PREFERENTIAL FLOW AND SCALE EFFECTS ON SOLUTE TRANSPORT IN INTACT AND REPACKED SOIL COLUMNS

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ABSTRACT

The preferential flow of solutes in porous media can greatly reduce the time needed for the solutes to be transported. The conventional models of predicting solute fronts and solute peaks greatly exaggerate the solute transport time. Several recent studies have shown strong bypass flow of water and solute in natural soil systems, resulting in accelerated flow of solute and water through preferential pathways.

A study of preferential flow phenomena in the vadose zone was conducted on intact and repacked 32.4-cm long soil columns at New Mexico Institute of Mining and Technology (NMIMT) in 1992 by Economy and Bowman. The current study was performed using 100-cm long soil columns from the same site to investigate the applicability of different transport parameters obtained from shorter columns to longer columns, so that solute transport can be predicted in the field scale using column study results. For this purpose an unsaturated, unit gradient, and steady state condition was created and maintained on two intact and two repacked soil columns using a constant water flux through drip emitters. Soil water tension in each column was monitored using tensiometers at various depths in each column. A slug input of m-TFMBA, an ideal tracer, and bromacil, a slightly retarded tracer, was made on the column surface. The column effluent was collected at the column bottom and analyzed using high performance liquid chromatography (HPLC) to obtain observed solute breakthrough curves (BTCs).

CXTFIT, a linear solute transport computer model, was used to fit the observed BTCs. The fitted and derived solute BTC parameters were compared to evaluate the presence of preferential flow in the columns. The results of Economy and Bowman's study and the current study were compared to evaluate scale effects. A dye experiment was performed to obtain visual evidence of the presence of preferential flow pathways.

The comparison of results from this study and the previous study done by Turney (1991) indicated significantly higher average pore water velocities in this study compared to Turney's previous study, in both the intact and the repacked columns. The degree of bypass flow was much higher in the intact than in the repacked columns. The dispersion coefficient was much higher in this study than in the previous study; high dispersion causes the solute front to migrate faster. The retardation factors of m-TFMBA and bromacil in both studies were about the same. The dye experiment offered vivid evidence of preferential flow; the dyed surface decreased with depth from the surface, indicating increased bypassing with depth.

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PREFERENTIAL FLOW AND SCALE EFFECTS ON SOLUTE TRANSPORT IN INTACT AND REPACKED SOIL COLUMNS

1. INTRODUCTION

The study of water and solute flow in the vadose zone, also known as the unsaturated zone, is still in its infancy despite recent efforts to model the flow in this zone. Due to the very nature of the vadose zone, it is a complex system with multiple factors affecting each other at any time.

The flow of water and solute through the porous media in the vadose zone is highly significant in the rate and time of groundwater contamination. The ability to accurately predict the rate of movement of water and solute in the vadose zone is critical in the evaluation, prevention and remediation of groundwater contamination. Nearly all of the traditional methods of estimating the rate of solute transport in the vadose zone consistently ignore the influence of preferential pathways. Some methods regard the preferential pathways effect as negligible. However, recent studies show that this effect may not only be non-negligible but can be the determining factor in some cases of groundwater contamination by different solutes. The preferential flow phenomenon increases the contamination potential of a water-borne chemical, because the flow becomes more concentrated and therefore faster and less susceptible to degradation and adsorption.

A study of preferential flow in the vadose zone and its effect in the adsorption of organic chemicals was previously conducted at NMIMT, using approximately 32.4-cm long and 14.2-cm diameter intact and repacked columns, by Economy and Bowman (1992); that particular study is hereafter referred as "the previous study." Results of the previous study indicated that significant preferential flow occurred under both saturated and unsaturated flow conditions, in both the intact and homogeneously repacked columns. This current study deals with basically the same phenomena, but focuses on the scale effect on the study results. Hence, in order to facilitate the comparison, this study was carried out in almost exactly the same manner as the previous study, except that the soil columns were 100-cm long. Most of the instruments used in the previous study were also used in this experiment, to eliminate the instrument effects. The experimental design was also the same, except that the intermittent flooding part of the previous study was omitted from this study due to time constraints. A dye experiment was performed for visual evidence of presence of preferential pathways in the columns. To facilitate comparison the format of this report is similar to the report of the previous study. This study complements the previous study regarding the possible effect of scale on the experimental results.

1.1. Historical Developments

Researchers began to notice the effect of preferential flow as early as the late 1800's (Lawes et al., 1882). Most scientists, however, ignored the importance of preferential flow. Lack of tools to quantitatively analyze the flow of fluid and solute in the unsaturated zone led many researchers to ignore the effect of bypass flow. One more reason the preferential flow phenomenon was not studied was its complexity due to interdependent multiple variables. Because of the ever increasing power of computers and a higher level of understanding in the field of flow through porous media, more attempts have been made recently to study the preferential flow phenomenon quantitatively.

Green and Ampt (1911) developed a quantitative relationship between velocity of solute movement and volumetric water content under unsaturated conditions, assuming a steady wetting front. This model is also known as the piston flow model. This model ignores the effect of dispersion and diffusion, and treats fluid movement as a function of potential difference, hydraulic conductivity and water content.

$$v_s = K_s \{[(h_0 - h_L) / L] + 1\} / \theta_s \qquad (1)$$

where v_s = velocity of wetting front [L/T]

θ_s = volumetric water content at the wetting front [L^3/L^3]

$h_0 - h_L$ = potential difference [L]

K_s = hydraulic conductivity of porous medium [L/T]

L = distance between two points [L]

Biggar and Nielson (1967) described a relationship between concentration gradient and concentration as a function of time, of a reactive solute. This model is called the 1-dimensional convection-dispersion model (CD model).

$$R\ (\delta C\ /\ \delta t) = D\ (\delta^2 C\ /\ \delta x^2\ ) - v\ (\delta C\ /\ \delta x) \qquad (2)$$

R = retardation factor of a solute = $[1 + (\rho\ K_D/\theta)]$

$\delta C/\delta t$ = rate of change of solute concentration with time $[M/L^3\text{-}T]$

$\delta C/\delta x$ = change of solute concentration with distance $[M/L^3\text{-}T]$

D = hydrodynamic dispersion coefficient $[L^2/T]$

= mechanical dispersion + molecular diffusion

v = average pore water velocity = q/θ $[L/T]$

ρ = average bulk density of porous medium $[M/L^3]$

K_D = linear partition coefficient; θ = volumetric water content

q = flux rate = Q/A $[L/T]$

Q = discharge rate $[L^3/T]$; A = cross sectional area of flow $[L^2]$

R, D, and K_D are discussed in more detail in Section 3.

Equation 2 is a simplified form of the CD equation. The inherent assumptions in this equation are: the sorption isotherm is linear, and D and v are constant and independent of time and space. For D and v to be constant the soil under study must be homogeneous and the water content, porosity and solute flux have to be constant.

Barring the effect of bypass flow, Equation 2 can accurately predict the breakthrough curve (BTC) of a solute of known properties in a homogeneous porous medium. Most of the currently available computer codes for solute transport use the CD model. Because of the differences in the solute BTCs predicted from the piston flow and CD model and the observed BTCs, most scientists are questioning the applicability of the piston flow model and CD model in solute transport predictions.

1.2 Recent Evidence of Preferential Flow Phenomena in Natural Soil

Numerous recent studies confirm the presence of preferential flow of water and solute in porous media under both saturated and unsaturated conditions. A few selected studies and their findings follow. Sharma and Hughes (1985) found that only 50% of the soil matrix participated in solute flow in the deep coastal sands of Western Australia. Recently, Bowman and Rice (1986b) found significantly higher average pore water velocities of solute in the vadose zone than would be predicted by the CD model. Seyfried and Rao (1987) found, from a dye experiment in undisturbed columns, that the leaching solution was bypassing a significant part of the soil matrix. Bouma and Dekker (1978) found that blue dye occupied only about 2% of the available vertical surface of soil peds, thus signifying a significant bypass flow in the soil. Booltink and Bouma (1991) found a rapid decrease in dye-stained area below the 45-cm depth. A similar finding has been reported by Ghodrati and Jury (1990) in a study of field soils. Kladivko et al. (1991)

found strong evidence of preferential movement of bromide in disturbed and undisturbed field soil. Hendrickx (1991) found that only 10% to 20% of soil volume participated in water flow in a homogeneous wettable sand soil under natural precipitation. Quisenberry et al. (1991) found that in structured soil more than 75% of water and solute moved through less than 25% of soil matrix. In light of all this evidence it is only natural that focus should shift from testing the existence of preferential flow to the factors that control this phenomenon.

1.3. Hypothesis, Goal, and Objectives of This Research

Hypothesis: Preferential flow phenomena can affect the relative retention of sorbed chemicals. The flow length, or the length of column studied, can influence the apparent degree of preferential flow.

Goal: To investigate, for a single soil and a single sorbed chemical, the relationship between degree of preferential flow and relative retardation, and the scale effect on this relationship.

Objectives:

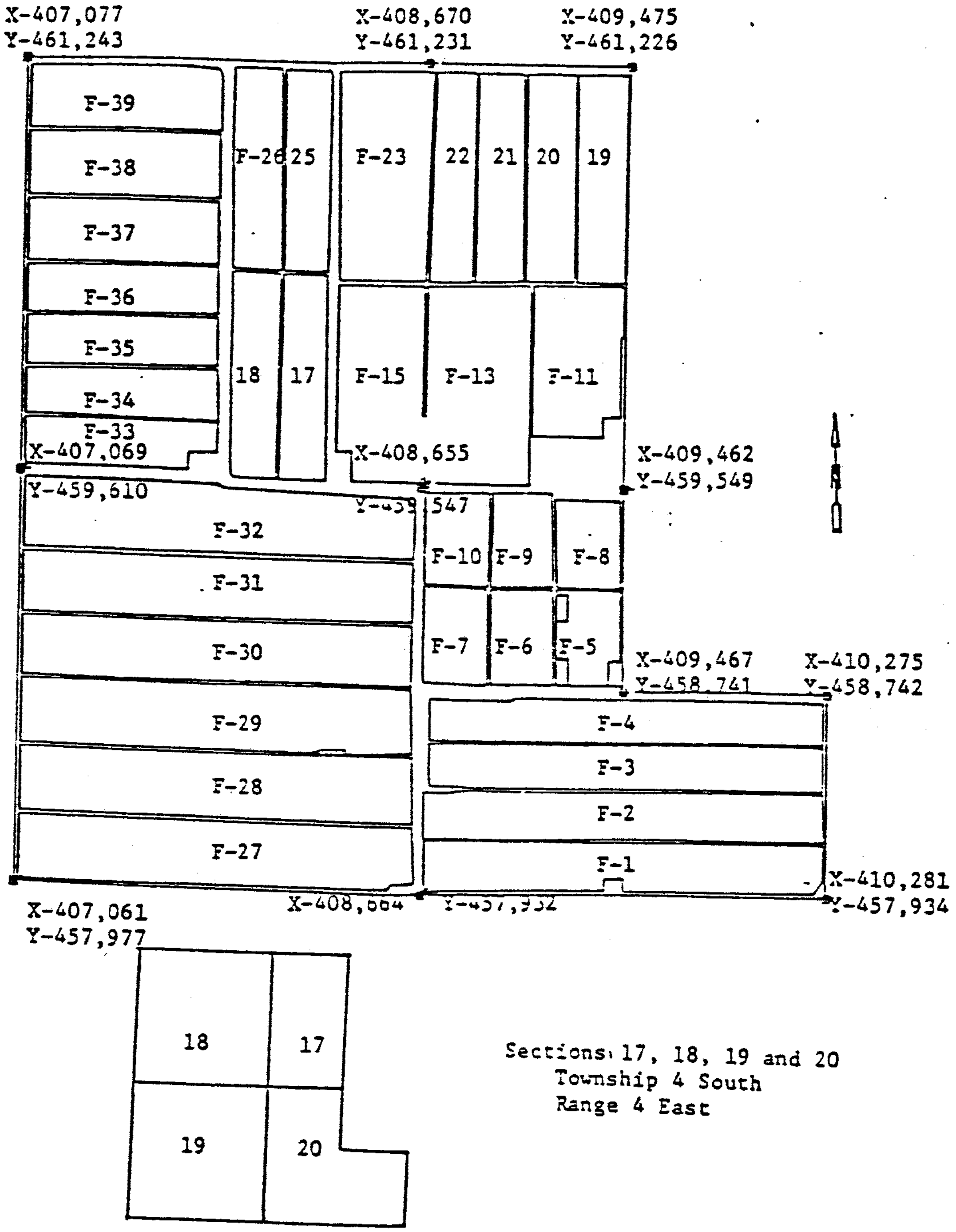
1. Determine the degree of preferential flow in intact and repacked soil columns.
2. Determine the scale effect on degree of preferential flow and its effect on relative retardation of chemicals.

2. METHODS AND MATERIALS

For the purpose of this study, four intact soil columns, each approximately 15.24 cm in diameter and 100 cm in length, were hand-carved and brought from the Maricopa Agricultural Center (MAC) of the University of Arizona. MAC is located about three miles north of the Casa Grande-Maricopa Highway and about three miles east of Maricopa in Pinal County, AZ. The intact columns were prepared using the techniques described by Economy and Bowman (1993). The best two of the four intact columns were used in the study. The soil excavated during the process of carving the intact columns was used to construct two repacked columns of same dimensions and average bulk density as the intact columns. The site was located on plot F-5 at the MAC, as shown on Figure 2.1. The exact location of the pits dug to carve the intact columns are given on Figure 2.2. Appendix 2.1 shows the details of hand carving intact soil columns and color photographs of carved intact columns before they were removed from the field.

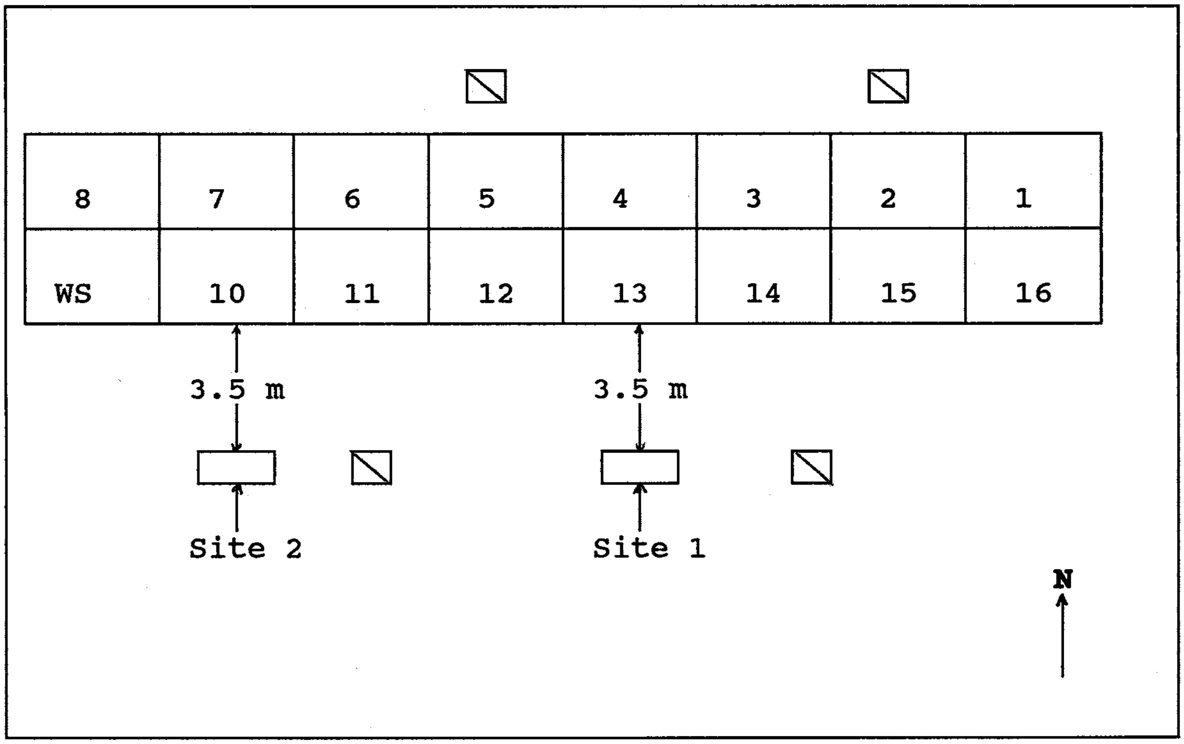
2.1. Soil Characterization

The site location was selected to facilitate comparison of the results of this study with previous studies at the same location. The soil at the MAC has been studied by



Sections: 17, 18, 19 and 20
Township 4 South
Range 4 East

Figure 2.1 Map of MAC farm located in central Arizona



SECTION OF PLOT F-5 AT MARICOPA AGRICULTURAL CENTER
(not to scale)

☐	Grids used for Turin's (1992) field study on contaminant transport
WS	Micrometeorological Weather Station
⧅	Site of the previous study
▭	Site of this study (Note : Intact Column 1 is from site 1 and Intact Column 2 is from site 2)

Figure 2.2 Specific Location of Column Sites.

Bowman and Rice (1986b), Post et al. (1988), Turney (1991), and Turin (1992). The information obtained from previous studies aid in understanding the results of this study and thus provides a more comprehensive picture of actual soil water processes.

The soil at this location is a Casa Grande deep sandy clay loam (fine-loamy, mixed, hyperthermic Typic Natrargrids) (Turney, 1991). The top 30 cm of the soil was relatively homogeneous, after which the amount of calcium carbonate visibly increased with depth. This observation was consistent with the general soil characterization by Post et al. (1988). No visible macropores were detected during the column carving and no major root systems were found below the top 15-cm of the soil surface.

The soil characteristics of this specific site were needed in order to evaluate and compare the results of this study with the previous study, so soil samples from the site were brought to NMIMT for characterization. The description of different properties and the determination methods follows.

2.1.1. Air Dried Water Content and Bulk Density

The air-dried water content, W_{ad}, of the soil was needed to calculate the mass of air-dried soil required to pack the repacked columns to the same average bulk density, ρ, as the intact columns. The W_{ad} of the intact columns were determined by cutting one of the unused intact columns into five pieces, with cuttings made at 7, 30, 60, and 90 cm from the surface. The cut pieces of columns were wetted to facilitate precise sampling. The soil was sampled at different depths with 110 cm^3 (5.08 cm diameter and 5.43 cm height) ring samplers. The soil samples were air-dried for one week, and then dried in an oven at 105^{0}C for 48 hours. A total of eight samples, two at each depth, were obtained and the two values at each depth were averaged. The mass of soil needed to pack repacked columns was calculated by multiplying the volume of column by air dried bulk density, ρ_{ad}, of the soil. The ρ, W_{ad}, and ρ_{ad} of the soil at different depths are given in Table 2.1.

Table 2.1
The Bulk Density, W_{ad}, and ρ_{ad} of Intact Soil Columns

Sample No.	Depth (cm)	ρ (g/cm^3)	Ave.ρ (g/cm^3)	W_{ad}	Ave. W_{ad}	ρ_{ad} (g/cm^3)
1	10	1.566	1.57	0.024	0.025	1.609
2	10	1.576		0.025		
3	34	1.534	1.54	0.027	0.026	1.580
4	34	1.546		0.025		
5	65	1.612	1.62	0.027	0.026	1.672
6	65	1.625		0.024		
7	96	1.816	1.80	0.029	0.028	1.850
8	96	1.795		0.027		

2.1.2. Saturated Moisture Contents and Porosity

To obtain saturated volumetric moisture content (θ_s) and porosity, the intact soil samples in the ring samplers that were used to determine bulk density were reused. Since the density of both samples at each depth were close, only one sample from each depth was used in θ_s determination. The 10-cm depth samples were accidentally destroyed during handling. To determine θ_s and porosity of the repacked columns, 184.5 g air-dried soil was packed in a 110 cm^3 ring sampler, with an average bulk density of 1.63 grams per cubic centimeter. The soil samples were saturated from the bottom, using deaired water, by placing the samples on Buchner funnels with ceramic porous plates and gradually raising deaired-water-filled flexible tubes connected to the bottom of the funnel. The deaired water was prepared by applying in-house vacuum pressure for 24 hours on an Erlenmeyer flask with tap water. The samples were considered saturated when a thin film of water developed on the soil surface. After one week of saturation, the samples were weighed, dried in an oven at 105°C for 48 hours, cooled to room temperature inside a vacuum chamber, and weighed again. About 1 mm swelling was observed on all samples when the samples were saturated; this swelling was disregarded in the volume calculation of the bulk soil.

Assuming that there were no entrapped air bubbles when the saturated soil samples were weighed and that the oven-dried, vacuum-chamber-cooled samples were completely dry when weighed, the soil porosity should equal θ_s.

Porosity can also be approximated by using the relation

$$\text{Porosity} = 1 - (\rho \,/\, \rho_s) \qquad (3)$$

where ρ_s [M/L^3] is the soil particle density. The average soil particle density is 2.65 g/cm^3 (Koorevaar et al., 1983). Table 2.2 gives the θ_s values of the soil at different depths and the soil porosity, using Equation 3 and as an approximation of θ_s. Post et. al (1988) found the porosity range of Casa Grande soil to be between 0.42 to 0.45.

Table 2.2
Saturated Moisture Content and Porosity at Different Depths

Sample No.	Depth (cm)	θ_s	Porosity = θ_s	Porosity=1-(ρ/ρ_s)
3	34	0.434	0.434	0.419
5	65	0.451	0.451	0.388
7	96	0.399	0.399	0.321

From Table 2.2 it is apparent that the intact soil columns were not homogeneous, and the soil particle density was not equal to 2.65 g/cm^3.

2.1.3 Soil Moisture Characteristic Curve

To determine the soil moisture characteristic curve, the "traditional method" described by Klute (1986) was used. The soil samples in the 110 cm^3 ring samplers were kept in Buchner funnels with ceramic porous plates. A hanging column of deaired water, connected to a graduated burette, was used to saturate the sample and to determine the sample's matric potential and water retention. Figure 2.3 is the plot of equilibrium points of matric potential (suction) and water content of the soil samples.

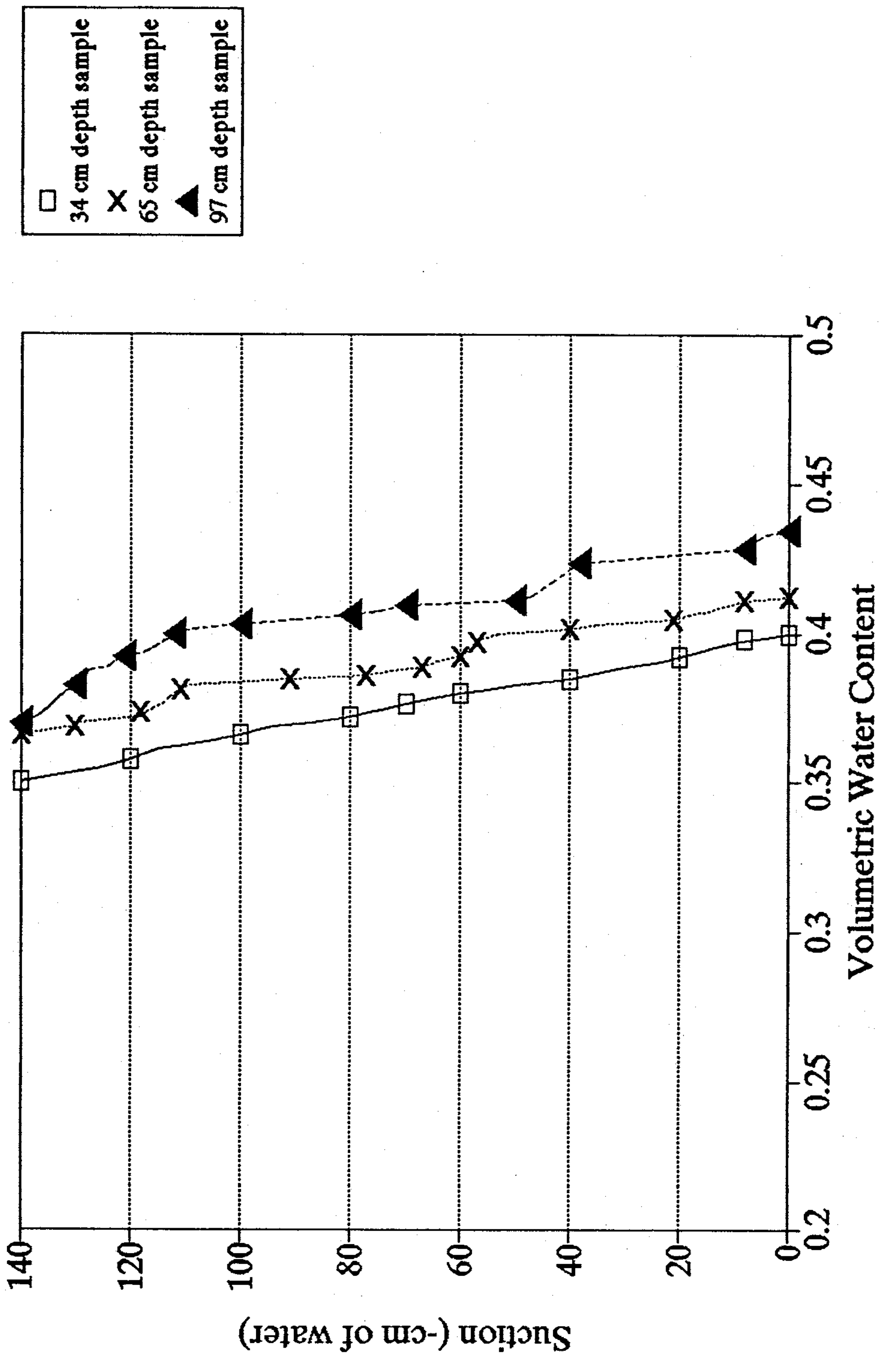


Figure 2.3 Soil Moisture Charactersitic Curves

Since the columns were saturated and then unsaturated, only the drying curve was studied. The suction was increased from 0 to 140 cm of water. A rubber septum with a hypodermic needle at the top of the burette prevented evaporation and allowed free water movement inside the burette.

