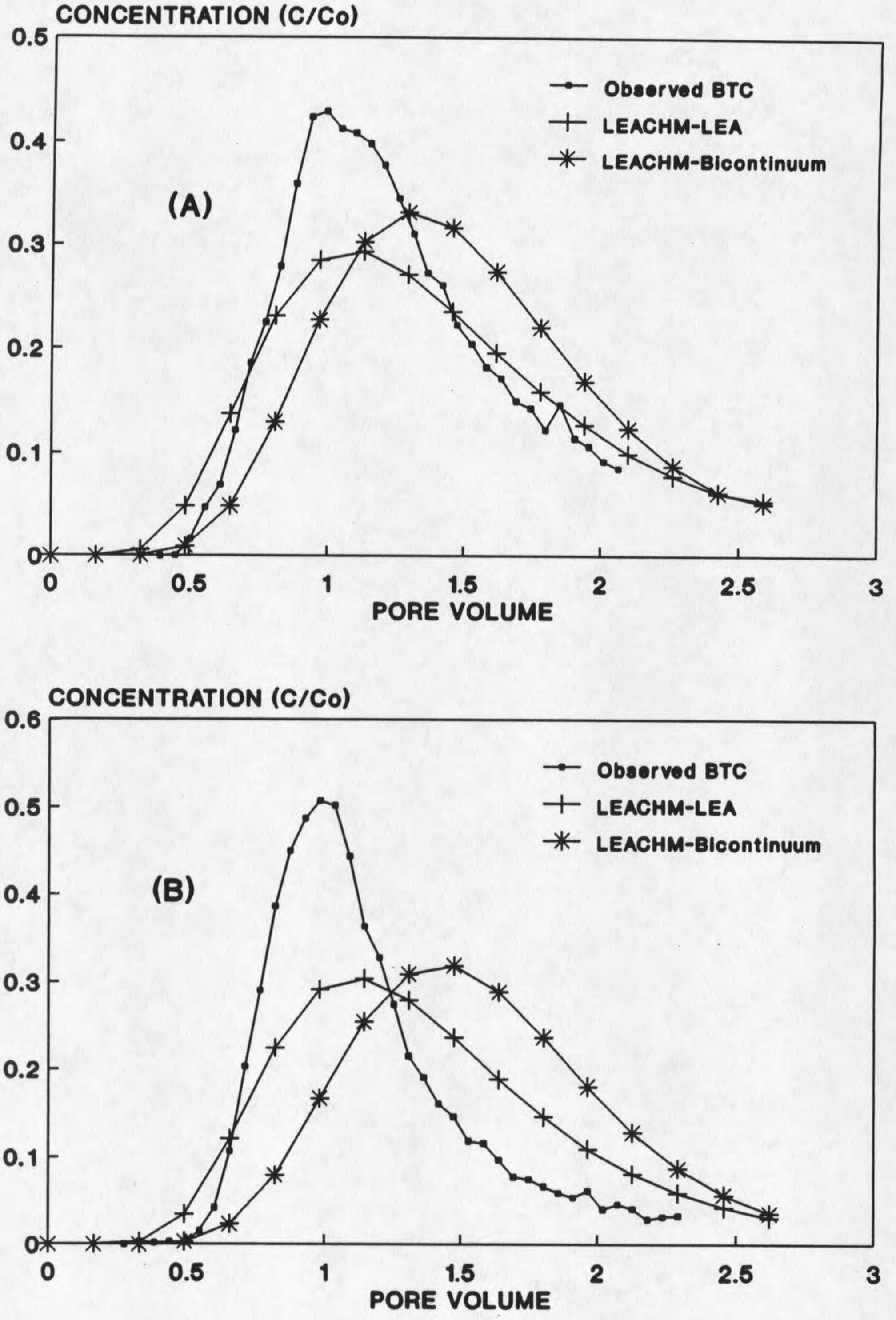


Figure 5. Comparison of observed chlorsulfuron BTCs in disturbed soil columns of (A) Amsterdam silt loam (Column 1, Rep. 1) and (B) Haverson silty clay loam (Column 5) with BTCs generated using LEACHM.

R which more adequately predict observed BTCs. In both cases, the predicted BTCs show lower apex concentrations than observed BTCs (Figure 5).

Input of accurate K_s values in LEACHM is important in obtaining predicted chlorsulfuron BTCs. LEACHM predictions were generally based on K_s values calculated from the Campbell's equation and the measured $K(\theta)$ specific to each column experiment. Experimentally measured K_s values for disturbed columns of the Amsterdam soil averaged 228 mm day^{-1}, very close to the calculated value of 231 mm day^{-1} (Table 5). However, this approach resulted in qualitatively reasonable predictions of chlorsulfuron BTCs (Figure 6B) using LEA inputs for K_{oc} and λ (as discussed above). For comparison, K_s values were estimated using regression equations based on measured soil texture and bulk density described by Rawls and Brakensiek (1989). Estimated K_s values were consistently 5 to 10 times lower than calculated K_s values (Table 5), and where used as input values to LEACHM, resulted in significant right-handed displacement of predicted chlorsulfuron BTCs (Figure 6A). These comparisons suggest that the applicability of generalized regression equations for estimating soil hydraulic properties for predicting solute transport may be limited.

Peclet number ($P = vL\,D^{-1}$; where v is pore water velocity, L is column length, and D is the apparent dispersion coefficient) and collection interval (sample size per fraction) both have been shown to affect the accuracy of estimating dispersion coefficients by assignment of effluent concentration values to the end of the sampling interval (Parlange and Starr, 1978; Schnabel and Richie, 1987). Peclet numbers for these experiments with chlorsulfuron ranged from 11 to 25 with an approximate sample size

Table 5. Input parameters to LEACHM for predicting chlorsulfuron breakthrough curves.

		Chlorsulfuron			Soil Properties							
Soil	Column	K_{oc}	Applied Cone.	θ	Bulk Density	Profile depth	Dispersivity	AEV #	BCAM #	K (θ) ‡	K_s calc.§	K_s est.¶
		(L kg^{-1})	(mg L^{-1})		(Mg m^{-3})	(mm)	(mm)	(k Pa)		mm day^{-1}		
Amsterdam silt loam	1, Disturbed-Rep. 1	2.23† (3.76)	0.073	0.43	1.29	295	22.6† (9.3)	-4.23	3.28	40.8	231	64
	3, Undisturbed	2.99 (7.70)	0.073	0.43	1.42	305	16.9 (4.5)	-5.59	3.36	45.5	96	28
Haverson silty clay loam	4, Disturbed*	-2.35 (0.37)	0.365	0.44	1.18	302	13.4 (9.8)	-3.89	4.16	43.3	581	63
	5, Disturbed	-2.70 (3.88)	0.073	0.44	1.11	295	16.8 (6.2)	-3.30	4.03	42.0	1036	105

† Unbracketed values are LEA derived; bracketed valves are bicontinuum derived

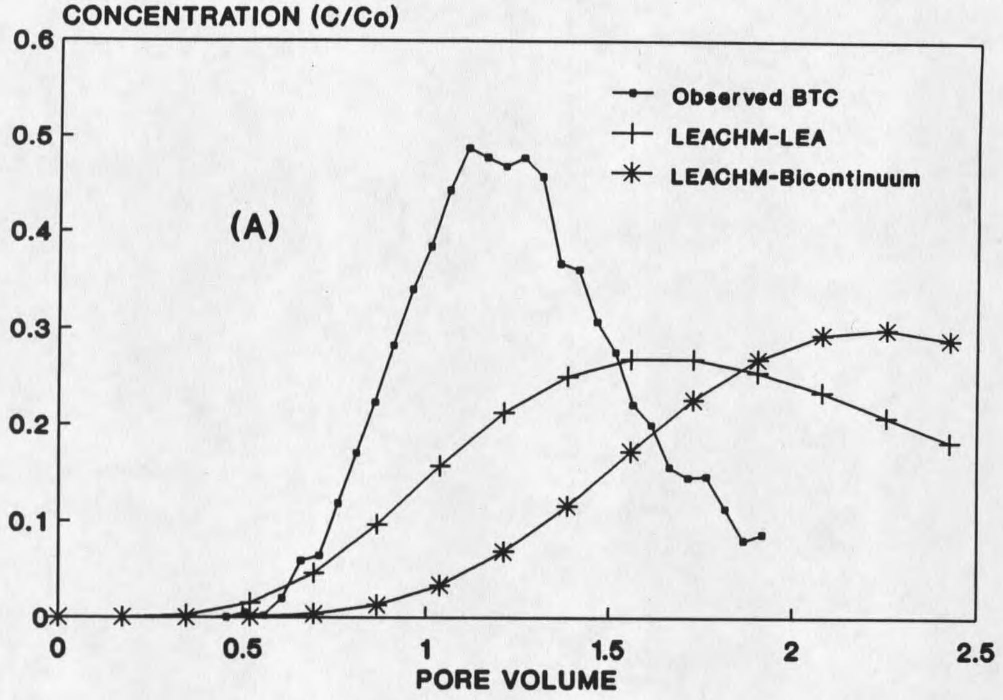
‡ Hydraulic conductivity at given θ value is equivalent to rate of solution application

§ Calculated from Campbell's Equation and measured K(θ)

¶ Estimated from Rawls and Brakensiek (1989)

AEV = air entry value; BCAM = exponent in Campbell's equation

* Chlorsulfuron at 5X field rate



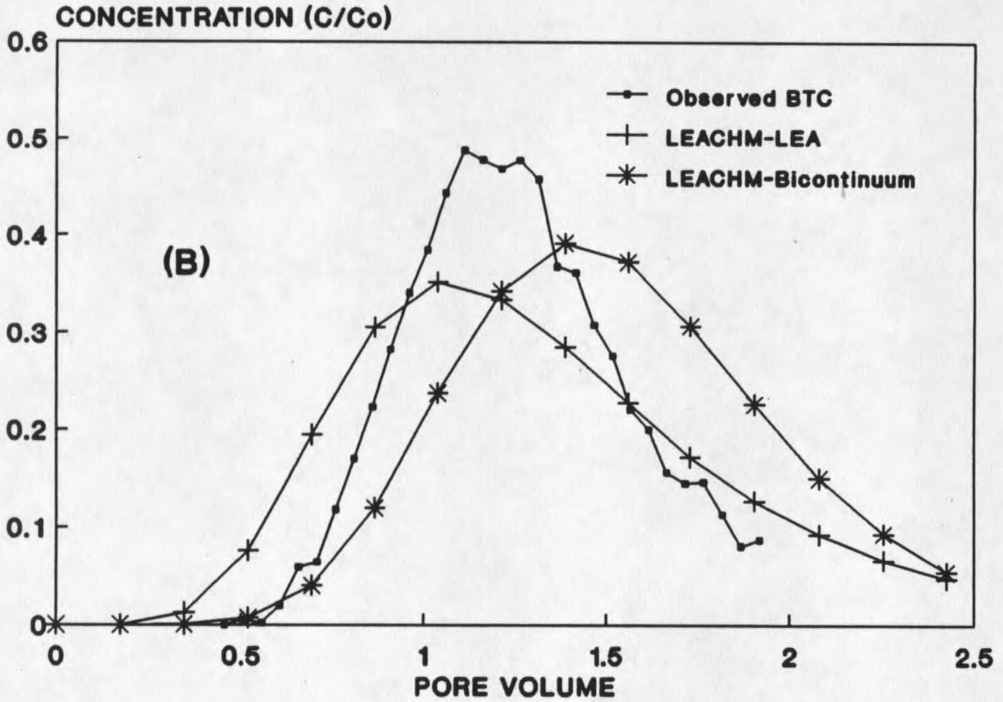


Figure 6. Comparison of observed and LEACHM-generated BTCs for chlorsulfuron in an undisturbed soil column of Amsterdam sil (Column 3), using (A) estimated K_s value and (B) calculated K_s value.

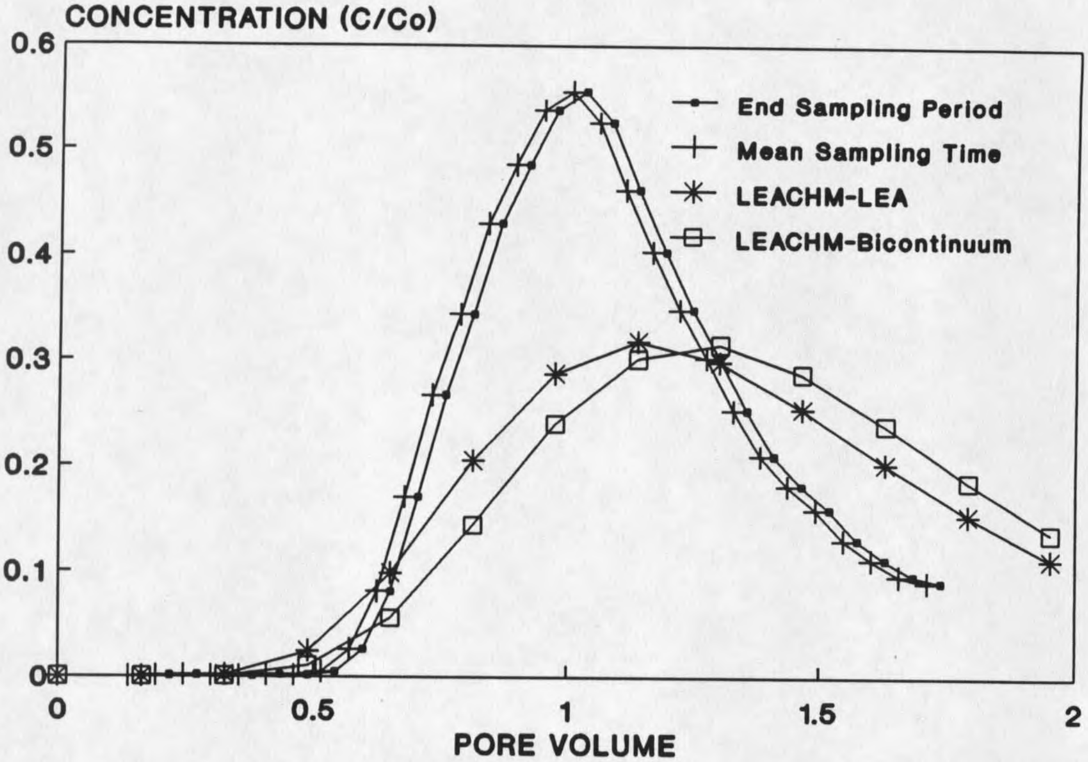


Figure 7. Effect of assigning sampling time to the end or mean of the sampling period on the observed chlorsulfuron BTC in a disturbed soil column of Haverson sicl (Column 1).

of 0.05 pore volumes. Observed column effluent data and predicted effluent data using LEACHM were generally assigned to the end of the sample interval. An alternative approach to generating BTCs is to assign solute concentrations to the medium sample interval. A comparison of observed BTCs assigning chlorsulfuron concentrations to the end versus the middle of each sampling interval was made for a disturbed column of the Haverson soil (Figure 7). A comparison of our experimental conditions (i.e. Peclet number and sample size) with comparable conditions in Table 1 of Schnabel and Richie (1987) suggests that an approximate error of 10% in the concentration vs. pore volume plot should have resulted from assignment of effluent data to the end instead of the middle of the fraction collection period. However, our data suggests an approximate deviation of only 3-4% in terms of pore volumes. Consequently, assigning effluent concentration data to the end of the sampling interval appears satisfactory for column conditions in the current study.

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CHAPTER 3

SOIL DEPTH AND TEMPERATURE EFFECTS ON DEGRADATION RATES OF 2,4-D

Introduction

The transport and degradation of soil contaminants within the unsaturated vadose zone is of national concern as we attempt to assess the potential for contamination of our groundwater systems. It is well known that microbial degradation is an important process for the fate of contaminants in soil systems. Traditionally, microbial numbers have been assumed to decrease with soil depth (Alexander, 1977), thus increasing the likelihood of persistence of mobile compounds which readily move out of the biologically active surface layer. This assumption has been supported by studies in which the maximum degradation rate of organic contaminants like phenol (Dobbins et al., 1987) and metribuzin (Moorman and Harper, 1989) has been shown to decrease significantly with increasing soil depth. Lower relative degradation rates in subsurface soils have been attributed to differences in temperature, soil water content, soil type, and decreasing microbial populations with depth (Kempson-Jones and Hance, 1979; Dobbins et al., 1987). Soil water content directly influences soil oxygen content and microbial activity and therefore can influence pesticide persistence. For example, the half-life of alachlor increased from 23 days in surface soil (aerobic conditions) to over 100 days in the vadose zone (anaerobic conditions) (Pothuluri et al., 1990). Also, the aerobic environment of an upland Maahas clay soil promoted greater 2,4-D degradation than in the same soil in a submerged condition (Yoshida and Castro, 1975). One of the established enzymatic degradation pathways of 2,4-D by Arthrobacter sp. (Loos et al., 1967; Bollag et al., 1968a; Bollag et al., 1968b; Tiedje et al., 1969, Tiedje and Alexander, 1969) proceeds by an oxidative process. Consequently, degradation rates may be lower in subsurface soil horizons as a result of reduced O_2 contents.

