TRANSPORT OF A
CONSERVATIVE AND MILDLY RETARDED TRACER
IN
IN SITU AND REPACKED SOIL COLUMNS

by

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ABSTRACT

The objective of this study was to investigate the presence of preferential flow and its affect on the transport of a conservative tracer, m-trifluoromethylbenzoic acid (m-TFMBA), and a mildly retarded tracer, 5-bromo-3-sec-butyl-6-methyluracil, (bromacil) through two in situ and two repacked soil columns. All columns were of the same bulk density and soil type. Each measured 15-cm in diameter and 32-cm high. Soil in the in situ columns showed no visible cracks or macropores. A comparison of the degree of preferential flow between steady state unsaturated and intermittent ponding flow regimes was investigated.

Curve fitting average pore water velocities to solute flux-averaged breakthrough curves (BTCs) indicated all columns had some degree of preferential flow for both flow regimes. Preferential flow during the intermittent ponding flow regime was much more pronounced in the in situ soil columns. The repacked soil columns showed close to ideal miscible displacement for both flow regimes. A comparison of BTCs between the two column types implied that soil structure of the in situ columns promoting preferential flow was destroyed during the sieving and repacking process.

During the steady state-unsaturated flow regime, the appearance of both tracer peaks required less cumulative effluent than that of the intermittent ponding flow regime. It is speculated that molecular diffusion and concentration gradients drove both tracers into the less mobile fluid-filled pores during the quiescent period of the intermittent ponding flow regime. This would make the tracers more resistant to miscible displacement during subsequent ponds.

The results from this study lead to three deductions. One, that preferential flow is highly possible in a seemingly structureless soil profile during steady state-unsaturated flow and intermittent ponding and therefore solute transport may be underestimated using conventional transport models. Two, due to the presence of preferential flow and the time interval between ponding events, intermittent ponding can be less effective than steady state-unsaturated flow in flushing surface applied salts out of a homogenous soil profile. Three, retardation factors (R_fs), derived from batch isotherm partitioning coefficients (K_ds), are good indicators of predicting solute movement of the mildly retarded bromacil during the steady state-unsaturated flow regime. For the intermittent ponding flow regime, high R_fs underestimated the initial appearance of bromacil for the in situ columns , yet adequately described the movement of bromacil BTC peaks. Underestimation of the initial appearance of bromacil relative to m-TFMBA was a result of preferential flow. Preferential flow caused such rapid solute movement through the soil profile that bromacil adsorption kinetics did not come to equilibrium. Bromacil R_fs were higher for the intermittent ponding flow regime than for the steady state-unsaturated flow regime. This was due to all columns having lower moisture contents during the long quiescent period between ponding events.

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1 INTRODUCTION

Increased world population in the past 100 years has been followed by industrial growth around urban centers and more intensive agricultural development in rural areas. Consequently, extra burdens have been placed on the soil. It is used by industry as a disposal site for undesirable industrial waste products, as well as a recipient of accidental chemical spills. As an example, organic chemical production grew from 1 to 300 billion pounds per year between 1940 and 1966. This was followed by an equally staggering growth in abandoned and/or improperly designed waste disposal sites. Agribusinesses have increased the use of fertilizers and pesticides, indiscriminately and ignorantly applied in many instances, to insure higher crop yields. This point is illustrated by a United Kingdom study done over a 34 year period indicating the source of nitrate contaminants in groundwater from inorganic fertilizers grew from 2 to 23 %. (Canter et al. 1988). These pesticides, fertilizers, and chemicals from spills and improperly designed disposal sites are causing an increasing threat to groundwater quality.

More accurate prediction methods to determine the fate and transport of contaminants through the soil profile to the water table are needed. Chemicals must be designed and used with groundwater protection in mind. Research to determine more efficient application rates and quantities of fertilizers and pesticides is becoming an imperative to safeguard groundwater supplies for future generations.

1.1 Historical Perspective

Scientific examination and modeling of fluid flow and its constituents through the soil to the water table is a relatively young science. One of the first scientific reports of flow processes was given in the late 1800's by Lawes et al. (1882) while studying the composition of effluent collected in field tile drains. Lawes et al.'s analysis led them to label two modes of flow affecting effluent composition, that of direct (preferential) flow and general (piston) flow. Lawes et al. described direct flow as bypassing the majority of the soil matrix and occurring in larger or open channels and pores. General (piston) flow was defined as moving through the bulk of the soil via micro channels. Lawes et al.'s observations were dismissed by most soil scientists at that time (Steenhius and Goehring, 1990).