2.2. Laboratory Setup

2.2.1. Intact Columns Setup

As already mentioned, two of the four hand-carved intact soil columns were used in this experiment. These intact columns were labelled Column 1 and Column 2. The bottom surfaces of the columns were wetted and cut horizontally with a butcher knife to obtain a better fit between the soil surface and a porous plate. A base assembly was constructed by gluing a 15.24-cm diameter stainless steel porous plate, with an air entry pressure of 250 mbar (Soil Measurement Systems, Tucson, AZ), to a 15.24-cm diameter transparent acrylic drain plate which, in turn, was glued to a 7.5-cm-long 15.24-cm internal diameter polyvinylchloride (PVC) tube. A thin slurry of silica flour was poured on the porous plate and the intact column was placed on the silica flour slurry, to avoid large air pockets between the bottom surface of the column and the porous plate. A 22.86-cm long 15.24-cm internal-diameter PVC collar was attached near the top of the column to support a drip emitter. Figure 2.4 shows the details of the intact column attachments before instrumentation. After the base assembly and the PVC collar were attached, both intact

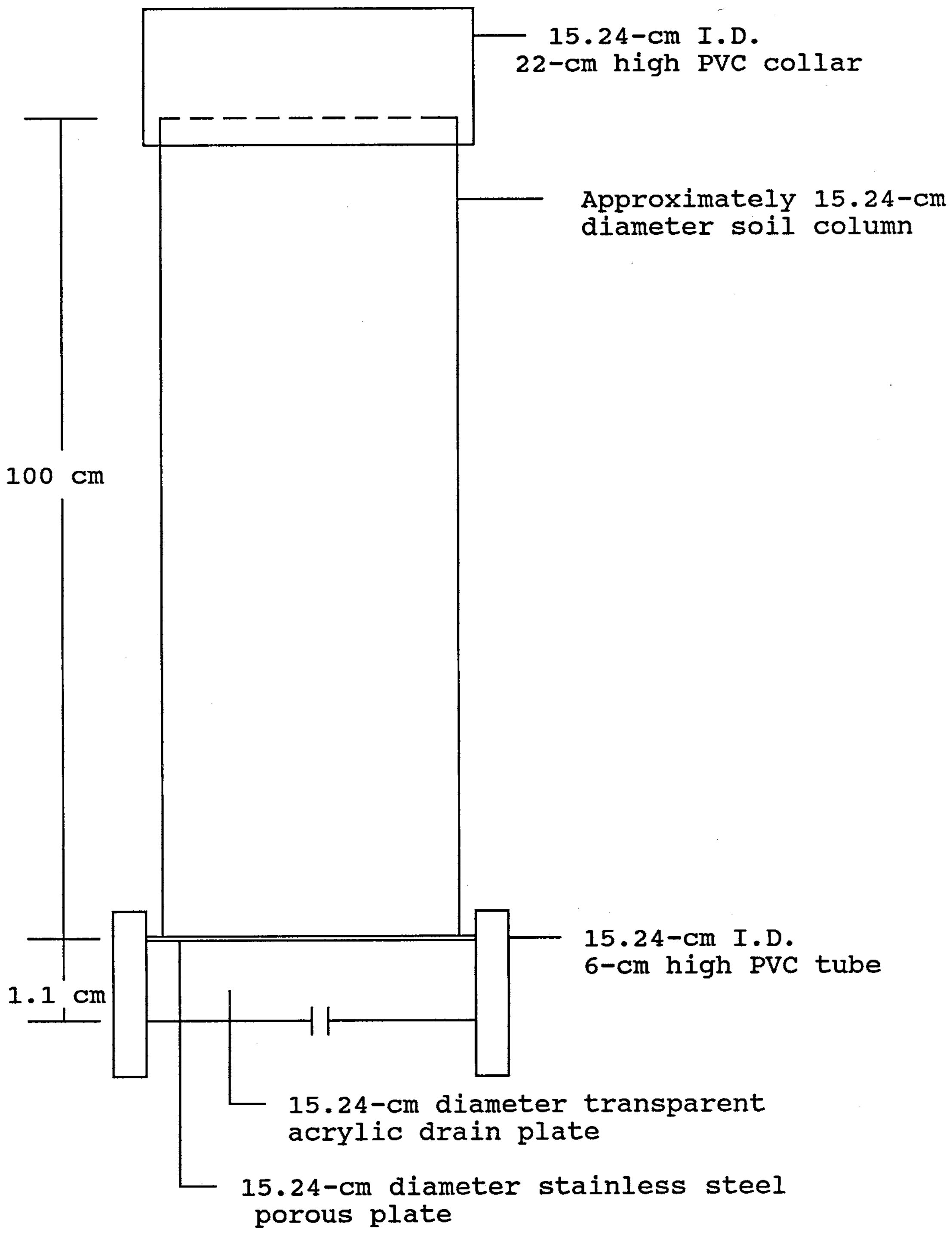


Figure 2.4 Details of Intact Column Attachments
(not to scale)

columns were erected on hand-made angle-iron frames. The angle-iron frames were made so that a cylindrical steel vacuum chamber (Soil Measurement Systems, Tucson, AZ) would fit easily underneath the frame. The vacuum chambers and the accessories used in the previous study were reused in this study. Readers are referred to Turney's (1991) thesis for details of the vacuum chamber. The distance between the columns' base assembly and the top of the vacuum chamber was approximately 9 cm. A 122-cm long bubble level was used to ascertain that the columns were vertical. The column base assembly was connected to the vacuum chamber by a 9-cm long vinyl tube and a bottle stopper attached to the chamber lid. The 9-cm distance between the column base assembly and the vacuum chamber allowed easy access to the vinyl tube. To maintain a constant potential at the column bottom, the tube was clamped each time the vacuum chamber was opened.

2.2.2. Repacked Columns Setup

The soil excavated during the column carving was brought to the laboratory, and soil from the upper and lower layers was mixed and sieved using a No. 10 sieve (2-mm opening). Two repacked soil columns of the same dimensions and the same average bulk density as the intact columns were prepared by homogeneously packing the soil inside 15.24-cm internal diameter transparent acrylic tubes. These columns were labelled Column 3 and Column 4. Appendix 2.2 contains details of packing the repacked columns and a photograph of the repacked columns in the laboratory.

The base assemblies for the repacked columns were the same as those on the intact columns. Unlike the intact columns, however, the repacked columns had no PVC collar at the top; the acrylic tube itself supported the drip emitter. The details of the repacked column attachments are given in Figure 2.5.

The repacked columns were erected on iron frames in the same manner as the intact columns. The repacked columns' connection between the base assemblage and the vacuum chambers were also the same as in the intact columns.

2.2.3. Column Instrumentation

Five equally spaced tensiometers were inserted on each of the four columns. The tensiometers were inserted at an angle of 65 degrees from horizontal to facilitate the upward migration of air bubbles formed inside the tensiometer. The approximate relative elevations of the tensiometers in each column were 95 cm, 72.5 cm, 50 cm, 27.5 cm and 5 cm; the base line was the column base. The tensiometers were connected to the Scanivalve pressure transducer system by urethane tubing, to measure the soil water tension in the column around the tensiometers. The details of construction, testing and insertion of tensiometers into the columns are given in Appendix 2.3.

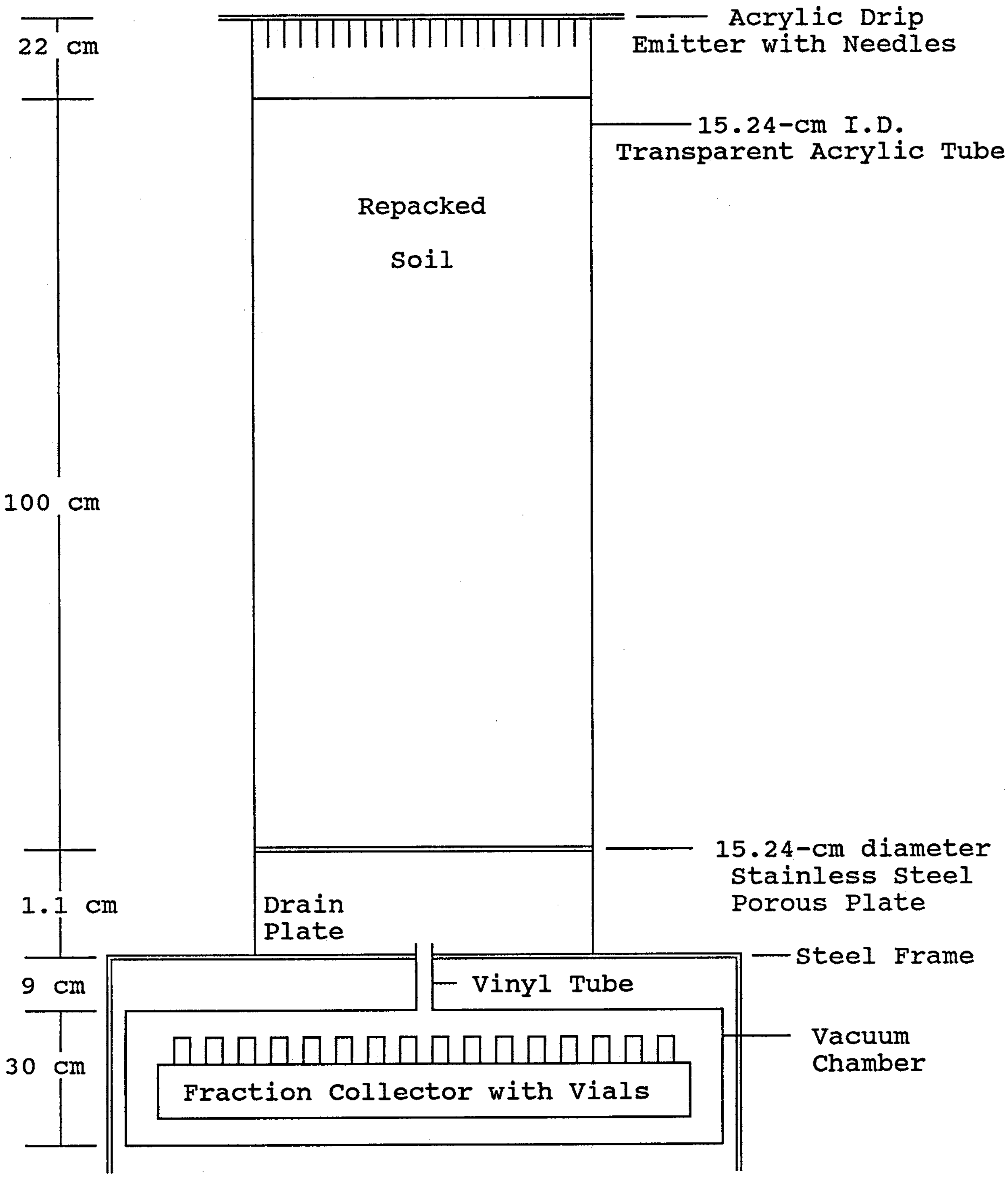


Figure 2.5 Details of Repacked Column Attachments
(not to scale)

2.2.4. Other Instruments

The water supply system consisted of a multichannel syringe water pump (Soil Measurement Systems, Tucson, AZ) and drip emitters. The water and solute flux to the columns were controlled by setting the pump cycle. Turney (1991) provided details of drip emitter construction.

The purpose of using the drip emitters to input water and tracer solution in the soil was to simulate a trickle irrigation in a field. The uniformly distributed needles in the drip emitters ensured virtually uniform application of water and solutes. Moreover, the uniformity of water flow through each needle in the drip emitters was checked by running the water pump with empty vials underneath each needle. The needles were replaced if the water collected in a specific vial differed 1% or more from the mean. Two layers of nylon screens at the soil surface prevented the water drops from disturbing the soil surface. All four ports of the water pump were also checked to make sure that the volume of water delivered per pump cycle was same from all ports. Kluitenberg and Horton (1990) found that the solute application method can significantly affect the BTC of the solute exiting a column. But the significance decreased when the "drained porosity" decreased. For the purpose of this study, the drip emitter method to introduce solute in the columns was deemed satisfactory. The "frozen disk method" of solute application, used in the previous study, was abandoned in this study because numerous complications developed in that method (Turney, 1991).

The effluent collection system on each column consisted of a 46-cm diameter and 30-cm height steel cylindrical vacuum chamber (Soil Measurement Systems), a Moore Model Series 44 pneumatic null-balance pressure regulator (Moore Products Co., Spring House, PA), and an ISCO Retriever II fraction collector (Isco, Inc., Lincoln, NE). The vacuum chamber allowed application of negative potential at the column bottom, which enhanced the flow of water and solute through the soil columns while maintaining a unit gradient in the columns. The vacuum pressure was controlled by the pressure regulator. The effluent amount in each vial was controlled by setting the fraction collection cycle.

The data acquisition system consisted of a 24-port scanning fluid switch wafer (Scanivalve model # W0602/1P-24T 303 S.S., Sam Diego, CA), a Druck PDCR 22 differential, strain gauge pressure transducer (Druck Incorporated, New Fairfield, CN), an AD-500 data acquisition board (RTD A/D500, State College, CA), and an IBM-XT personal computer. The method of use and the purpose of these instruments were the same as in the previous study (Turney, 1991), so readers are referred to that thesis for details of these instruments. Both studies used the same software to collect and store the pressure data on the computer; the source code of this software is given in the appendix of Turney's thesis (1991). The software triggered the scanning valve to rotate every 30 minutes. As the scanning valve rotated through each fluid switch wafer port, the pressure transducer measured the pressure in each tensiometer. The millivolt (mV) outputs from the transducer were stored on the computer. The schematic of the use of these instruments is given in Figure 2.6.

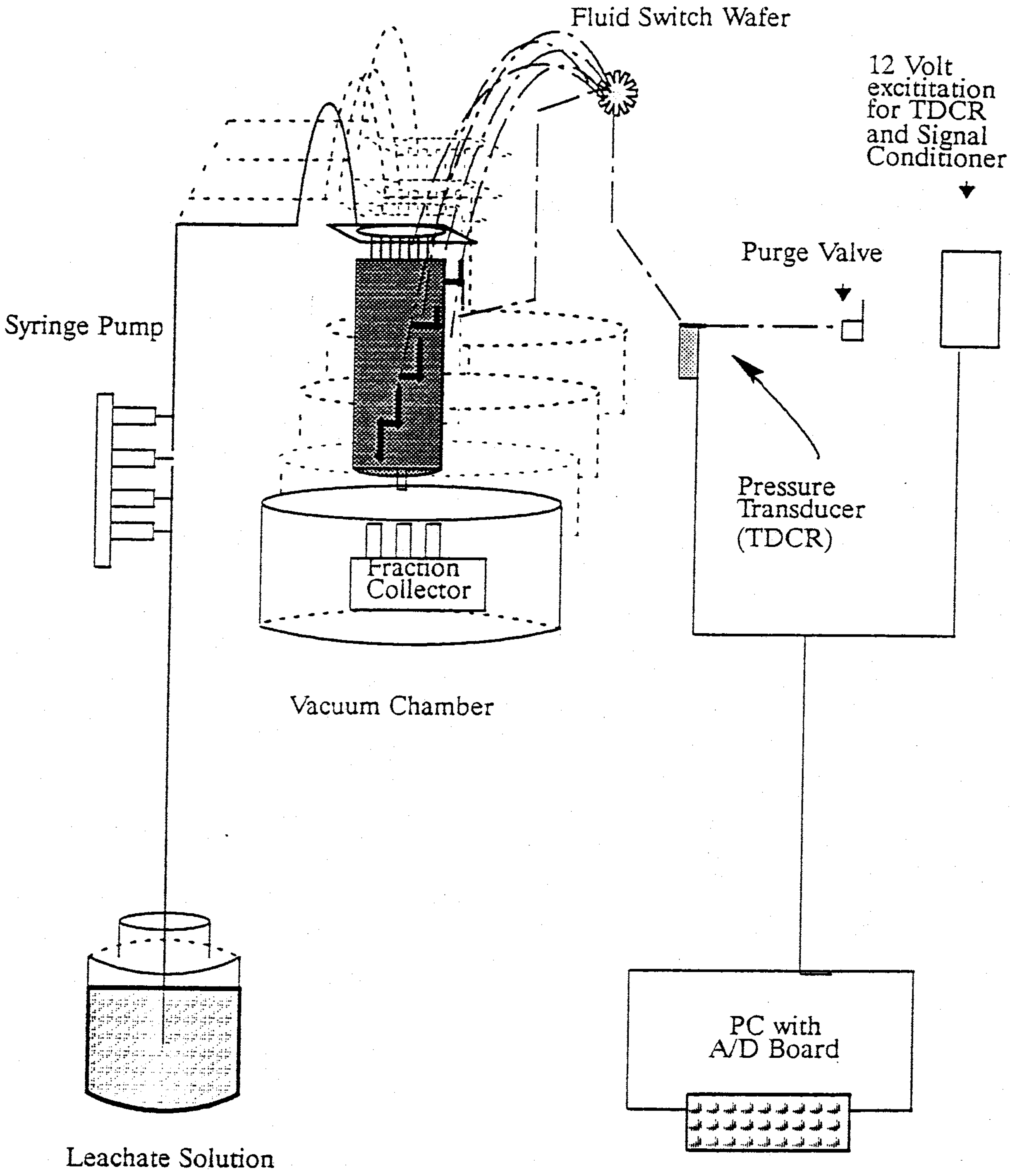


Figure 2.6 Schematic of Laboratory Setup

(from Turney, 1991)

2.3. Experimental Design

Two intact and two repacked soil columns were subjected to unsaturated conditions using constant flux, 0.67 cm/day (123.05 mL/day), of simulated Maricopa well water, using the water supply system and the vacuum chambers mentioned above. The composition of Maricopa well water is given in Table 2.3. The flux rate used in the previous study was in this study used as a guide in setting initial inflow rate. The final constant flow rate was determined by the outflow rate, which maintained a constant rate of 123.05 mL/day (0.015 pore volume (PV) per day). The outflow rate was determined by collecting the outflow in 42 21-mL vials and dividing the total amount of outflow by the duration of effluent collection. The outflow rate was monitored throughout the experiment.

Table 2.3
Maricopa Well Water Composition

Constituents	Molarity	Concentration (mg/L)
Ca^{+2}	0.0036	144.28
Mg^{+2}	0.0016	40.10
Na^{+}	0.0184	423.00
SO_4^{-2}	0.0092	883.35
Cl^{-}	0.0108	382.28

The soil suction, which indicated the dryness of the columns, was monitored by tensiometers (Section 2.2.3). The soil water tension measurements were taken every 30 minutes, using the data acquisition system. A total of 65 days was required to establish a near unit gradient and steady-state condition. The tension in each tensiometer continued to fluctuate slightly throughout the duration of the experiment. This fluctuation was caused by small air bubbles that gradually accumulated in the urethane tubing that connected the tensiometers to the pressure transducer. The tensiometers and the urethane tubes were flushed every three or four days to eliminate accumulated air bubbles, as suggested by Cassel and Klute (1986).

Once a unit gradient was achieved, as indicated by constant suction at all elevations of each column and by inflow rate equalling outflow rate, a slug input of tracer solution was made at the top of all four columns simultaneously, at the same steady-state flux rate. The tracer solution consisted of 500 mg/L bromacil (5-bromo-3-sec-butyl-6-methyluracil) and 250 mg/L meta-trifluoromethylbenzioc acid (m-TFMBA); both chemicals were obtained from Aldrich Chemical Company, Milwaukee, Wisconsin. The amount of solute introduced was 200 mL (0.025 PV) in each column, so each column received 100 mg of bromacil and 50 mg of m-TFMBA. The tracer solution was introduced for 38 hours. The m-TFMBA served as tracer of water movement; m-TFMBA has been found to be a nonreactive stable anionic tracer in vadose zone tracer tests (Bowman and Gibbens, 1992). The previous study also used m-TFMBA as an ideal tracer.

After a slug input of solutes the water supply system was switched back to Maricopa well water.

The column effluent was collected in labeled 21-mL plastic scintillation vials, using vacuum chambers and fraction collectors. The 9-cm distance between the column bottom attachments and the vacuum chamber (Figure 2.5) was small enough to minimize mixing of the effluent before it was collected in the vials. The fraction collector was set such that each vial collected effluent for four hours. At the set inflow rate, the amount of effluent collected in each vial was approximately 20.5 mL (0.0025 PV). A new set of 42 empty vials was needed every seven days. Constant potential at the column bottom was maintained by clamping the tube that connected the base assemblage to the vacuum chamber before opening the vacuum chamber to collect effluent filled vials. The vials were weighed and capped as soon as possible. It took approximately 10 to 15 minutes per column to replace the vials in the chamber and cap the effluent vials.

The effluent was collected and the soil water tension was monitored for 110 days.

A dye experiment was performed on all four columns at the end of this study for visual evidence of preferential pathways in the columns. The Erioglaucine dye (Aldrich Chemical Company, Milwaukee, WI), also known as FD&C Blue #1, with dye content approximately 70%, was prepared at a concentration of 100 mg/L and introduced on the soil surface for 12 days via the water supply system, at the steady-state flux rate. This period of dye introduction was selected for several reasons. The volume of intact columns had to be determined after the end of the experiment by removing the soil in the column and filling the column with water. The intact and the repacked columns needed to be weighed to determine their water content. So the columns could not be dissected after the dye introduction i.e., the soil in the columns had to be hand-removed. It was determined that soil removal below the top 40 cm would not be feasible without cutting the column. Since the approximate derived water velocity in the columns was 2.7 cm/day, a longer period of dye introduction can uniformly dye the upper 30 cm of the column by diffusion. Hence, it was decided to observe the beginning of the bypass flow. In 12 days the dye front was expected to travel between 30 and 40 cm. The soil was removed from each column in 5-cm depth increments. Each new exposed soil surface was photographed to record the dye pattern. The color photographs of exposed surfaces of different columns at different depths appear in Appendix 3.2.

2.4. Chemical Analysis

The effluent samples were analyzed for m-TFMBA and bromacil using HPLC. A small sample from each of the vials was used to check the effluent pH with a Beckman pH Meter Model 45 (Beckman Instruments, Inc., Fullerton, CA)

The HPLC hardware consisted of five major parts -- a pump (Model 501, Waters Associates, Inc., Milford, MA); an autosampler (Model ISS-200, Perkin-Elmer Corp., Analytical Instruments, Norwalk, CT); a stationary phase consisting of a 15-cm x 4.6-mm

I. D. Rex-chrom ODS (C18) column packed with 5 micron particles (Regis Chemical Co., Morton Grove, IL); a spectrophotometer (Waters Lamba-Max Model 481); and an integrator (Waters Model 745).

For chemical analysis of the effluent, the wavelength was set at 220 nm because bromacil absorption maxima occur at 220 and 270 nm, while m-TFMBA also shows strong absorbance at 220 nm. The mobile phase consisted of a 60/40 $MeOH/KH_2PO_4$ (0.02 M) solution with pH adjusted to 3.0 using orthophosphoric acid. The flow rate was set at 1.0 mL per minute. The injection volume was set at 10.0 microliter. The integrator was set to calculate the area under the peak on the chromatogram. The retention times (RT) of bromacil and m-TFMBA are a function of mobile phase pH. If mobile phase pH decreases, the RT of both tracers increase; however the RT of m-TFMBA increases to a much higher degree than the RT of bromacil. Several trials of different mobile phase pH were required to optimize bromacil and m-TFMBA peak separation in the chromatogram.

2.5. Dyed Area Calculation

Several color photographs of the exposed surfaces of all four columns at different depths were taken for visual evidence of the solute transport mechanism. The photographs were traced onto plain paper and enlarged by a photocopy machine. A transparent graph paper was overlaid on the enlarged figures and the approximate areas of dyed and clear portions at each depth were estimated by counting the squares on each figure.

2.6. Computer Model and BTC Analysis

CXTFIT (Parker and van Genuchten, 1984), a non-linear least squares curve-fitting program for simulating one-dimensional advective-dispersive flow, was used to estimate different transport parameters and to fit BTCs of m-TFMBA and bromacil. A comparison between simulated and observed BTCs was made to determine the presence of preferential flow. The results of this experiment were compared to the previous study to check any scale effect on the results of the experiments. The details of CXTFIT and scale effect study are given in Section 3.

3. RESULTS AND DISCUSSION

3.1 Unit Gradient in Columns

The experiment was conducted under unit gradient condition in all four columns. The constant suction in all five tensiometers of each column indicated a unit gradient. The suction in each tensiometer fluctuated continually but intermittently as a result of air bubble accumulation in the tensiometers and in the urethane tubes that connected the tensiometers to the pressure transducer. The intermittent fluctuation in tensiometer readings did not indicate change in column water content because the outflow rate from all columns remained constant throughout the experiment.

A near unit gradient condition was deemed satisfactory when that condition was observed for seven consecutive days. Figures 3.1 to 3.4 represent the soil water tension in different tensiometers of different columns at different times. As indicated in Figures 3.1 and 3.2, in both of intact columns the near unit gradient condition deteriorated a week after the tracers were applied. The upper part of the intact columns, which were relatively less dense, became slightly drier and the lower part of the columns, which were more dense, became wetter. This condition was maintained throughout the experiment. The lower part of the columns contained more clays, and thus held more water. The unit gradient conditions in the repacked columns were relatively more stable.