Although subsurface environments were often thought to be devoid of microbial activity, recent studies show considerable microbial activity in aquifers and sediments. For example, at a depth of 7 m below the water table, Hirsch and Rades-Rohkohl (1983) characterized 90 morphological types of microbes of which 20 were identified as facultative anaerobes. Bacteria isolated in this study grew well at groundwater temperature (9 °C) and developed best on oligotrophic media. Other studies indicate that appreciable numbers of microbes exist in subsurface aquifer sediments (Ghiorse and Balkwill, 1983; Balkwill and Ghiorse, 1985; Beloin et al., 1988; Bone and Balkwill, 1988; Konopka and Turco, 1991). These microbial populations were characterized as entirely different from those found to be dominant in the surface soils and generally much lower in total biomass; they were nutritionally versatile and adapted to survive under low-nutrient stress. Turco and Konopka (1989) reported that a microbial population located at 26 m in a sandy aquifer had the capability to degrade C sources equal to that of the population in the overlying surface soil. The most microbially active strata were those associated with the aquifer, which had organic C levels in excess of

1.6% and also higher amounts of total N and P compared to much lower levels found near the surface (0.37% organic C at 1.8 m). This implied that microbial activity was nutrient-limited in the vadose zone above the aquifer. These findings together with the observations that pesticide degradation rates decrease with soil depth in the rooting zone (Moorman and Harper, 1989; Pothuluri et al., 1990; Adams and Thurman, 1991) suggest that (i) soil depth is an important variable for predicting the fate of pesticides in modeling efforts, and (ii) the dependence of degradation rate on soil depth may be at least partially related to nutrient conditions.

Temperature has also been shown to significantly affect degradation kinetics of organic contaminants in soils. Walker and Zimdahl (1981) studied the effects of temperature on the persistence of atrazine and metolachlor in three soil types and linuron in two different soils. For temperature treatments that increased from 5°C to 35°C, corresponding half-lives decreased for atrazine by factors ranging from 7 to 9, for metolachlor by factors ranging from 6 to 8, and for linuron by a factor of about 4.5. Ou (1984) found that the disappearance rate of 2,4-D was reduced in two soils incubated at 35°C compared to the same two soils incubated at 25°C. Padilla et al. (1988) used the Arrhenius and Van't Hoff equations in a transport model (MELEF-3v) to predict the effect of temperature variations on the concentration profile of atrazine in the subsurface. Two model simulations with respective temperature gradients of 15°C to 5°C and 25°C to 15°C from the soil surface to a 1 m soil depth were used to predict atrazine concentration profiles after one year. When these results were compared to atrazine concentration profiles generated assuming uniform profile temperatures (5°C and 15°C), the predicted atrazine peak concentrations increased by 70% and 90%, respectively. Consequently, temperature effects may increase the persistence of pesticides in soils and groundwater in temperate climates, where dramatic seasonal temperature variations occur. In northern latitudes many soils are classified in the frigid or cryic temperature regimes. Mean annual soil temperature (50 cm) in these soils is less than 8°C; therefore, increased persistence of pesticides can be expected, especially if leaching into the subsurface occurs.

Accurate assessment of degradation kinetics of organic contaminants in soils is critical to transport model predictions. Boesten and van der Linden (1991) investigated the effects of transformation rate on pesticide leaching and persistence models. They reported that changing the degradation rate by a factor of 2 changed the fraction of pesticide leached by about a factor of 10. Calculations in the models showed that fall application of nonsorbing pesticides with short half-lives increased pesticide leaching by two orders of magnitude over the same pesticides applied in the spring. A sensitivity analysis of an unsaturated zone transport model (PRZM) performed by Villeneuve et al. (1988) showed that a 15-22% variation in the degradation constant lead to a 100% uncertainty in the various simulation results of the amount of aldicarb leached below the root zone. Cohen et al. (1984) discussed the effectiveness of the one-dimensional transport model, PESTANS, and suggested that models of this type must allow the user to vary the transformation rate of a contaminant with depth in order to account for differences in parameters such as dissolved oxygen and microbial populations which occur in heterogeneous (layered) systems.

Of the herbicides used extensively in Montana, 2,4-D is still the most commonly used herbicide for broadleaf weed control in cereal grain production. Regional groundwater monitoring programs (DeLuca et al., 1989) have shown a number of wells contaminated with 2,4-D; consequently, there is significant concern about the fate and transport of 2,4-D under regional environmental conditions in surface and vadose zone soils. Thus, the objectives of the current study were to determine the effects of soil depth and soil temperature on the degradation rates of 2,4-D in representative Montana soils. Results from this work were intended to yield a preliminary indication of how degradation subroutines in transport models may be modified to account for changes in degradation rate as a function of soil depth and soil temperature.

Materials and Methods

Soils

Soil samples were taken from two sites in Montana from the 0-30 cm, 30-60 cm, and 60-120 cm depths, corresponding to the A, B, and C horizons of each soil. One of the soils was an Amsterdam silt loam (fine-silty mixed Typic Haploboroll) from a site near Bozeman, MT, and the other was a Haverson silty clay loam (fine-loamy mixed (calcareous) Mesic Ustic Torrifluvent) from Huntley, MT (Table 6). The pipette method of particle-size analysis was performed on the 0-30 cm depth increment of each soil; the 30-60 cm and 60-120 cm depths of each soil were characterized for soil texture using the hydrometer method of mechanical analysis (Day, 1965). Each soil was also analyzed for total organic C (Snyder and Trofymow, 1984), cation exchange capacity (Chapman,

Table 6. Characteristics of soils used in the degradation experiments and associated bacterial plate counts.

Soil type and (Classification)	Soil depth (cm)	clay	silt	sand	organic carbon	Soil pH (1:1)	CEC mmol charge kg^{-1}	R2A media	2,4-D media	% 2,4-D degraders
		---------------- g kg^{-1}	----------------					-- CFU†/g soil x 10^5 --		
Amsterdam silt loam	0-30	231	606	163	10.6	6.9	0.21	123.0	31.7	25.8
	30-60	300	610	90	8.1	7.4	0.21	26.3	2.3	8.7
(Typic Cryoboroll)	60-120	280	650	70	4.7	8.0	0.17	17.4	2.2	12.6
Haverson silty clay loam	0-30	404	414	182	10.1	7.1	0.24	174.0	12.0	6.9
	30-60	500	360	140	6.1	7.8	0.25	34.7	---‡	---‡
(Mesic Ustic Torrifluvent)	60-120	530	390	80	4.4	8.3	0.26	10.6	0.5	4.7

† CFU = colony forming units

‡ data not reported; CFU in control media (i.e. mineral salts media without 2,4-D) > CFU in presence of 2,4-D

1965), and soil pH using a 1:1 soil-water ratio.

Degradation Experiments

Soil samples were air-dried and passed through a 2 mm sieve. Subsamples of 75 g from each soil type and depth were weighed into 250 ml Erlenmeyer side-arm flasks to include 3 replicates and 1 control for each soil type/depth treatment. Three separate temperature experiments were conducted at 10°C, 17°C, and 24°C (± 1°C) by incubating the flasks in a constant temperature water bath (Figure 8).

A 25 ml solution of 2,4-D was applied to each flask to approximate a normal field rate application of 0.84 kg ha^{-1} and a gravimetric water content of 33% (dry soil basis). The applied solution per flask included approximately 0.145 μCi (5349 Bq) of carboxyl-^{14}C-labeled 2,4-D (specific activity = 8.5 mCi/mmol (3.145 x 10^{8} Bq/mmol); Sigma Chemical Company, St. Louis, MO), 28.56 μg of unlabeled 2,4-D (99% purity), and 0.11 mg of $CaCl_2$ at a pH of 7.3.

Each reaction flask was subjected to a flow rate of 1.9 ml min^{-1} of humidified, CO_2-free, compressed air. Evolved $^{14}CO_2$ was collected in a series of two 10 ml, 0.5 M NaOH traps. One ml aliquots from each trap were sampled every 24 hrs for the duration of the experiment (generally 10 to 12 d), added to 6 ml of scintillation cocktail (ScintiVerse E, Fisher Scientific), and analyzed by liquid scintillation techniques using a 2200CA Tri-Carb Liquid Scintillation Analyzer (Packard Instrument Company, Laguna Hills, CA). At the termination of each experiment, 1-2 g of soil from each reaction flask (duplicate subsamples) were combusted at 800°C for 4 minutes in a biological oxidizer

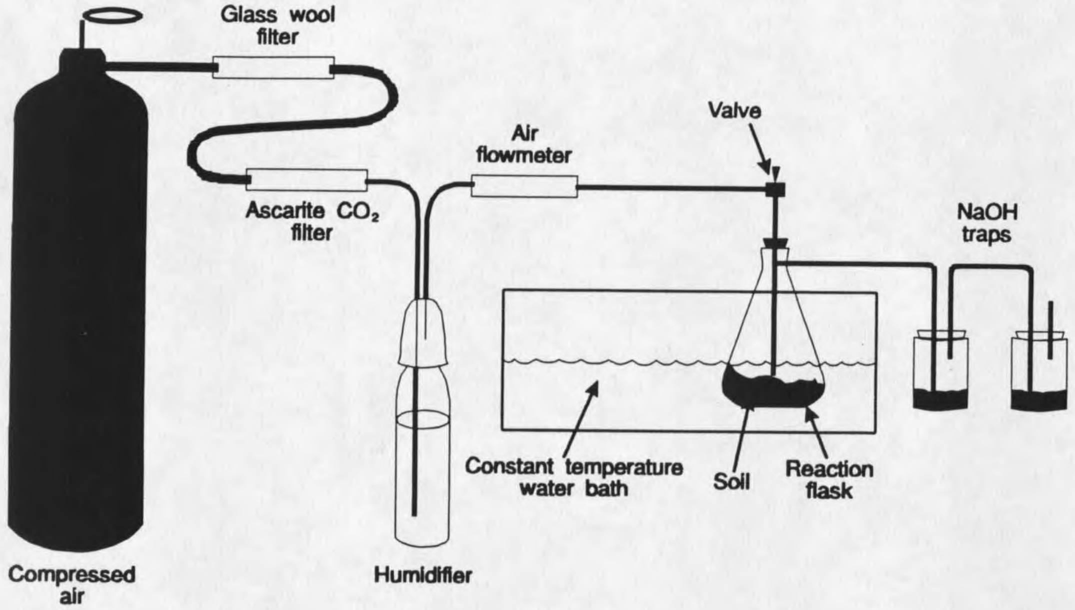

Figure 8. Schematic of apparatus used in 2,4-D degradation experiments.

(Model OM300, R.J. Harvey Instrument Corp., Hillsdale, N.J.). The $^{14}CO_2$ evolved from this oxidation was trapped in liquid scintillant (Part No. OX-161 Carbon-14 cocktail, R.J. Harvey Instrument Corp., Hillsdale, N.J.) and analyzed as described above. The overall average ^{14}C-recovery using the above method was 92%.

Logistic Equation and First-Order Kinetics

Cumulative disintegrations per minute (DPM) of evolved $^{14}CO_2$ were graphed as a function of sampling time (days). The resulting degradation curves were interpreted by fitting these data using SAS (SAS NLIN procedure, SAS Institute, 1985) to solve the integrated form of a logistic equation (Characklis, 1990), which can be used to describe accumulation of various components in batch reactor systems. The differential form of the equation is as follows:

$$\frac{dX}{dt} = k_1 X(1 - \frac{X}{X_m}) \tag{5}$$

where X is the component produced (fitted), k_1 is the effective process rate coefficient (fitted), and X_m is the maximum attainable product level (fitted), and t is time (known). The integrated form of Equation 5 is:

$$X = \frac{X_0 \, e^{k_1 t}}{1 - [(X_0/X_m)(1 - e^{k_1 t})]} \tag{6}$$

where X_o is the initial reactor component concentration. This form of the logistic equation does not assume any particular dependence of growth rate on substrate concentration (other than to state that X_m cannot be exceeded) and therefore cannot be used as a growth rate equation. However, despite this limitation the above form of the logistic equation can be used for empirically describing the accumulation rate (or evolution) of various components in a reactor (Characklis, 1990). A mathematically equivalent expression of Equation 6 can be derived using the phenomenological logistic equation of Simkins and Alexander (1984) in which k_1 includes effects of both growth rate and total substrate availability and X_m results directly from substrate availability.

The applicability of first-order degradation kinetics was also investigated by determining a rate constant from the equation:

$$\ln \frac{A}{A_0} = -kt \tag{7}$$

where A is DPM remaining at time t (which can be assumed to equal $[A_o]$ - cumulative DPM evolved), A_o is the initial amount of DPM added to the reaction flask, t is time, and k is the first-order rate constant. Half-lives were then calculated for all treatments using the following relationship for a first-order reaction:

$$t_{1/2} = \frac{0.693}{k} \tag{8}$$

where $t_{1/2}$ is half-life (d) and k (d^{-1}) is the first-order rate constant.

Bacterial Plate Counts

A relative estimate of total bacterial numbers was determined for each soil type and depth utilizing an oligotrophic plating medium, R2A (Difco Laboratories, Detroit, MI). The number of 2,4-D degrading organisms present was determined using mineral salts medium consisting of 12 g/L Noble agar (Difco Laboratories, Detroit, MI), 7 g/L K_2HPO_4, 3 g/L KH_2PO_4, 1 g/L $(NH_4)_2SO_4$, 0.1 g/L $MgSO_4$, and 0.46 mg/L 2,4-D, which approximated the initial concentration of 2,4-D applied to the soil in the reaction flasks. Control samples for each soil type and depth were also plated using the mineral salts medium in the absence of 2,4-D, so that final enumeration of 2,4-D degraders was obtained by difference.

Two 5 g subsamples of each soil type and depth were diluted in 9 ml of sterile deionized water and vortexed for approximately 3 minutes. Seven serial 1:10 dilutions were performed, and 100 μl aliquots of each serial dilution were transferred to triplicate plates of each medium. The plates were incubated at 24°C for 4 days (R2A) and 6 days (Noble agar). Colony forming units (CFU) per g soil were determined from geometric means of plate counts for dilutions which ranged from about 30-100 CFU per plate.

Results and Discussion

Soil Type and Depth Effects on 2,4-D Degradation

The two soils used in this study had similar soil properties; however, the Haverson soil contained significantly greater clay contents and showed higher CEC values at all depths than the Amsterdam soil (Table 6). The Haverson soil contained slightly higher total bacterial colony forming units (CFU) on R2A medium yet showed lower amounts of 2,4-D degrading organisms (Table 6). Consequently, the Haverson soil showed a lower percentage of 2,4-D degrading organisms than the Amsterdam soil. Figures 9 and 10 illustrate the effects of soil depth at 10, 17, and 24°C on degradation rates of 2,4-D in terms of cumulative disintegrations per minute (DPM) evolved as $^{14}CO_2$ for the Amsterdam and Haverson soils, respectively. An initial lag phase of minimal degradation was observed for all treatments. This initial lag phase has been observed in other studies on 2,4-D degradation (Audus, 1960; Mullison, 1970) and has been characterized as a period of adaptation in which the enzymes needed for decomposition of the substrate and its metabolites are synthesized from closely related enzymes (Torstensson, 1978). The lag phase increased and the maximum degradation rate of 2,4-

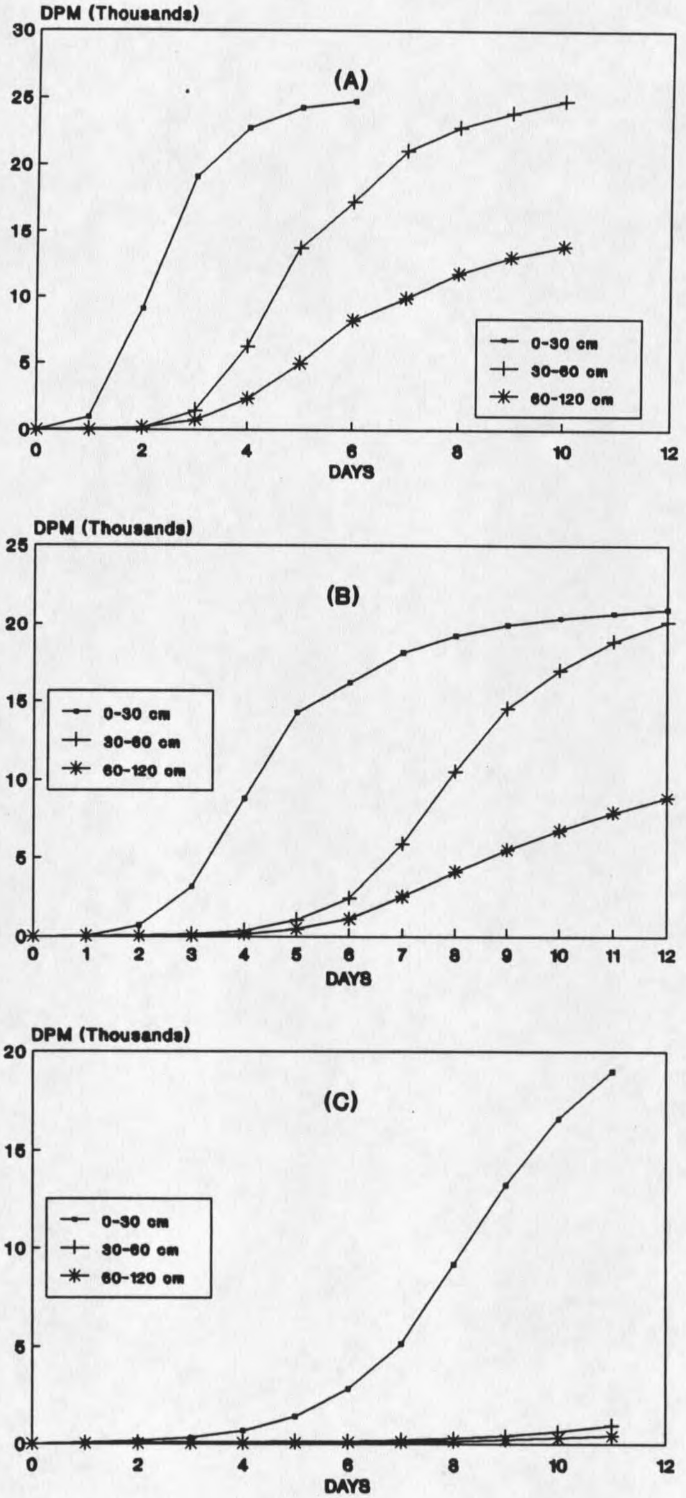

Figure 9. Soil depth effects on 2,4-D degradation rates in Amsterdam silt loam at (A) 24°C (B) 17°C and (C) 10°C.