A more commonly accepted infiltration model was developed by Green and Ampt (1911) which described the mechanical properties of fluid movement through an unsaturated soil profile. This theory assumes 100% of the soil matrix participates in vertical flow, moving in a piston like fashion. The following equation is used to describe the Green-Ampt theory

$$\theta_s v_s = k_s\left(\frac{(h_o - h_L)}{L} + 1\right) \qquad [1]$$

where

θ_s = volumetric water content of the wetting profile (L^3/L^3)

v_s = the velocity of the wetting front (L/T)

h_o = the pressure head at the soil surface (L)

h_L = the pressure head at the wetting front (L)

L = the depth of the wetting front

The preceding equation is the integrated form of Darcy's flow equation given below

$$\Theta v = -k\left(\frac{dH}{dz}\right) \qquad [2]$$

where

Θ = the volumetric water content of the soil (L^3/L^3)

v = the average pore water velocity of the water (L/T)

H = the hydraulic head (the sum of the pressure head, h (L), and the gravitational head, -z (L))

z = the vertical distance from an a priori designated reference point (L).

k = the hydraulic conductivity (L/T)

Biggar and Nielsen (1967) developed a flow equation for the transport of an infiltrating fluid through an unsaturated soil profile which is miscible with the background fluid. This is written as follows

$$R_f \frac{\delta C}{\delta t} = D\frac{\delta^2 C}{\delta x^2} - v\frac{\delta C}{\delta x} \qquad [3]$$

where

C = solute concentration (M/L^3)

x = the distance (L) from where the solute is introduced

t = time (T) since solute introduced to system

D = hydrodynamic dispersion coefficient (L^2/T)

v = average pore water velocity (L/T).

R_f = retardation factor of a solute

Dispersion coefficients, D, describe the processes of mechanical dispersion and molecular diffusion together. They are written as $D = D_m + \alpha v$. The mechanical dispersion term is a function of average pore water velocity, v, and the physical properties of the porous medium, such as variations in flow path tortuosities, pore sizes and textures. These physical variations are lumped together and labeled the dispersivity, α (L), of the porous medium. Because molecular diffusion is very much smaller, in most transport situations, than mechanical dispersion it is usually not considered a major contributing factor in D values. Therefore the dispersion coefficient is usually written only as $D = \alpha v$.

Partitioning coefficients, K_d, (mass of solute adsorbed to a unit mass of soil surface/concentration of solute in solution (L^3/M)) are used to calculate the retardation factor, R_f, of a solute as it moves from the source point. R_fs are defined with the following

$$R_f = 1 + \frac{\rho_b K_D}{\Theta} \qquad [4]$$

where

ρ_b = soil bulk density

Idiosyncracies of predicted fluid movement, using miscible displacement flow theory, in homogeneous and nonhomogeneous soils were explained by the phenomenon of hydrodynamic dispersion. Large dispersion coefficients were used as correction factors in the miscible displacement theory. Biggar and Nielsen's model had become widely accepted by most soil scientists up until the late 1960's and early 1970's and is referred to as the classical miscible displacement or convection-dispersion, CD, model.

Numerous soil scientists were finding predicted movement of fluid flow underestimating, in many instances, arrival times of solute free and laden water using this theory. This stemmed from several erroneous assumptions made in developing the CD model; that infiltrating fluid always displaces the background fluid as it moves through the soil matrix, and 100% of the soil matrix always participates in the infiltration process.

Calculation of R_f's had been overestimated in many cases, using laboratory derived K_d values. This was due to the misconception that all the solute participates in miscible displacement as it moves away from its source point, contacting all potential adsorbing sites of the soil and thus becoming retarded. Because of the preceding arguments, many soil scientists have been compelled to reevaluate the classical CD and piston flow models in order to more adequately describe fluid flow through a porous medium.

1.2. Preferential Flow - Theoretical Development

In the early 1970's numerous researchers were finding the Green-Ampt (piston flow) and miscible displacement models underestimating the velocities of solutes as they passed through a soil profile, whether they are nonreactive (conservative) or reactive with the media. The theory of piston flow, especially that occurring in layered soils, and total miscible displacement was challenged by Hill and Parlange (1972), Raats (1973), and Phillip (1975 a,b). These researchers noted several parameters that can disrupt the front stability of piston flow, causing accelerated leaching through a fraction of the soil matrix. At this time most soil scientists still accepted the theory of piston flow and miscible displacement as representing the primary mode of fluid transport through nonlayered, homogeneous, and uniform soils. However, the idea of accelerated leaching and/or delayed release of tracers due to the interactive processes between micro- and macropore flow was becoming more widely discussed and tested.