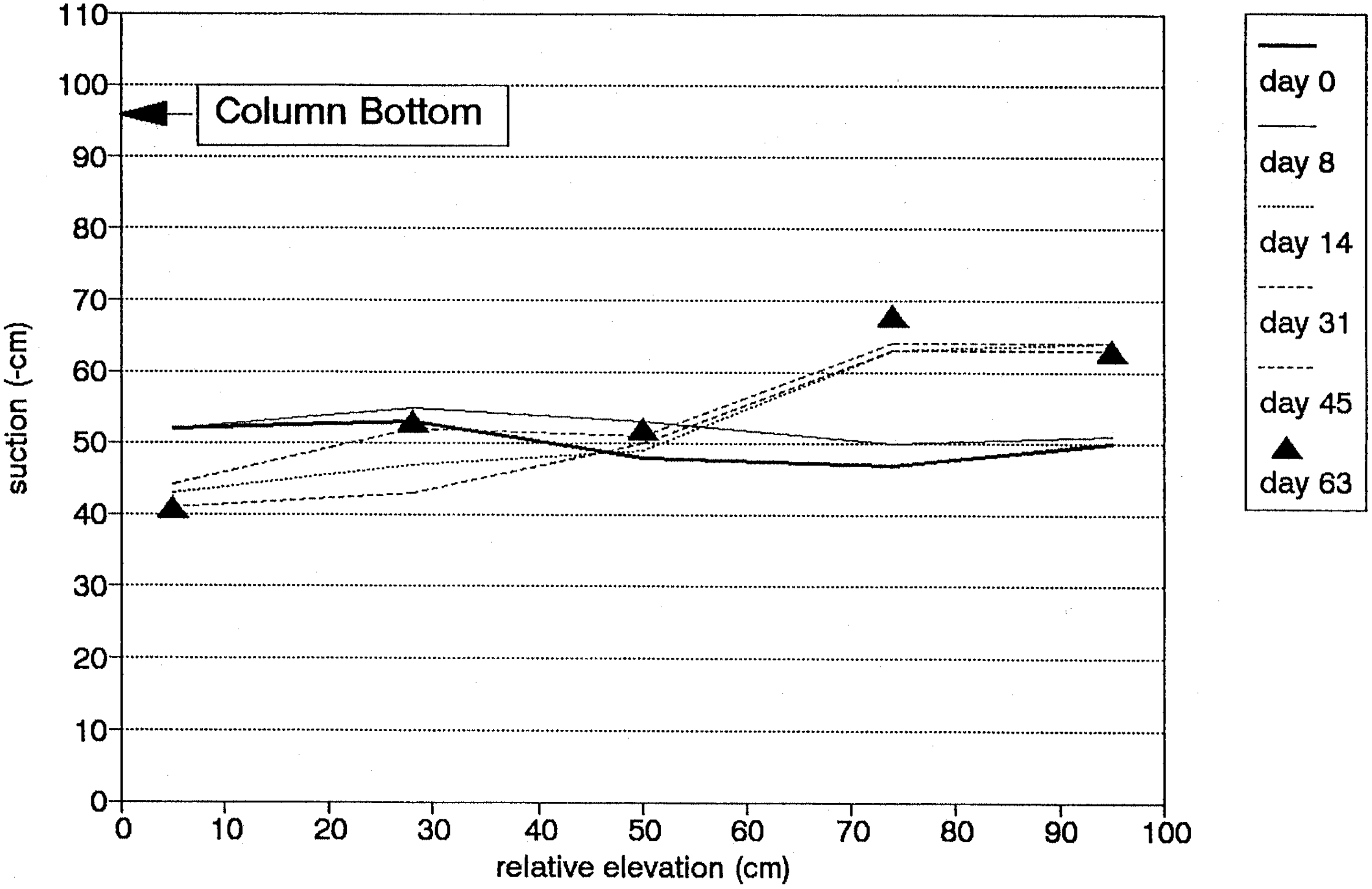


Figure 3.1 Potential versus Elevation in Column 1

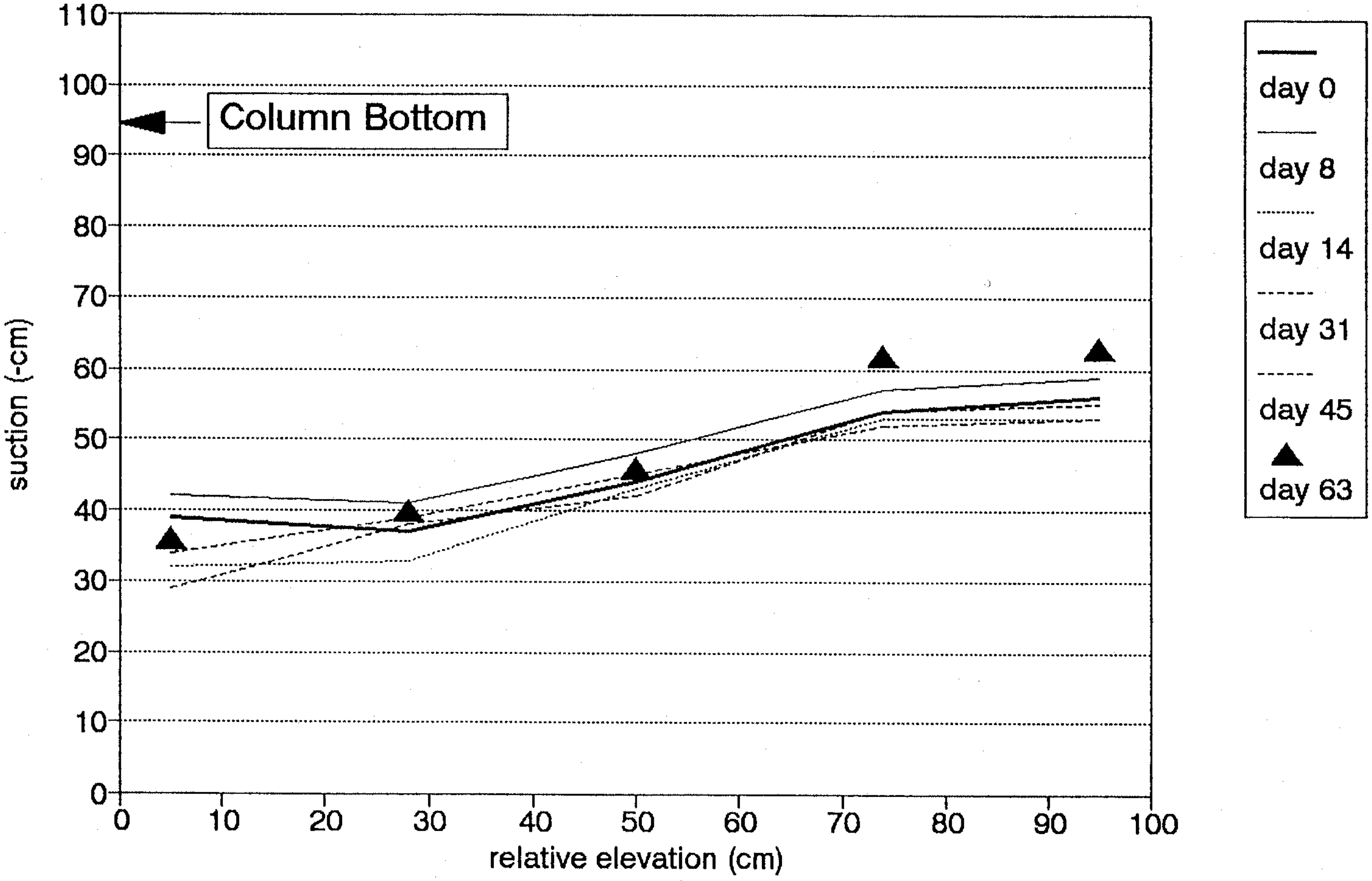


Figure 3.2 Potential versus Elevation in Column 2

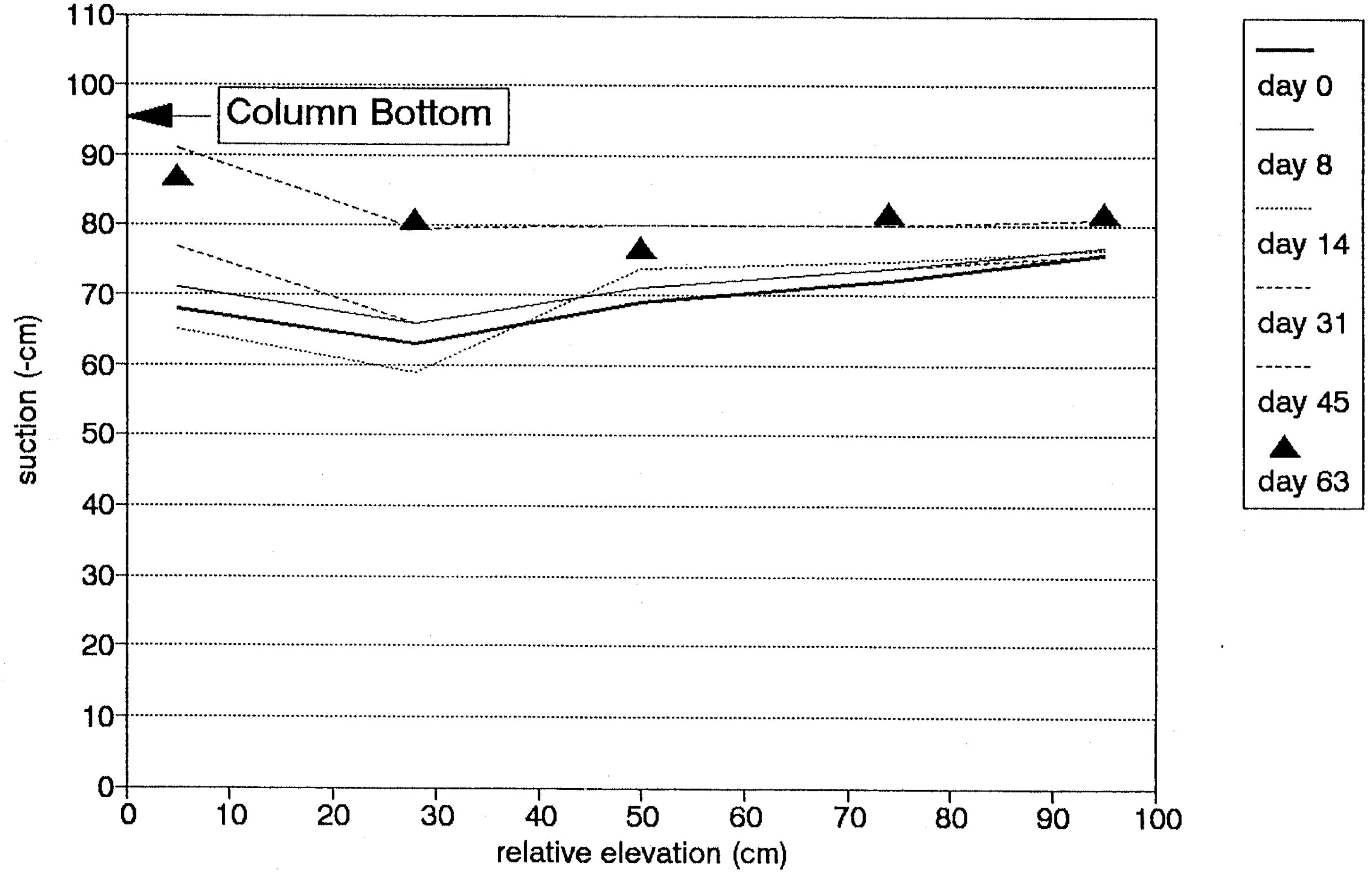


Figure 3.3 Potential versus Elevation in Column 3

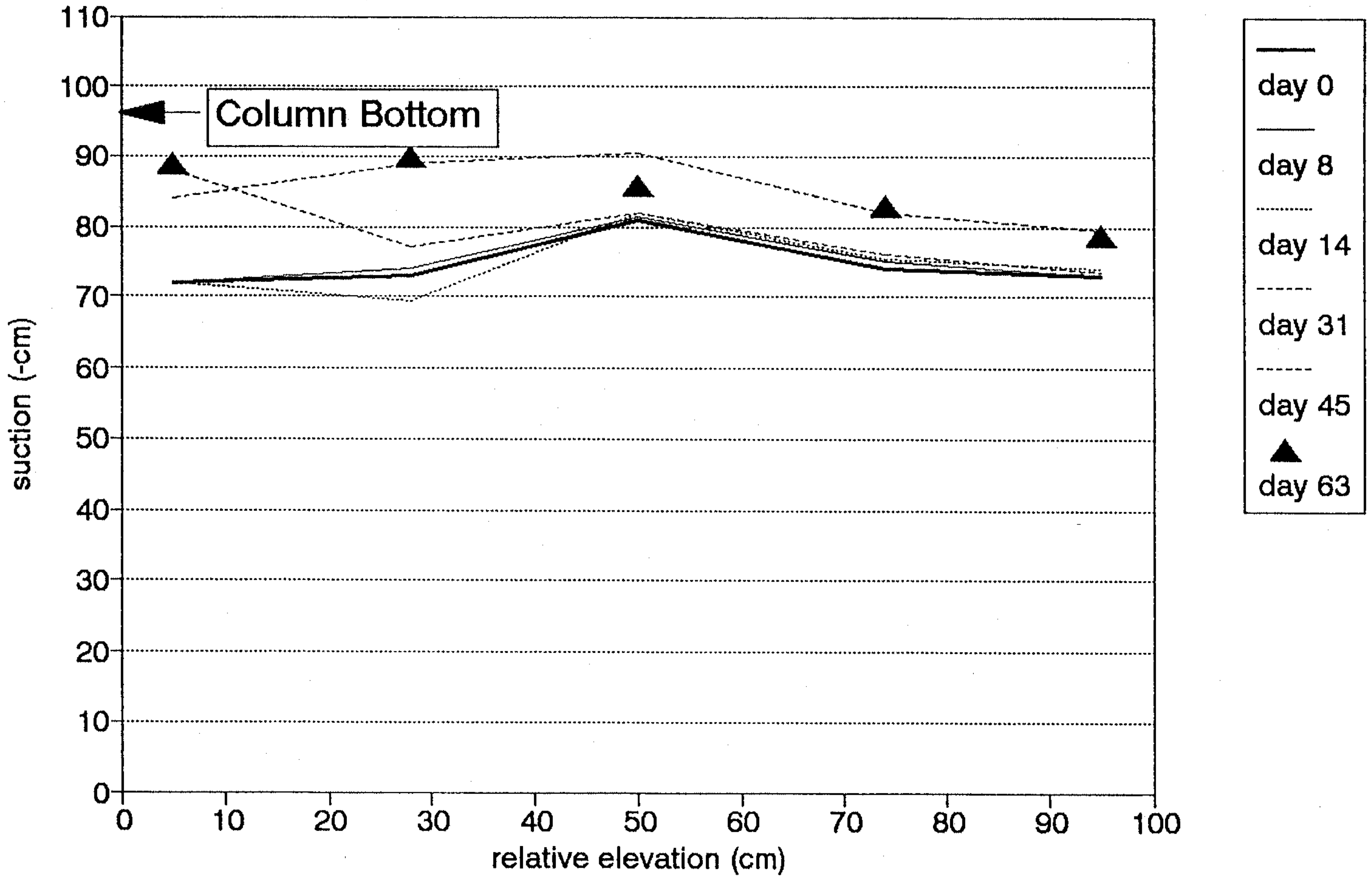


Figure 3.4 Potential versus Elevation in Column 4

3.2 Observed BTCs

Using HPLC, the column effluent was analyzed to obtain observed BTCs of bromacil and m-TFMBA. The area under the peak (AUP) of the chromatogram was calibrated using standard solutions of different concentrations. The relation between area and concentration was approximately linear, as shown in Figure 3.5. Figures 3.6a and 3.6b are chromatogram standards of bromacil (30.0 mg/L) and m-TFMBA (20.0 mg/L). Figure 3.7 is a chromatogram of an effluent sample with both tracer peaks identified.

The relation between absolute values of area and concentration varied continuously, i.e., for the same concentration in a standard solution the AUP fluctuated depending on the exact volume of effluent injection. Similarly, depending on the mobile phase flow rate at any given time, the retention time (RT) of solutes fluctuated. The pressure gauge in the pump, which injected the mobile phase, fluctuated occasionally. Every decrease in water pump pressure resulted in an increase in RT of both tracers. For example, as shown in Figures 3.6a and 3.6b, for bromacil at 30 mg/L the AUP varied from 1449069 to 1529476 and the RT changed from 3.29 to 3.28 minutes. Similarly, for m-TFMBA at 20 mg/L, the AUP varied from 1032834 to 1053340 and the RT changed from 4.93 to 4.92 minutes. Note that these two samples were analyzed within 7 minutes of each other. Therefore, when operating the HPLC, every sixth sample analyzed was a standard solution to continuously calibrate the area under the peak, assuming a linear relationship between AUP and solute concentration.

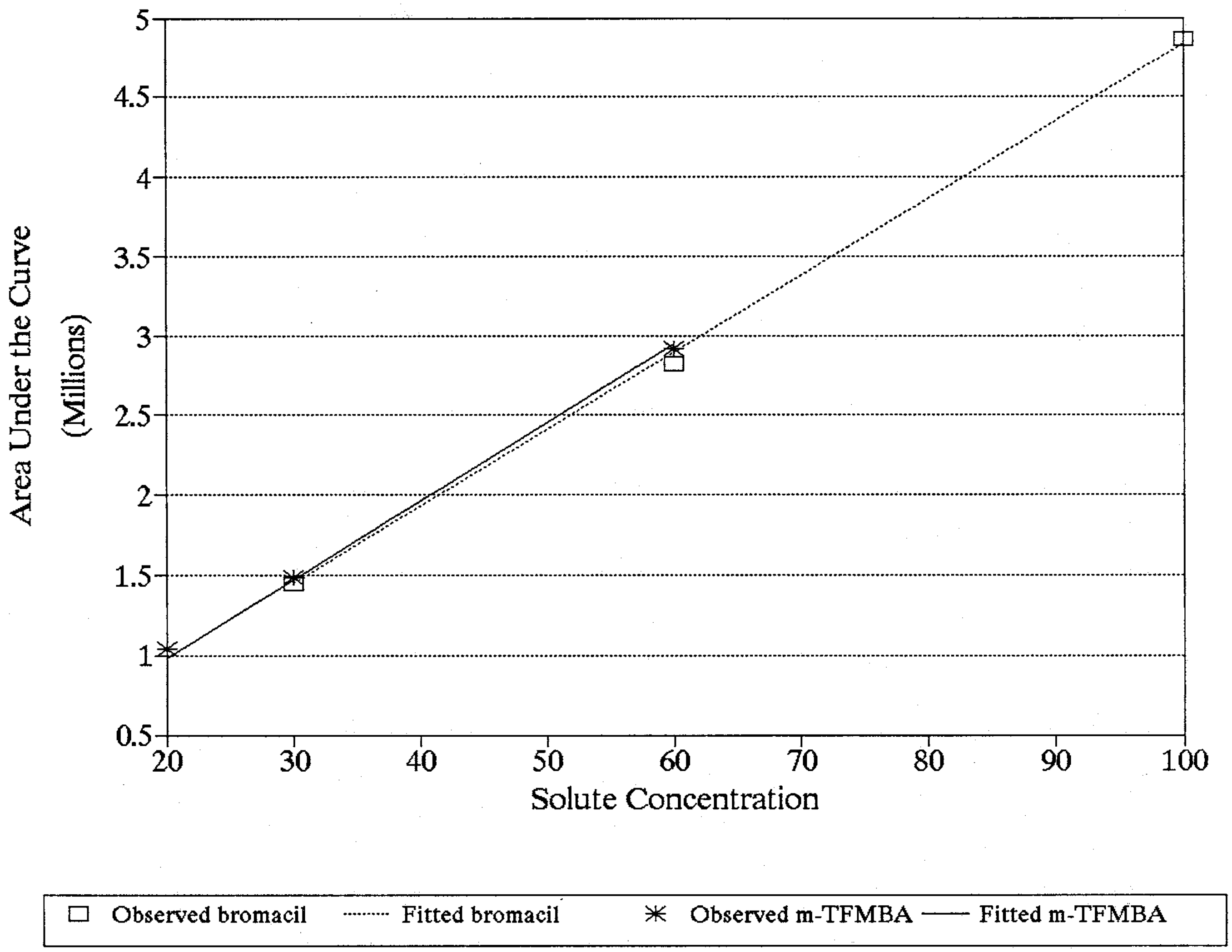
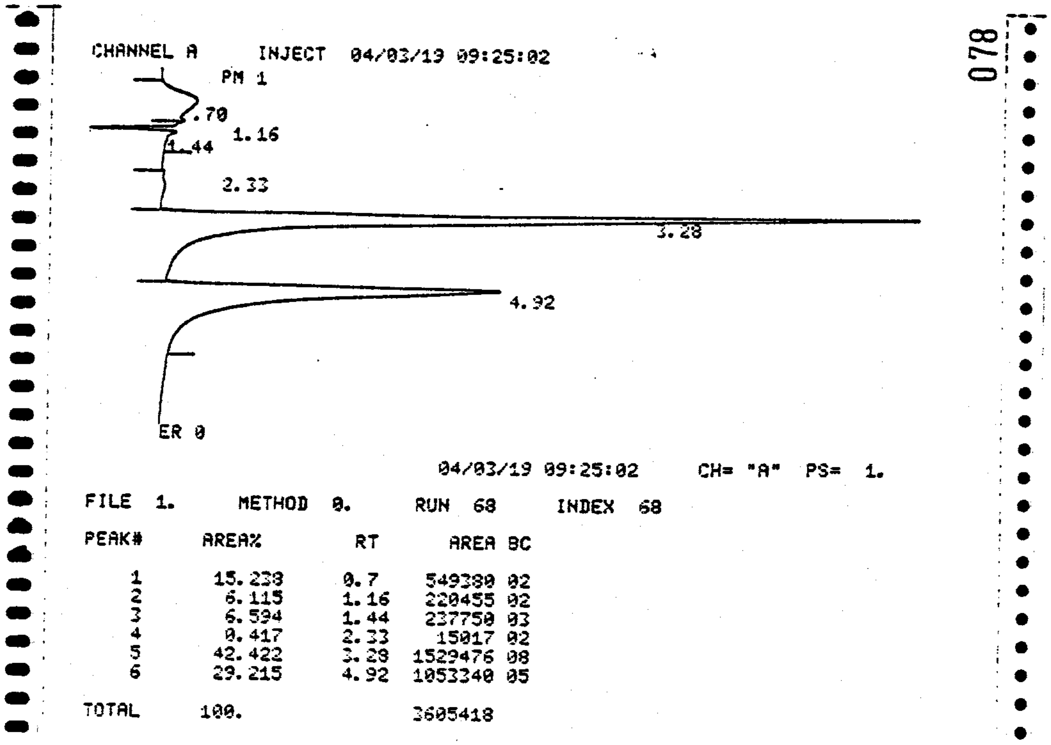


Figure 3.5 Relation Between Area Under the Curve and Solute Concentration



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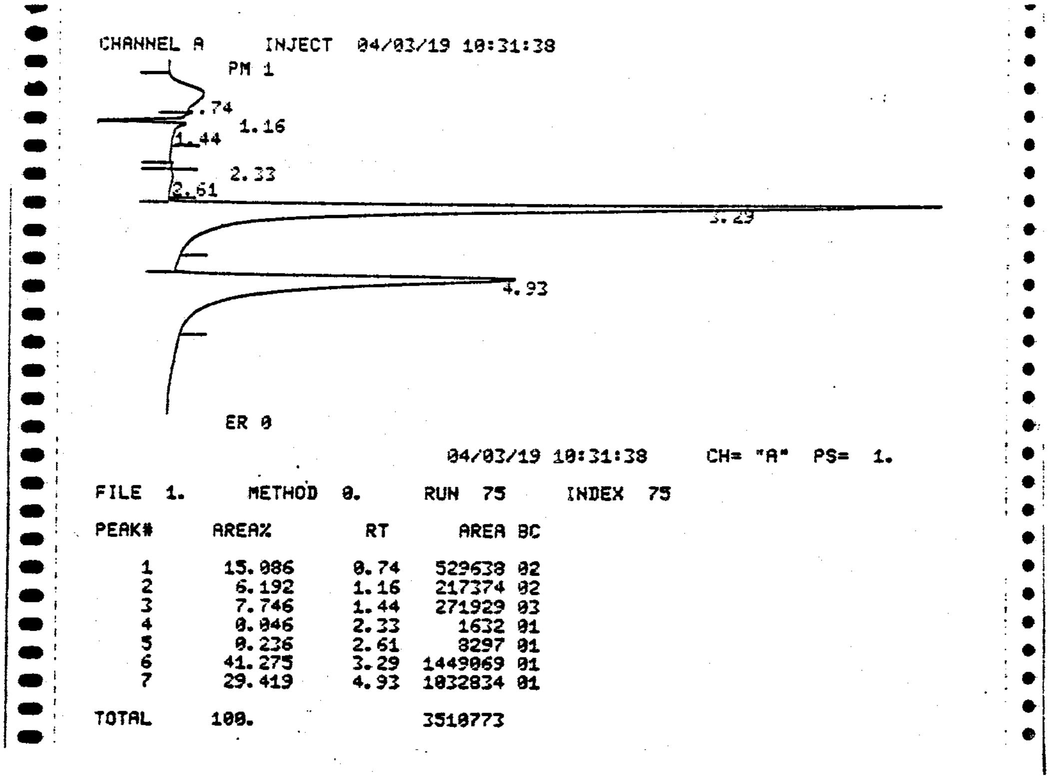
FILE  1.     METHOD  0.      RUN  68      INDEX  68

PEAK#      AREA%        RT       AREA BC

    1       15.238     0.7     549380 02
    2        6.115     1.16    220455 02
    3        6.594     1.44    237750 03
    4        0.417     2.33     15017 02
    5       42.422     3.28   1529476 08
    6       29.215     4.92   1053340 05

TOTAL      100.               3605418
```

Figure 3.6a Example of Chromatogram of Standard Solution.



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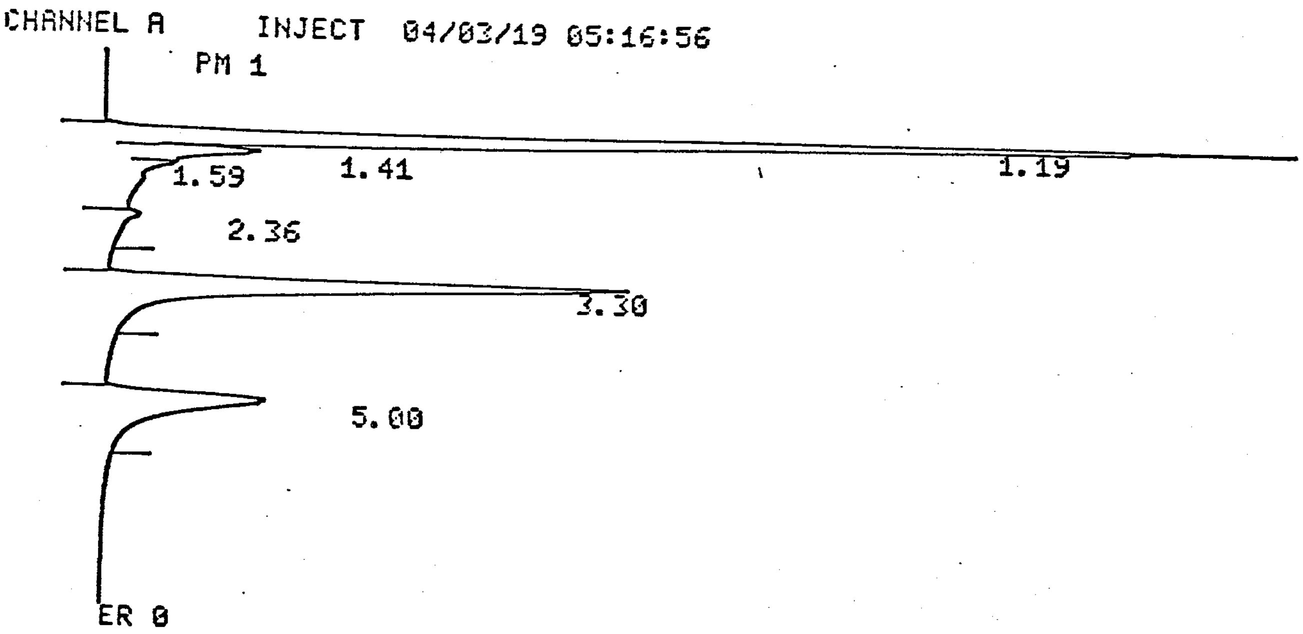
PEAK#      AREA%        RT       AREA BC

    1       15.086     0.74    529638 02
    2        6.192     1.16    217374 02
    3        7.746     1.44    271929 03
    4        0.046     2.33      1632 01
    5        0.236     2.61      8297 01
    6       41.275     3.29   1449069 01
    7       29.419     4.93   1032834 01

TOTAL      100.               3510773
```