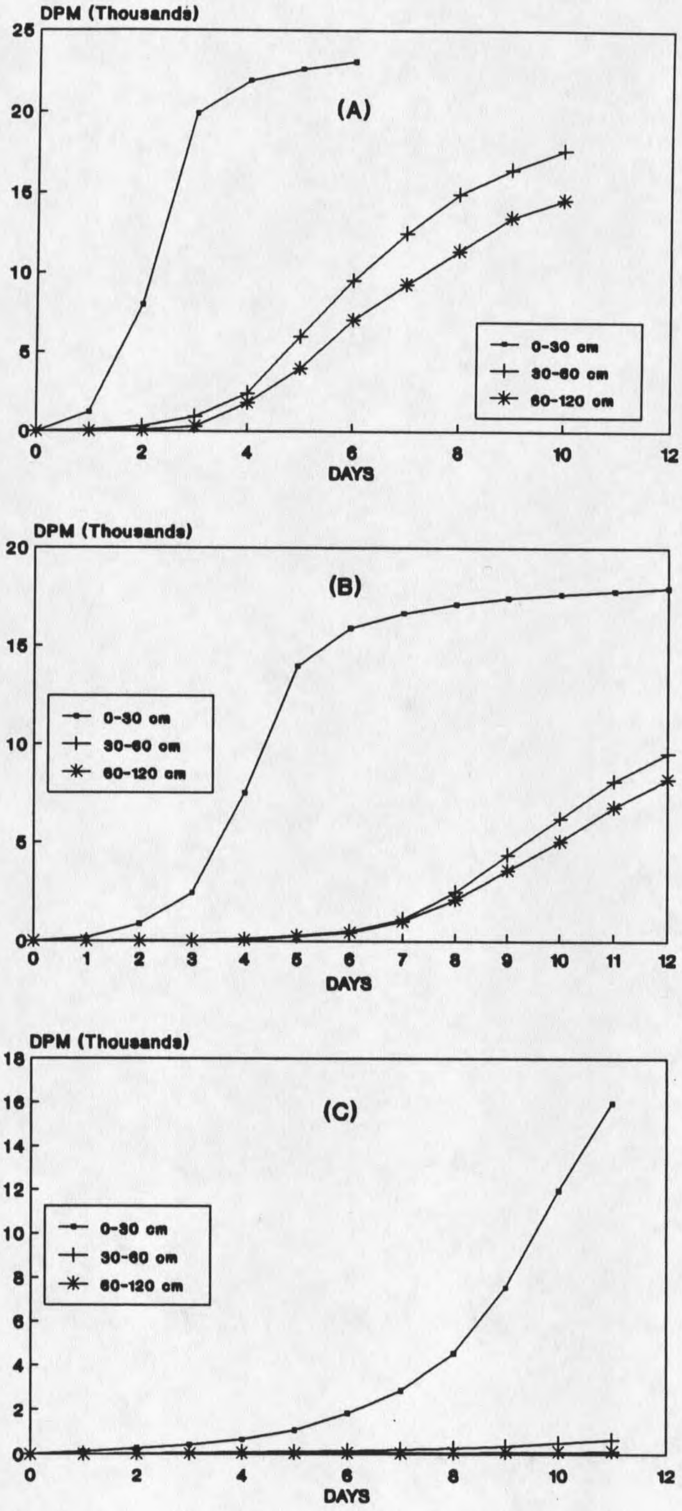

Figure 10. Soil depth effects on 2,4-D degradation rates in Haverson silty clay loam at (A) 24°C (B) 17°C and (C) 10°C.

D decreased with depth for each set of degradation curves for both soils. However, the difference in degradation rates between the 30-60 cm and 60-120 cm depths was more pronounced for the Amsterdam soil than for the Haverson soil, especially at 17°C and 24°C.

Process rate coefficients (k_1) obtained from fitting the degradation curves to a logistic model (Table 7) and first-order rate constants (k) and calculated half-lives ($t_{1/2}$) (Table 8) show the effects of soil depth on degradation rate. Rate coefficients and constants decreased and half-lives increased significantly with increasing soil depth. Degradation rate constants obtained from the logistic model decreased by a factor of 1.5 to 2 between the 0-30 cm and 60-120 cm depths within a given temperature treatment for the Amsterdam soil and by a factor of 2 to 3 for the Haverson soil (Table 7). First-order rate constants (Table 8) decreased by a factor of about 4 for the two highest temperature treatments for both soils and by a factor of 100 and 150, respectively, for the 10 °C treatment. The decrease in degradation rate coefficients with depth was consistent with a decrease in bacterial populations (Table 6). The Haverson soil generally showed lower degradation rates than the Amsterdam soil, which is consistent with the number of 2,4-D degrading bacteria (CFU) counted on 2,4-D media (Table 6). These findings agree with other studies showing a significant decrease in degradation rates of phenol, metribuzin, and alachlor in subsurface soils (Dobbins et al, 1987; Moorman and Harper, 1989; Pothuluri et al.,1990). In addition, these results are consistent with other studies showing a negative correlation between 2,4-D degradation rate (and microbial activity) and clay content (Smith, 1980; Beloin et al., 1988).

Table 7. Comparison of k_1 (hr^{-1}) and X_m (DPM) values obtained by fitting degradation curves (Figures 9 and 10) to a logistic equation.

Soil depth (cm)	Temperature °C	Amsterdam silt loam			Haverson silty clay loam		
		k_1	X_m	r^2	k_1	X_m	r^2
0-30	10	0.033	21322	0.99	0.024	31546	0.99
	17	0.045	20121	0.99	0.062	17483	0.99
	24	0.080	24272	0.99	0.104	22676	0.99
30-60	10	0.019	14681	0.99	0.013	4717	0.99
	17	0.039	20080	0.99	0.034	10384	0.99
	24	0.046	23981	0.99	0.036	17730	0.99
60-120	10	0.016	2817	0.99	0.008	730	0.99
	17	0.031	9174	0.99	0.032	9174	0.99
	24	0.037	13812	0.99	0.034	14993	0.99

Table 8. Rate constants (k [=] d^{-1}), half-lives ($t_{1/2}$ [=] d), and r^2 values calculated from fit of first-order kinetics to degradation curves in Figures 9 and 10.

Soil depth (cm)	Temperature °C	Amsterdam silt loam			Haverson silty clay loam		
		k	$t_{1/2}$	r^2	k	$t_{1/2}$	r^2
0-30	10	0.10	7	0.77	0.06	11	0.68
	17	0.11	7	0.93	0.08	8	0.87
	24	0.29	2	0.94	0.26	3	0.90
30-60	10	0.003	273	0.73	0.002	352	0.88
	17	0.09	8	0.84	0.03	25	0.77
	24	0.17	4	0.94	0.09	8	0.93
60-120	10	0.001	593	0.81	0.0004	1691	0.95
	17	0.03	25	0.86	0.02	31	0.77
	24	0.06	12	0.94	0.07	10	0.91

Temperature Effects on 2,4-D Degradation

Generally, there was an increase in the lag phase and a decrease in the maximum rate of degradation for both soils with decreasing temperature (Figures 9 and 10). This effect is particularly apparent between the 10°C and 17°C treatments for the 30-60 cm and 60-120 cm depths in both soils. Again, rate coefficients (k_1) obtained from fitting the degradation curves to a logistic model (Table 7) and first-order rate constants (k) and calculated half-lives ($t_{1/2}$) (Table 8) illustrate the effects of soil temperature on 2,4-D degradation. A comparison of the 10°C and 24°C treatments shows that values of k_1 in the logistic model (Table 7) increased by a factor of 2.5 to 3 for the Amsterdam soil and by a factor of 3 to 4 for the Haverson soil. A similar increase in the first-order rate constants (k) with increasing temperature was observed for the 0-30 cm depth for both soils (Table 8). However, k values for the 30-60 cm and 60-120 cm depths increased by a factor of 45 to 175 over the two temperature extremes.

The temperature effects reported here are consistent with other published results of the effect of temperature on the persistence of 2,4-D. For example, Parker and Doxtader (1983) reported a significant increase in first-order rate constants for 2,4-D degradation from 20°C and to 27°C at four moisture tensions ranging from 0.10 to 1.00 bars. However, rate constants decreased significantly between 30°C and 35°C for the 0.10 bar moisture treatment, indicating that an optimum degradation temperature existed. In addition, Smith and Hayden (1981) studied the persistence of 2,4-D in a Regina heavy clay soil. They observed rapid degradation of 2,4-D with half-life values of approximately 7 days at soil temperatures ranging from 15-25°C. However, a significant decrease in degradation was noted at lower soil temperatures.

Kinetics of 2,4-D Degradation

Two empirical kinetic models (i.e. logistic and first-order) based on dissimilar degradation mechanisms (Alexander and Scow, 1989) were evaluated to fit the experimental data. An example of the results of fitting both models to one set of degradation curves is shown in Figure 11. The logistic equation of Characklis (1990) provided excellent fit to the experimental data ($r^2 = 0.99$) (Table 2). The fit of degradation curves to the first-order kinetic model was poorer as indicated by lower r^2 values for all treatments (Table 8). The logistic model contains three empirical parameters, whereas the first-order model contains only one empirical parameter. Generally, the regression r^2 values for the first-order model were poorest at the low temperature (10°C). This is probably due to the fact that our experiments were terminated prior to the onset of log phase growth in the 10°C treatments. Although first-order kinetics provided only marginal fits to the experimental data, the half-life values (Table 8) are generally in agreement with those reported in other studies (Altom and Stritzke, 1973; Foster and McKercher, 1973; Smith, 1980; Smith and Hayden, 1981).

First-order biodegradation is usually observed when the process is limited by a reactant (e.g. substrate). Simkins and Alexander (1984) describe the necessary conditions for first-order mineralization of substrate as $X_o >> S_o$ and $S_o << K_s$, where X_o is initial biomass concentration, S_o is initial substrate concentration, and K_s is the saturation rate coefficient. This leads to the derivation of the first-order rate constant, $k = \mu_{max}X_o/K_s$. The logistic equation described by Characklis (1990) assumes no dependence

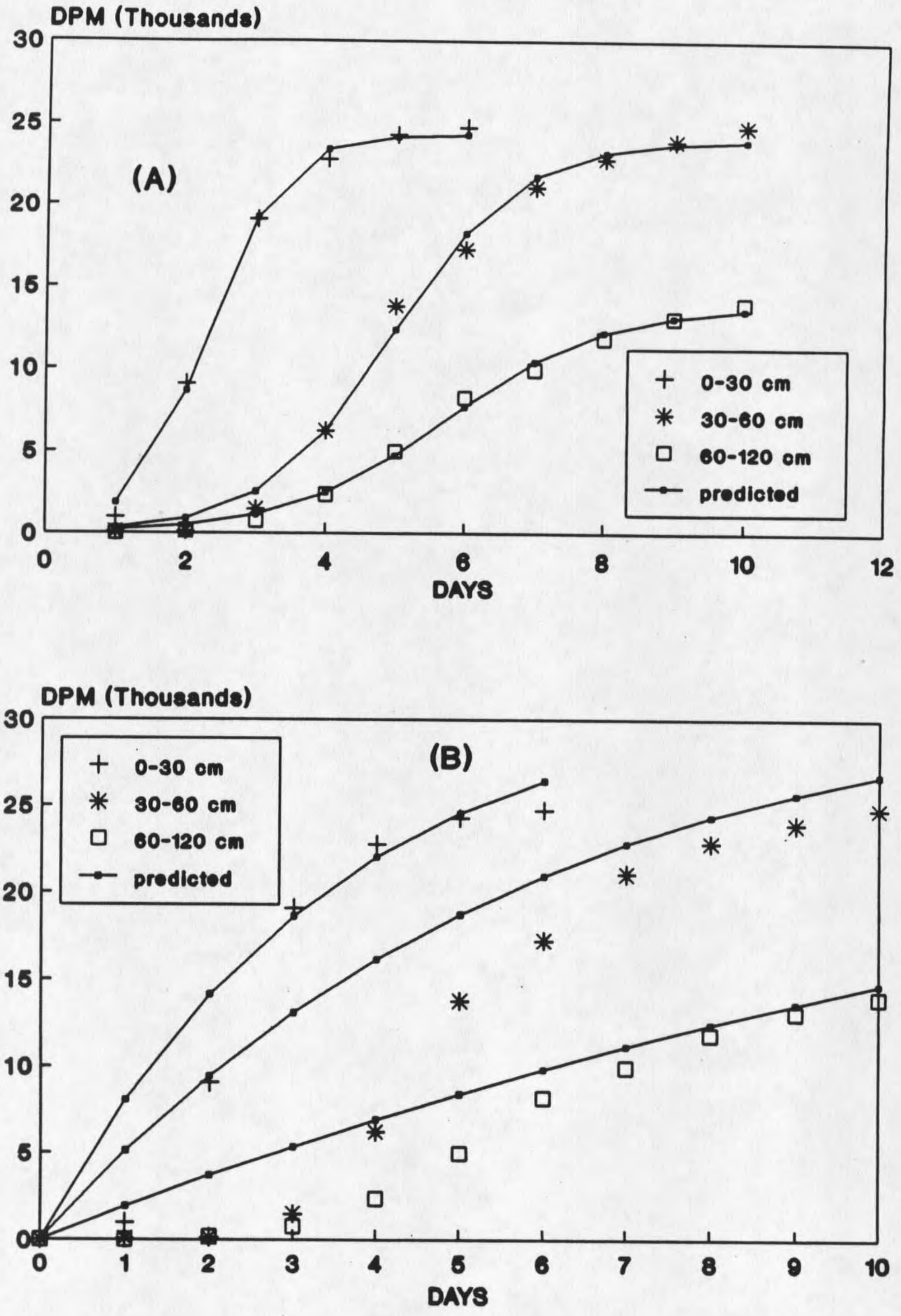

Figure 11. Observed and predicted degradation curves at 24 °C for Amsterdam silt loam (Figure 9A) fit to (A) a logistic model and (B) first-order kinetics.

of growth rate on substrate concentration and simply describes the accumulation rate of a reactor component. We conclude that the reason this form of the logistic equation fit the experimental degradation curves so well is that (i) substrate was not limiting in our reactors ($S_o >> K_s$) except possibly near values of X_m and (ii) the logistic model more adequately describes lag phase and stationary phase growth stages, which was a characteristic feature of our observed data. The first-order model does not assume or include either of these two criteria (Alexander and Scow, 1989). The results of the present study are consistent with other studies in which degradation of pesticides could not be described by a simple first-order kinetic model (Hamaker, 1972; Rahn and Zimdahl, 1973; Parker and Doxtader, 1983; Moorman and Harper, 1989).

Correlation of Organic C with Microbial Activity

Bacterial numbers as determined using plate counts decreased with depth in both soils for both types of growth media (Table 6). A linear regression analysis was performed to determine the correlation between CFU and % organic C over all depth increments for both soils. A positive correlation between CFU and % organic C was observed for both media with regression r^2 values of 0.61 (2,4-D media) and 0.75 (R2A media). This is consistent with Lavy et al. (1973) showing a positive regression correlation ($r^2 = 0.66$) between microbial numbers and % organic matter for three soil depths in two texturally different soil types. Foster and McKercher (1973) also found 2,4-D degradation rates to be positively correlated to soil organic C and microbial plate counts. These findings suggest that changes in soil organic C as a function of soil depth may be a reasonable indicator of microbial activity and subsequent degradation rate changes as a function of soil depth.