Green et al. (1972) emphasized the need to investigate the interaction between pore geometry and velocity distributions to explain the presence of early "breakthrough" of a solute which was currently explained by large D coefficients. The label "preferential flow" was used to describe this accelerated movement of displacing water along macropores otherwise interpreted as extensive hydrodynamic dispersion in the piston flow and CD model. Preferential flow became widely accepted as describing non-piston flow or anomalous flow processes where miscible displacement occurs in only a fraction of the soil profile. These flow processes may be characterized by distinct fingers as well as more subtle nonpiston type flow porcesses not satisfactorily described by the currently accepted flow theories.

Researchers such as Bouma (1981) and van Genuchten and Wierenga (1977), to name a few, were coining terms such as "short circuiting" and " mobile/immobile water" to explain more accurately the variable rate of solute fronts through a soil matrix. Research and investigations of fluid flow on regional, field and laboratory soils were reporting more and more frequently the presence of preferential flow phenomenon.

Regional studies investigating the occurrence of natural isotopes, such as Cl^-, and their relationship to groundwater recharge and movement in Western Australia, indicated that preferential flow paths are responsible for transport of up to 50% of the annual aquifer recharge there (Sharma and Hughes ,1981). These flow paths bypass most of the mitigating, filtering, and adsorption processes that take place in the soil matrix.

Field studies such as those carried out by Steenhuis and Geohring (1990) on effluent collected from subsurface tile drains, called attention to the accelerated movement of conservative and retarded tracers that were not adequately explained by piston flow or the CD model. Preferential flow was found prevalent in the Netherlands using iodide coloring techniques by Hendrickx et al. (1988) in fields soils that were hydrophobic. Bowman and Rice (1986a, b) measured the transport of conservative and retarded tracer concentrations vs. depth in a "homogeneous" soil. Their findings indicate accelerated movement of these tracers via preferential flow paths as a dominant process.

Column studies such as those done by De Smedt et al. (1986), indicate the presence of preferential flow given changes in various flow regimes. Many investigators have shown that solute transport parameters derived from "intact" soil samples vary considerably from those obtained using repacked samples. For example, McMahon and Thomas (1974) compared breakthrough curves (BTC) of intact and repacked soil columns presaturated with distilled water than eluted with a solution of .002N $CaCl_2$ in tritiated water. Much earlier BTCs were found in the intact as compared to repacked soil columns. Smith et al. (1985) found considerably faster transport of Escherichia coli through intact soil columns as opposed to repacked columns. Jardine et al. (1988) compared R_fs of retarded inorganic ions derived from batch isotherms on disturbed and intact soil columns. They found derived R_fs from disturbed soil samples overestimated solute retardation in the intact soil columns and suggest modeling solute transport properties derived from repacked soil columns may give erroneous values. It is clear from these and similar studies that a marked difference exists between solute breakthrough of repacked and in situ soil columns, with strong preferential flow seen in the in situ columns.

It has become increasingly apparent that the phenomenon of preferential flow needs to be further investigated. In order to understand what processes seem to dominate and/or dampen preferential flow, further laboratory and field experiments need to be undertaken with controls and monitors given to specified properties such as tensions, flow regimes, solute concentration and type.

1.3 Purpose

The purpose of this study was to;

- compare and contrast the degree of preferential flow in intact vs. repacked soil columns, given different flow regimes,
- determine the impact of preferential flow on retardation factors,
- aid in predicting variables that might enhance or impede the presence of preferential flow phenomena.

2. MATERIALS AND METHODS

2.1 Soil Characterization

Two intact and two repacked columns of the same dimensions were used for this study. The soil for each column was a Casa Grande deep sandy clay loam (fine-loamy, mixed, hyperthermic Typic Natrargrids) well drained and slowly permeable, located on Plot F-5 at the Maricopa Agricultural Center (MAC) of the University of Arizona. The field from which soil was used for this study had been uncropped for the past 4 years and upon visual inspection exhibited no discernible macropores. No major root systems were found.

MAC is located three miles east of Maricopa and three miles north of the Casa Grande-Maricopa Highway. Figure 1 is map of MAC and gives the legal description and Universal Transverse Mercator grid notations for the section corners.