Figure 3.6b Example of Chromatogram of Standard Solution



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FILE  1.      METHOD  0.      RUN  42      INDEX  42

PEAK#       AREA%        RT      AREA BC

    1      40.364      1.19    837515 02
    2       6.795      1.41    140993 02
    3       6.854      1.59    142210 02
    4       2.097      2.36     43504 03
    5      29.682      3.3     615869 01
    6      14.209      5.      294819 01

TOTAL      100.                2074910
```

Figure 3.7 Example of Effluent Chromatogram

3.3 Mass Balance

The observed mass balances of m-TFMBA and bromacil were calculated from the observed BTCs of the tracers, using trapezoidal integration. The following relation was used to calculate mass recovered in each duration:

$$M = (Q\ C\ \Delta t)/1000 \tag{4}$$

where M = mass recovered in time Δt [mg]

Q = steady-state flow rate [mL/day]

C = solute concentration [mg/L]; Δt = time [day]

The fitted mass balance was checked from the fitted value of pulse, a parameter in CXTFIT that indicates the time duration of tracer solution application. The mass recovery of a species depends on several factors, such as its biological and chemical degradation rate, duration of the experiment, and experimental conditions. The observed and fitted BTC concentrations of both chemicals in each column are given in Appendix 3.1.

As indicated in Table 3.1, the mass of m-TFMBA recovered was approximately 97% of the input in both the intact and repacked columns, except in Column 2. This mass recovery was expected because m-TFMBA is a nonreactive tracer and flows along with the leaching solution without being retarded or degraded. This result is consistent with previous study by Bowman and Rice (1986a) but is not consistent with the result of the previous study. The mass recovery of bromacil was also approximately 97% in both the intact and repacked columns, again except in Column 2.

The specific reasons for low recovery of m-TFMBA in Column 2 could not be pinpointed; however, considerably more biological growth was detected on this column than on any other column. When the soil was extracted from Column 2 at the end of the experiment, it released a strong foul smell.

Table 3.1
Mass Recovery of m-TFMBA and Bromacil in
Intact and Repacked Columns Based on Observed and Fitted BTCs

	Intact Columns				Repacked Columns			
	Column 1		Column 2		Column 3		Column 4	
Tracer	Observed	Fitted	Observed	Fitted	Observed	Fitted	Observed	Fitted
m-TFMBA	97%	98%	92%	92%	96%	95%	98%	96%
Bromacil	97%	98%	89%	88%	96%	94%	98%	96%

The less-than-100% mass recovery of both chemicals can be attributed to several possible factors: (1) The tracer retention time during HPLC analysis fluctuated, which made it difficult to detect all of the tracer peaks. The fluctuation in retention time was controlled by using a buffer solution in the mobile phase. Therefore the error resulting from this factor was minor. (2) The sorbed bromacil and entrapped m-TFMBA in relatively immobile regions diffused slowly; hence the tracers were not totally recovered during the duration of the experiment. The m-TFMBA was not reactive, but some of the solute can be trapped in relatively immobile regions of the soil matrix and can be released slowly through the diffusion process. The same mechanism can cause the bromacil to retard its migration. This retardation can cause incomplete recovery of the solute during the experiment. (3) The chemical and biological degradation can cause less than 100% mass recovery. Bowman and Rice (1986a) found some mass loss of m-TFMBA in Arizona field studies. Similar mass losses can contribute to less than 100% mass recovery in this experiment. Biological growth was noted in all four columns during this experiment. The biological growth is discussed in detail in Section 3.9 of this report.

3.4 Effluent pH

The pHs of the effluent samples were tested to see if there was any dramatic or consistent change in effluent pH. Extreme pH variation can affect the solute BTC by reacting with the soil matrix. The effluent pHs from all four columns were fairly stable all through the experiment, mostly between 8.0 and 8.4, as shown on Figure 3.8. The pH of the tracer solution before being introduced on the soil was 7.56; the pHs of column effluent before tracer introduction were 7.70, 7.37, 7.80, and 7.99 in Columns 1, 2, 3, and 4, respectively. Thus no significant changes in effluent pH were observed.

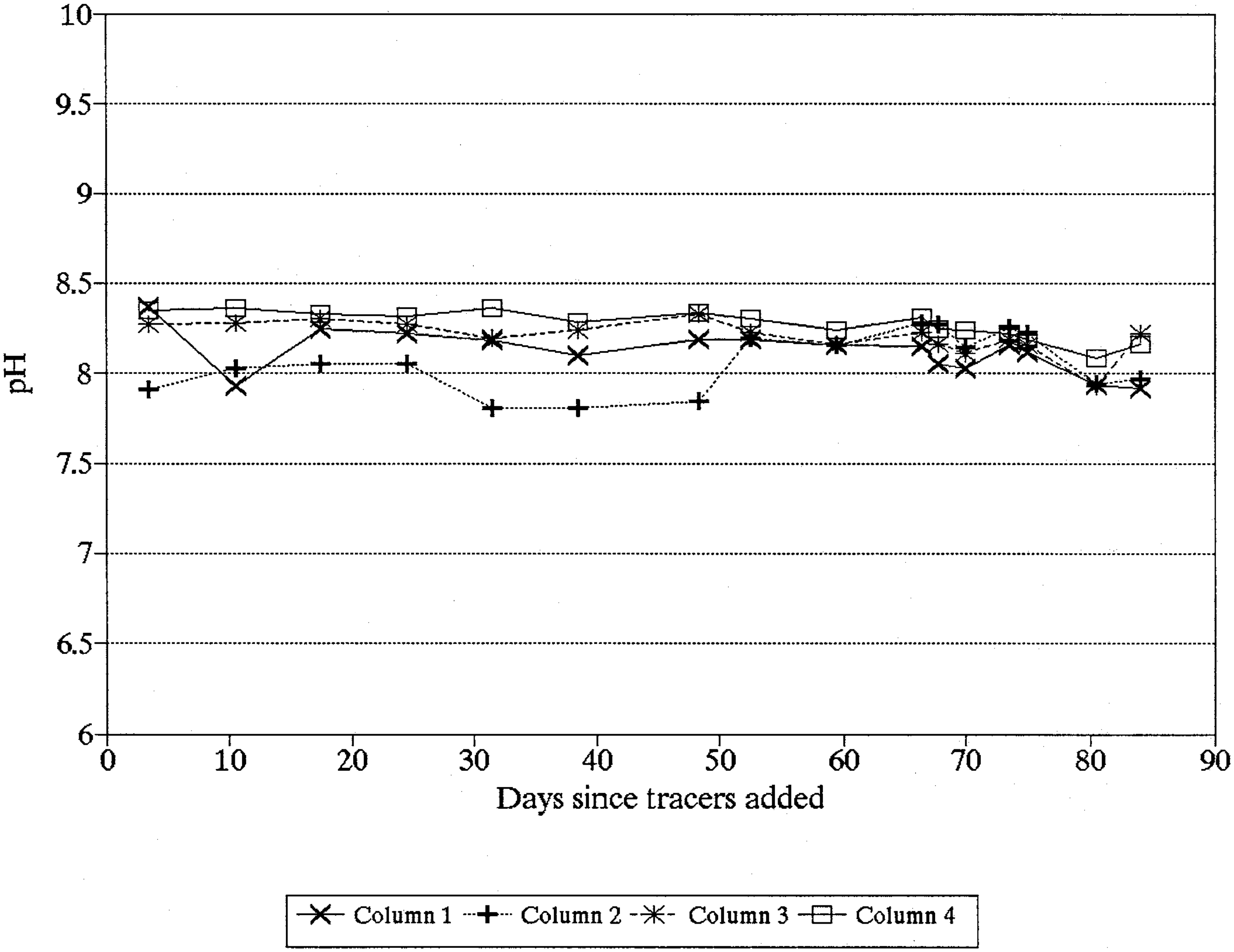

Figure 3.8 pH versus Time in Different Columns

3.5 Analytical Model

Based on the shape of the observed BTCs of m-TFMBA in the intact columns, the appropriate solute transport model for this study was deemed to be the two-region concept of CXTFIT, a one-dimensional deterministic two-site/two-region nonequilibrium model for pulse type injection with no production or decay (Parker and van Genuchten, 1984). In the two-region concept all solute transport occurs in the mobile (dynamic) region and solute moves from the immobile (stagnant) region to the mobile region through diffusion only. This diffusion of solutes from the immobile region causes tailing of both reactive and non-reactive tracers BTCs. The governing equations for the two-region concept are:

$$(\theta_m + f\rho K_D)(\delta C_m/\delta t) + [\theta_{im} + (1\text{-}f)\ \rho K_D]\ (\delta C_{im}/\delta t) = \theta_m D_m\ (\delta^2 C_m/\delta x^2) - v_m\ \theta_m\ (\delta C_m/\delta x) \quad (5)$$

$$[\theta_{im} + (1\text{-}f)\ \rho K_D]\ (\delta C_{im}/\delta t) = \lambda^* (C_m - C_{im}) \quad (6)$$

where C_m = resident solute concentration in mobile region [M/L^3]

C_{im} = resident solute concentration in immobile region [M/L^3]

θ_m = mobile volumetric water content [L^3/L^3]

θ_{im} = immobile volumetric water content [L^3/L^3]

D_m = dispersion coefficient for the mobile region [L^2/T]

f = fraction of the sorption sites that equilibrates with the mobile liquid phase

λ^* = first-order rate constant governing solute exchange rate between mobile and immobile regions.

The initial and boundary conditions for a flux averaged solution are:

$C(x,0) = 0$ - initial solute concentration in soil column = 0

$$C(0,t) = \begin{cases} C_o, & 0 < t \leq t_o \\ 0, & t > t_o \end{cases}$$ - at the upper boundary

$$\frac{\delta C(\infty,t)}{\delta x} = 0$$ - at the lower boundary

where C_o = input solute concentration $[M/L^3]$

t_o = duration of input concentration (also called pulse) [T]

x = distance along the coordinate axis which is parallel to flow direction at any time [L]

The assumptions made in the application of the governing equations was that all available sorption sites equilibrated with the mobile liquid phase.

The tracer concentration in the effluent was flux averaged. Therefore, Model 4 of CXTFIT was used to determine transport parameters of the solutes. The parameters pertinent to this study were the average pore water velocity (v), hydrodynamic dispersion coefficient (D), retardation coefficient (R), pulse (t_o), and the two dimensionless parameters, β and ω. The v, D, and R are discussed later, in Section 3.4. The t_o is the duration of influx of tracer solution, and can be used to estimate the total amount of influx of each tracer. For the mass balance to be met, the fitted t_o value should closely correspond to the known amount of time of solute influx. In this particular study, since the solute was introduced for 1.5 days, the closer the fitted value of t_o is to 1.5 days, the better the mass balance will be, assuming no errors in solute concentration and solute delivery through the syringes. The parameter β indicates the relative amount of mobile water in the soil. An increase in immobile water decreases β from 1.0.

$$\beta = (\theta_m + f \rho K_D) / (\theta + \rho K_D) \tag{7}$$

where θ = volumetric water content = $\theta_m + \theta_{im}$

ρ = soil bulk density [M/L^3]

K_D = partitioning coefficient [L^3/M]

The partitioning coefficient is the ratio of mass of solute adsorbed to a unit mass of soil to the concentration of solute in solution. For a particular soil and solute the K_D value is a constant at low concentration (van Genuchten and Wierenga, 1986).

ω is a function of several variables:

$$\omega = \lambda^* L / q \tag{8}$$

where L = an arbitrary positive distance from the origin

λ^* = a first-order rate constant that governs the rate of solute exchange between the mobile and immobile regions.

The parameter ω is not directly related to any specific soil property (Seyfried and Rao, 1986). Therefore, the significance of ω is difficult to interpret with regard to mechanism and degree of preferential solute flow.

Model 4 of CXTFIT was used to fit v, D, t_o, β, and ω in the case of m-TFMBA, and D, R, t_o, β and ω in the case of bromacil. For the purpose of this study, the R of m-TFMBA was assumed to be 1 because it is a nonreactive tracer. By fixing R, the fitted v, D, t_o, β and ω of m-TFMBA were obtained from CXTFIT. And since the flow was steady-state, the fitted v of m-TFMBA was used as fixed parameter to obtain fitted parameters of bromacil. In CXTFIT, at least one of the three parameters (v, D or R) must be known to run the program. Parker and van Genuchten (1984) recommend minimizing the number of parameters to be fitted to the observed data as much as possible to avoid uniqueness problems.

3.6 Observed and Fitted BTC Parameters

The observed and the fitted BTCs for each tracer in each column are given in Figures 3.9 to 3.12. The fitted BTCs were obtained by using the fitted parameters as the fixed values in CXTFIT and simulating the BTCs for these values. The different derived and fitted parameters for all four columns are given in Table 3.2.

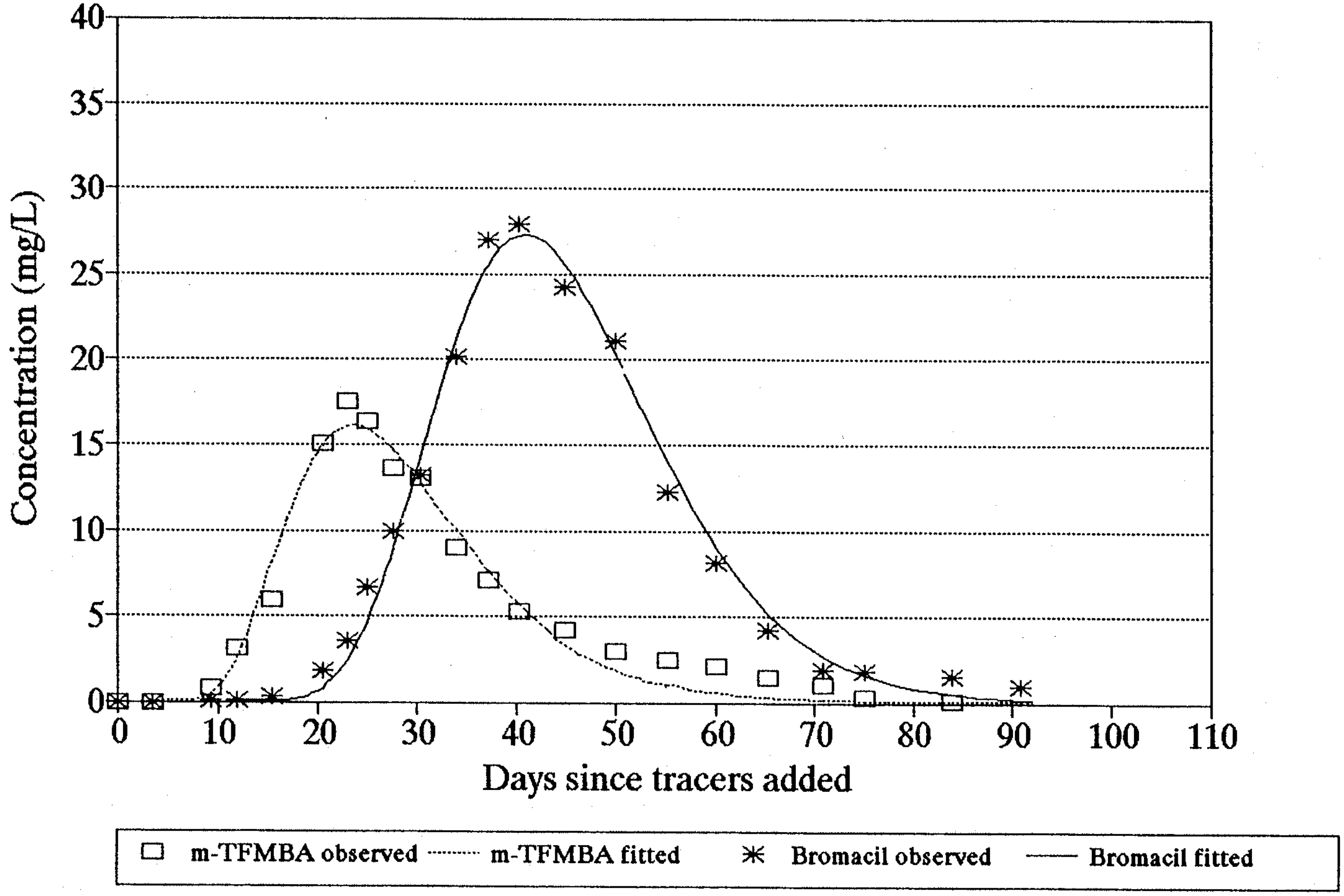

Figure 3.9 Observed and Fitted BTCs in Column 1

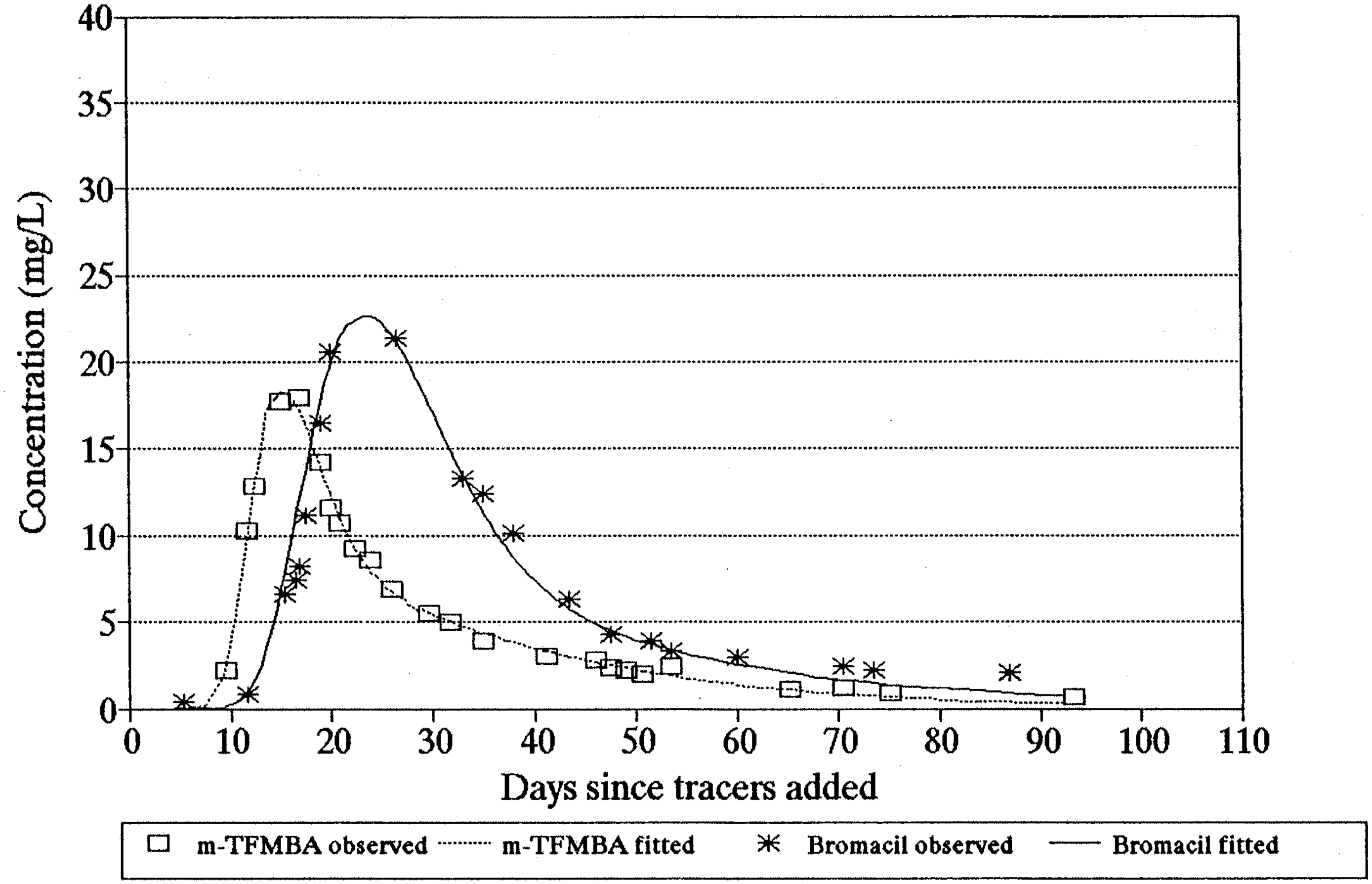

Figure 3.10 Observed and Fitted BTCs in Column 2

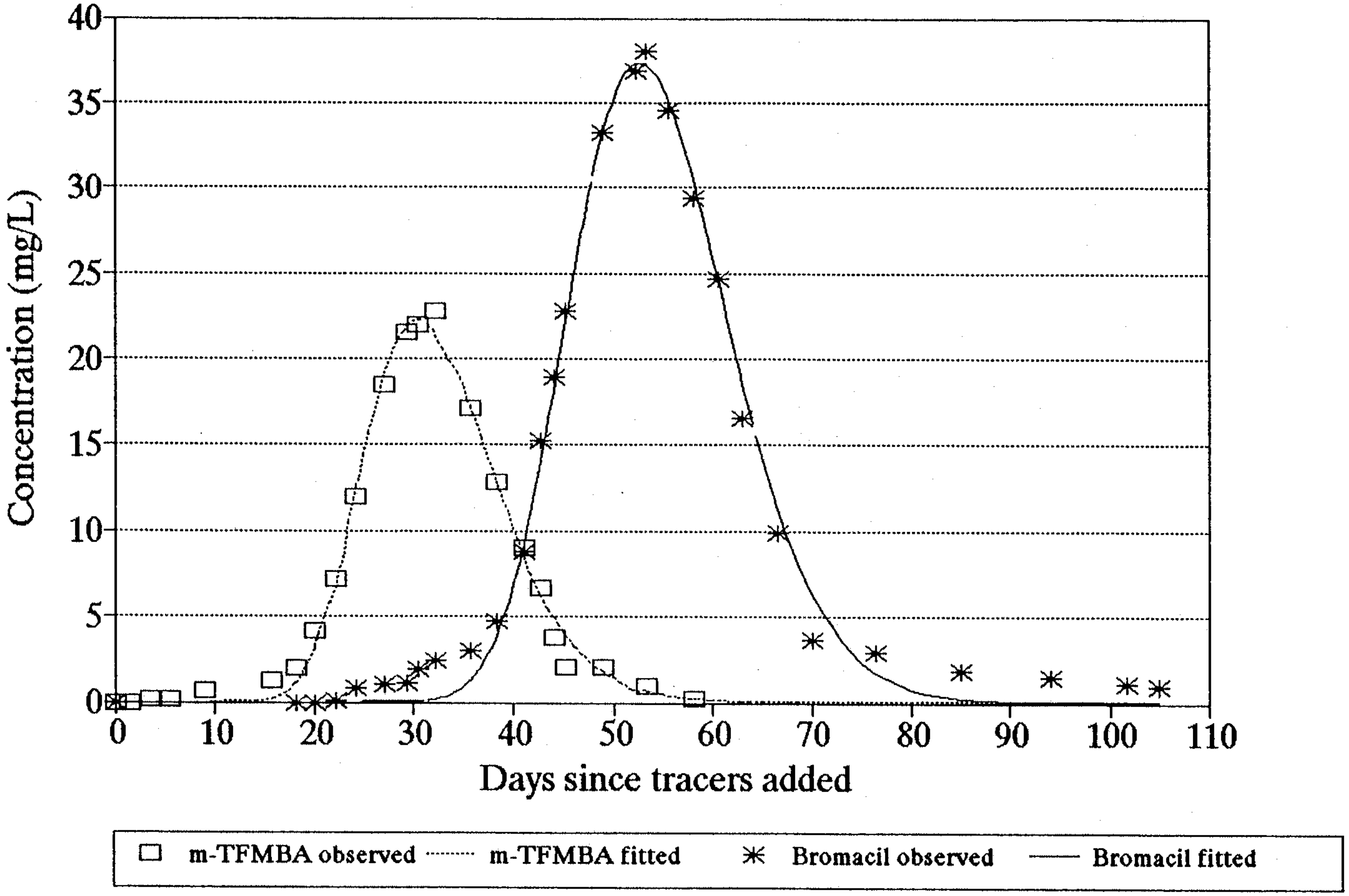

Figure 3.11 Observad and Fitted BTCs in Column 3

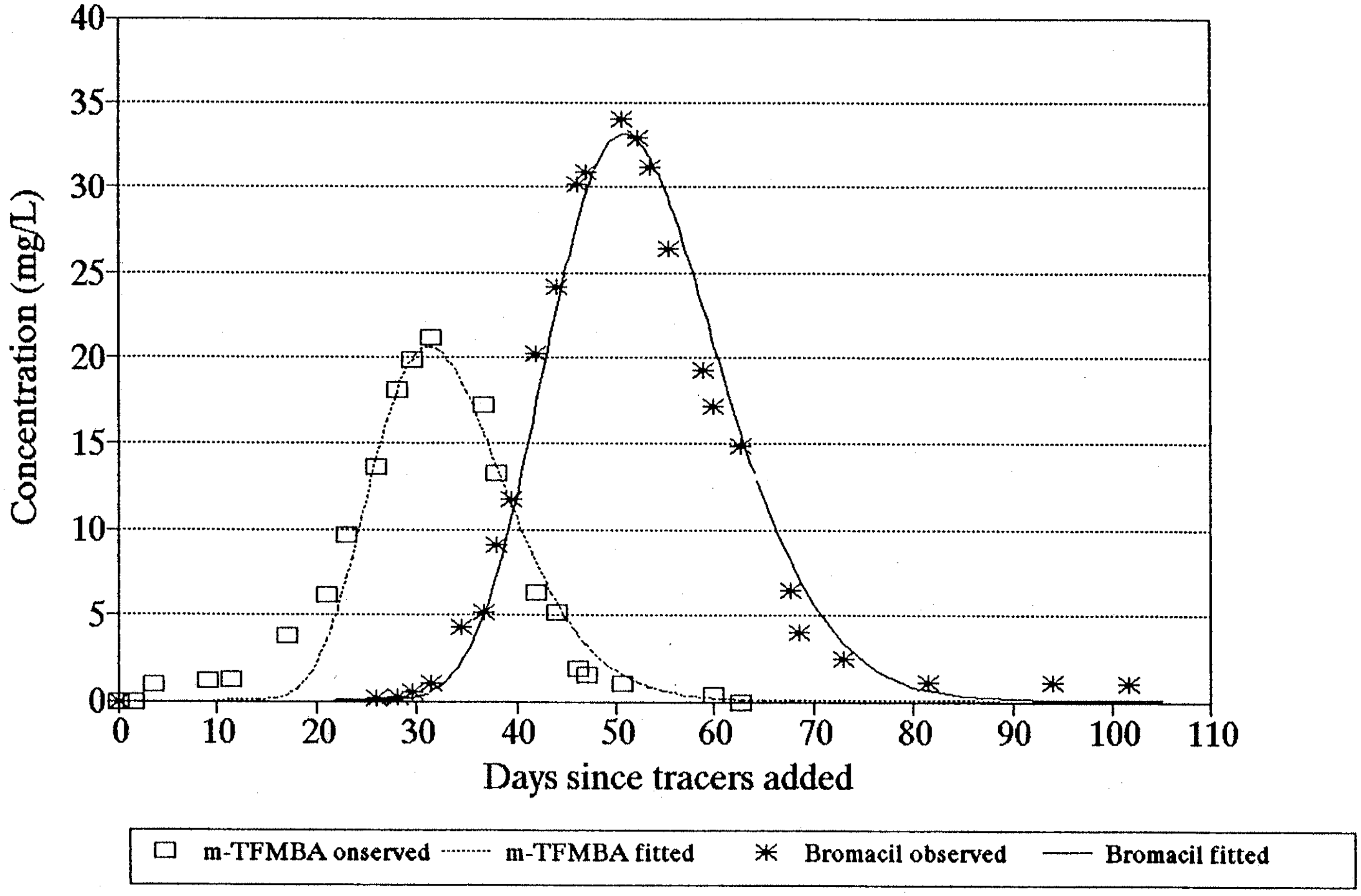

Figure 3.12 Observed and Fitted BTCs in Column 4

Table 3.2
The Derived and Fitted BTC Parameters

Parameters	Intact Columns Column 1	 Column 2	Repacked Columns Column 3	 Column 4
v-derived (cm/day)	1.751	1.576	1.758	1.576
v-fitted (cm/day)	3.615	3.623	3.163	3.054
θ-gravimetric	0.234	0.260	0.233	0.260
θ-fitted	0.185	0.185	0.212	0.219
$\frac{\theta\text{-fitted}}{\theta\text{-gravimetric}}$	0.803	0.711	0.908	0.845
PV-bypassed	0.197	0.289	0.092	0.155
D-fitted (cm^2/day)	10.53	14.01	3.21	3.41
α-fitted (cm)	2.913	3.878	1.015	1.117
R-fitted	1.602	1.341	1.701	1.606
β-fitted	0.809	0.689	0.912	0.849
ω-fitted	6.639	1.166	5.345	6.637

If the wetting front of the fluid or solute is stable and the whole soil matrix takes part in the fluid and solute movement, then the fitted v should equal the derived v. But if the water or solute bypass a portion of the soil matrix, then the fitted v will be higher than the derived v.

As shown in Table 3.2, a large difference existed between the derived and fitted v value in all four columns. The v-fitted values were 2.06, 2.30, 1.80, and 1.93 times higher than the v-derived values in Columns 1, 2, 3, and 4, respectively. The derived v value was obtained using the relation $v = q/\theta$. The θ-gravimetric of each column was determined by weighing the column after the experiment. θ was calculated using the relation

$$\theta = [(\rho \ / \ \rho_L) \ \theta\text{-gravimetric}]$$

The liquid density, ρ_L, was assumed to be 1.0 g/cm^3. The q was the constant flux rate of the leaching solution and was equal to 0.67 cm/day. The average v-fitted values of intact and repacked columns were 3.619 cm/day and 3.108 cm/day, respectively. Due to the ped structures, intact columns have higher v-fitted values than repacked columns.

The possible reasons for higher v-fitted values compared to v-derived values were as follows:

1. A bypassing by a part of the matrix in solute movement can increase the v value because for a specific flux the area of flow is smaller. The derived method assumes a complete mixing of incoming fluid with resident fluid, which is not necessarily true, especially in structured soil. Similar higher solute velocities, under similar experimental conditions, have been reported by numerous investigators including Bowman and Rice (1986b) and Turney (1991).

2. Since most natural soil particles are negatively charged on the surface they repel negatively charged particles, which tends to accelerate the movement of negatively charged solute. This mechanism of solute transport is known as anion exclusion. m-TFMBA is an anion with a charge of -1. Therefore this mechanism could contribute to the higher fitted v value of the tracers. But the non-uniformity of the dye patterns in the dye experiment results (Section 3.7) indicated that the negative charge of m-TFMBA was not the main cause of the higher v-fitted value. If anion exclusion was the main cause of higher fitted v values then the dye patterns would be much more uniform than that observed.

3. The capillary end effect (also called wall effect) can accelerate the solute breakthrough. In this mechanism, the solute travels the column mostly along the column walls; the capillary effect at the contact point between the soil mass and the column wall changes abruptly and induces the water and solute to travel along the column wall. To check the wall effect in this experiment, blue dye was introduced on the columns for 12 days. The dye fronts along the wall were visible and relatively horizontal during dye addition. The total vertical distance travelled by the dye front in each column was measured and divided by 12 to get an approximate rate of dye front movement. The average dye front velocity in the columns were 3.4, 2.6, 2.7, and 2.7 cm/day in Columns 1, 2, 3, and 4, respectively. These rates were similar to those calculated from m-TFMBA (Table 3.2). The dye supply to Column 2 was inadvertently interrupted for a day, and this interruption in the advection

process of solute movement caused the dye front to migrate much more slowly in this column. If the dye was travelling mostly along the column walls then it would have traveled much faster than the fitted v value. Moreover, the cross-sectional photographs (Appendix 3.2) showed no noticeable wall effect. Thus the effects of this mechanism of solute transport, if any, were also deemed insignificant. The dye experiment, discussed later, showed that most of the solute transport followed preferred paths, bypassing a significant portion of the soil matrix. Thus it was concluded that the increased v-fitted values were in fact due to the preferential flow of the solutes.

The θ-fitted values, which were the average fitted volumetric water content in each column, were obtained by dividing the constant flux, q, by the v-fitted value of the respective column.

The PV-bypassed was calculated using the relation

$$\text{PV-bypassed} = 1 \,/\, (\,\theta\text{-fitted} \,/\, \theta\text{-gravimetric}\,) \qquad (9)$$

The pore volume of the column bypassed by the solute is an indication of the degree of preferential flow. In a perfectly stable solute front the pore volume bypassed should be close to zero. As shown in Table 3.2, the average PV-bypassed were approximately 24.3% in the intact columns and 12.35% in the repacked columns, indicating that preferential flow was present even in homogeneous repacked soil columns. The difference in PV-bypassed between the intact and the repacked columns was due to the difference in their homogeneity. As expected, the PV-bypassed was greater in the intact columns because of their structure. The visual evidence of the bypass flow is provided in Appendix 3.2, in the photographs taken after the dye experiment.

The hydrodynamic dispersion coefficient, D, is a function of fluid velocity, dispersivity, and molecular diffusion.

$$D = D_m + D_d = \alpha v^n + D_d \approx \alpha v^n \tag{10}$$