A regression analysis was performed to assess the relationship between 2,4-D half-life values (Table 8) for the 17°C and 24°C treatments over all depths and % soil organic C content (Table 6). Although we only collected data for two soil types, a strong negative correlation was observed between half-life values of 2,4-D and % organic C (Figure 12). Regression r^2 values were 0.88 and 0.94 for the 17°C and 24°C treatments, respectively. These results are consistent with the observation that degradation of phenol was greatest in surface and 26 m-deep aquifer samples from strata that were highest in organic C (Turco and Konopka, 1989). Experimental results of Beloin et al. (1988) also showed that microbial activity in subsurface soils and aquifers depends on the presence of organic compounds leached from recalcitrant soil organic matter into the groundwater. A negative correlation between half-life and organic C may explain the contributions of microbial biomass and activity to degradation rate; however, this relationship may only hold for organic contaminants which are not strongly bound to soil organic matter (Hurle and Walker, 1980). Sorption of 2,4-D by most soils is low with K_d values generally ranging from 0.05 to 1.5 cm^3 g^{-1} (Grover, 1973; Moreale and Van Bladel, 1980). However, it has been shown that 2,4-D sorption is highly dependent on organic matter content, and K_d values as high as 23.9 cm^3 g^{-1} have been reported for soils with 6% organic matter (Moreale and Van Bladel, 1980). Sorption of organic contaminants to solid phases such as organic matter may in fact increase their half-lives because they are not accessible to microbial attack in the bound state (Smith and Muir, 1980; Stott et al., 1983). Consequently, for sorbed compounds the relationship between

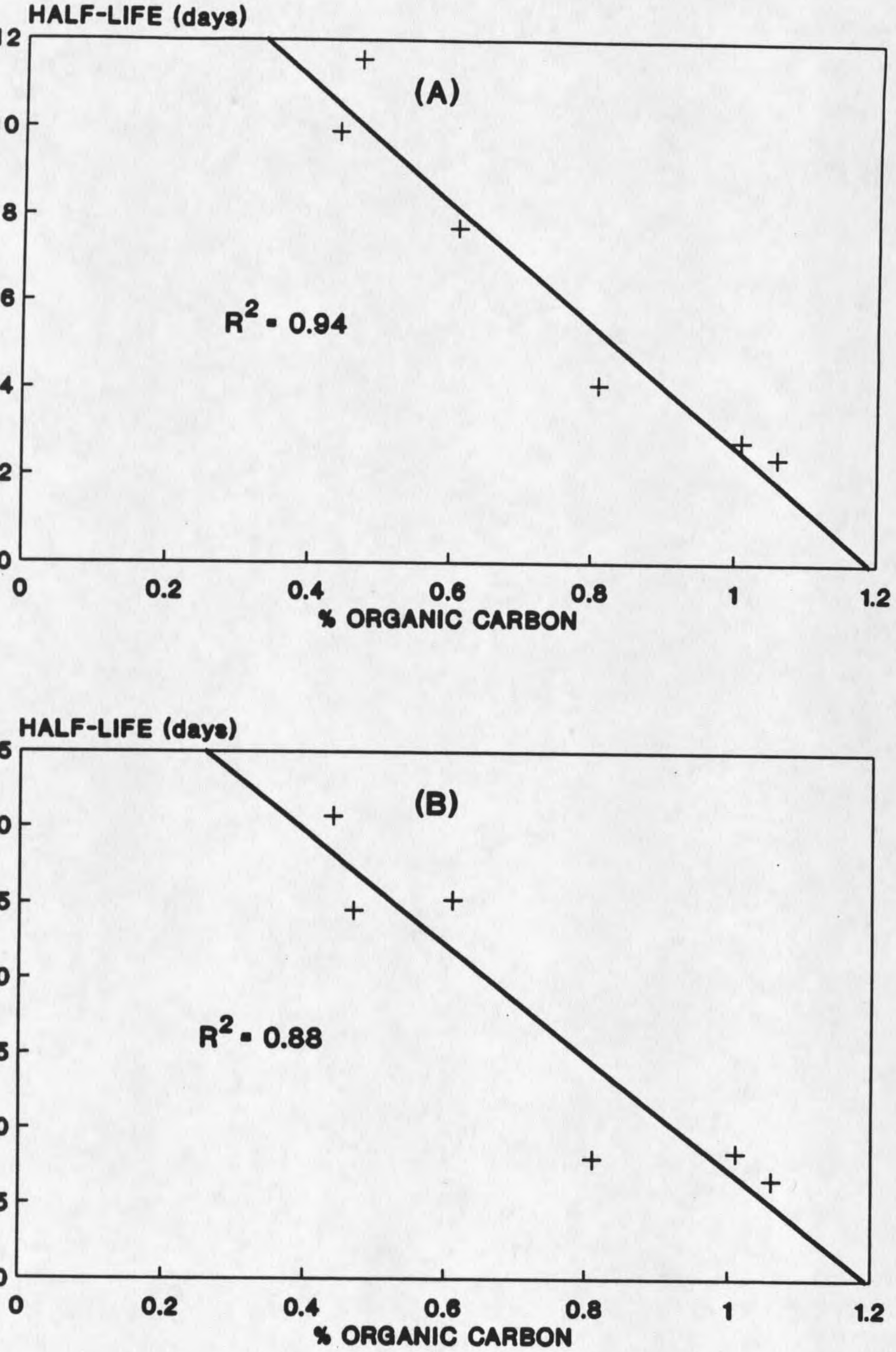

Figure 12. Correlation of 2,4-D half-life and % organic C for 0-30 cm, 30-60 cm, and 60-120 cm depths of Amsterdam sil and Haverson sicl for (A) 24°C and (B) 17°C treatments.

organic C and microbial biomass may be confounded.

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CHAPTER 4

COSOLVENT EFFECTS ON TRANSPORT OF NAPHTHALENE IN UNSATURATED SURFACE SOIL

Introduction

An understanding of sorption mechanisms of hydrophobic organic chemicals (HOC) in the presence of organic solvents is important for predicting the fate and transport of organic contaminants in soils and groundwaters. Groundwater contamination from hazardous organic wastes has occurred in many disposal and land treatment sites which contain a suite of mixed solvents (Bedient et al., 1984; Goerlitz et al., 1985; Aamand et al., 1989; Klecka et al., 1990; Aelion and Bradley, 1991). Naphthalene, for example, has been found in groundwater and has migrated significant distances in aquifers low in organic carbon (Bedient et al., 1984; Goerlitz et al., 1985). Existing data and theories for sorption and transport of HOC in soils have dealt primarily with aqueous solutions. Extrapolation of these data and theories to mixed solvent systems is not appropriate, due to solvent effects on the solubility and subsequent sorption of HOC by soil organic matter (Rao et al., 1985).

Several recent studies on the transport of HOC in the presence of miscible solvents have established that miscible solvents generally reduce the amount of HOC sorption, resulting in accelerated transport through porous media (Nkedi-Kizza et al., 1987; Staples and Geiselmann, 1988). Transport of HOC and other nonionic organic compounds in aqueous systems is primarily influenced by sorption to soil organic matter. Karickhoff (1981) as well as others have shown that variations in the equilibrium sorption coefficient, K_d (L kg^{-1}), for many pesticides and HOC among different soils and sediments were significantly reduced by normalizing the K_d value to the soil organic carbon (OC) content. This K_{oc} value (K_d/OC) generally has been shown to vary within only a factor of two and is proportional to η^w/η^{oc}, where η^w and η^{oc} are the sorbate activity coefficients in the aqueous and organic carbon phases, respectively. Because variations in η^w for various HOC may be several orders of magnitude while η^{oc} only vary by a comparatively small factor, η^w appears to be the primary determinant of K_{oc} for HOC. Since there is a reciprocal relationship between η^w and mole-fraction solubility (X^w), HOC concentration in an aqueous solution is controlled by its solubility. Other solution parameters can also modify HOC sorption and solubility. For example, naphthalene K_d values decreased by a factor of about 4.5 over a range in soil pH of 3.1-11.0 (Stauffer and MacIntyre, 1986). This is consistent with results from a transport study in which calculated retardation factors (R) for naphthalene decreased from pH 5 to pH 9, particularly at low naphthalene concentrations (Kan and Tomson, 1990a). An examination of the kinetics of sorption of HOC by soils in mixed solvents revealed that increases in the reverse sorption rate constant were log-linearly related to an increase in volume fraction of organic cosolvent (Brusseau et al., 1991a). The addition of cosolvent appeared to influence the conformation of soil organic matter, thus increasing the rate of sorbate diffusion. The sorptive mechanism of polycyclic aromatic hydrocarbons

(PAH) like naphthalene in mixed solvent-soil systems has been related thermodynamically to retention of PAH by reversed-phase liquid chromatography columns (Woodburn et al., 1989). It is probable that organic cosolvents increase transport of HOC by both increasing HOC solubility and the degree of reversible partitioning (i.e. decrease in K_{oc} and increase in rate of diffusion in soil organic matter).

Another equilibrium constant used to characterize the behavior of organic chemicals in aqueous systems is the octanol-water partition coefficient (K_{ow}), where octanol is assumed to behave similarly to soil organic C in the partitioning process. The ratio of an organic solute's maximum solubility in pure octanol its solubility in pure water can be used as a good approximation of the K_{ow} (Yalkowsky et al., 1983). Yalkowsky et al. (1988) reported that the solubility of an organic solute in water (S_w) can be estimated from the equation:

$$\log S_w = -\log K_{ow} + 0.8 \tag{9}$$

Karickhoff et al. (1979) developed an empirical relationship between K_d and K_{ow} such that $K_d = (0.63)(K_{ow})(OC)$. This relationship has been used successfully to predict ^{14}C-naphthalene transport in field column tracer tests conducted in sediments with OC content as low as 0.03-0.04% (Winters and Lee, 1987). Equations based on K_{ow} have also been derived to model enhanced transport of naphthalene by dissolved organic matter (Kan and Tomson, 1990b).

Yalkowsky et al. (1976) used a molecular and group surface area approach to describe the exponential increase in solubility observed for a variety of HOC in mixed solvent systems of water and a miscible organic cosolvent. They showed that

$$\ln X^m = \ln X^w + \sigma^c f^c \tag{10}$$

where X^m is mole fractional solubility of the HOC in the mixed solvent, X^w is the mole fraction solubility of the HOC in water, f^c is the fraction of organic cosolvent in the mixed solvent, and σ^c is defined by the following equation:

$$\sigma^c = \frac{(\Delta\gamma)(HSA) + (\Delta\epsilon)(PSA)}{k\,T} \tag{11}$$

where $\Delta\gamma$ and $\Delta\epsilon$ are the interfacial free energy changes of the hydrophobic and polar portions of the HOC molecule (kJ/nm^2), respectively, in the mixed solvent, *HSA* and *PSA* are the hydrophobic and polar surface areas of the molecule (nm^2), respectively, k is the Boltzmann constant, and T is temperature (°K). For a low-polarity solute like naphthalene the above equation reduces to:

$$\sigma^c = \frac{(\Delta\gamma)(HSA)}{k\,T} \tag{12}$$

Thus, the above solubility model is based on thermodynamic considerations where the energy required to create a cavity in the solvent for a solute molecule is the primary determinant.

The "cavity model" of solvophobic interactions between solute and solvent in mixed solvent systems was the basis for the sorption and transport model developed by

Rao et al. (1985) to predict sorbate-sorbent interactions in soils. This model has been used successfully to predict the sorption of HOC, including naphthalene, in a variety of soils. These studies have shown that the mixed solvent sorption partition coefficient (K^m) decreases in a log-linear manner with increasing cosolvent fraction (Nkedi-Kizza et al., 1985; Fu and Luthy, 1986; Lee et al., 1990). Nkedi-Kizza et al. (1985) derived the following definition for K^m from Equation 10:

$$\ln K^m = \ln K^w - \alpha\sigma^c f^c \tag{13}$$

where K^w is the aqueous partition coefficient, σ^c and f^c are as defined above, and α has been determined to be 0.83 for HOC sorption on soils and sediments (Karickhoff, 1981).

The presence of organic cosolvents has been shown to increase the transport of HOC in saturated soil columns. Staples and Geiselmann (1988) used mixed solvent sorption partition coefficients obtained from batch sorption experiments to calculate retardation factors (R) and predict kepone transport. Solvophobic theory was used to describe transport of the herbicides diuron and atrazine in saturated soil columns in the presence of cosolvents (Nkedi-Kizza et al., 1987). A log-linear decrease in the mixed solvent retardation factor, R^m, was observed with increasing organic cosolvent fraction:

$$R^m = 1 + \frac{\rho(OC)P^m}{\theta} \tag{14}$$

where ρ is soil bulk density, OC is the soil fraction of organic carbon, P^m is the K_{oc} value in the mixed solvent, and θ is the volumetric liquid phase content.

Transport studies such as those cited above have quantified the effect of organic cosolvents on HOC transport under saturated conditions. However, the influence of cosolvents on the transport of HOC in the vadose zone in soils has received little attention. The fate of PAH, including naphthalene, has been evaluated with regard to interphase transfer potential in soils under aqueous unsaturated conditions (Park et al., 1990). Losses of PAH due to volatilization and biotic and abiotic reactions were significant. Consequently, the objectives of the current study were to: (i) assess transport in a single sorbate (i.e. naphthalene)-mixed solvent system using soil columns under slightly unsaturated flow conditions, and (ii) assess the relative importance of degradation and volatilization during naphthalene transport in the presence of cosolvents.

Materials and Methods

Soil

Soils used in both transport and degradation/volatilization experiments were sampled from the A.H. Post Montana State University Experiment Station near Bozeman, MT, from the 0-30 cm depth. The soil has been classified as an Amsterdam silt loam (fine-silty mixed Typic Haploboroll) and is described in Table 9.

Table 9. Characteristics of soils used in transport and degradation experiments.

		Clay	Silt	Sand	Organic Carbon	Soil pH	CEC
Soil Series	Classification	------------(g kg^{-1})------------				(1:1)	mmol charge g^{-1}
Amsterdam silt loam	Typic Haploboroll	231	606	163	10.6	6.9	0.21

The pipette method of particle-size analysis (Day, 1965) was performed on each soil. Each soil was also analyzed for total organic C (Snyder and Trofymow, 1984), cation exchange capacity (Chapman, 1965), and soil pH using a 1:1 soil-water ratio.

Batch Adsorption Experiments

Batch experiments were conducted to establish independent partition coefficients (K_d) for the aqueous and four cosolvent treatments. Five g of soil and approximately 35 mL of a 6 mM KCl aqueous or cosolvent solution (no headspace) containing naphthalene corresponding to either 0.5, 1, 5, and 20 ppm (aqueous treatment only) or 2, 20, 50, and 200 ppm (four cosolvent treatments) were added to 40 mL Teflon centrifuge tubes. The five solvent treatments at each level of naphthalene were run in triplicate with one control (no added soil). The centrifuge tubes were placed on a G24 Environmental Incubator Shaker (New Brunswick Scientific Co., Inc.; Edison, NJ) maintained at 24 °C for 96 hours, then centrifuged for 20 minutes at 10,000 rpm. Duplicate subsamples of the supernatant liquid were analyzed for ^{14}C-naphthalene to establish adsorption isotherms for each solvent treatment.

Transport Experiments

Disturbed soil columns were constructed using homogeneous air-dried, sieved (2 mm) soil uniformly packed in 5.1 cm diameter by 30 cm long plexiglass columns (Soil Measurement Systems; Tucson, AZ.) or 5.1 cm diameter by 25.4 cm long glass columns. Soil columns were fitted with stainless steel porous plates to seal the bottom of the columns and with tensiometer ports (plexiglass columns only) near the top and bottom of the column to monitor water potential.

Column displacement experiments were performed under unsaturated flow conditions as described by van Genuchten and Wierenga (1986). A timer-controlled syringe pump was used to apply an intermittent pulse of solution to the top of the column. Two different methods were used to collect column effluent. In one set of experiments, a vacuum chamber with a regulated vacuum of 65 mm Hg (Nullmatic Pressure Regulator; Moore Products Co.; Spring House, PA) connected to the bottom of the respective columns was used to control the soil matric potential at approximately 35 mbars throughout the soil column. A fraction collector (Retriever II; Isco, Inc.; Lincoln, NE.) placed inside the vacuum chamber was used to collect column effluent at intervals of 4 hours (see Figure 2, Chapter 1). In a second set of experiments, the same vacuum was applied to the bottom of respective columns by connection to a manifold system without the use of a vacuum chamber. Instead, two 3-way valves (B14DK1-075; Skinner Valve Division, Honeywell, Inc.; New Britain, CT) with a Manostat barrel (B-D Multifit 10 cc Luer-Lok Tip Interchangeable Syringe; Becton-Dickinson and Co.; Rutherford, NJ) mounted between the valves were used to control effluent collection for each column during the 4 hour collection period (Figure 13). At the end of the collection period, a signal from the fraction collector through a 15-pin monitor plug to an external controller allowed the 3-way valves to switch to a 30 second dumping cycle during which effluent collected in the Manostat drained into a tube in the fraction collector. The latter effluent collection method allowed immediate sampling of collected fractions. In order to mimimize naphthalene volatilization, one mL of mineral oil (Swan Heavy Mineral

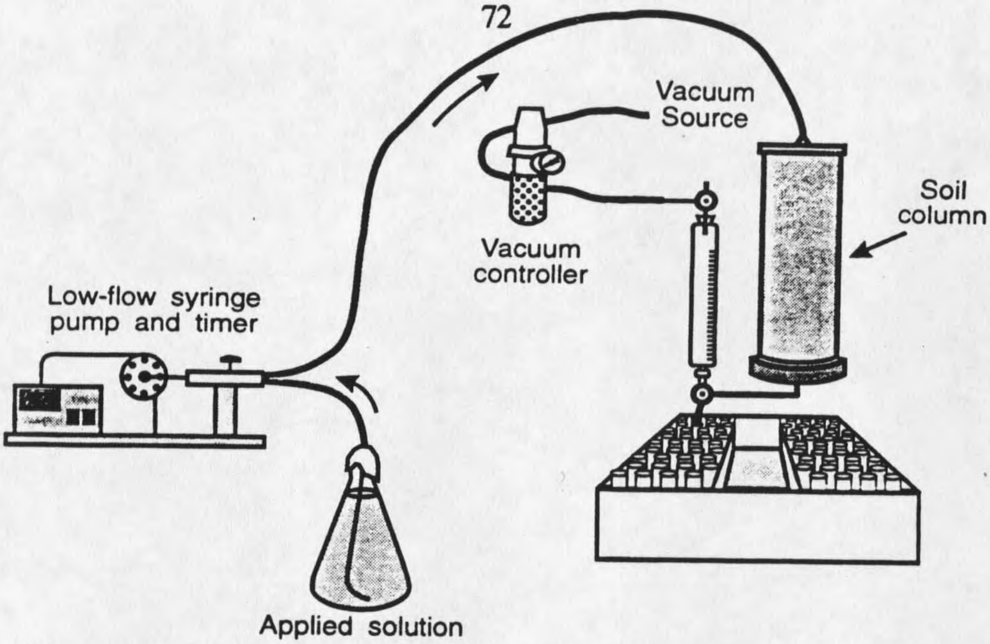

Figure 13. Soil column apparatus used in naphthalene transport experiments.