where α is dispersivity, n is an empirical constant (generally taken as 1.0), D_m is mechanical dispersion, and D_d is molecular diffusion (van Genuchten and Wierenga, 1986). Unless the solute velocity is extremely low, the molecular diffusion effect is generally negligible. For laboratory experiments involving repacked and uniform intact columns, the α is close to 1 cm or less; for heterogeneous intact soil columns the α can be one or two orders of magnitude larger (van Genuchten & Wierenga, 1986). The α values of 1.015 cm and 1.117 cm in the repacked columns were as expected because of the uniformity of the columns. The α values of 2.913 cm and 3.878 cm in the intact columns indicated the degree of preferential flow in the intact columns compared to the repacked columns.

The D, which incorporates the effects of both mechanical dispersion and molecular diffusion, causes variation in the velocity of tracer particle movement; some particles will move faster and some slower than the average linear velocity of water movement (Freeze & Cherry, 1979). The mechanical dispersion is caused by the variation in the size, shape and direction of pores, and by the velocity variation of fluid within a pore and among the pores. The molecular diffusion is caused by concentration gradient; molecular diffusion occurs even in the absence of fluid movement. In the absence of both dispersion and diffusion the BTC of a chemical would be a step function, with the concentration of the species suddenly jumping to inflow concentration from zero at the solute front. The D value of a species indicates the spreading of solute from the center of mass of solute. The presence of preferential flow can cause a large D value because some of the solute introduced in the column will travel much faster than the rest. Seyfried and Rao (1987) noted that dispersion decreased with increase in tension. De Marsily (1982) claimed, from the results of a field experiment, that D is time and space dependent. In this study the D was assumed to be constant with time and space.

As shown in Table 3.2, the D value is much higher in the intact columns than in the repacked columns, indicating a wider range of pore water velocities in the intact columns than in the repacked columns. The average D values in the intact and repacked columns were 12.29 cm^2/day and 3.31 cm^2/day, respectively. This difference was expected because the soil composition in the intact columns changed with depth, while the repacked columns were essentially homogeneous. The bulk density of the intact columns increased significantly with depth (see Table 2.1); also, the calcium carbonate content visibly increased below the first 30 cm of field soil. Unlike the repacked columns, the intact columns contained a significant amount of calcium carbonate pellets bigger than 2 mm; this was observed after taking the intact columns apart at the end of the experiment. This variation in soil properties induced variation in water velocity which, in turn, increased the D value. The soil composition in the repacked columns was homogeneous, any soil structures present in the intact columns were destroyed, and the bulk density was constant with depth. Thus variation in water velocity along the column was limited and relatively low D values were observed in the repacked columns.

For a specific soil and θ, the retardation factor (R) of a species indicates the reactivity of the species with the soil matrix.

$$R = 1 + \rho K_D / \theta \tag{11}$$

where K_D is the partitioning coefficient. If a chemical does not react with the soil matrix and is transported along with the fluid, then K_D becomes zero and R becomes 1.0. R is also defined as a ratio of fluid velocity to solute velocity (Davis and DeWiest, 1966). An ideal tracer does not react with the soil, and thus has an R value of 1. If only a fraction of the liquid phase participates in the solute transport process, R can be less than one (van Genuchten and Wierenga, 1986). As shown in Table 3.2, in the intact columns the R of bromacil varied from 1.602 in Column 1 to 1.341 in Column 2. The average Rs of bromacil in the intact and repacked columns were 1.441 and 1.65, respectively, implying that the solute reacted slightly less with the intact than with the repacked columns.

3.7 Dye Experiment

The relative amount of undyed area to dyed area at various depths from the soil surface was interpreted as an indication of degree of bypassing. The results of this experiment, given in Table 3.3, indicated that at a depth of 25 cm from the surface the stained area was only 90% and 40% of the cross sectional area in intact Columns 1 and 2, respectively. The amount of stained area decreased significantly at 35 cm depth, indicating a progression in bypassing with depth. A similar trend was observed, although to a lesser degree, in both of the repacked columns. The very little bypassing observed at the upper part of the columns was due to diffusion of dye in the area not dyed by fluid flow.

Table 3.3
Approximate Percent of Unstained Area in Different Columns at Various Depths

Depth (cm)	Column 1	Column 2	Column 3	Column 4
15	0	0	0	0
20	5	6	0	0
25	10	60	11	6
30	24	64	15	33
35	65	74	58	43

A very similar phenomenon has been observed by numerous investigators, including Seyfried and Rao (1987), Booltink and Bouma (1991), and Ghodrati & Jury (1990). Booltink and Bouma (1991) found increased bypassing below the first 45 cm in a dye experiment. Bouma and Dekker (1978) observed that very little available vertical surface area was dyed by blue dye in another column experiment. Some color photographs of the dye experiment appear in Appendix 3.2.

The pattern of dyed and undyed areas confirmed that most of the flow occurred via preferential pathways. If the apparent higher solute velocities of the tracers had been due to negatively charged solutes then the columns would be uniformly dyed. The dye pattern also eliminated the possibility of higher solute velocity due to wall effect. If the wall effect was significant then most of the dyed area would be along the column perimeter. The photographs in Appendix 3.2 show that flow did not occur mostly along column walls.

The dye experiment results are consistent with the tracer experiment results. As shown in Table 3.3, at 35-cm depth the average bypassing was 70% and 50% in the intact and repacked columns, respectively. This difference in bypassing caused a higher hydrodynamic dispersion coefficient and higher PV-bypassed in the intact columns (Table 3.2).

3.8 Scale Effect

To study the scale effect the soil properties and the resulting transport parameters of the previous study and this study were compared. The soil properties considered were average bulk density, saturated water content, and column dimensions. The BTC parameters from this study were compared to the previous study's trickle-flow results. The transport parameters considered for comparison were v, D, R, α, θ, and PV-bypassed. Since the previous study used Model 2 of CXTFIT, the two parameters β and ω could not be compared. Also, no dye experiment was conducted in the previous study, so no comparison could be made based on dyed versus clear area. Using the fitted parameters from the previous study, BTCs of m-TFMBA and bromacil for this study were extrapolated. The solute BTC peak arrival times from the two studies were compared to determine the implications of the results in solute migration prediction.

3.8.1 Soil Properties, Column Dimensions, and Constant Flux

The soil properties affect the results of transport experiments. If the soil properties are very different then the resulting BTCs from the two studies cannot be compared. The soil for this and the previous study was collected from the same general area. The different averaged soil properties, column dimensions, and constant flux rate in the intact columns of this and the previous study are given in Table 3.4.

To minimize input variables the column diameters in this study were kept close to those of the previous study. The average porosity in this study was much higher because of the high clay content at the bottom half of the column. The column-diameter-to-column-length ratio was much lower in this study; however, this should not significantly

Table 3.4
Soil Properties, Column Dimension and Flux Rate
in the Intact Columns of This and the Previous Study

Parameters	This study	The previous study
Average Bulk Density (g/cc)	1.635	1.634
Average Porosity	0.428	0.371
Volumetric Water Content	0.428	0.308
Average Column Dimensions (cm)	Diameter : 15.24 Length : 100	Diameter : 14.2 Length : 32.4
Column Diameter to Length Ratio	0.1524	0.4383
Constant Flux (cm/day)	0.67	0.65

affect the results of the study because no wall effect was observed in either study. The biggest difference between the soil of the two studies was in mineral content. The previous study was carried out on the top 32.4 cm of the soil; this study also included the bottom 70 cm of the soil from the same plot. The bottom 70 cm of the soil was significantly different from the top 32.4 cm. As mentioned in Section 1, the calcium carbonate content increased markedly below the top 30 cm of the soil. The average percentage of calcium carbonate content increased from 4% in the top 30 cm to a maximum of 20% in the next 70 cm (Post et. al, 1988). The bulk density of the lower half of the column of this study was much higher than the upper half (see Table 2.1).

3.8.2 Transport Parameters and BTCs

The transport parameters of the intact and repacked columns from the previous study's trickle-flow results were averaged separately. The fitted v values of two intact columns in the previous study were 3.13 and 3.11 cm/day. Since the constant flux rates in both studies were very close, the "predicted v from the previous study" was obtained by averaging the two v's of the intact columns from the previous study. No correction was made for the difference between the two studies in the θ values. The fitted D value of the two intact columns in the previous study were 1.46 and 2.46 cm^2/day; the predicted D value was obtained by averaging the two D's of the intact columns of the previous study. Similarly, all other predicted parameters for intact and repacked columns were obtained by simply averaging the respective values found in the previous study. The resulting transport parameters from the two studies are summarized in Table 3.5.

Table 3.5
Comparison of Parameters from This and the Previous Study

	Intact Columns			Repacked Columns		
Parameters	Predicted from previous study	Column 1	Column 2	Predicted from previous study	Column 3	Column 4
v	3.12	3.615	3.623	2.38	3.163	3.054
D	1.96	10.53	14.05	3.195	3.21	3.41
R	1.55	1.602	1.341	1.566	1.701	1.606
PV-bypassed	0.27	0.197	0.289	0.166	0.092	0.155
α-fitted	0.63	2.913	3.878	1.345	1.015	1.117

Besides the soil parameters and the column dimensions, some other major differences exist between this and the previous study. The previous study used Model 2 of the CXTFIT, and this study used Model 4. The difference between these two models is that Model 4 takes into account the effects of two-site/two-region (Parker and van Genuchten, 1984). The solute application method was different in the two studies; in the previous study, in order to apply the tracers uniformly on the soil surface, the tracer solution was frozen as a thin disk; the disk was placed on the soil surface and allowed to melt. The melting of the solute disk disrupted the steady-state situation in the columns. In this study, to maintain unit gradient and unsaturated steady-state conditions, the solute was applied at the steady-state flux rate using the drip emitter. Since the current study omitted the intermittent flooding part of the previous study, the results of this study were compared to the trickle-flow results of the previous study.

The average fitted v of the intact and repacked columns in this study were 3.619 cm/day and 3.108 cm/day, respectively. Thus there was an increase of approximately 16% and 30% in the fitted v of this study compared to the fitted v of the previous study (see Table 3.5). The increase in v of this study can be caused by several reasons. As mentioned earlier, in the intact columns the bulk density increased with depth. For the same type of soil an increase in bulk density decreases porosity which, in turn, increases the average pore water velocity. In the previous study the intact column was carved from the top 32.4 cm of the field soil; thus, in the intact columns, the lower, denser part of the field soil was missing. In this study relative bypassing increased with depth, as indicated by decrease of dyed area with depth in the dye experiment results. Under steady-state conditions, increase in bypassing decreases the area of flow and thus increases fluid velocity. Due to the length of the column, the relative bypassing was higher in this study which increased the v-fitted value.

In the repacked columns, although the columns were repacked homogeneously in both studies, the mineral content of the soil of this study was different from the previous study. Again, as mentioned earlier, the calcium carbonate content of the field soil increased significantly below the first 30 cm. Since the previous study used the top 32.4 cm of the soil, it missed the bottom soil with higher calcium carbonate content which was included in this study. Moreover, in the previous study the fitted v of one of the repacked columns was lower than the derived v. This decrease in fitted v caused a lower average v in the repacked columns of the previous study.

The average D value of the intact columns in this study is 12.27 cm^2/day, which is 6.3 times higher than the average D value of the intact columns in the previous study. This dramatic increase in D value was caused by higher heterogeneity in this study. Increase in calcium carbonate pellets in the lower half of the intact columns increased the heterogeneity. This increased the randomness in fluid velocity which, in turn, increased the D value. In the repacked columns all structures present in the intact columns were destroyed. The fitted D values of the repacked columns are essentially the same in the previous study and this study.

The average fitted R values of this study in both the intact and repacked columns were close to the average R values of the previous study, except in Column 2 of this study. The slightly lower θ-fitted values caused slightly higher R values in this study.

To compare the fitted BTCs of this study with the BTCs that would have been predicted by the average fitted parameters of the previous study, new BTCs were extrapolated for 100-cm long columns using the average values of v, D and R of the previous study. The average v, D, and R of the intact columns in the previous study were 3.21 cm/day, 1.96 cm^2/day and 1.55, respectively (Table 3.5). To simulate the same total mass transport, the solute concentration and the solute input duration of this study were used. For example, to extrapolate m-TFMBA BTC of intact columns the input values used in CXTFIT were 3.21 cm/day, 1.96 cm^2/day, 1.55, 1.5 days, 500 mg/L, and 100 cm for v, D, R, t_o, C_o, and column length, respectively. The BTCs of m-TFMBA in the repacked columns and bromacil in the intact and repacked columns were extrapolated following the same procedure. The extrapolated BTCs and the fitted m-TFMBA and bromacil BTCs of this study are presented together in Figures 3.13 to 3.16.

The comparison of m-TFMBA and bromacil BTC peak arrival time for a 100-cm long soil column from the extrapolated BTCs and the observed BTCs are given in Table 3.6. The peak arrival time for the extrapolated BTCs were obtained from Figures 3.13 to 3.16.

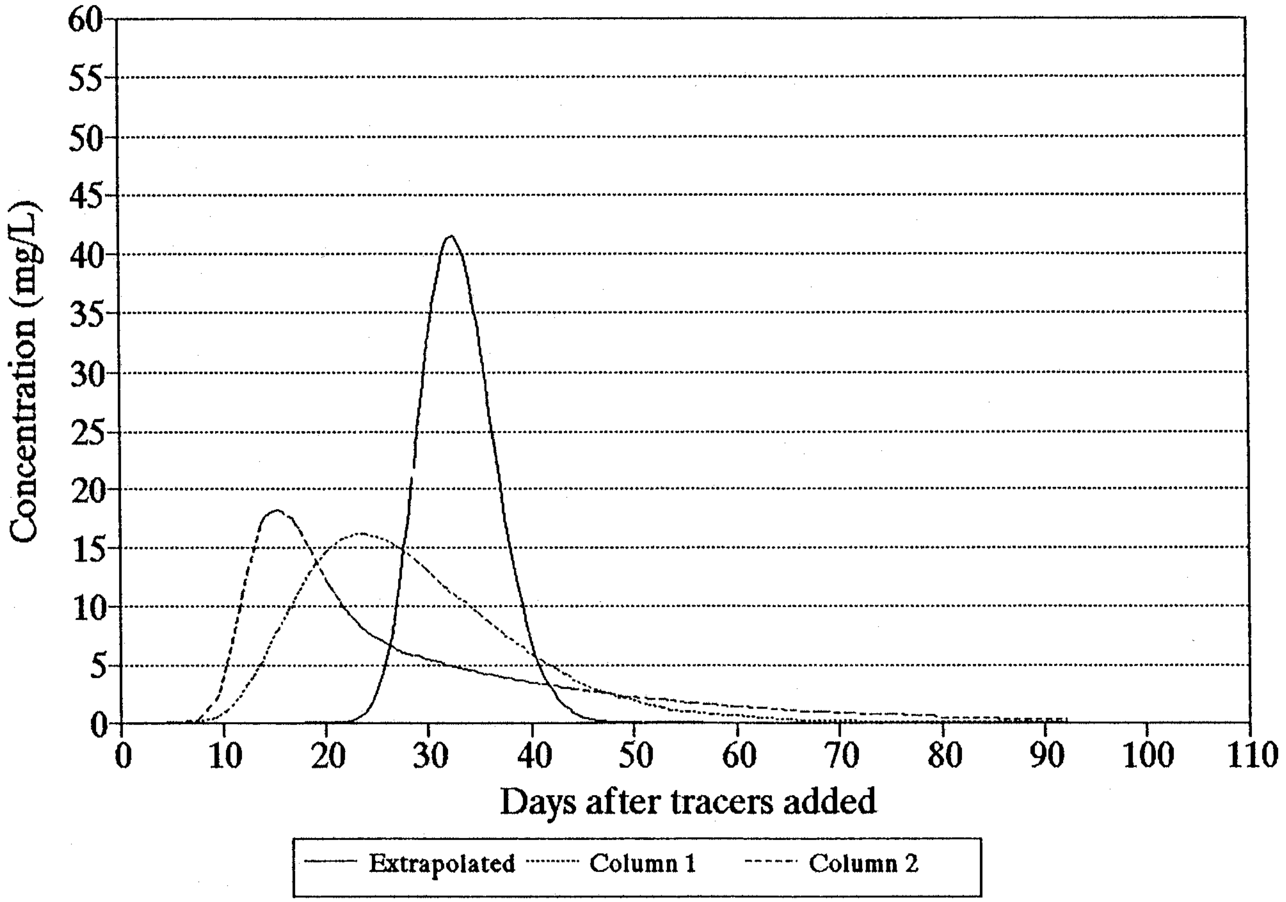

Figure 3.13 Extrapolated and Fitted m-TFMBA BTCs in Intact Columns

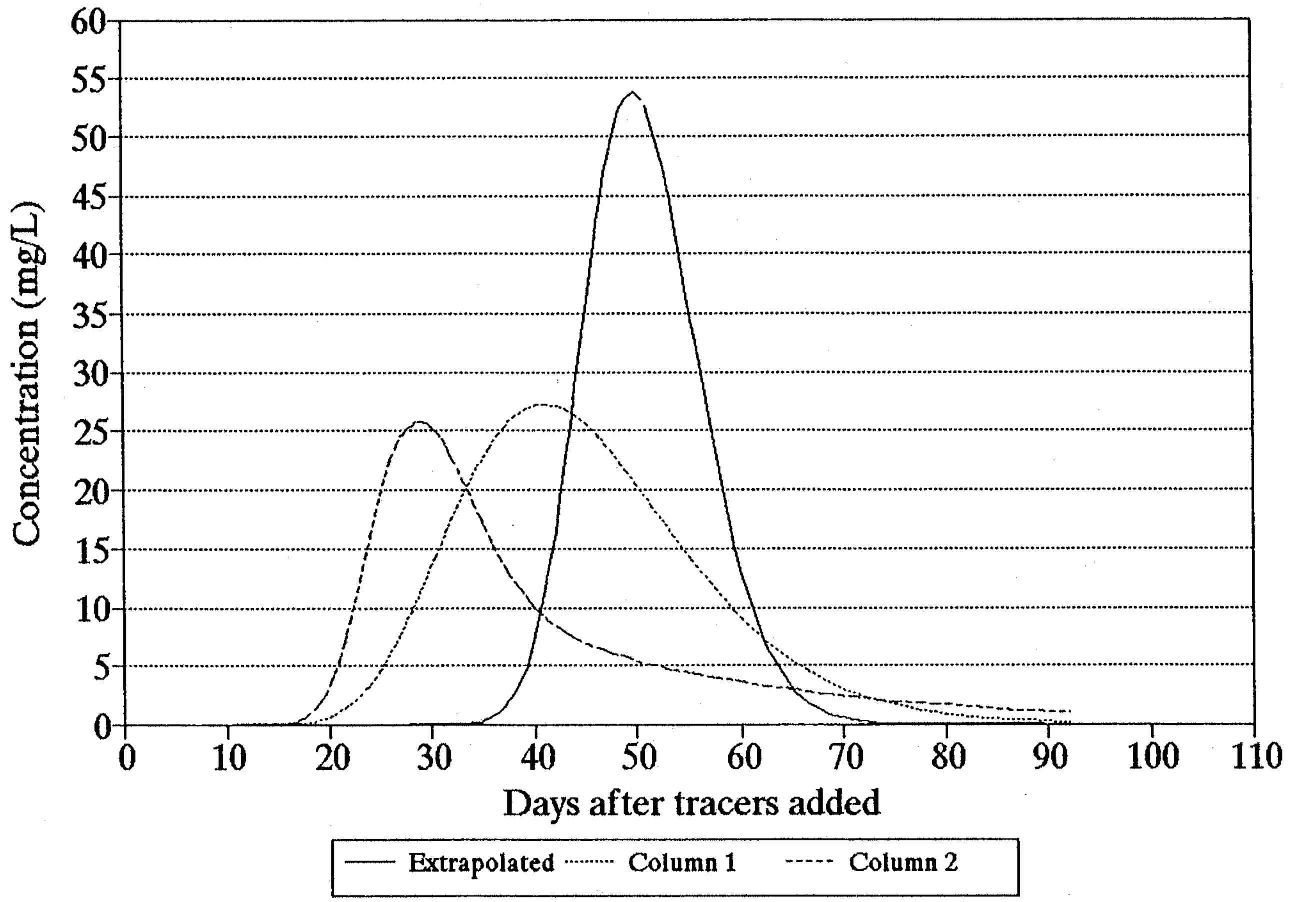

Figure 3.14 Extrapolated and Fitted Bromacil BTCs in Intact Columns

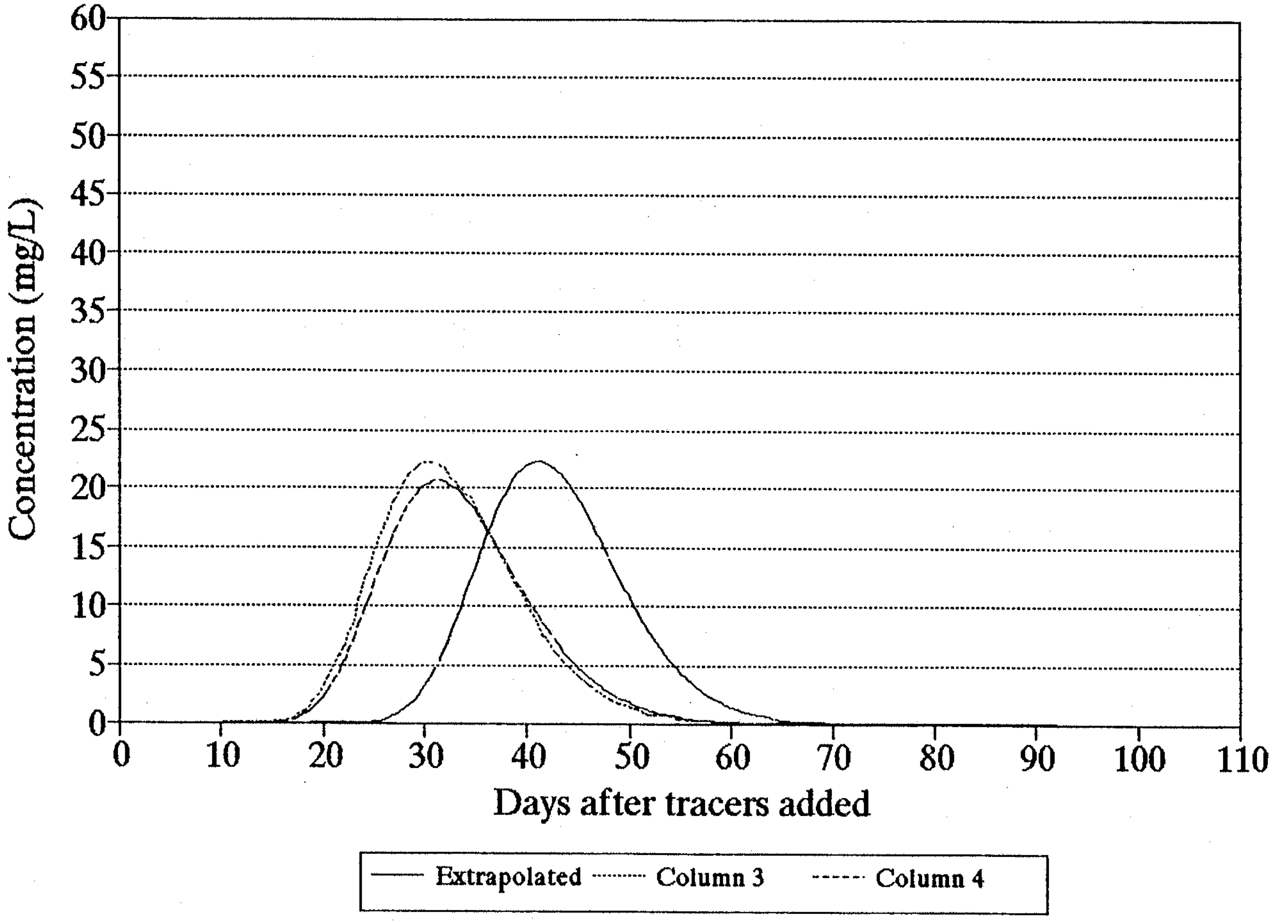

Figure 3.15 Extrapolated and Fitted m-TFMBA BTCs in Repacked Columns

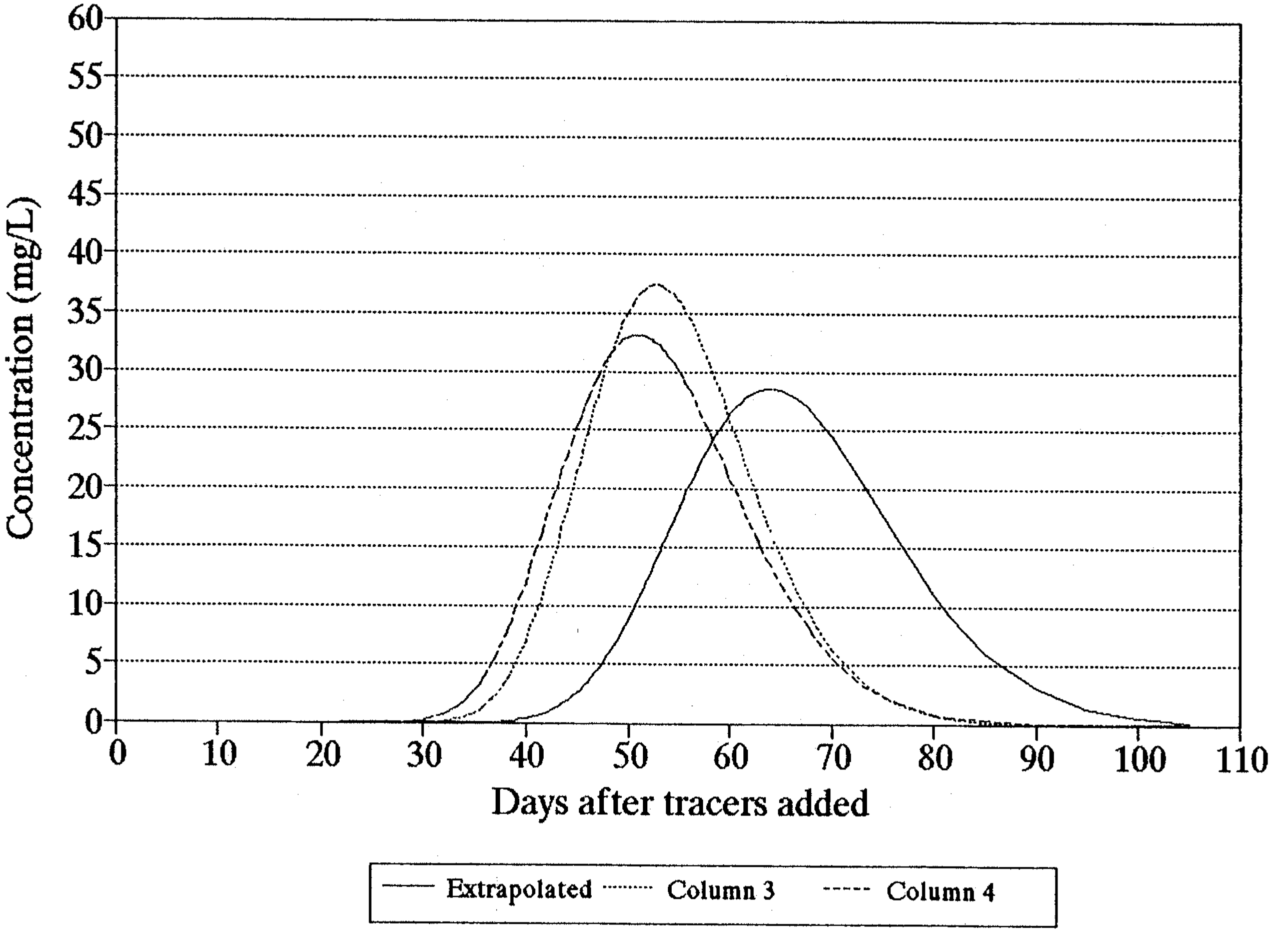

Figure 3.16 Extrapolated and Fitted Bromacil BTCs in Repacked Columns

Table 3.6
Comparison of Observed and Predicted BTC Peak Arrival Time (days)

	Intact Columns			Repacked Columns		
	From Extrapolated BTC	Observed		From Extrapolated BTC	Observed	
		Column 1	Column 2		Column 3	Column 4
m-TFMBA	32	23.5	15.5	41.5	30.4	31.4
bromacil	51	41.0	29.0	64.5	52.5	50.7

As shown in Table 3.6, the BTCs extrapolated from the average fitted transport parameters of the previous study over-estimated the BTC peak arrival time of m-TFMBA by approximately 36%, 106%, 37%, and 32% and bromacil by approximately 24%, 76%, 23%, and 27% in Columns 1, 2, 3, and 4, respectively. This dramatic reduction in BTC peak arrival time indicates that the solute transport parameters obtained from small column experiments cannot be safely applied to field scale problems.

The 32.4-cm long columns of the previous study were far from being representative elementary volume (REV) because these columns missed the lower part of the field soil which was more dense and rich in calcium carbonate. A soil sample is a REV of a porous medium if it includes sufficient pores and matrix to permit meaningful statistical averages representing the porous medium (Freeze and Cherry, 1979). The 100-cm long columns represented the field soil better than did the short columns because they included the part of the field soil that has properties different from the top 30 cm of the soil. Bouma (1983) recommends a sample volume of 10000 cm^3 for clay soils with medium peds. The approximate volume of soil in the previous and the present studies were 5131 cm^3 and 18241 cm^3, respectively.

Seyfried and Rao (1987) noted that the BTC of a chemical can vary widely if P is less than 5.0. Van Genuchten and Wierenga (1986) found that for P = 1 the analytical solutions deviate drastically, but when P increased the BTCs converged for different boundary conditions. So a final check was made on the fitted parameters of the two studies to see the effect of the Peclet number (P) on the resulting BTCs. The Peclet number is defined as

$$P = vL/D = L/\alpha \tag{12}$$

where L is the column length. The Peclet number provides a measure of the relative importance of advective and dispersive processes. Large D values and small P values indicate large dispersive solute flux relative to conductive solute flux (Kluitenberg and Horton, 1989). Very small P values are indicative of an extremely broad range of pore water velocities in the mobile water region (Seyfried and Rao, 1987). Table 3.7 is a tabulation of the P values of different columns in the two studies.

Table 3.7
The Peclet Number of Different Columns in the Previous and This Study

	Previous study				Current study			
	Column 1	Column 2	Column 3	Column 4	Column 1	Column 2	Column 3	Column 4
Peclet number	69.593	40.731	27.357	21.505	34.32	27.04	98.0	89.5

Table 3.7 shows that the P values of all columns in both studies were much higher than 5.0. Therefore the differences in BTCs and the resulting parameters between the two studies were due to the scale effect and not due to low P values.

3.9 Biological Growth in Columns

As mentioned earlier, significant biological growth was observed in all four columns during the experiment. This growth was expected, as the experiment was conducted with the column surface open to the atmosphere. Moreover, the soil was not treated in any way before the experiment, and the leaching solution was made from tap water. In the previous experiment, biological growth also occurred in the urethane tubing that connected the tensiometers to the pressure transducer. In this experiment the tensiometer tubes and urethane tubing were filled with 1000 mg/L sodium azide water to prevent disruption in pressure recording due to biological growth in the urethane tubing. Since the experiment was designed to simulate trickle flow irrigation of Maricopa well water in the field, sodium azide was not mixed in the leaching solution.

Approximately 2-mm-diameter circular green patches on the column surface, indicating algae growth, were noted before the tracer application. This algae growth was arrested by minimizing the light availability in the laboratory. After keeping the laboratory mostly dark for two weeks all the green patches turned black and no further growth was noted for several weeks. Similar green patches were noted three weeks after the tracer introduction in the columns. During that time the laboratory was used for several research projects; therefore, the laboratory could not be kept dark. The columns received light approximately 8 to 10 hours a day and the quantity of green patches continued to grow during the experiment. The approximate diameter of the green patches ranged from 2 to 8 mm by the end of the experiment. Appendix 3.3 contains color photos of algae growth in the columns. Lack of appropriate data prevented evaluation of tracer biodegradation.

This algae growth can be minimized by reducing the amount of light that the soil columns receive. The experiment can be conducted in a room that can be kept dark most of the time, or the columns can be wrapped in aluminum foil to minimize light reception by soil columns. The algae growth stopped when the laboratory was lighted only 2 to 3 hours a day. The length of the experiment also affects the amount of algae growth. In this study the algae were not detected for the first three weeks. A low concentration of sodium azide or similar other chemicals in the leaching solution can prevent biological growth in the columns while not significantly affecting the experiment results.

3.10 Summary of Results

New Heading

In summary, both the o [illegible] experiment showed a bypassing of the soil matrix in the w [illegible] in both the intact and the homogeneously repacked columns. The bypassing was much higher in the intact columns than in the repacked columns. The results of this study support the findings of several previous studies concerning the presence of preferential flow in soil under unsaturated conditions. The presence of bypass flow can significantly reduce the time required for the solute to travel a certain distance i.e., solute can be transported much farther in a certain time than would be predicted by the conventional advection-dispersion model.

The results of this study also indicate that the transport parameters obtained from the repacked column underestimate the average velocity of the solute in the field soil. Therefore, better site characterization can be accomplished by tracer studies in the field soil rather than in repacked soil columns. The transport parameters obtained from column studies may or may not be applicable in the field condition if the depth of interest is much higher than the length of columns studied. A short column may not represent the REV of the field soil under study. Therefore, to reliably predict the solute movement in a field soil, column studies should be carried out so that the columns represent the REV.

Some of the transport parameters obtained from the previous study were very different from the results of this study. The average pore water velocity was much lower in the previous study than in this study. The hydrodynamic dispersion coefficients of the intact columns were much higher in this study. The retardation factors in both studies were similar.

3.11 Sources and Discussion of Errors

Some of the sources of error in this experiment were as follows :

1. The effect of gas on the solute transport was ignored. Since the experiment was conducted under unsaturated conditions, there was abundant air in the soil columns. A buildup in air pressure in the entrapped air ahead of a wetting front influences the rate of propagation of the front through a soil (Freeze and Cherry, 1979).

2. Air bubbles in the urethane tubing, connecting the tensiometers to the scanivalve lines, were a nuisance during the experiment because the tensiometers had to be flushed every three or four days to obtain accurate tension readings. Once the tubes were flushed it took one or two days for the pressure recording system to stabilize.

3. The rubber septum used on the tensiometers was large enough to conceal air bubbles. Air bubbles were removed only when they could be seen in the acrylic tube. Concealed air pockets in the tensiometers can influence the pressure reading.

4. The vacuum source was house line and fluctuated continuously. Use of air pressure somewhat stabilized the vacuum pressure. The vacuum pressure was checked once a day using a Tensicorder (Soil Measurement Systems, Tucson, AZ).

5. Wall effects can confound results. A dye was used at the end of the experiment to check for any visible wall effects. The results of the dye experiment indicated negligible wall effects in this study.

6. The porous plate was glued to the column using general purpose glues and 2-Ton Epoxy (Devcon Corp. Wood Dale, IL). The columns continued to leak for several days. Visible leaks were sealed with more epoxy, but nonvisible leaks can be sources of air leaks. This leakage could have caused fluctuation in the suction pressure at the bottom of the porous plate.

7. The volume of effluent collected on the drain plate and in the tube which connected the base assembly to the vacuum chamber was approximately 15 mL. There were ample chances of further mixing of the solute with the resident effluent in the drain plate. This could easily affect the BTC of the solutes.

8. The following assumptions made in this study may or may not be valid:

   a) the exponent n in $D = \alpha v^n$ was assumed 1.0,

b) the sorption of bromacil was linear and reversible,

c) decay of tracers was negligible, and

d) all other inherent assumptions in the governing equations were valid.

9. The effect of biological growth on the columns was considered negligible, although a significant biological growth was noted on some columns. Excessive biological growth can block interconnected pores and increase the amount of dead-end pores. Increase in dead-end pores can increase the hydrodynamic dispersion coefficient by increasing heterogeneity in fluid flow paths. The biological growth can also reduce the hydraulic conductivity of a porous medium. In a steady-state experiment, biological growth can enhance preferential flow by blocking micropores.

4. SUMMARY AND CONCLUSIONS

Two intact, hand-carved soil columns were brought from MAC, Arizona. Two repacked columns, of the same dimensions and average bulk density, were constructed using soil from the same pits. All four columns were instrumented with tensiometers. Other instruments for the water supply system, the effluent collection system, and the data acquisition system were put in place. All four columns were subjected to unsaturated steady flux conditions until a unit gradient was achieved.

Two tracers, m-TFMBA and bromacil, were introduced on the soil surface, and the effluent was collected using fraction collectors and vacuum chambers. The effluent was analyzed to determine the concentration of both tracers using HPLC. Using CXTFIT, the observed BTCs were used to obtain different fitted transport parameters to assess the presence or absence of preferential flow in the soil columns. A dye experiment was performed to obtain visual evidence of the presence of preferential pathways. To study the scale effect on the results of the experiment, the fitted parameters were compared to the results of a previous study done on approximately 32.4-cm long soil columns from the same site.

The results of this study indicated a presence of strong preferential flow in both the intact and the repacked columns; the preferential flow was more obvious in the intact columns than in the repacked columns. The reason for preferential flow was the non-participation of a significant part of the soil matrix in the water and solute transport. This was evidenced by the patches of blue colors in the soil columns at different depths, instead of a uniform blue coloring of the whole soil matrix.

Comparison of the results of this study with the results of the previous study indicated that considerable caution should be used in extrapolating the results of a column study onto field scale problems.

The following conclusions are based on the results of this study:

1. The presence of preferential flow in natural soil conditions must always be considered in predicting the transport of solutes in the vadose zone. The solute front can arrive in the water table two to three times faster than will be predicted by conventional models based only on advection and dispersion. In this study the fitted average pore water velocities in repacked and intact columns were approximately twice as fast as the derived velocities. Bowman and Rice (1986b) found measured tracer velocity two and one-half times faster than the mean pore water velocity in a field tracer study.

2. The flow and transport of water and solutes is different in repacked and intact columns. The parameters obtained from repacked columns cannot be used to estimate solute fronts in the field. Generally, the solute front moves faster in the intact soil than

in the repacked soil. The parameters from intact colum tual field situation because of the boundary effect, but they field situations because of the preservation of ped structures hon and Thomas, 1974).

3. If the length of the column studied does not represent the REV, then the transport parameters obtained from the column study cannot be safely applied to field scale problems. Due to the scale effect, the result of a short-column study can be very different from a long-column experiment. The fitted v values in this study were 16% and 30% higher than the fitted v values of the previous study, in the intact and repacked columns, respectively. This difference in fitted v values between the two studies would be even higher if the difference in θ values between the two studies were considered when predicting the v of the previous study.

4. A dye experiment is an effective technique to obtain visual evidence of the preferential flow pathways. The dye experiment results in this study eliminated the possibility of wall effects as a cause of higher fitted pore water velocities than the derived velocities.

5. RECOMMENDATIONS

Air bubbles in the urethane tubing connecting the tensiometers to the pressure transducer continued to be a source of confusion throughout the experiment. The tensiometers had to be flushed every three or four days in order to that they provide true pressure readings. But it took about the same amount of time for the system to restabilize after each flushing cycle. Thus the actual pressure measurements were made for only a short period. The suspected sources of air in the system were numerous. Since the experiment was conducted under unsaturated conditions there was plenty of air in the soil columns. The leaching solution was made from tap water, which also contained plenty of air. Under continued negative pressure for a long period of time, air diffused through the urethane tubing and passed on to the tensiometers. Once air bubbles exist in the tube the pressure transducer cannot read the pressure accurately. Determining the establishment and maintenance of a unit gradient in the columns was thus a difficult task. The tensiometer should be checked for air leak under long durations of negative pressure. Use of thick-walled urethane tubing is recommended.