Oil; Cumberland-Swan, Inc.; Smyrna, TN) was added prior to the dumping cycle to fraction collection tubes that could not be sampled immediately.

Cosolvent treatments included methanol-water (1:3 and 1:1) and acetone-water (1:9 and 1:3) with an aqueous control (see Table 10). Both organic solvents were Certified A.C.S. grade (Fisher Chemical; Fair Lawn, NJ). Disturbed columns were prepared in triplicate for the aqueous and 50% methanol treatments and in duplicate for each of the other three treatments. Soil columns were initially conditioned with at least 2 pore volumes of the solvent system used during the transport experiment, in the presence of 6 m$\underline{M}$ KCl to provide constant background ionic strength. The solution was applied at a rate of approximately 2 ml hr^{-1} with the syringe pump set at 3 cycles hr^{-1}. A pulse of 1-^{14}C-naphthalene (6.8 mCi mmol^{-1} (251.6 MBq mmol^{-1}); Sigma Chemical Co.; St. Louis, MO.) or UL-^{14}C-naphthalene (8.7 mCi mmol^{-1} (321.9 MBq mmol^{-1});

Table 10. Properties of experimental solvents.

Solvent	boiling point (°C)	density* (g cm^{-3})	viscosity* (cp)	surface tension* (dynes cm^{-1})	dipole moment (D)	dielectric constant*
Water	100	1.0	0.89	73	1.84	78.5
Methanol	65	0.79	0.55	22	1.66	32.6
Acetone	56	0.79	0.32	23	2.72	20.7

* values at 25°C

Sigma Chemical Co.; St. Louis, MO) with tritiated water (^3H_2O) (0.013 mCi mmol^{-1} (0.48 MBq mmol^{-1}); NEN Products; Boston, MA) was applied for approximately 48 hours at the above rate. Naphthalene was applied at a concentration of 20 ppm with enough ^{14}C-naphthalene and ^3H_2O added to achieve a solution activity of about 3 μCi (0.11 Bq) L^{-1}, respectively.

After the pulse application, fraction collection of the column effluent proceeded for approximately 30 days to establish breakthrough curves for both ^3H_2O and ^{14}C-naphthalene. Fraction collection tubes were either capped and weighed or the liquid volume measured directly to establish an average pore water velocity. Subsamples of effluent and mineral oil were analyzed for ^3H_2O and ^{14}C-naphthalene using liquid scintillation analysis for dual-labeled samples. Six mL of ScintiVerse E scintillation cocktail was added to each 1 mL effluent subsample and counted on a 1900CA Tri-Carb Liquid Scintillation Analyzer (Packard Instrument Co.; Laguna Hills, CA). Subsamples of the applied solution were also analyzed for ^3H_2O and ^{14}C-naphthalene to establish initial concentration levels. At the termination of each experiment, the soil columns were frozen and sectioned into 2 cm segments. The soil segments were thawed, homogenized, and 1-2 g duplicate subsamples were combusted at 800 °C for 4 minutes in a biological oxidizer (Model OM300, R.J. Harvey Instrument Corp., Hillsdale, N.J.) to determine residual ^{14}C content. The $^{14}CO_2$ evolved from the oxidation step was trapped in liquid scintillant (Part No. OX-161 Carbon-14 cocktail, R.J. Harvey Instrument Corp., Hillsdale, N.J.) and analyzed as described above.

CXTFIT

The computer program CXTFIT (Parker and van Genuchten, 1984b) was used to provide a nonlinear least-squares solution of the one-dimensional convection-dispersion equation:

$$R\frac{\partial c_r}{\partial t} = D\frac{\partial^2 c_r}{\partial x^2} - v\frac{\partial c_r}{\partial x} - \mu c_r + \gamma \qquad (15)$$

where R = the retardation factor, D = the apparent dispersion coefficient, c_r = the volume-averaged resident concentration of the solute in the soil liquid phase, t is time, x = a positive distance from the input boundary, μ = the combined soil liquid and solid phase rate constant for first-order decay, and γ = the combined soil liquid and solid phase rate constant for zero-order production.

The deterministic linear equilibrium adsorption (local equilibrium assumption, LEA) and two-site/two-region (i.e. bicontinuum model) modes for pulse injection and either flux-averaged or resident concentrations (Parker and van Genuchten, 1984a) were used to interpret the ^3H_2O and naphthalene BTCs as reduced concentration versus reduced time (i.e. pore volume). Time values at the middle of the collection period were used. Equations describing the linear equilibrium adsorption (LEA) model and the bicontinuum model are given in Parker and van Genuchten (1984a) and are not repeated here. The primary parameters estimated using the LEA model include the dispersion coefficient (D), and the retardation factor (R). D represents the contribution of hydrodynamic dispersion to transport, while R represents the influence of sorption. R has the following relationship to K_d under equilibrium conditions:

$$R = 1 + \rho K_d / \theta \tag{16}$$

where ρ = soil bulk density, K_d = the equilibrium partition coefficient, and θ = total volumetric liquid phase content. The additional parameters estimated using the bicontinuum model include β and ω, which specify the degree of either chemical or physical nonequilibrium. β represents the distribution of sorption between instantaneous and rate-limited domains, and ω represents the ratio between hydrodynamic residence time and characteristic time of sorption. The degree of system nonequilibrium increases as either β or ω decrease. For chemical nonequilibrium, the following equations define β and ω:

$$\beta = \frac{\theta + F\rho K_d}{\theta + \rho K_d} \quad \textit{and} \quad \omega = \alpha(1-\beta)RL/v \tag{17}$$

where F = fraction of total adsorption sites which react instantaneously with the solute, L = an arbitrary positive distance from the boundary inlet, v = pore water velocity, and

α = first-order rate constant for the adsorption of solute on time-dependent adsorption sites. For physical nonequilibrium, β and ω are defined as:

$$\beta = \frac{\theta_m + F\rho K_d}{\theta + \rho K_d} \quad and \quad \omega = \alpha^* L / q \tag{18}$$

where F = fraction of total adsorption sites that equilibrate with the mobile liquid phase, θ_m = mobile volumetric water content, α^* = rate constant for solute exchange between mobile and immobile soil water, and q = volumetric liquid phase flow rate (i.e. vθ).

CXTFIT was used to fit breakthrough curves (BTCs) for ^3H_2O and naphthalene using flux-averaged concentrations in several different scenarios. First, apparent dispersion coefficients (D) and retardation factors (R) for the ^3H_2O BTCs were estimated with the linear equilibrium adsorption (i.e. local equilibrium assumption or LEA) model using measured values of pore water velocity (v) and pulse length (t_o) (first-order decay and zero-order production rate constants also fixed at 0). Secondly, ^3H_2O BTCs were analyzed with R fixed at 1 for a conservative nonadsorbing solute, rate constants and t_o fixed as above, and D and v were fitted. Thirdly, the bicontinuum model was used to analyze ^3H_2O BTCs for nonequilibrium conditions (i.e. fitted β and ω values) by either fixing R at 1 or allowing R to float (if necessary), fixing t_o, and fixing D and v from values obtained from fitting the LEA model. Fourthly, BTCs for naphthalene were fit with the LEA model by fixing D and v at the fitted values obtained for ^3H_2O (as in Scenario 3 above), fixing t_o and the zero-order production constant (as in Scenario 1 above), while R and μ (first-order rate constant for decay) were allowed to float.

Finally, BTCs for naphthalene were analyzed with the bicontinuum model by fixing D and v values optimized from the ^3H_2O BTCs (Scenario 2), fixing t_o, and allowing the model to fit R, β, and ω. Collectively, this series of CXTFIT analyses were performed to: (i) optimize the nonadsorbing tracer dispersion coefficient and (ii) determine the extent of physical or chemical nonequilibrium occurring during transport.

CXTFIT was also used to predict naphthalene equilibrium resident concentrations in the soil columns at 2 cm depth increments at the end of each experiment. Resident concentrations were calculated from total residual naphthalene concentrations and θ, ρ, and K_d (either batch or literature-derived) values in Table 11 in the following equation:

$$c_r = \frac{total\ DPM/column\ volume}{\theta_v + \rho K_d} \tag{19}$$

where c_r is the resident concentration of naphthalene, *total DPM/column volume* is disintegrations per minute as an average measure of both residual sorbed and solution phase naphthalene per column volume for each 2-cm depth increment, θ_v is volumetric liquid phase content, ρ is soil bulk density, and K_d is the equilibrium partition coefficient. These predicted concentration profiles were generated using the LEA model by fixing t_o to the measured value, fixing D and v to the optimized values obtained with ^3H_2O BTCs, fixing the rate constants for decay and production at 0, and fixing R at two different values. In one case, naphthalene K_d values obtained from the batch experiments were used to calculate R (Equation 16). In the second case, aqueous K_d (K^w) values calculated from average K_{oc} values reported in Montgomery and Welkom (1990) were used to

Table 11. Comparison of measured K_d (cm^3 g^{-1}) values from batch Freundlich adsorption isotherms (slopes (1/n), constants (log K_d), and r^2 values included) and calculated K_d values from the literature.

Treatment	1/n[*]	Constant[*] (log K_d)	r^2	measured K_d	calc. K_d[¶]	calculated literature K_d
Aqueous	0.91 (0.04)	0.41 (0.09)	0.98	2.57	------	13.83[§]
Methanol-Water (1:3)	0.99 (0.08)	-0.07 (0.18)	0.94	0.86	0.53	2.87[‡]
Methanol-Water (1:1)	1.11 (0.05)	-0.68 (0.13)	0.98	0.21	0.11	0.60[‡]
Acetone-Water (1:9)	0.95 (0.07)	0.11 (0.13)	0.97	1.27	0.81	4.37[‡]
Acetone-Water (1:3)	1.11 (0.05)	-0.17 (0.09)	0.99	0.68	0.14	0.77[‡]

[*] standard error coefficients in parentheses

[¶] calculated from measured aqueous K_d and Equation 13 (Nkedi-Kizza et al., 1985)

[§] calculated from average K_{oc} values in Montgomery and Welkom (1990)

[‡] calculated from literature aqueous K_d (§ above) and Equation 13 (Nkedi-Kizza et al., 1985)

calculate mixed solvent partition coefficients (K^m) (Equation 13); these K^w and K^m values were then used to calculate R (Equation 16).

Degradation/Volatilization Experiments

Degradation experiments were conducted with the same soil as that used for the transport experiments. Subsamples of 15 g were weighed into 25 ml flasks (Supelco, Inc.; Bellefonte, PA) with 2-3 replicates and 1 control (no added naphthalene) for each soil treatment. The treatments included an aqueous system, methanol-water (1:3) and acetone-water (1:9) cosolvent systems, and diesel fuel. The flasks were incubated in a constant temperature water bath maintained at 24 °C by a Model 9100 Isotemp Refrigerated Circulator (Fisher Scientific; Pittsburgh, PA). Four ml of 6 m<u>M</u> KCl aqueous solution, cosolvent solution, or diesel fuel containing 20 ppm naphthalene with ^{14}C-naphthalene added to achieve a solution activity of 0.02 μCi (7.4E-4 MBq) was applied to the soil in each flask to approximate the same volumetric solvent content as that in the transport experiments (≈ 40%).

A regulated gas cylinder was used to introduce compressed air as a carrier gas into the reaction flasks. The air was passed through a series of glass wool filter and ascarite filter (to eliminate CO_2), a gas washing cylinder filled with distilled water to humidify the air, a flowmeter, and into a manifold system of 1 mm i.d. Tygon tubing to distribute the air to each of the reaction flasks (Figure 14). A mini-valve (MNV-1K, Clippard Minimatics; Clippard Instrument Laboratory, Inc.; Cincinnati, OH) at the top of each flask was used to control air flow through a sealed Teflon-lined cap and into the reaction flask headspace at approximately 2.5 ml min^{-1}. Continuous evacuation of reaction flask headspace occurred through 1/16" stainless steel tubing connected to a series of two traps, one for volatilized naphthalene and one for evolved $^{14}CO_2$. The volatilization traps were either ORBO-32 activated coconut charcoal (20/40 mesh) or ORBO-43 Supelpak 20U (20/40 mesh) filters (Supelco, Inc.; Bellefonte, PA). The $^{14}CO_2$ trap was 10 ml of 0.5 M NaOH. Each of the two traps were extracted or subsampled and replaced every 24 hours for the duration of the experiment (14 days). Volatilization filter sorbent was extracted in 7 ml scintillation vials with 1 ml of toluene. One ml subsamples from the NaOH traps were transferred to 7 ml scintillation vials. Both sets of samples were then combined with 6 ml of ScintiVerse E scintillation cocktail (Fisher Chemical; Fair Lawn, NJ) and analyzed by liquid scintillation techniques.

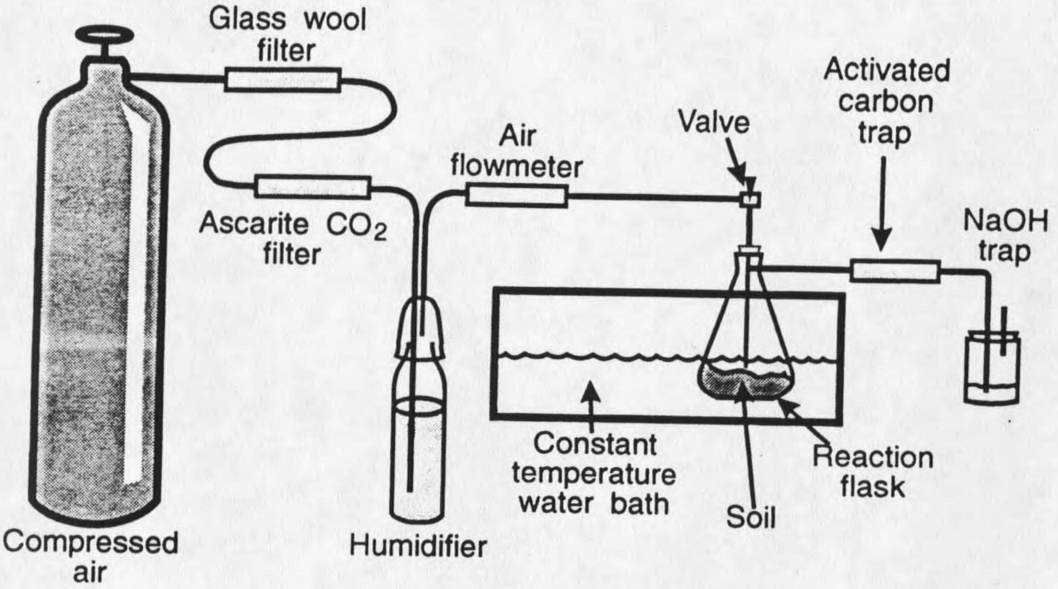

Figure 14. Schematic of apparatus used in naphthalene degradation/volatilization experiments.

Results and Discussion

Batch Adsorption Isotherms

The linear form of the Freundlich adsorption model can be written:

$$\log Q = \frac{1}{n} \log C + \log K_d \tag{20}$$

where Q is the concentration of solute in the sorbed solid phase (g g^{-1}) and C is the concentration of solute in the liquid phase (g cm^{-3}). The y-intercept of a linear regression analysis of log Q vs. log C is used to calculate log K_d, provided 1/n is approximately 1. Data collected from the batch adsorption studies with naphthalene were fit to the Freundlich model to obtain measured K_d values for the various cosolvent treatments

(Table 11). In order to evaluate the applicability of Equation 13 to these results, the measured aqueous batch K_d value (2.57) was used to calculate K_d values for the four cosolvent mixtures (Table 11). For comparison, a literature K_d value (13.83) obtained from average naphthalene K_{oc} values reported in Montgomery and Welkom (1990) was used in the same way to calculate the four cosolvent mixture K_d values (Table 11). Values for σ^c in Equations 12 and 13 were calculated with the following parameters: HSA = 156 Å^2 (Rao et al., 1985), $\Delta\gamma$ = 1.99 x 10^{-15} ergs/Å^2 for methanol-water mixtures and 3.65 x 10^{-15} ergs/Å^2 for acetone-water mixtures (Nkedi-Kizza et al., 1985), k = 1.38 x 10^{-16} ergs °K^{-1}, and T = 297°K. Cosolvent mixture K_d values calculated from the measured aqueous batch K_d value were consistently less than the corresponding measured values, generally within a factor of two. In contrast, calculated cosolvent mixture K_d values using the literature aqueous K_d value were consistently greater than those measured in the batch experiments, generally by a factor of about 4-5. Measured K_d values decreased as the cosolvent fraction increased in a log-linear relationship (Figure 15). These results are consistent with those reported by Nkedi-Kizza et al. (1985), Fu and Luthy (1986), and Staples and Geiselmann (1988) and support the use of solvophobic theory for describing sorption of HOC from mixed solvents in unsaturated systems. It is also important to note that the measured K_d value for the acetone-water mixture is less than that of the methanol-water mixture at the same cosolvent fraction (25%). This is consistent with the fact that an HOC like naphthalene is more soluble in a less polar solvent like acetone (Table 10), and thus would be less likely to partition into the soil organic matter phase.

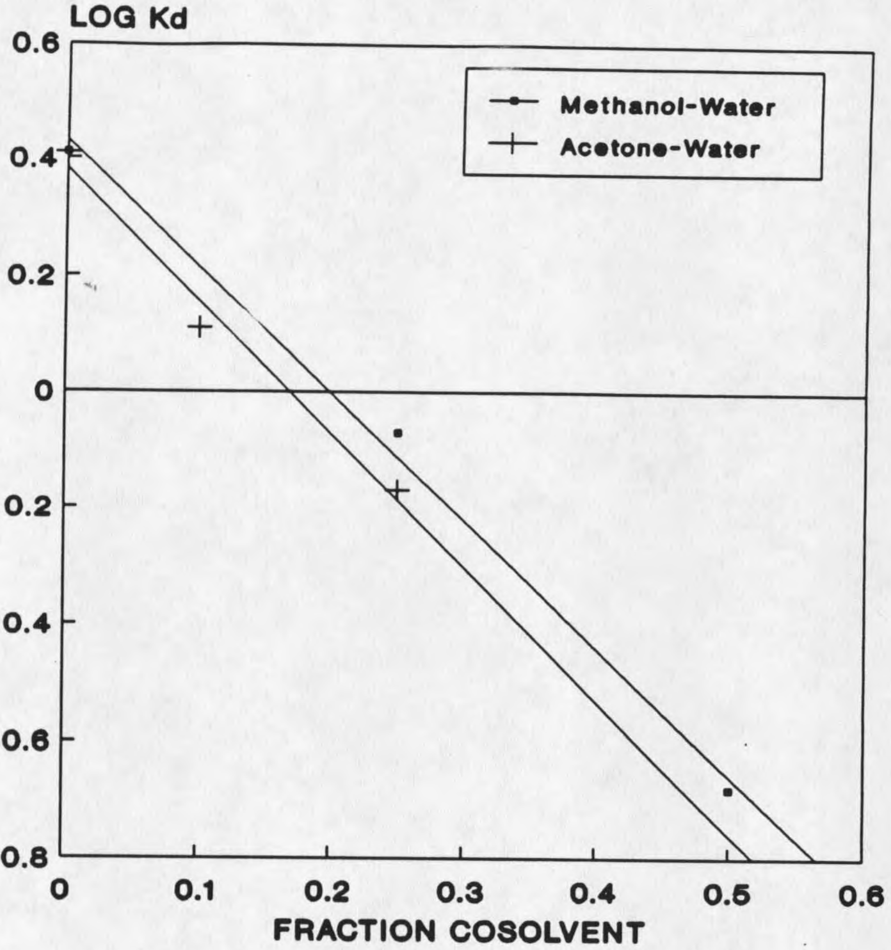

Figure 15. Log-linear relationship between K_d and fraction of organic cosolvent for naphthalene sorption by soils from methanol-water and acetone-water mixtures.

The fact that measured batch K_d values did not agree with literature values may reflect differences in experimental conditions, particularly the solid:solution ratio. An inverse relationship between concentration of adsorbing solids up to 100 g L^{-1} (1:10 solid to solution ratio) and partition coefficient has been observed for inorganic as well as organic sorbates (O'Connor and Connolly, 1980; Staples and Geiselmann, 1988). O'Connor and Connolly (1980) suggested that a solid-solid interaction may affect the adsorption process, causing a decrease in the partition coefficient with increasing solids concentration. However, they also postulated the existence of a limiting (minimum) partition coefficient at a critical level of high concentration of solids. Batch experiments in our study were conducted at a soil:solution ratio of about 1:7 for both aqueous solutions and cosolvent mixtures. Differences in methodologies (e.g. soil:solution ratio) may have contributed to the differences in measured and calculated K_d values in Table 11. O'Connor and Connolly (1980) advocate the development of standardized laboratory tests for evaluation of partition coefficients. Furthermore, Staples and Geiselmann (1988) suggest that the observed effect of solid concentration on measured partition coefficients demonstrates the need for conducting sorption experiments at solid concentrations appropriate to the system being studied. O'Connor and Connolly (1980) also reported a greater dependence of measured partition coefficients on concentration of solids with increasing degree of sorbate-sorbent affinity. The strong affinity of naphthalene for soil organic carbon is reflected by a relatively large partition coefficient ($K_{oc} \cong 1300$ cm^3 g^{-1} in Montgomery and Welkom, 1990); therefore, naphthalene sorption would be expected to be strongly influenced by the concentration of organic solid phase in batch experiments.

CXTFIT Analysis of Breakthrough Curves

The local equilibrium assumption (LEA) represents one possible solution to the convection-dispersion equation for describing solute transport (Equation 15). In order for the LEA to be valid, the rate of the sorption process must be fast relative to other transport processes such as advection and hydrodynamic dispersion, so that equilibrium between the sorbent and the pore fluid has been established (Bahr and Rubin, 1987;

Brusseau and Rao, 1989). Rate-limited (nonequilibrium) sorption has been grouped into three mechanistic categories by Brusseau and Rao (1989): (1) physical (i.e. transport-related) nonequilibrium, which results from rate-limited mass transfer in hetergeneous porous media, (2) chemical nonequilibrium, which is caused by rate-limited sorbate-sorbent interactions, and (3) rate-limited intrasorbent diffusion, which is thought to occur within organic matter or microporous mineral particles.

It is common to use nonsorbing tracers such as ^3H_2O to assess the degree of physical nonequilibrium in solute transport experiments in uniformly packed soil columns and to establish soil column D values with R fixed at unity (Brusseau et al., 1991a; Brusseau et al., 1991b). Table 12 presents values for D, R, v, β, ω, and r^2 obtained from CXTFIT analyses (both LEA and bicontinuum models) of ^3H_2O BTCs observed in the soil column experiments. Tritiated water BTCs were generally symmetical in shape with only slight tailing (Figures 16-18), and a good fit to the LEA model (r^2 range of 0.95-0.99) indicated the absence of any physical nonequilibrium. The lack of physical nonequilibrium was also confirmed by results of fitting ^3H_2O BTCs to the bicontinuum model where the Damkohler numbers (ω values) were significantly $>$ 100 in all but one case. Damkohler numbers $>>$ 100 are indicative of the absence of physical nonequilibrium transport conditions (Bahr and Rubin, 1987; Brusseau et al., 1991). There was no consistent effect of cosolvent mixtures on D values obtained by fitting ^3H_2O BTCs using the LEA model. Fitted R values were consistently the greatest for the methanol-water (1:1) mixture. It is perhaps not coincidental that 4 of the 5 replicates for which LEA-fitted R values were greater than 1 were at the highest cosolvent fractions.

Table 12. Comparison of fixed and fitted dispersion coefficients (D [=] cm^2 hr^{-1}), retardation factors (R), pore water velocities (v [=] cm hr^{-1}), β, ω, and r^2 values (standard error coefficients in parentheses) from CXTFIT (LEA and bicontinuum models) analyses of ^3H_2O breakthrough curves.

		Local Equilibrium Adsorption (LEA) Model							Bicontinuum Model			
						R, fixed = 1						
Treatment	Rep. #	D, fitted	R, fitted	v, fixed	r^2	D, fitted	v, fitted	r^2	R†	β	ω	r^2
Aqueous	1	0.16(0.007)	1.11(0.004)	0.30	0.99	0.15(0.006)	0.27(0.001)	0.99	1.00	0.27(0.010)	1144(51)	0.90
	2	0.39(0.021)	1.24(0.009)	0.36	0.97	0.32(0.017)	0.29(0.002)	0.97	1.24	0.22(0.004)	987(113)	0.97
	3	0.16(0.005)	1.11(0.004)	0.20	0.99	0.15(0.004)	0.18(0.001)	0.99	1.00	0.13(0.031)	325(22)	0.92
Methanol-Water (1:3)	1	0.52(0.015)	0.96(0.005)	0.29	0.99	0.54(0.016)	0.30(0.002)	0.99	1.00	0.56(0.015)	351(11)	0.98
	2	0.48(0.009)	0.94(0.003)	0.30	0.99	0.51(0.009)	0.32(0.001)	0.99	1.00	0.57(0.159)	88(23)	0.98
Methanol-Water (1:1)	1	0.82(0.019)	1.42(0.007)	0.38	0.99	0.58(0.013)	0.27(0.001)	0.99	1.42	0.37(0.007)	427(46)	0.99
	2	0.21(0.016)	1.63(0.012)	0.36	0.95	0.13(0.010)	0.22(0.002)	0.95	1.63	0.34(0.005)	659(16)	0.95
	3	0.29(0.005)	1.45(0.003)	0.34	0.99	0.20(0.004)	0.24(0.001)	0.99	1.45	0.87(0.003)	387(10)	0.99
Acetone-Water (1:9)	1	0.64(0.015)	1.11(0.006)	0.33	0.99	0.57(0.013)	0.30(0.002)	0.99	1.00	0.23(0.013)	182(15)	0.95
	2	0.16(0.006)	1.01(0.004)	0.26	0.99	0.16(0.006)	0.26(0.001)	0.99	1.00	0.51(0.008)	1565(146)	0.99
Acetone-Water (1:3)	1	0.19(0.008)	1.06(0.006)	0.27	0.98	0.18(0.008)	0.25(0.001)	0.98	1.00	0.34(0.047)	501(75)	0.95
	2	0.25(0.008)	1.23(0.005)	0.31	0.99	0.20(0.006)	0.26(0.001)	0.99	1.23	0.36(0.003)	433(8)	0.99

† R either fixed = 1.00 or fitted at stated value.

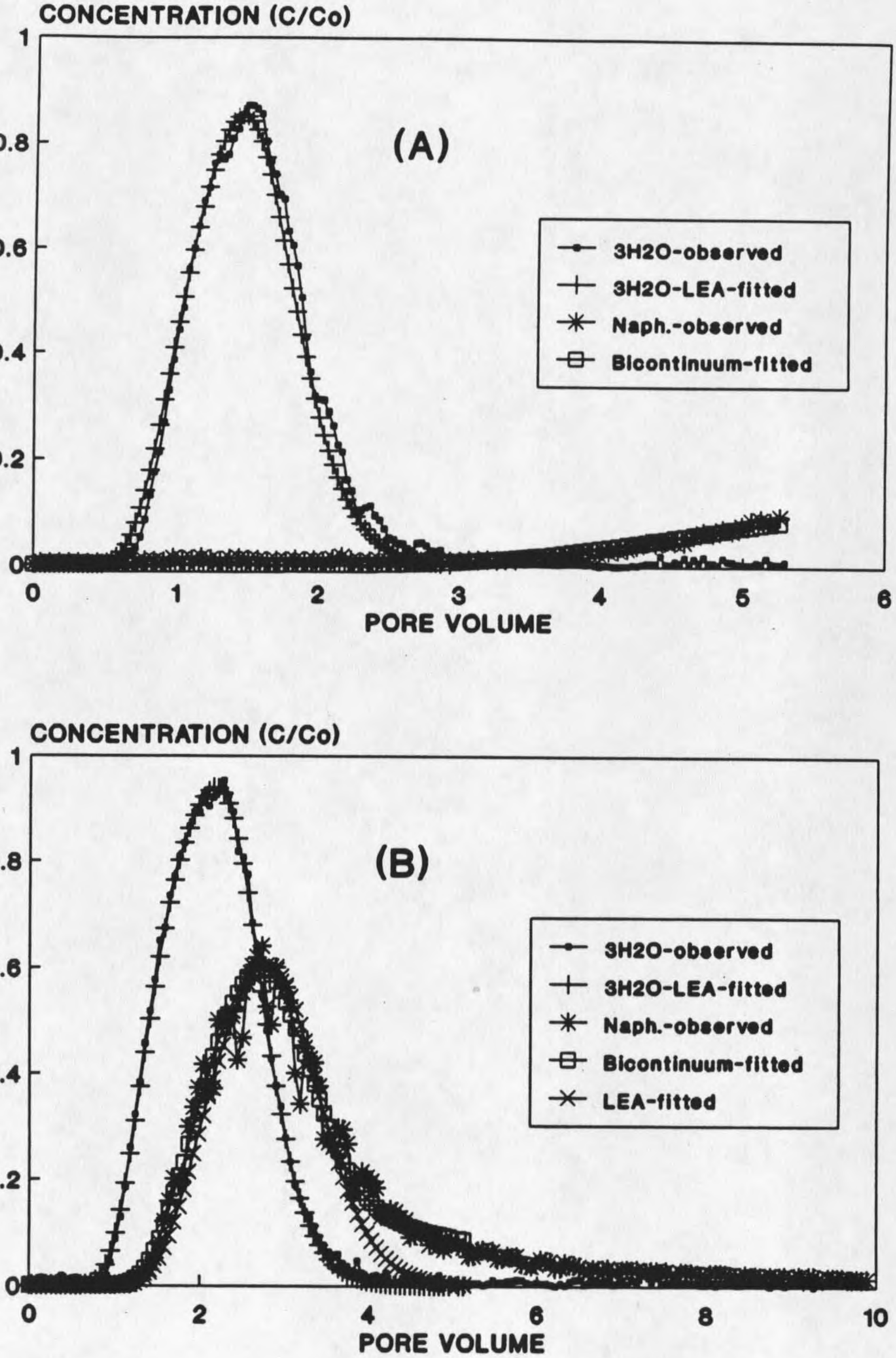

Figure 16. Observed and CXTFIT-fitted BTCs for ^3H_2O and naphthalene from soil columns treated with (A) aqueous solution, Rep.#3 and (B) methanol-water (1:1), Rep.#3 (Tables 12 and 13).

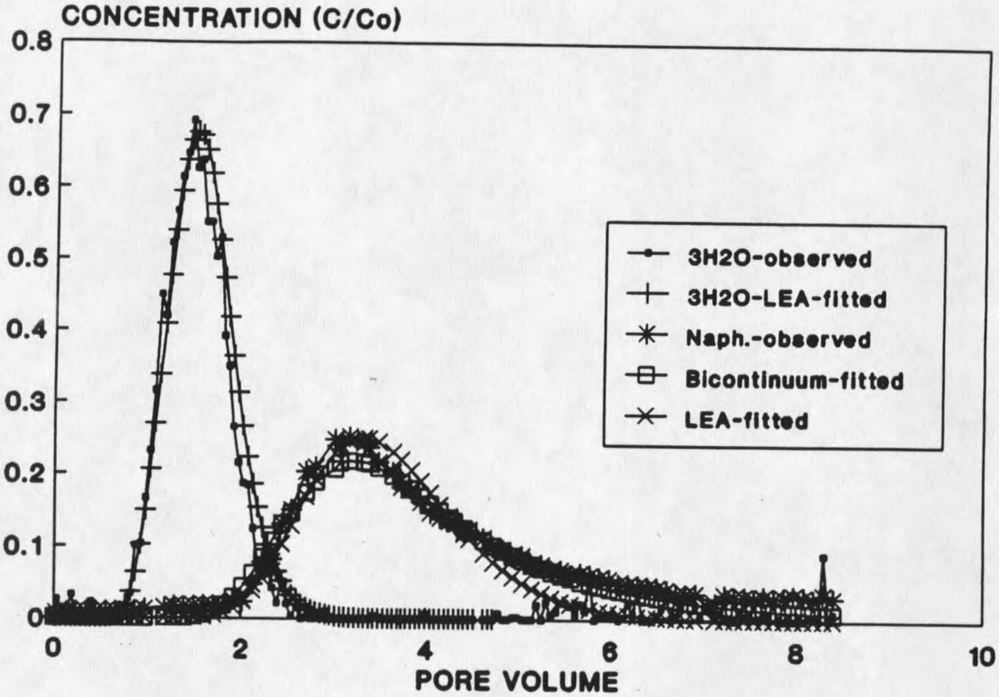

Figure 17. Observed and CXTFIT-fitted BTCs for ^3H_2O and naphthalene from a soil column treated with acetone-water (1:3) solution (Rep.#2 in Tables 12 and 13).