The columns were initially saturated from the bottom to avoid entrapment of large air pockets in the column but this method of removing air is not reliable; this way as much as 15 to 20% of the pore volume can be filled with air (Wan and Wilson, 1992). Moreover, entrapped air in large pores can reduce the hydrodynamic dispersion by reducing the velocity of water in the larger pores (Orlob and Radhakrishna, 1958). It is, therefore, recommended that in the future the columns be saturated with CO2 before being saturated with water. The head difference should be high when the columns are saturated from the bottom because the higher velocity of saturation ensures less entrapped air in the column (personal communication, Jiamin Wan).

The use of drip emitters to introduce solute on the soil columns worked satisfactorily. But flow through each needle should be checked to ensure uniform solute application on the soil surface. The flow from each syringe on the pump should be checked for consistency. The syringes in the water pump wear out quickly and must be replaced every two to three weeks.

The vacuum chambers must be protected from high temperature fluctuations. During this experiment the relatively high afternoon temperature and the vacuum inside the chamber caused the effluent to evaporate, and the low evening temperature caused condensation of effluent on the bottom surface of the chamber lid. This can affect the solute concentration of the effluent. The effect can be reduced by collecting the samples in the chamber every day, but this will increase the work tremendously since it takes about two hours of hard work to change the vials in the fraction collectors, and every time the vials are changed the effluent flow is interrupted. Covering the vacuum chamber lid with cloth significantly reduced the effluent condensation on the chamber lid.

A dye experiment can provide visual evidence of preferential pathways, hence a dye experiment is recommended at the end of this type of experiment to ensure the mechanism of apparent higher pore water velocity. Unless the columns will be dissected after the dye is introduced, for a long column study the dye should be introduced for the top 30 to 40 cm only because soil extraction from the top of the column blurs the coloring. The appropriate dye concentration should be tested for a particular soil. High dye concentration results in faster diffusion in initially clear areas and makes the initially clear and dyed areas indistinguishable.

The fiberglass cloth encasement discussed in Appendix 2.1 provided strength to the intact columns. But tiny holes can remain in the resin coated fiberglass cloth supporting the intact columns, even after several coating of polyester resin. When the intact columns were subjected to 200-cm of water pressure during the saturation process, water leaked from several spots. All leaky spots were sealed using general purpose 2-Ton epoxy (Devcon Corp., Wood Dale, IL).

To minimize biological growth the column study should be conducted in a laboratory that can be kept dark most of the time. A low concentration of sodium azide water mixed with the leaching solution can prevent biological growth in the columns. Turney (1991) successfully prevented biological growth in urethane tubing with a sodium azide concentration of 10 mg/L.

APPENDICES

Appendix 2.1

The procedure followed in hand-carving 100-cm long intact soil columns is given below:

Selecting Site and Digging Trench:

Two sites were selected to obtain four 100-cm long intact soil columns from the field, two columns from each site. Since the columns had to be carved intact, it was not possible to work from the soil surface all the way to the bottom of the column. So, using a back-hoe, 45-cm wide and 1.5 m deep trenches were dug on each side of the selected site, as shown in Figure 4.1. A 60-cm wide soil wall was left after digging the trenches; this ensured enough soil width to carve intact 15.24-cm diameter soil columns from the middle of the wall.

Figure 4.1 Picture of 60-cm wide Soil Wall and the Trenches

Treating the Top of Column Surface:

The specific sites from which the columns were carved, on the 60-cm wide soil wall, were marked by painting with liquid rubber latex (Kwickmold, Adhesive Product Corp., Bronx, New York), with a 60 cm center-to-center distance between the specific sites. The "specific site" was the exact location in the field from which the column was carved. The rubber latex painting was made thin, since a thick coat can take more than twelve hours to set, especially on a cloudy day. A chimney flange was used as a guide when painting the site with rubber latex. Once the rubber latex paint was set on the soil surface, it gave support to the surface soil while the column was being carved. Without this support at the surface the soil tends to crack and fall apart while it is being carved.

Carving the Column:

A rough initial carving was made slightly bigger in dimension than needed. Then a vertical soil column of desired dimension was carefully carved. The column was checked every 2 or 3 centimeters with a water level to ensure that the column was vertical; it was very difficult to estimate whether the column was vertical when standing close to it. All sides of the column needed periodic sprinkling with water during carving because the surface dried quickly. Big chunks of soil tend to come apart and fall unexpectedly when columns are being carved under dry conditions. A spray bottle was used to sprinkle water on the column surface to keep it wet. After the first 40 cm of carving, a 120-cm long water level was used to check the vertical direction of the column. The diameter of the column was checked by measuring the circumference of the column, and dividing by π.

Supporting the Column with Fiberglass Cloth:

After the carving was finished, the soil column surface was painted with a mixture of polyester resin and methyl ethyl ketone peroxide (MEKP) catalyst, 50:1 ratio, using a 5-cm natural-bristle brush. Both the polyester resin and the MEKP were obtained from Evercoat Marine Resin, Fiber Glass-Evercoat, Inc. 660 Cornell Road, Cincinnati, OH. On hot, sunny days a ratio of 70:1 is preferable, as the mixture can set quickly. The procedure described by Economy and Bowman (1993) was followed when encasing the soil column with the fiberglass colth. A graduated beaker and a graduated cylinder were used to mix the resin and the hardener.

The polyester resin was applied on a 30 cm wide and 70 cm long precut fiberglass cloth using a 5-cm natural-bristle brush. The resin-coated fiberglass cloth was wrapped aorund the top 30 cm of the column. The 70-cm length of the fiberglass cloth allowed approximately 20 cm of overlapping at the ends. The next strip of fiberglass cloth was wrapped with an overlap of 5 cm at the lower edge of the first strip. The same procedure was followed all the way to the column bottom. Four 30-cm by 70-cm fiberglass strips were required per column per coating of fiberglass cloth. Any air space created after wrapping the column with fiberglass cloth was filled with resin. This was done by applying several coats of resin over the fiberglass cloth on the column while the fiberglass cloth was still soft. Two coatings of fiberglass cloth were needed for a stable column.

A gas mask and long-sleeved clothing were required while working with the resin. The vapor from the resin can be irritating to some people, and direct contact with the resin irritates the skin.

Lifting the Column from the Trench:

The time for the fiberglass cloth to set depends on weather; the total setting time is 24 to 30 hours in hot and dry weather and about 48 hours in cold and humid weather. The setting time can be significantly reduced by blowing warm, dry air on the resin-coated fiberglass cloth. Once the fiberglass cloth was set, the columns were marked for future identification. About 10 cm of soil was dug around the column bottom. Holding the column at the top, the extra column length at the bottom was carefully trimmed underneath with a trowel. A shovel was used to cut the remaining soil at the trimmed part of the column. The column was then broken by gently pushing it to one side. Because of the trimming at the extra length of the column, the broken column was about 105-cm long. This extra column length was carved out later with a butcher knife.

Figures 4.2 and 4.3 are photographs of intact carved columns in the field.

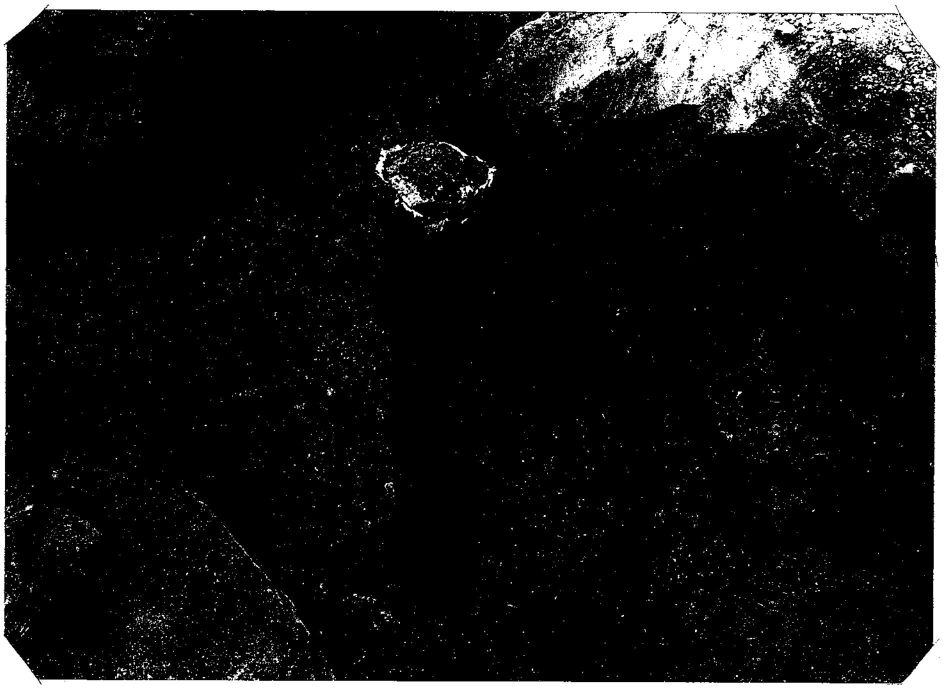

Figure 4.2 Photograph of a Intact Carved Column in the Field.

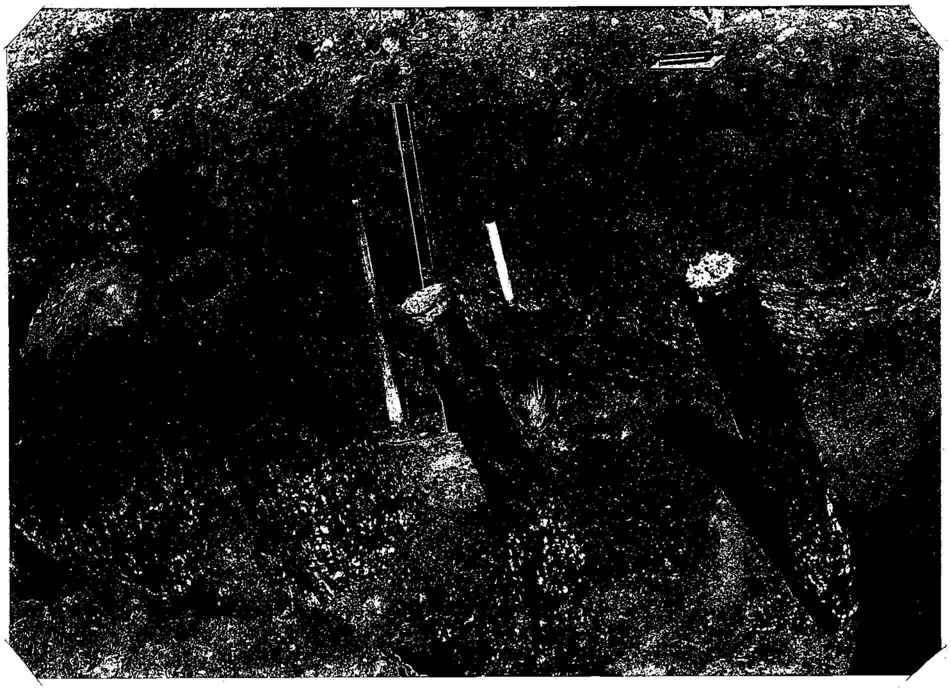

Figure 4.3 Photograph of Intact Carved Columns in the Field.

Appendix 2.2

Details of packing repacked columns:

Soil from the two pits which were the source of the intact columns was collected separately and brought to the laboratory. The soil from each pit was sieved using a Number 10 (2-mm opening) sieve and mixed homogeneously using a spade and a trowel.

A 15.24-cm internal diameter, 120-cm long transparent acrylic tube was fitted with a 15.24-cm diameter stainless steel porous plate and a drain plate at one end, using commercially available silicon glue and 2-Ton Epoxy (Devcon Corp., Wood Dale, IL). The water-resistant 2-Ton Epoxy was painted around the non-porous edge of the stainless steel porous plate. Care was taken not to put the Epoxy on the porous part of the plate. A transparent 15.24-cm diameter drain plate was carefully placed over the porous plate on the side with the Epoxy. The 2-Ton Epoxy set in about 4 hours, gluing the porous plate to the drain plate. The porous plate was then glued to the acrylic tube.

The soil required to pack 10 cm of the column was poured inside the acrylic tube from the open end of the tube through a multilayer screen funnel (MSF); the soil particles passed through the screens. The MSF, shown in Figure 4.4, was made by joining a 15-cm diameter, 10-cm long PVC tube with two 10-cm diameter, 10-cm long PVC tubes with different sizes of screens in between. A total of 3 screens were used, with the finest screen (2-mm opening) at the very end of the funnel. The 3-mm opening screen was inserted 10 cm above the funnel bottom. The 4-mm opening screen was inserted 10 cm above the 3-mm screen. The total length of the MSF was 30 cm.

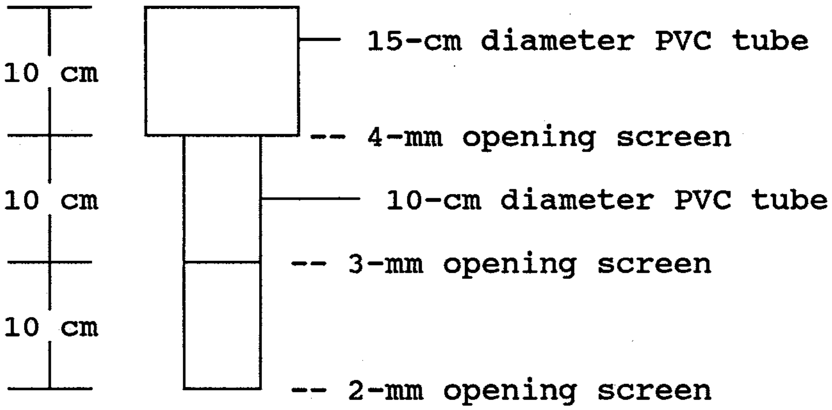

Figure 4.4 A Line Sketch of a Multilayer Screen Funnel

The bottom-most screen of the MSF was kept about 5 cm above the surface to be poured to eliminate layer formation. The soil inside the column was hand-mixed, using a putty knife fitted on a broomstick handle, until the soil was visually homogeneous. A 2-pound hammer was dropped 50 times in all sides of the tube, from approximately 10 cm above the soil surface. Care was taken not to drop the hammer at the same spot every time. A 3-mm thick rubber mat was placed under the drain plate to prevent crack formation in the glue between the acrylic tube and porous plate. The top 1- to 2-cm of the compacted soil was scratched with a spatula to eliminate layering. More soil was poured and the whole process was repeated until a 100-cm long column was prepared. It took four trials to pack columns that did not exhibit layering when the columns were wetted. Figure 4.5 is a photograph of a repacked column.

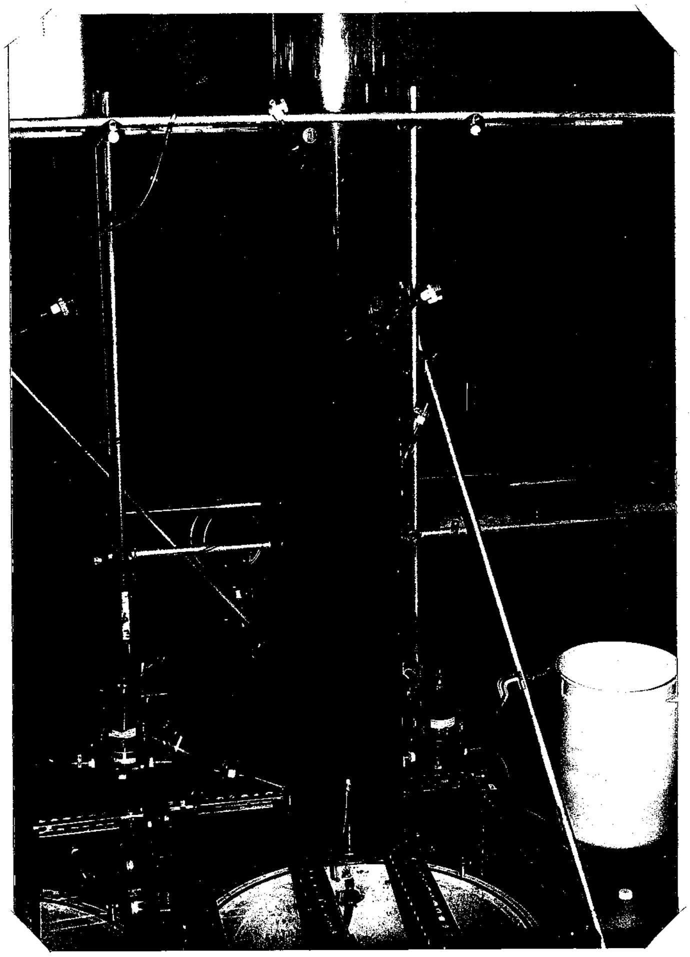

Figure 4.5 Photograph of a Repacked Column in the Laboratory

Appendix 2.3

Tensiometer Construction, Testing, and Insertion in Columns:

The tensiometers were constructed of two major components. A 6-mm external-diameter and 8-cm long ceramic porous cup, with air entry pressure of 1 Bar, (part #652X02-B1M1, Soil Moisture Equipment Corp., Santa Barbara, California) was inserted about 10 mm inside a transparent acrylic tube of 7-mm internal diameter and 5-cm length. The 2-Ton Epoxy (Devcon Corp.) was used to glue the porous cup to the acrylic tube. About 2 cm of the porous cup from its open end was also covered with the epoxy. This was done to minimize the wall effect, if any, on the pressure reading of the tensiometers. A 7-mm serum bottle sleeve stopper was used at the other end of the acrylic tube.

To test them, the tensiometers were soaked in deaired water overnight so that any entrapped air bubbles inside the porous cup could escape or dissolve. Then the whole tensiometer was dipped in deaired water and a pressure of up to 1000 mbar was applied using a 3-cc syringe. The pressure was measured using a Tensicorder (Soil Measurement Systems, Tucson, Arizona). If air bubbles continued to escape out of the porous cup after one minute of applied pressure the tensiometers were rejected. The tensiometers were kept in the deaired water until it was time to insert them in the soil column.

To insert the tensiometers the soil column was hand drilled, at an angle of 65 degrees from horizontal, using a 5-mm drill bit. The acrylic wall around the hole was enlarged with a 6-mm drill bit. The porous cup of the tensiometer was then inserted in the hole by rotating the tensiometer. A 6-mm diameter porous cup in a 5-mm diameter hole ensured tight fitting of the tensiometer and thus a minimum of air pockets between the porous cup and the soil. The tensiometers were slanted in order to get any air bubbles to the upper end of the tensiometers; there the bubbles could be eliminated by opening a syringe needle that was inserted through the rubber septum. The urethane tubing connected the tensiometers with the Scanivalve pressure transducer system.

Appendix 3.1

COLUMNS 1-4; OBSERVED AND FITTED BTC'S VALUES

COLUMN 1							
m-TFMBA				Bromacil			
Days	Obsrvd	Days	Fitted	Days	Obsrvd	Days	Fitted
3.5	0	3.5	0	3.5	0	3.5	0
		5.5	0.0004			5.5	0
		7.5	0.0408			7.5	0
9.33	0.842	9.33	0.4067	9.33	0.001	9.33	0
		9.7	0.5708			9.7	0
		10.5	1.071			10.5	0
		11.7	2.2333			11.7	0.0001
12	3.123	12	2.6009	12	0.012	12	0.0001
		12.5	3.2763			12.5	0.0003
		13	4.0217			13	0.0008
		13.7	5.1604			13.7	0.0022
		14	5.6744			14	0.0034
		14.7	6.9117			14.7	0.0081
		15.2	7.8105			15.2	0.0143
15.5	6.002	15.5	8.1254	15.5	0.31	15.5	0.0197
		16.5	9.6754			16.5	0.0518
		16.7	9.9722			16.7	0.0618
		17	10.6376			17	0.0798
		17.5	11.4288			17.5	0.1194
		18.5	12.86			18.5	0.2463
		19	13.4879			19	0.3234
		19.5	14.0515			19.5	0.4395
		20	14.5483			20	0.5856
		20.2	14.7279			20.2	0.6685
20.5	15.159	20.5	14.9768	20.5	1.78	20.5	0.7839
		21	15.3366			21	1.0536
		21.5	15.6284			21.5	1.3312
		21.7	15.7263			21.7	1.4556
		22	15.8535			22	1.6573
		22.5	16.014			22.5	1.99
23	17.53	23	16.1125	23	3.52	23	2.4131
		23.5	16.1522			23.5	2.8914
		23.7	16.1523			23.7	3.0986
		24	16.1364			24	3.4264
		24.5	16.0689			24.5	4.0182
25	16.416	25	15.9535	25	6.65	25	4.6664
		25.5	15.7941			25.5	5.3696
		26	15.5948			26	6.1256
		26.5	15.3595			26.5	6.9312
		27	15.0921			27	7.7827
		27.2	14.977			27.2	8.1351
		27.5	14.7964			27.5	8.6754
27.67	13.61	27.67	14.69	27.67	9.99	27.67	8.9874
		28	14.476			28	9.6042
		28.5	14.1344			28.5	10.5633

Days	Obsrvd	Days	Fitted	Days	Obsrvd	Days	Fitted
		28.6	14.0638			28.6	10.7583
		29	13.775			29	11.5467
		29.5	13.4008			29.5	12.5477
		29.7	13.2476			29.7	12.9515
		30	13.0147			30	13.5596
30.33	13.04	30.33	12.7548	30.3	13.2	30.33	14.2301
		30.5	12.6196			30.5	14.5755
		31	12.1634			31	15.5886
		31.5	11.7677			31.5	16.592
		31.7	11.572			31.7	16.9891
		32	11.3763			32	17.5789
		32.5	10.9806			32.5	18.543
		33	10.6849			33	19.478
		33.5	10.3892			33.5	20.3783
34	9.058	34	10.0935	34	20.2	34	21.2384
		34.5	9.7			34.5	22.0534
		34.7	9.544			34.7	22.3658
		35	9.3118			35	22.8191
		35.5	8.9299			35.5	23.5315
		35.6	8.8544			35.6	23.6673
		36	8.5553			36	24.1873
		36.5	8.1886			36.5	24.784
		37	7.8305			37	25.3192
37.17	7.08	37.17	7.7108	37.17	26.99	37.17	25.4869
		37.5	7.4816			37.5	25.7914
		38	7.1423			38	26.1994
		38.5	6.813			38.5	26.5427
		39	6.4938			39	26.8213
		39.5	6.1851			39.5	27.0354
		40	5.8869			40	27.186
40.3	5.301	40.3	5.713	40.3	27.94	40.3	27.2407
		41	5.3222			41	27.3042
		41.2	5.2143			41.2	27.3006
		42	4.7996			42	27.1967
		42.5	4.5538			42.5	27.0519
		43	4.3182			43	26.8555
		43.2	4.2268			43.2	26.7631
		43.5	4.0926			43.5	26.6103
		44	3.7088			44	26.3192
45	4.212	45	3.3252	45	24.3	45	25.6117
		46	2.9415			46	24.7327
		46.2	2.8752			46.2	24.5468