Brindley et al. (1969) demonstrated a significant decrease in basal spacings of Ca-montmorillonite in equilibrium with methanol-water mixtures at mole percentages of methanol greater than about 45%. A similar decrease in basal spacings of Ca-montmorillonite was observed at mole percentages of acetone greater than 20%. It was postulated that the observed collapse of the expanded state of the clay fraction may be attributable to an increase in Coulombic attractions arising from the diminished dielectric constants of the cosolvent mixtures. It is possible that ^3H_2O associated with methanol or acetone in the collapsed clay fraction of the solid phase may be interpreted as a type of sorption behavior, in which case R values would be expected to be greater than 1.

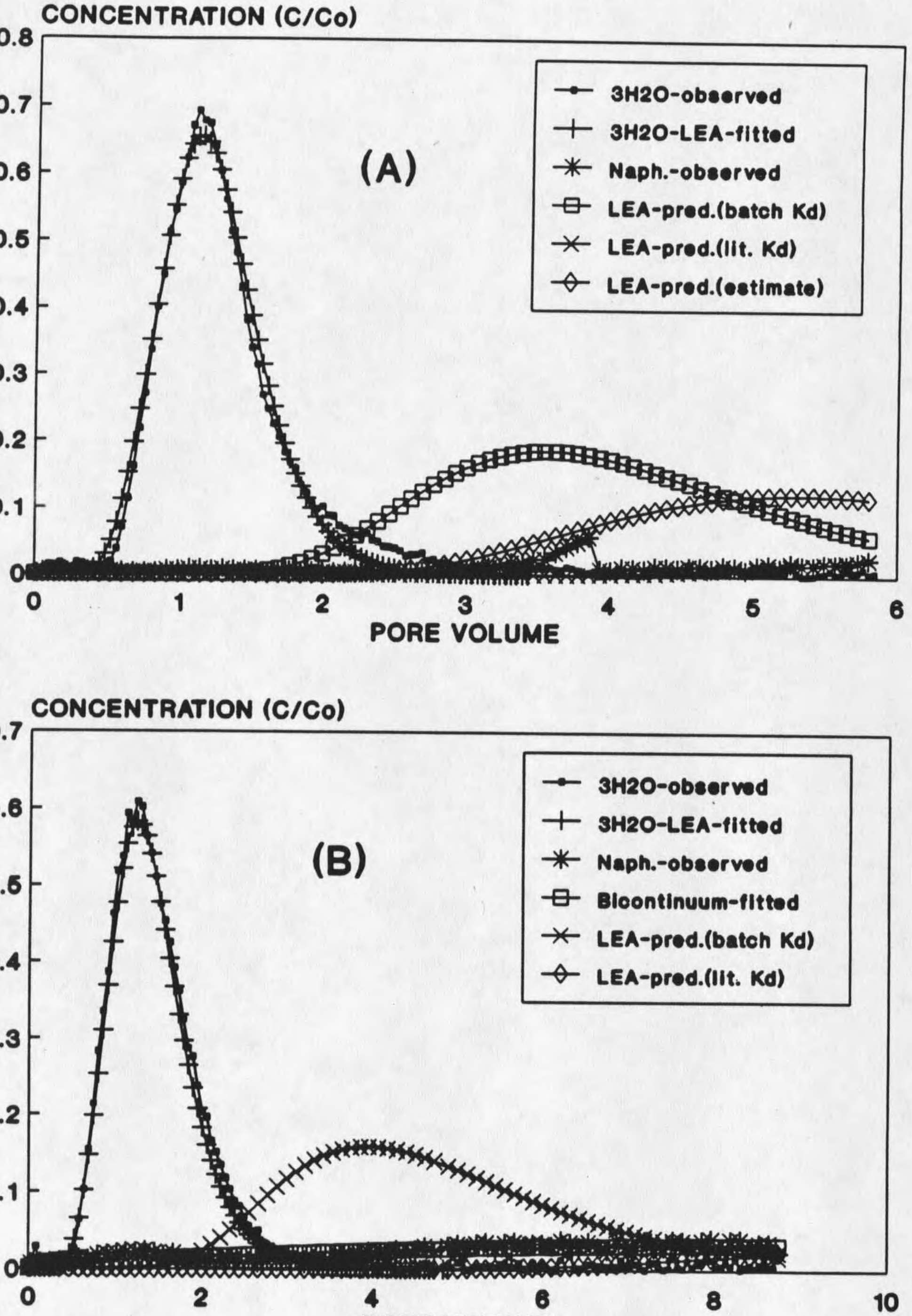

Figure 18. Observed and CXTFIT-fitted and -predicted BTCs for ^3H_2O and naphthalene from soil columns treated with (A) methanol-water (1:3), Rep.#1 and (B) acetone-water (1:9), Rep.#1 (Tables 12 and 13)

An estimation of the amount of immobile liquid phase involves interpretation of β values in Table 12. Assuming a K_d of zero for ^3H_2O, β reduces to θ_m/θ (Equation 18), and 1-β represents the immobile liquid fraction. This suggests that from 13% (methanol water (1:1), Rep.#3) to 87% (aqueous treatment, Rep.#3) of the volumetric liquid fraction was immobile. However, the lack of physical nonequilibrium reflected by large ω values suggests that the rate of exchange between mobile and immobile regions was relatively fast (i.e. α^* in Equation 18 was a large number).

The results of CXTFIT analyses of selected naphthalene BTCs are presented in Table 13, as well as calculated R values (Equation 16) using the appropriate solvent K_d (Table 11), θ and ρ (Table 13). One set of R values was calculated using experimental batch K_d values, while a corresponding set of R values was calculated from the average of K_d values for naphthalene reported in Montgomery and Welkom (1990). These two sets of predicted R values follow the same decreasing trend with increasing cosolvent fraction as that observed for the respective K_d values in Table 11. Missing data in Table 13 for CXTFIT analysis of naphthalene BTCs was the result of extremely poor fit of the LEA or bicontinuum models to observed BTCs due to inadequate breakthrough or losses of naphthalene by volatilization and degradation. This problem will be discussed further in a subsequent section.

Generally, R values derived from fitting naphthalene BTCs to both the LEA and bicontinuum models fell within the range predicted by calculated R values. There was a significant increase in transport of naphthalene observed at the two highest cosolvent fractions (Figures 16B and 17), and this is consistent with the lower R values (Table 13)

Table 13. Comparison of retardation factors (R) calculated from equilibrium K_d values (Table 11) to R values generated from CXTFIT (LEA and bicontinuum models) analyses of naphthalene BTCs.

						LEA Model			Bicontinuum Model			
Treatment	Rep.#	θ	ρ (g cm^{-3})	R†	R‡	R	μ§ (hr^{-1})	r^2	R	β	ω	r^2
Aqueous	1	0.34	1.20	10.2	50.4							
	2	0.29	1.10	10.9	54.0							
	3	0.48	1.28	7.9	38.0				7.9(0.1)	0.500(0.066)	10.0(1.20)	0.83
Methanol-Water (1:3)	1	0.34	1.13	3.9	10.6							
	2	0.31	1.09	4.0	11.0							
Methanol-Water (1:1)	1	0.26	1.15	1.9	3.6	2.5(0.03)	0.012(0.0003)	0.90	5.0(0.3)	0.200(0.052)	5.00(1.37)	0.32
	2	0.27	1.21	1.9	3.6	2.4(0.02)	0.011(0.0004)	0.87	3.7(0.2)	0.025(0.004)	7.66(1.16)	0.37
	3	0.26	1.28	2.0	4.0	2.2(0.02)	0.0053(0.0003)	0.91	3.3(0.1)	0.602(0.019)	0.54(0.01)	0.97
Acetone-Water (1:9)	1	0.31	1.13	4.6	16.8				13.4(0.3)	0.005(0.0005)	7.52(0.49)	0.56
	2	0.37	1.15	4.0	14.7							
Acetone-Water (1:3)	1	0.31	1.22	2.7	4.1	3.3(0.04)	0.010(0.0004)	0.73	5.0(0.3)	0.005(0.002)	5.72(0.60)	0.28
	2	0.33	1.20	2.5	3.8	3.3(0.04)	0.002(0.0004)	0.84	3.8(0.1)	0.795(0.012)	0.79(0.09)	0.95

† R calculated from batch K_d values.

‡ R calculated from literature K_d and Equation 13 (Nkedi-Kizza et al., 1985).

§ first-order rate constant for decay.

associated with these treatments. Nkedi-Kizza et al. (1987) reported a similar decrease in retardation factors for two herbicides, diuron and atrazine, as the volumetric fraction of methanol was increased in a binary methanol-water mixture. Our observations are also consistent with results from a transport study by Staples and Geiselmann (1988) in which several alcohol-water mixtures decreased kepone retardation in soil columns.

Naphthalene BTCs for one replicate of each of the methanol-water (1:1) and acetone-water (1:3) treatments (Rep.#3 and Rep.#2 in Table 13, respectively) were described relatively well by both the LEA and bicontinuum models. Figure 16B and Figure 17 illustrate for these two replicates, respectively, that although the LEA model fit the front and middle of the observed naphthalene BTCs, the bicontiuum model provided a better fit to the tailing observed in these BTCs. This tailing phenomenon is associated with the presence of nonequilibrium conditions (Brusseau and Rao, 1989). The existence of nonequilibrium is also supported by the results of fitting naphthalene BTCs to the bicontinuum model. Values for ω are ≤ 10 (Table 13), which is indicative of nonequilibrium conditions (Brusseau et al., 1991b). Also, β values in Table 13 are significantly less than 1. Interpretation of the β values in terms of Equation 17 indicates that a substantial fraction of sorption sites were rate-limited. Brusseau et al. (1991c) found that nonequilibrium behavior exhibited by naphthalene was a sorption-related process and probably controlled by the rate-limiting mechanism of intraorganic matter diffusion. The minimal influence of physical nonequilibrium determined by CXTFIT analysis of ^3H_2O BTCs in our study is consistent with this observation.

Figure 18 illustrates the use of the LEA model of CXTFIT to predict flux-averaged naphthalene BTCs at the pore volume corresponding to time of termination of the column experiment. This is accomplished by using a mode of CXTFIT in which only time and distance from the boundary inlet are specified and any observed concentration data are ignored. In addition, all six model parameters were fixed. D and v were fixed in all cases at respective values from Table 12 (columns 7 and 8), rate constants for production and decay were fixed at zero, pulse length (t_o) was fixed at the known value, and R was fixed at either of the respective calculated values in Table 13 (columns 5 and 6). Therefore, the only difference in LEA-predicted BTCs was due to the input value of R. Figure 18 clearly shows that a much earlier naphthalene BTC of greater magnitude is predicted by the input R value determined from the batch K_d. In contrast, very little naphthalene breakthrough was predicted with the greater input R value calculated from the literature K_d. In Figure 18A an intermediate estimated input R value of 6.0 was also used to generate an LEA-predicted BTC and provided a much better fit to the observed time of initial breakthrough. In Figure 18B the bicontinuum model provided a good fit to the observed BTC and resulted in a fitted R value of 13.4 (Table 13), again a value intermediate to the two calculated R values used to generate the LEA-predicted BTCs.

Although success was limited in describing naphthalene BTCs for all solvent treatments, Figure 19 clearly illustrates the effect of increasing cosolvent fraction on naphthalene transport. Total residual naphthalene (see Materials and Methods section) decreased significantly with increasing cosolvent fraction for both methanol-water and acetone-water mixtures. In Figures 20 and 21, LEA-predicted resident concentrations of naphthalene at 2-cm incremental soil column depths (generated in the same manner

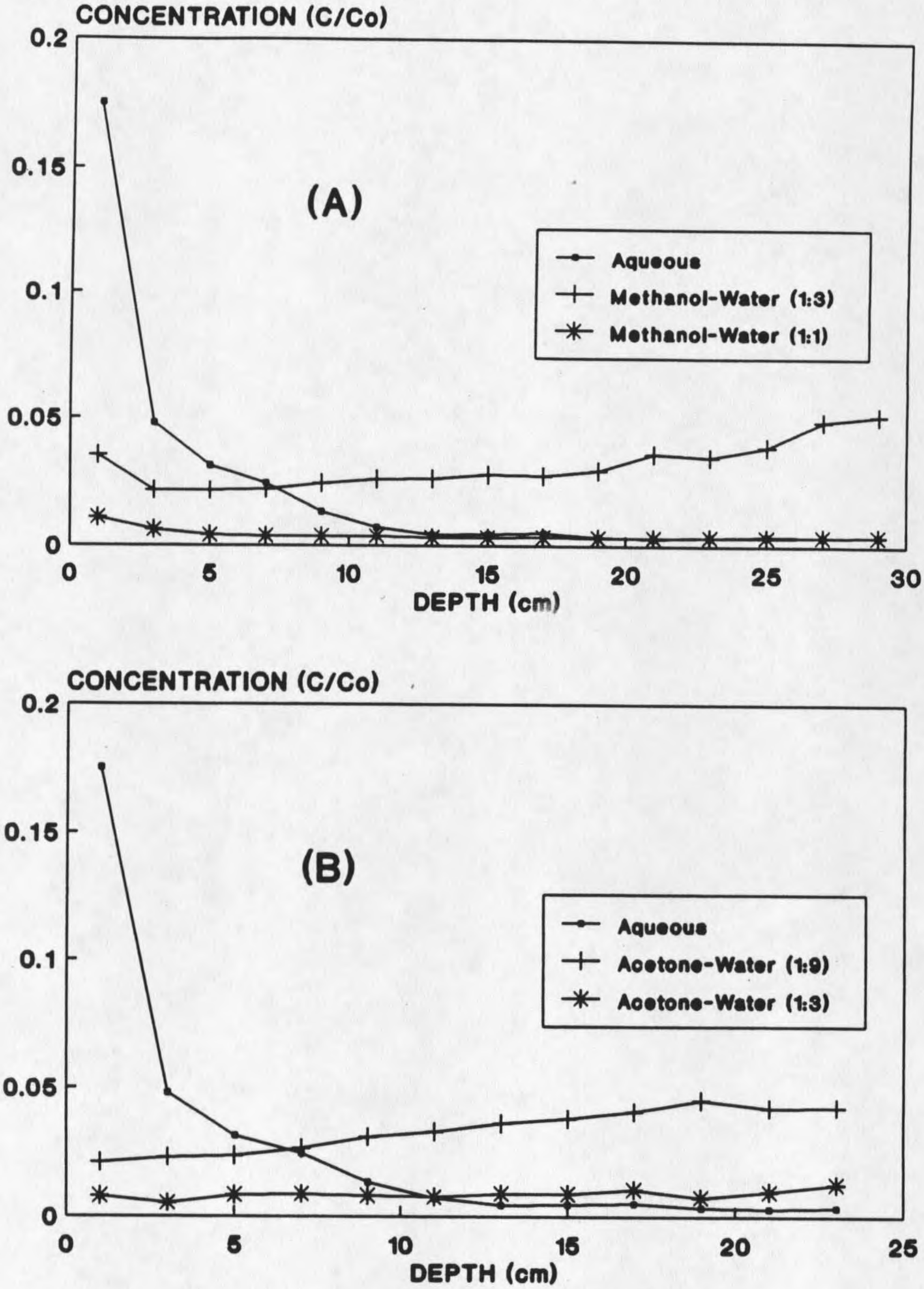

Figure 19. Comparison of total residual naphthalene concentration in soil columns for (A) a methanol-water system and (B) an acetone-water system (soil columns represented are Rep.#1 for respective treatments in Table 13).

as predicted flux-averaged BTCs above) were compared to resident concentrations calculated from total residual naphthalene concentrations (Figure 19). As expected, resident concentrations calculated by Equation 19 followed the same trend as total residual naphthalene, decreasing with increasing cosolvent fraction. At the higher cosolvent fractions for both methanol-water and acetone-water systems, resident naphthalene concentration profiles predicted by the LEA model consistently reflected greater transport of naphthalene than profiles calculated by Equation 19 using respective equilibrium K_d values (Figures 20B and 21B). However, at the lower cosolvent fractions for both methanol-water and acetone-water mixtures, the LEA-predicted resident concentrations were lower than calculated profiles only when the lower batch K_d values were used (Figures 20A and 21A). These results are consistent with the relationship between observed naphthalene BTCs at the two lower cosolvent treatments and LEA-predicted BTCs where either batch or literature K_d values were used to calculate input R values (Figure 18).