		46.5	2.7781			46.5	24.2596
		47	2.6228			47	23.7855
		47.5	2.4752			47.5	23.2621
		48.5	2.202			48.5	22.1554
		49	2.0759			49	21.5778
50	3.013	50	1.843	50	21.1	50	20.3879
		50.7	1.6945			50.7	19.5362

m-TFMBA				Bromacil			
Days	Obsrvd	Days	Fitted	Days	Obsrvd	Days	Fitted
		51	1.6343			51	19.1683
		51.5	1.5382			51.5	18.5533
		52.5	1.4088			52.5	17.3229
		52.7	1.2795			52.7	17.0778
		53.5	1.1501			53.5	16.1044
55.33	2.51	55.33	1.0207	55.33	12.25	55.33	13.9455
		55.7	0.9746			55.7	13.5244
		57.5	0.7769			57.5	11.5695
		59.5	0.602			59.5	9.6044
60.13	2.105	60.13	0.5551	60.13	8.12	60.13	9.0341
		62.5	0.4083			62.5	7.1031
		62.5	0.4083			62.5	7.1031
65.33	1.412	65.33	0.2816	65.33	4.2	65.33	5.2282
		66.5	0.2412			66.5	4.5803
		68	0.1975			68	3.8488
		68.5	0.1847			68.5	3.628
		70.5	0.1412			70.5	2.8517
71	1.011	71	0.132	71	1.9	71	2.6817
		73	0.1007			73	2.0877
		73.5	0.0941			73.5	1.9589
75.1	0.306	75.1	0.0757	75.1	1.82	75.1	1.5934
		77.5	0.0649			77.5	1.1615
		79	0.042			79	0.9469
		80	0.0366			80	0.8259
84	0.051	84	0.0211	84	1.56	84	0.4721
		87	0.014			87	0.3067
		88	0.0122			88	0.2651
		91	0.008	91	0.95	91	0.1701
		92	0.007			92	0.1465

COLUMN 2							
m-TFMBA				Bromacil			
Days	Obsrvd	Days	Fitted	Days	Obsrvd	Days	Fitted
		3.5	0			3.5	0
5.5		5.5	0.0004	10.5	0.36	5.5	0
		7.5	0.1302			7.5	0
		9.33	1.8839			9.33	0
9.7	2.27	9.7	2.7042			9.7	0
		10.5	5.0969			10.5	0
11.7	10.24	11.7	9.7658	14.7	0.8	11.7	0
		12	10.9836			12	0
12.5	12.77	12.5	12.925			12.5	0.0002
		13	14.6607			13	0.0005
		13.7	17			13.7	0.0024
		14	17.5			14	0.0042
		14.7	18			14.7	0.0142
15.2	17.7	15.2	18.2109			15.2	0.0308
		15.5	18.23	20.7	6.64	15.5	0.0474
		16.5	17.7457			16.5	0.17
		16.7	17.5397	21.7	7.46	16.7	0.2135
17	17.94	17	17.182	22	8.18	17	0.296
		17.5	16.4833	23	11.15	17.5	0.4905
		18.5	14.8626			18.5	1.1799
19	14.17	19	14.0155	24	16.5	19	1.7252
		19.5	13.1815			19.5	2.4349
20	11.54	20	12.3803	25	20.62	20	3.3264
		20.2	12.0722			20.2	3.7365
		20.5	11.6252			20.5	4.4097
21	10.66	21	10.9244			21	5.6849
		21.5	10.2819			21.5	7.1418
		21.7	10.0415			21.7	7.7711
		22	9.6985			22	8.7593
22.7	9.25	22.5	9.1727			22.5	10.506
		23	8.7012			23	12.342
		23.5	8.2798			23.5	14.2212
		23.7	8.1242			23.7	14.9739
24	8.54	24	7.9038			24	16.0939
		24.5	7.5682			24.5	17.9098
		25	7.2682			25	19.6208
		25.5	6.9992			25.5	21.1836
26	6.93	26	6.757			26	22.5616
		26.5	6.5377	27.7	21.4	26.5	23.7262
		27	6.3379			27	24.4692
		27.2	6.2628			27.2	24.7024
		27.5	6.0125			27.5	25.1
		27.67	5.9634			27.67	25.2
		28	5.8706			28	25.4667
		28.5	5.7356			28.5	25.7751

m-TFMBA				Bromacil			
Days	Obsrvd	Days	Fitted	Days	Obsrvd	Days	Fitted
		28.6	5.7094			28.6	25.8094
		29	5.74			29	25.8591
		29.5	5.5904			29.5	25.734
29.7	5.49	29.7	5.5332			29.7	25.6296
		30	5.4499			30	25.4194
		30.33	5.3614			30.33	25.1189
		30.5	5.317			30.5	24.9381
		31	5.2207			31	24.3148
		31.5	5.0938			31.5	23.5749
31.7	5.01	31.7	5.0448			31.7	23.252
		32	4.9731			32	22.7437
		32.5	4.8297			32.5	21.8452
		33	4.7248	34.7	13.2	33	20.9019
		33.5	4.6227			33.5	19.9339
		34	4.5231			34	18.9591
		34.5	4.426			34.5	17.9928
		34.7	4.3877			34.7	17.6115
35	3.95	35	4.331	36.7	12.31	35	17.0474
		35.5	4.2382			35.5	16.1332
		35.6	4.2198			35.6	15.9548
		36	4.1473			36	15.2579
		36.5	4.0583			36.5	14.427
		37	3.9711			37	13.6442
		37.17	3.9418			37.17	13.3894
		37.5	3.8856			37.5	12.9116
		38	3.8018	40	10.13	38	12.2299
		38.5	3.7197			38.5	11.5985
		39	3.6392			39	11.0162
		39.5	3.5602			39.5	10.4808
		40	3.4828			40	9.9899
		40.3	3.437			40.3	9.7155
		41	3.3324			41	9.1299
41.2	3.01	41.2	3.303			41.2	8.9757
		42	3.1878			42	8.4115
		42.5	3.1177			42.5	8.0977
		43	3.0489			43	7.8103
		43.2	3.0217			43.2	7.702
		43.5	2.9814	46.2	6.3	43.5	7.5464
		44	2.9153			44	7.3036
		45	2.787			45	6.8721
45.7	2.74	46	2.6638			46	6.6
		46.2	2.6398			46.2	6.55
		46.5	2.6041			46.5	6.4378
		47	2.5455			47	6.2636
47.5	2.34	47.5	2.4882	50.7	4.25	47.5	6.1003
		48.5	2.377			48.5	5.9
49	2.2	49	2.3231			49	5.7568
		50	2.2186			50	5.3747
50.7	1.95	50.7	2.148			50.7	5.2157

m-TFMBA				Bromacil			
Days	Obsrvd	Days	Fitted	Days	Obsrvd	Days	Fitted
		51	2.1184			51	5.1498
		51.5	2.0699	54.8	3.87	51.5	5.0428
		52.5	1.9758			52.5	4.8381
		52.7	1.9575			52.7	4.7985
54.5	2.39	53.5	1.8857	59.5	3.33	53.5	4.6442
		55.33	1.7305			55.33	4.3127
		55.7	1.7006			55.7	4.2489
		57.5	1.5618			57.5	3.9523
		59.5	1.42			59.5	3.6471
		60.13	1.3778	66.5	2.93	60.13	3.5558
		62.5	1.2295			62.5	3.2316
		62.5	1.2295			62.5	3.2316
61.5	1.06	65.33	1.072			65.33	2.8812
		66.5	1.0126			66.5	2.7473
		68	0.9409			68	2.5841
		68.5	0.9181			68.5	2.5317
70	1.22	70.5	0.832	75	2.43	70.5	2.3323
		71	0.8117			71	2.2848
		73	0.7352			73	2.104
		73.5	0.7171	80.5	2.23	73.5	2.061
75.5	0.94	75.1	0.6622			75.1	1.9288
		77.5	0.5872			77.5	1.7457
		79	0.5445			79	1.6398
		80	0.5177			80	1.5726
		84	0.4227			84	1.3294
		87	0.3626	93.3	2.03	87	1.1712
		88	0.3445			88	1.1226
		91	0.2952			91	0.9882
		92	0.2803			92	0.947
93.3	0.67	93.3	0.2711			93.3	

COLUMN 3							
m-TFMBA				Bromacil			
Days	Obsrvd	Days	Fitted	Days	Obsrvd	Days	Fitted
1.5	0	1.5	0	1.5		1.5	0
3.5	0.09	3.5	0	3.5		3.5	0
5		5	0			5	0
5.5	0.14	5.5	0	5.5		5.5	0
9	0.65	9	0	9		9	0
11.5		11.5	0.0002			11.5	0
14.2		14.2	0.0236			14.2	0
15.7	1.23	15.7	0.1394	15.7		15.7	0
		16	0.1885			16	0
		17	0.4623			17	0
		17.5	0.6848			17.5	0
		18	0.9815			18	0
18.2	1.93	18.2	1.1238	18.2	0	18.2	0
		18.5	1.365			18.5	0
		19	1.8464			19	0
		19.5	2.4344			19.5	0
		20	3.1347			20	0
20.1	4.18	20.1	3.2885	20.1	0	20.1	0
		20.5	3.9494			20.5	0
		21	4.8761			21	0
		21.5	5.9083			21.5	0
		21.7	5.815			21.7	0
		22	6.4429			22	0
22.1	7.17	22.1	6.6582	22.1	0.05	22.1	0
		22.5	7.5462			22.5	0
		23	8.7059			23	0
		23.5	10.5023			23.5	0
		24	11.8205			24	0
24.3	12	24.3	12.6134	24.3	0.81	24.3	0
		24.5	13.1397			24.5	0
		25	14.4365			25	0.0001
		25.5	15.6881			25.5	0.0002
		26	16.873			26	0.0004
		26.7	18.3832			26.7	0.0009
		27	18.9672			27	0.0013
27.1	18.5	27.1	19.1527	27.1	0.99	27.1	0.0014
		28	20.5947			28	0.004
		28.5	21.2076			28.5	0.0067
		29	21.6791			29	0.011
29.3	21.6	29.3	21.8934	29.3	1.1	29.3	0.0146
		29.5	22.0077			29.5	0.0177
		30	22.1943			30	0.0277
30.4	22	30.4	22.244	30.4	1.9	30.4	0.0391
		30.5	22.2429			30.5	0.0425
		31	22.1592			31	0.0606

m-TFMBA				Bromacil			
Days	Obsrvd	Days	Fitted	Days	Obsrvd	Days	Fitted
		31.4	22.0024			31.4	0.0828
		31.5	21.9513			31.5	0.0894
		32	21.6484			32	0.1293
32.2	22.83	32.2	21.2964	32.2	2.43	32.2	0.1492
		32.5	20.9445			32.5	0.1872
		33	20.5925			33	0.2618
		33.2	20.2406			33.2	0.2981
		33.5	19.8886			33.5	0.3603
		34	19.5366			34	0.5121
		34.5	19.1847			34.5	0.6828
		34.67	18.8327			34.67	0.7505
		35	18.341			35	0.8975
		35.5	17.5621			35.5	1.1396
35.7	17.1	35.7	17.2412	35.7	2.99	35.7	1.2594
		36	16.7519			36	1.4574
		36.5	15.9204			36.5	1.8407
		36.7	15.5839			36.7	2.014
		36.8	15.4151			36.8	2.1052
		37	15.0768			37	2.2969
		37.5	14.2296			37.5	2.8333
		38	13.3864			38	3.4563
		38.2	13.0517			38.2	3.7311
38.3	12.87	38.33	12.8353	38.3	4.79	38.33	3.9178
		38.5	12.5538			38.5	4.1718
		39	11.7376			39	4.984
		39.5	10.9428			39.5	5.8961
		40	10.115			40	6.9095
		40.52	9.2871			40.52	8.0702
41	9.05	41	8.4593	41	8.79	41	9.2359
		41.5	7.6314			41.5	10.5421
		41.67	7.4167			41.67	11.0064
		42	7.0119			42	11.9354
42.7	6.64	42.7	6.2051	42.7	15.22	42.7	14.0155
		43	5.8808			43	14.9468
		43.3	5.5693			43.3	15.898
		43.5	5.3686			43.5	16.5419
44	3.81	44	4.8913	44	18.97	44	18.1784
		44.5	4.4477			44.5	19.8412
		44.8	4.1974			44.8	20.8447
		45	4.0368			45	21.5139
45.2	2.09	45.2	3.8813	45.2	22.82	45.2	22.182
		45.5	3.6573			45.5	23.1795
		45.8	3.444			45.8	24.1683
		46	3.3076			46	24.8208
		46.17	3.1953			46.17	25.3702
		46.8	2.8065			46.8	27.353
		47	2.6919			47	27.9612
		47.5	2.4226			47.5	29.4272
		47.85	2.2482			47.85	30.4006

m-TFMBA				Bromacil			
Days	Obsrvd	Days	Fitted	Days	Obsrvd	Days	Fitted
		48	2.1769			48	30.803
		48.3	2.0401			48.3	31.5793
		48.3	2.0401			48.3	31.5793
49	2.06	49	1.75	49	33.22	49	33.2293
		49.5	1.5657			49.5	34.2565
		49.85	1.4473			49.85	34.8946
		49.85	1.4473			49.85	34.8946
		50	1.399			50	35.147
		50.5	1.2484			50.5	35.8938
		50.7	1.1923			50.7	36.1511
		51.3	1.0376			51.3	36.7779
		51.5	0.8302			51.5	36.9381
		51.7	0.7929			51.7	37.0737
		52	0.7399			52	37.2313
		52.3	0.6901	52.3	36.89	52.3	37.3341
		52.35	0.6821			52.35	37.3459
		52.4	0.6742			52.4	37.3562
		52.5	0.6586			52.5	37.3724
		53	0.7443			53	37.3639
		53.2	0.7093			53.2	37.3195
53.4	0.95	53.4	0.6757	53.4	38.01	53.4	37.2522
		53.5	0.6595			53.5	37.21
		54	0.5837			54	36.9166
		54.4	0.5289			54.4	36.5861
		54.5	0.516			54.5	36.4907
		54.8	0.479			54.8	36.1749
		55	0.4557			55	35.9404
		55.4	0.4122			55.4	35.4169
		55.67	0.3851	55.67	34.57	55.67	35.0243
		56	0.3543			56	34.5044
		56.5	0.3119			56.5	33.6391
		57	0.2744			57	32.6897
		57.67	0.2595			57.67	31.3052
58	0.19	58	0.2378	58	29.43	58	30.5833
		58.5	0.2082			58.5	29.4481
		58.9	0.1871			58.9	28.5105
		59.33	0.1394			59.33	27.4797
		59.5	0.1333			59.5	27.067
		59.7	0.1264			59.7	26.5785
		60	0.1167			60	25.8977
		60.5	0.1021	60.5	24.73	60.5	24.6664
		61	0.0893			61	23.431
		61.5	0.078			61.5	22.1429
		62.67	0.0567			62.67	19.3057
		62.8	0.0547			62.8	18.9983
		63	0.0518	63	16.505	63	18.529
		63.7	0.0427			63.7	16.9264
		64	0.0393			64	16.2604

m-TFMBA				Bromacil			
Days	Obsrvd	Days	Fitted	Days	Obsrvd	Days	Fitted
		64.3	0.0362			64.3	15.5413
		65	0.0297			65	14.0796
		66.5	0.0195	66.5	9.9	66.5	11.3003
		67.5	0.0147			67.5	9.6293
		67.8	0.0135			67.8	9.1641
		68.5	0.011			68.5	8.1426
		70	0.0071	70	3.6	70	6.2452
		73	0.003			73	3.5216
		75	0.0016			75	2.312
		76.5	0.001	76.5	2.9	76.5	1.668
		80	0.0004			80	0.745
		81.5	0.0002			81.5	0.5175
		85	0.0001	85	1.8	85	0.2128
		90	0			90	0.055
		94	0	94	1.4	94	0.0175
		95	0			95	0.0131
		98.33	0			98.33	0.0048
		100	0			100	0.0029
		101.67	0	101.67	1.1	101.67	0.0018
		105	0	105	0.952	105	0.0006

COLUMN 4							
m-TFMBA				Bromacil			
Days	Obsrvd	Days	Fitted	Days	Obsrvd	Days	Fitted
1.5		1.5	0			1.5	0
3.5	0	3.5	0			3.5	0
5	0.93	5	0			5	0
5.5		5.5	0			5.5	0
9		9	0			9	0
11.5	1.2	11.5	0.0002			11.5	0
14.2	1.25	14.2	0.0162			14.2	0
		15.7	0.0944			15.7	0
		16	0.1214			16	0
		17	0.3001			17	0
17.5	3.78	17.5	0.4751			17.5	0
		18	0.6859			18	0
		18.2	0.7878			18.2	0
		18.5	0.9617			18.5	0
		19	1.2905			19	0
		19.5	1.7171			19.5	0
		20	2.233			20	0
		20.1	2.3474			20.1	0
		20.5	2.843			20.5	0
		21	3.5488			21	0
21.5	6.16	21.5	4.3494			21.5	0
		21.7	4.6953			21.7	0
		22	5.2402			22	0.0001
		22.1	5.4286			22.1	0.0001
		22.5	6.2135			22.5	0.0001
		23	7.2584			23	0.0002
23.5	9.61	23.5	8.3614			23.5	0.0005
		24	9.5065			24	0.0009
		24.3	10.2066			24.3	0.0013
		24.5	10.6762			24.5	0.0016
		25	11.8519			25	0.0029
		25.5	13.0144			25.5	0.005
		26	14.1449			26	0.0084
26.7	13.61	26.7	15.6394	26.7	0.124	26.7	0.0164
		27	16.2385			27	0.0216
		27.1	16.4318			27.1	0.0236
		28	18.0062			28	0.0486
28.5	18.21	28.5	18.737	28.5	0.189	28.5	0.0722
		29	19.3541			29	0.1067
		29.3	19.6674			29.3	0.1324
		29.5	19.8519			29.5	0.1524
30	19.9	30	20.2274	30	0.449	30	0.2138
		30.4	20.4391			30.4	0.287
		30.5	20.4798			30.5	0.3055
		31	20.6106			31	0.4137

<========= m-TFMBA ==============>				<=========== Bromacil ============>			
Days	Obsrvd	Days	Fitted	Days	Obsrvd	Days	Fitted
		31.4	20.6299			31.4	0.5213
		31.5	20.6233			31.5	0.5431
32	21.22	32	20.5232	32	1.023	32	0.7133
		32.2	20.453			32.2	0.7922
		32.5	20.317			32.5	0.9236
		33	20.0127			33	1.18
		33.2	19.8654			33.2	1.2968
		33.5	19.619			33.5	1.4885
		34	19.1454			34	1.8548
		34.5	18.6018			34.5	2.2846
		34.67	18.4028	34.67	4.28	34.67	2.4461
		35	17.9982			35	2.783
		35.5	17.3445			35.5	3.3543
		35.7	17.0711			35.7	3.6041
		36	16.6503			36	4.0021
		36.5	15.9252			36.5	4.729
		36.7	15.6284			36.7	5.0422
36.8	17.32	36.8	15.4789	36.8	5.223	36.8	5.2037
		37	15.1778			37	5.5363
		37.5	14.4164			37.5	6.4241
		38	13.6485			38	7.391
38.2	13.32	38.2	13.3411	38.2	9.081	38.2	7.7993
		38.33	13.1416			38.33	8.0711
		38.5	12.8811			38.5	8.4342
		39	12.1201			39	9.5495
		39.5	11.371			39.5	10.7311
		40	10.6384	40	11.76	40	11.9721
		40.52	9.8982			40.52	13.3166
		41	9.2376			41	14.5974
		41.5	8.5754			41.5	15.9617
		41.67	8.3566			41.67	16.4306
		42	8.0918			42	17.3456
42.7	6.28	42.7	7.2455	42.7	20.22	42.7	19.2932
		43	6.9011			43	20.1242
		43.3	6.4162			43.3	20.949
		43.5	6.2027			43.5	21.4941
		44	5.6911			44	22.8344
44.4	5.21	44.5	5.2112	44.5	24.146	44.5	24.1331
		44.8	4.9382			44.8	24.8874
		45	4.7624			45	25.3784
		45.2	4.5914			45.2	25.859
		45.5	4.344			45.5	26.481
		45.8	4.1072			45.8	27.1589
		46	3.9552			46	27.5949
		46.17	3.8295			46.17	27.9549
46.8	1.87	46.8	3.3917	46.8	30.209	46.8	29.2792
		47	3.2616			47	29.6396
47.5	1.49	47.5	2.9544	47.5	30.887	47.5	30.47
		47.85	2.7541			47.85	30.9888

m-TFMBA				Bromacil			
Days	Obsrvd	Days	Fitted	Days	Obsrvd	Days	Fitted
		48	2.6719			48	31.195
		48.3	2.5136			48.3	31.6137
		48.3	2.5136			48.3	31.6137
		49	2.1752			49	32.3398
		49.5	1.9584			49.5	32.7216
		49.85	1.818			49.85	32.8856
		49.85	1.818			49.85	32.8856
		50	1.7606			50	32.9556
		50.5	1.5807			50.5	33.1146
		50.7	1.5134			50.7	33.1464
51.3	0.97	51.3	1.3266	51.3	34.005	51.3	33.135
		51.5	1.2691			51.5	33.0963
		51.7	1.2138			51.7	33.0406
		52	1.135			52	32.9256
		52.3	1.0608			52.3	32.7739
		52.35	1.0489			52.35	32.7451
		52.4	1.0371	52.4	33.027	52.4	32.7154
		52.5	1.0138			52.5	32.6529
		53	0.9045			53	32.2838
		53.2	0.8639			53.2	32.1104
		53.4	0.825			53.4	31.9229
		53.5	0.8061			53.5	31.824
		54	0.7176	54	31.226	54	31.2802
		54.4	0.6533			54.4	30.7892
		54.5	0.6381			54.5	30.6591
		54.8	0.5944			54.8	30.2525
		55	0.5668			55	29.9681
		55.4	0.5152			55.4	29.3699
		55.67	0.4829	55.67	26.459	55.67	28.9455
		56	0.446			56	28.406
		56.5	0.3847			56.5	27.5497
		57	0.3405			57	26.6533
		57.67	0.2997			57.67	25.4018
		58	0.2761			58	24.7687
		58.5	0.2437			58.5	23.7943
		58.9	0.2204			58.9	23.0052
		59.33	0.1977	59.33	19.285	59.33	22.1514
		59.5	0.1893			59.5	21.813
		59.7	0.1799			59.7	21.4147
		60	0.1667			60	20.8178
60.5	0.4	60.5	0.1466	60.5	17.238	60.5	19.8266
		61	0.1289			61	18.8442
		61.5	0.1132			61.5	17.8748
		62.67	0.0833			62.67	15.6785
62.8	0	62.8	0.0805	62.8	14.891	62.8	15.442
		63	0.0764			63	15.0814
		63.7	0.0634			63.7	13.8528
		64	0.0585			64	13.3432

m-TFMBA				Bromacil			
Days	Obsrvd	Days	Fitted	Days	Obsrvd	Days	Fitted
		65	0.0448			65	11.7235
		66.5	0.0298			66.5	9.5358
		67.5	0.0226			67.5	8.2439
		67.8	0.0208	67.8	6.522	67.8	7.8823
		68.5	0.0172			68.5	7.0843
		70	0.0113	70	3.991	70	5.5826
		73	0.0048			73	3.3454
		75	0.0027	75	2.5	75	2.3195
		76.5	0.0018			76.5	1.7417
		80	0.0006			80	0.8605
		81.5	0.0004			81.5	0.6269
		85	0.0001	85	1.103	85	0.2903
		90	0			90	0.0904
		94	0			94	0.0338
		95	0	95	1.05	95	0.0262
		98.33	0			98.33	0.0111
		100	0			100	0.0072
		101.67	0			101.67	0.0046
		105	0	105	1.029	105	0.0019

Appendix 3.2

This appendix contains some of the photographs from different columns at various depths. These photographs were used to estimate approximate bypassing in the dye experiment.

Figure 4.6 Dye Pattern in Column 1 (intact column) at a Depth of 30 cm.

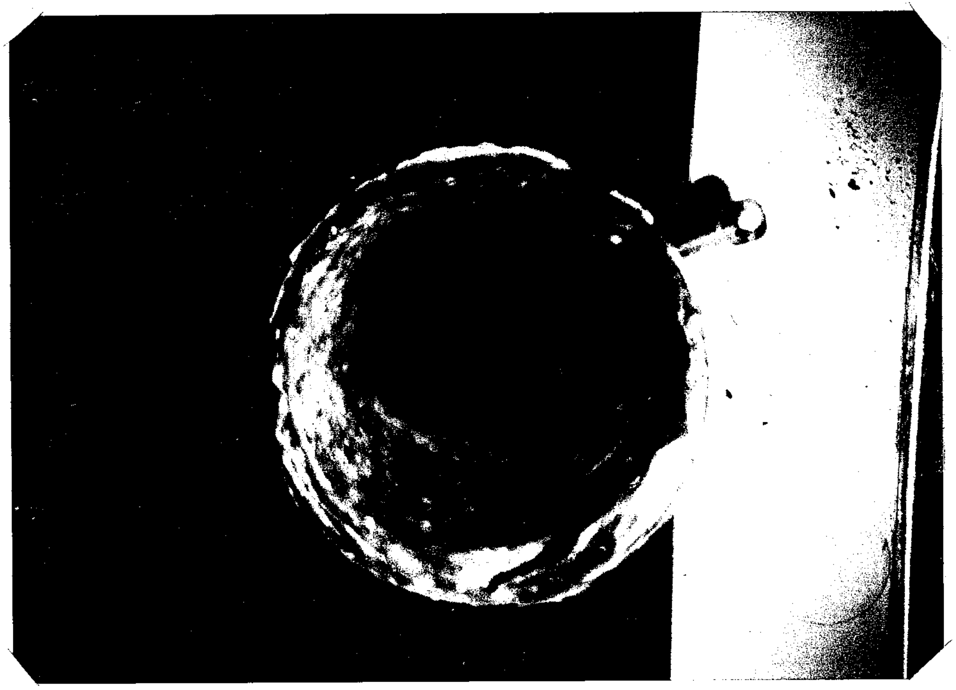

Figure 4.7 Dye Pattern in Column 1 at a depth of 35 cm.

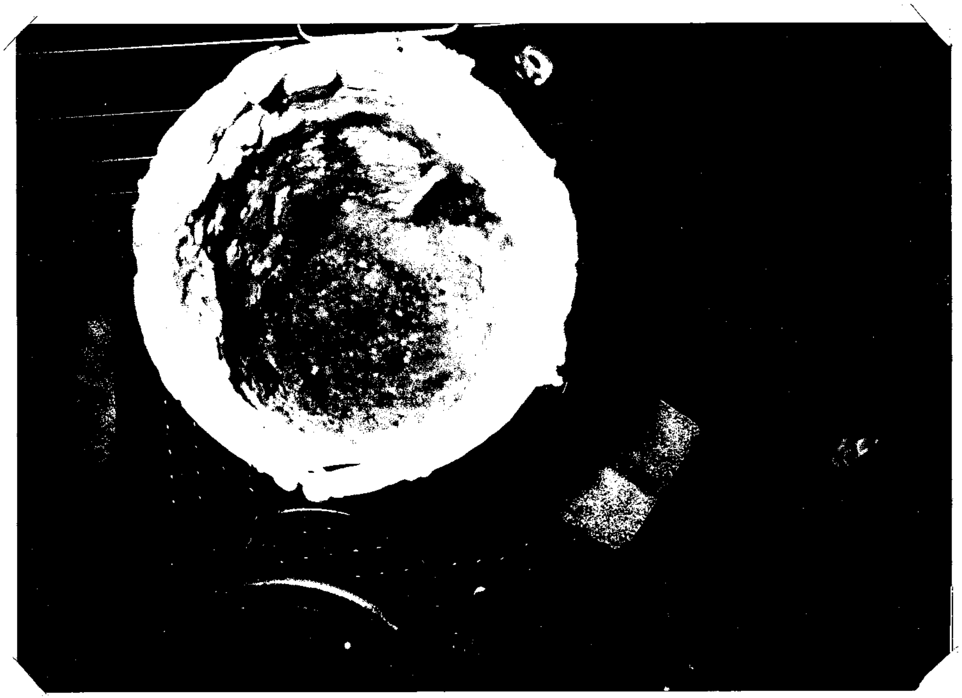

Figure 4.8 Dye Pattern in Column 2 (intact column) at a depth of 25 cm.

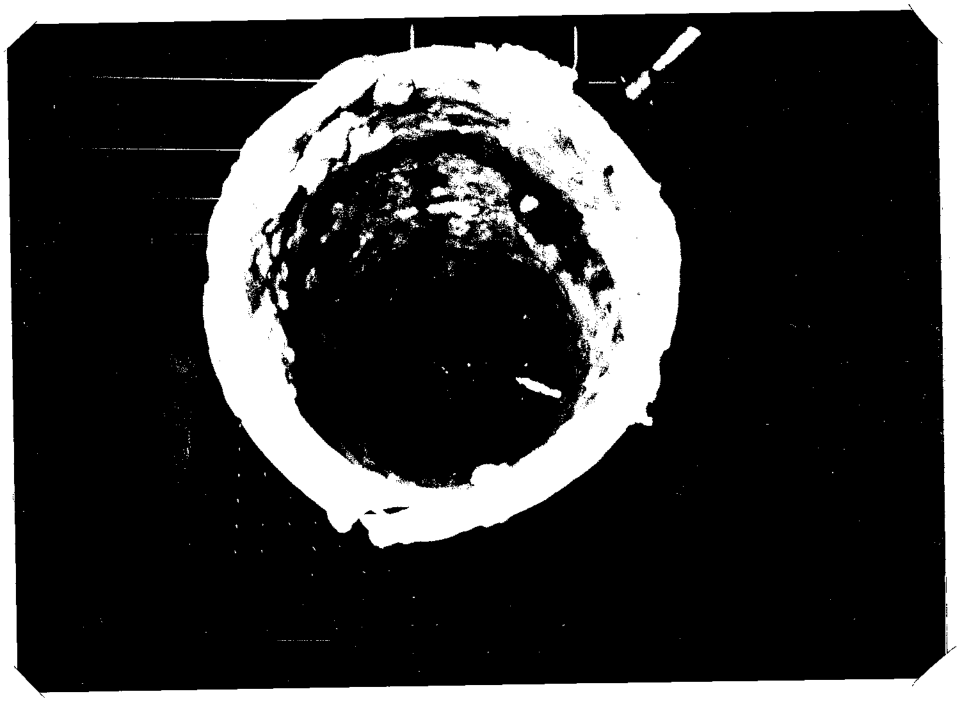

Figure 4.9 Dye Pattern in Column 2 at a depth of 35 cm.

Figure 4.10 Dye pattern in Column 3 (repacked column) at a depth of 25 cm.

Figure 4.11 Dye Pattern in Column 3 at a depth of 35 cm.

Figure 4.12 Dye Pattern in Column 4 (repacked column) at a depth of 5 cm.

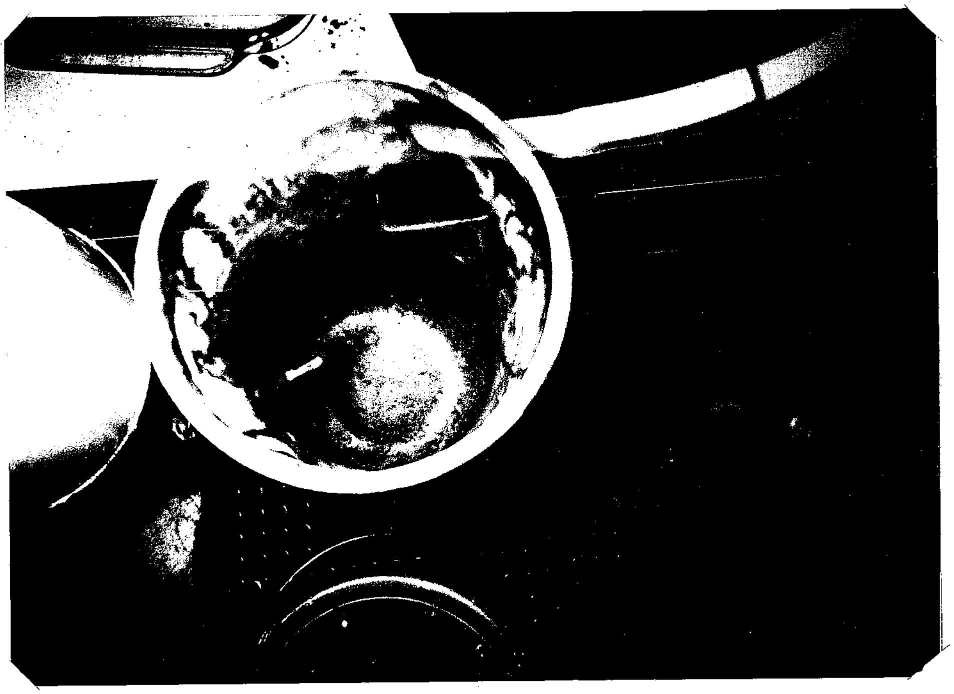

Figure 4.13 Dye Pattern in Column 4 at a depth of 20 cm.

Appendix 3.3

This appendix contains one photo of algae growth in a repacked column. The algae growth in the intact columns was not visible due to fiberglass coating of the columns.

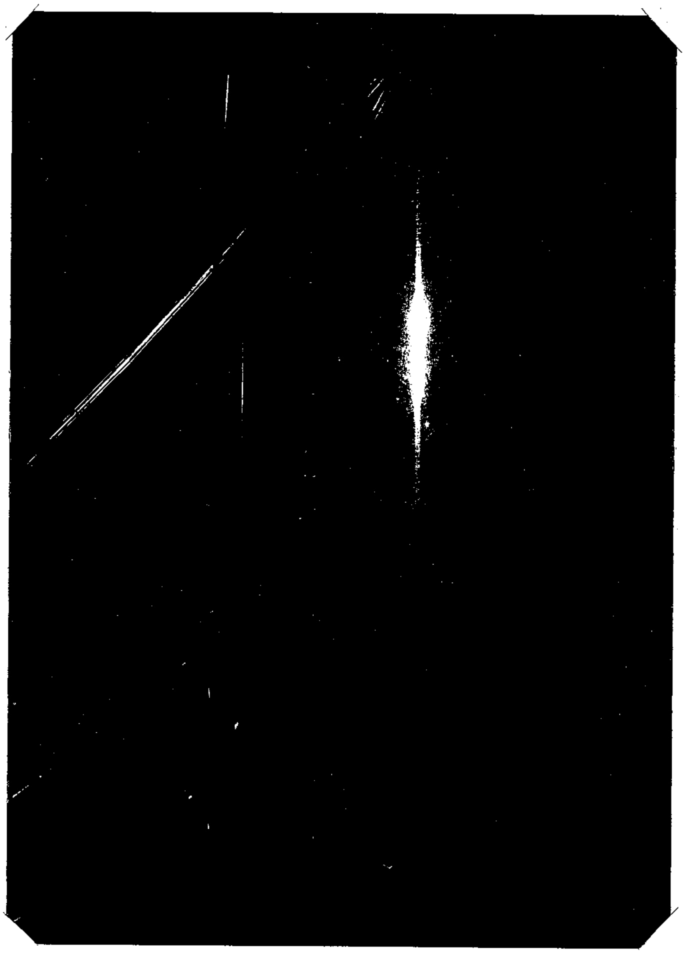

Figure 4.14 Algae Growth in Column 3.

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