Assessment of Naphthalene Volatilization/Degradation

The analysis of naphthalene BTCs using CXTFIT and interpretation of results of the transport experiments were complicated for several reasons: (i) total naphthalene recovery was generally poor, (ii) assessment of losses of napthalene due to volatilization and/or degradation was difficult, and (iii) there was not adequate breakthrough of naphthalene for the aqueous and lower cosolvent fraction mixtures. For example, total naphthalene recovery for the column experiments ranged from 53% to 118% with an

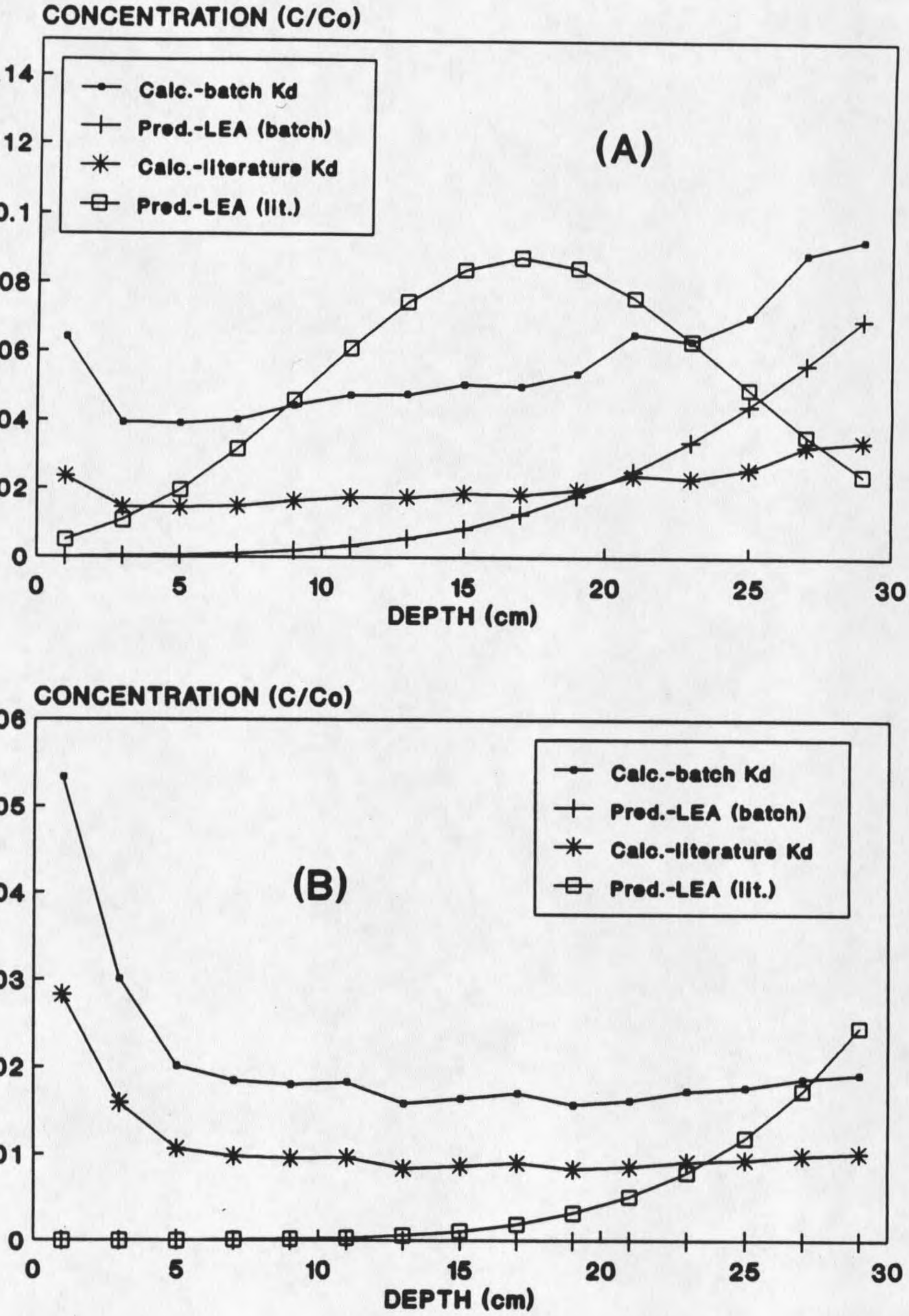

Figure 20. Comparison of calculated and CXTFIT-predicted residual naphthalene resident concentrations for (A) a methanol-water (1:3) system and (B) a methanol-water (1:1) system (Rep.#1, respectively, in Table 13).

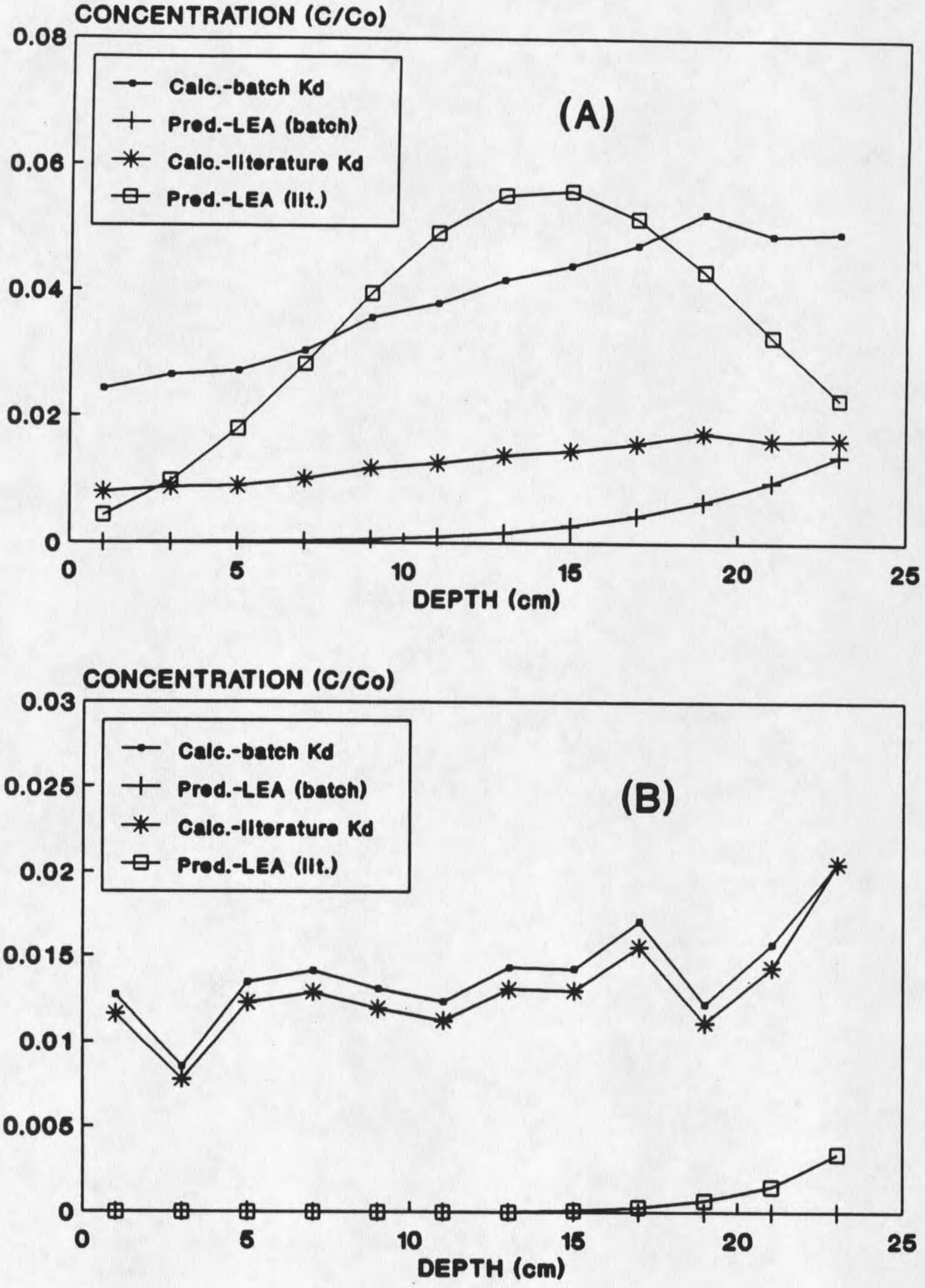

Figure 21. Comparison of calculated and CXTFIT-predicted residual naphthalene resident concentrations for (A) an acetone-water (1:9) system and (B) an acetone-water (1:3) system (Rep.#1, respectively, in Table 13).

average recovery of 70%. For six of the soil columns, mineral oil was used to minimize naphthalene volatilization from effluent samples (see Materials and Methods). However, this improvement in experimental design only increased the average recovery to 75%. In addition, experiments were conducted to assess the efficiency of recovery for total residual ^{14}C-naphthalene by combustion of soil subsamples in the biological oxidizer. An efficiency factor of 0.8 was used to correct total residual soil column naphthalene concentrations.

Volatilization contributed significantly to poor naphthalene recovery. These losses occurred primarily at three points in the experimental apparatus: (i) the pulse solution container prior to application to the top of the soil column, (ii) the collected effluent while it was under vacuum in either the vacuum chamber or manostat barrel (see Materials and Methods), and (iii) the effluent samples in fraction tubes prior to sampling. This latter loss due to volatilization is apparent in Figure 18A in which at about 4 pore volumes the observed naphthalene concentration is reduced because effluent tubes were held for later sampling. The solvent/cosolvent pulse solution containing both unlabeled and ^{14}C-naphthalene was sampled both at the start and the end of pulse application so that losses due to volatilization could be assessed by liquid scintillation analysis. Volatilization was greatest for the aqueous solution (approximately 45%) and decreased as the fraction of cosolvent increased. This trend would be expected on the basis of naphthalene solubility. Values (DPM) averaged from the starting and ending times of the pulse application were used as input concentration values in CXTFIT. Inaccuracies in these input values could have contributed to the lack of good fit of CXTFIT to the observed data. Losses from the manostat barrel during effluent collection were assessed by introducing naphthalene solutions representative of applied concentrations and also diluted 1:10 into the manostat barrel under vacuum for 4 hours (the effluent collection interval). Again, losses were pronounced and followed the same trend as that observed above for pulse solutions. Losses varied from about 82% for the aqueous and lower cosolvent mixtures to 29% for the methanol-water (1:1) mixture and 55% for the acetone--water (1:3) solution. Losses such as these probably contributed significantly to diminishing observed naphthalene BTCs, particularly for the aqueous and lower cosolvent treatments, and to poor overall naphthalene recovery. Activated carbon traps placed between the atmosphere and a vent in the stainless steel cap at the top of the soil column were used to assess volatilization of applied naphthalene from the soil surface for each of the columns treated with acetone-water mixtures. However, losses of only 0.2%-0.5% of total applied ^{14}C-naphthalene were measured.

Table 14 presents a summary of data collected from naphthalene volatilization and degradation experiments designed to assess the relative importance of these processes to naphthalene transport in the soil column study. The data represents averages of 2-4 replicates for each treatment. Because some adsorption of $^{14}CO_2$ had been observed by activated carbon traps in preliminary experiments with ^{14}C-$NaHCO_3$, duplicate experiments were performed with Supelpak traps, designed especially for sorption of polynuclear aromatic hydrocarbons (PAH) like naphthalene. Again, poor overall recovery of naphthalene complicated interpretation of the results, but several important points are suggested by the data in Table 14. First of all, volatilization of naphthalene

Table 14. Summary of batch naphthalene degradation and volatilization experiments.

	Treatment	% Degraded	% Volatilized	% Residual	% Recovery
with activated C traps	Aqueous	11.6	10.9	32.4	54.8
	Methanol-Water (1:3)	1.6	24.9	18.1	44.6
	Diesel Fuel	4.7	3.3	101.6	109.6
with Supelpak traps	Aqueous	35.2	11.6	23.7	70.5
	Methanol-Water (1:3)	1.5	32.1	8.2	41.8
	Acetone-Water (1:9)	21.1	23.6	17.2	61.9

from soil reflected a reverse in trends compared to the applied pulse solutions; that is, volatilization increased with increasing cosolvent fraction. This is consistent with values for K_d in Table 11, which suggest that decreased partitioning of naphthalene into the solid phase in the aqueous system would increase the naphthalene solution concentration and thus increase volatilization. Secondly, volatilization of naphthalene (23.6%) from soil treated with the acetone-water (1:9) mixture greatly exceeded the amount volatilized from the top of soil columns treated with the same solution (0.5% as determined by activated carbon traps placed at the top of the column). A plausible explanation for this discrepancy is that volatilization experiments were characterized by higher gas flow rates than the column experiments. The significance of naphthalene volatilization in aquatic systems has been verified in other studies (Rodgers et al., 1983; Saleh et al., 1984). Park et al. (1990) reported that volatilization accounted for approximately 30% loss of naphthalene from an unsaturated soil. This value is approximately 20% higher than the values reported for the aqueous treatments in the current study (Table 14). This suggests that low recoveries may have been due to inadequate assessment of volatilization losses.

Finally, the data in Table 14 suggest that degradation occurred in the soil columns treated with aqueous solution and the acetone-water (1:9) mixture, but that degradation was inhibited in columns the methanol-water (1:3) solution. These results complicate the interpretation of BTCs and total residual naphthalene in the transport experiments in that separation of ^{14}C-naphthalene from possible metabolites was not undertaken. The liklihood of naphthalene degradation is consistent with other studies showing that naturally-occurring microorganisms capable of naphthalene degradation are found in pristine and contaminated soils (Stetzenbach et al., 1985), deep aquifers (Fredrickson et al., 1991), and marine sediments (Bauer and Capone, 1985).

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CHAPTER 5

SUMMARY AND CONCLUSIONS

Breakthrough curves for Br$^-$ in disturbed and undisturbed soil columns showed no significant evidence of physical nonequilibrium. Consequently, Br$^-$ dispersion coefficients generated using CXTFIT were used to optimize R_f values for the transport of chlorsulfuron. A nonequilibrium model (bicontinuum model) involving chemical nonequilibrium conditions for chlorsulfuron transport was necessary to obtain adequate fit to observed chlorsulfuron BTCs. CXTFIT analysis of chlorsulfuron BTCs using the LEA model where both R_f and D were allowed to float resulted in adequate r^2 values; however, these apparent R_f and D values simply compensate for the observed nonequilibrium conditions. Retardation factors for Br$^-$ were consistently less than 1, averaging 0.65-0.78 for the soils used in this study. Although anion exclusion may have contributed to R_f values less than 1, our estimates of anion exclusion volume would not explain R_f values as low as 0.7. CXTFIT was used to generate fitted pore water velocities assuming that the R_f for Br$^-$ was 1.0. A comparison of fitted pore water velocities to measured values indicated that a significant percentage of soil water under unsaturated flow conditions may be considered immobile. The solute transport model, LEACHM, was used to generate predicted chlorsulfuron BTCs using inputs for K_{oc} and λ from either LEA or bicontinuum R_f and D values. LEACHM adequately predicted the position of the observed chlorsulfuron BTCs; however, apparent R_f and D values obtained using the LEA model were necessary since LEACHM does not accept coefficients related to nonequilibrium transport (e.g. β and w in the bicontinuum model). In general, LEACHM underestimated the apex concentrations compared to observed data, and may reflect uncertainties in the fitted D values or the soil hydraulic properties (e.g. Campbell's exponent and K_s values) used as inputs to the model. Results obtained in this study also confirmed that at soil pH values near 7, chlorsulfuron is highly mobile and may move out of the root zone prior to significant chemical hydrolysis or microbial degradation.

The results of this research support the conclusion that soil depth and soil temperature significantly affect 2,4-D degradation rate. The bacterial population decreased significantly in Amsterdam silt loam and Haverson silty clay loam soil types with increasing soil depth and was positively correlated to 2,4-D degradation rate. Soil temperature strongly affected 2,4-D degradation over the 10-24°C range. Degradation rate constants increased and half-lives decreased significantly.

In the present study, degradation of 2,4-D was described adequately by both a first-order kinetic model and a logistic model with the latter providing a better fit to the experimental data. A negative correlation was observed between 2,4-D half-life and % soil organic C content, and a positive correlation existed between % organic C and bacterial CFU. These results support the idea that % organic C could be used as an index for pesticide degradation potential for those compounds known to be subject to microbial attack. It is apparent from the results of this study that transport models that attempt to describe the fate and movement of organic contaminants in soil should include appropriate kinetic parameters that allow for variations in soil depth and temperature.

In this study, naphthalene partition coefficients (K_d) significantly decreased as organic cosolvent fractions in mixtures of both methanol-water and acetone-water increased and followed a log-linear relationship. Transport of naphthalene in soil columns increased as the fraction of organic cosolvent increased for methanol-water and acetone-water mixtures. Retardation factors (R) obtained from fitting observed BTCs using the computer program, CXTFIT, generally were intermediate to those R values calculated from batch K_d values and other K_d values obtained from the literature. Observed naphthalene BTCs exhibited tailing, which indicated that some type of sorption nonequilibrium process was occurring during transport. Assessment of naphthalene losses during transport experiments as well as volatilization/degradation studies with the manifold reactor system demonstrated that these are important processes that contribute significantly to overall recovery and interpretation of experimental results. These processes must be considered in the design of experimental apparatus to create unsaturated flow conditions. The lower partitioning and accelerated transport of naphthalene observed by the addition of organic cosolvents suggests that the presence of cosolvents must be considered in predicting HOC fate in mixed contaminant waste sites or spills in the vadose zone.

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