This location was picked to coincide with a concurrent field study, at the same location, on preferential flow and concentration effects of a suite of conservative and retarded tracers. The site was also used by Bowman and Rice's (1986a) field experiment on preferential tracer movement. Information gained from each study can be used to shed light and give a clearer picture of the overall physical and chemical processes of the site that affect pesticide transport. Figure 2 is a map of the portion of plot F-5 used for the concurrent field study. Figure 2 also denotes the location of soil taken for this study relative to the grids created for the concurrently run solute transport study. A brief description of the Casa Grande soil and list of soil parameters found by the Department of Soil and Water Science at the University of Arizona is given in Appendix A.

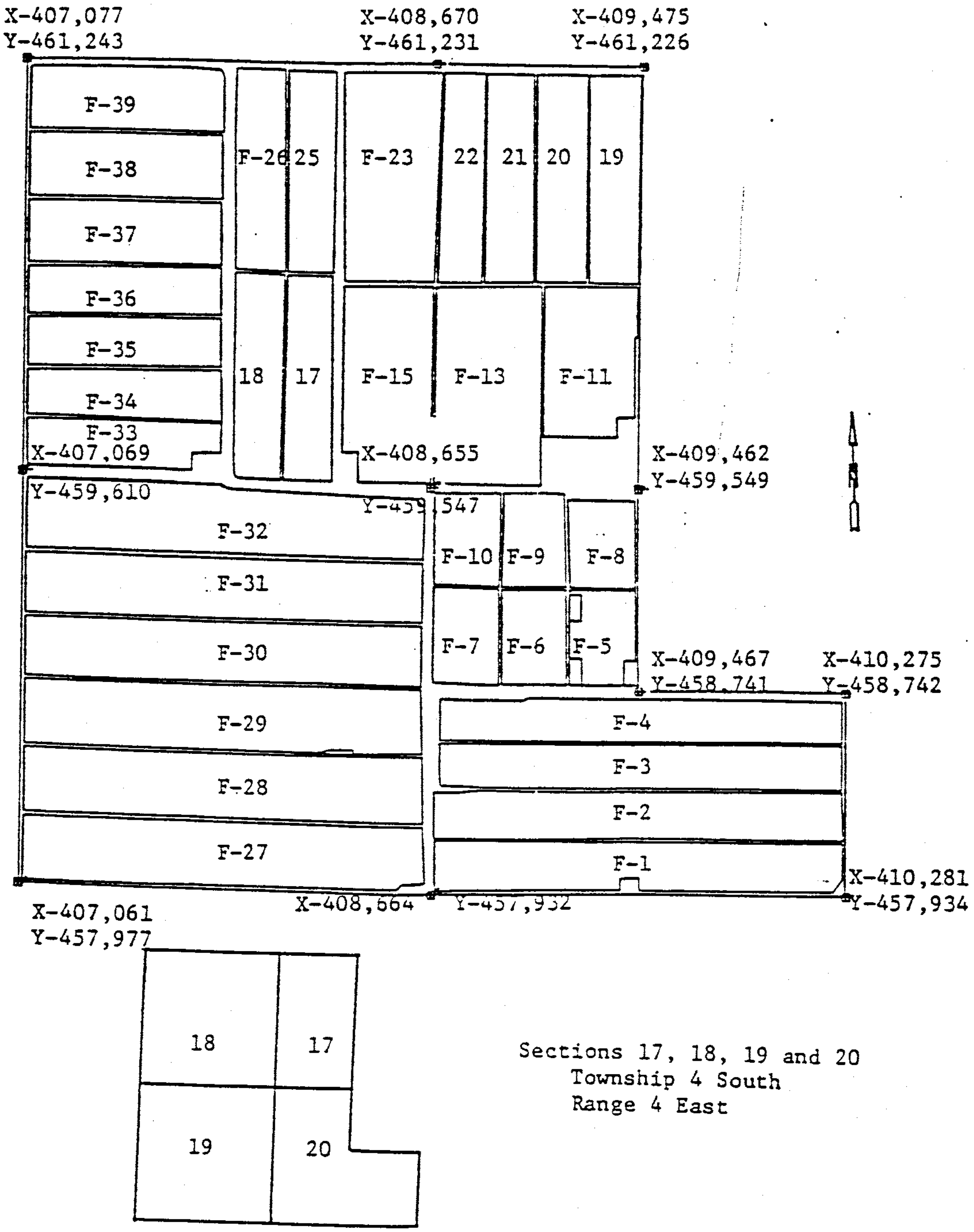


Fig. 1. Map of MAC farm located in central Arizona. (Post, 1988)

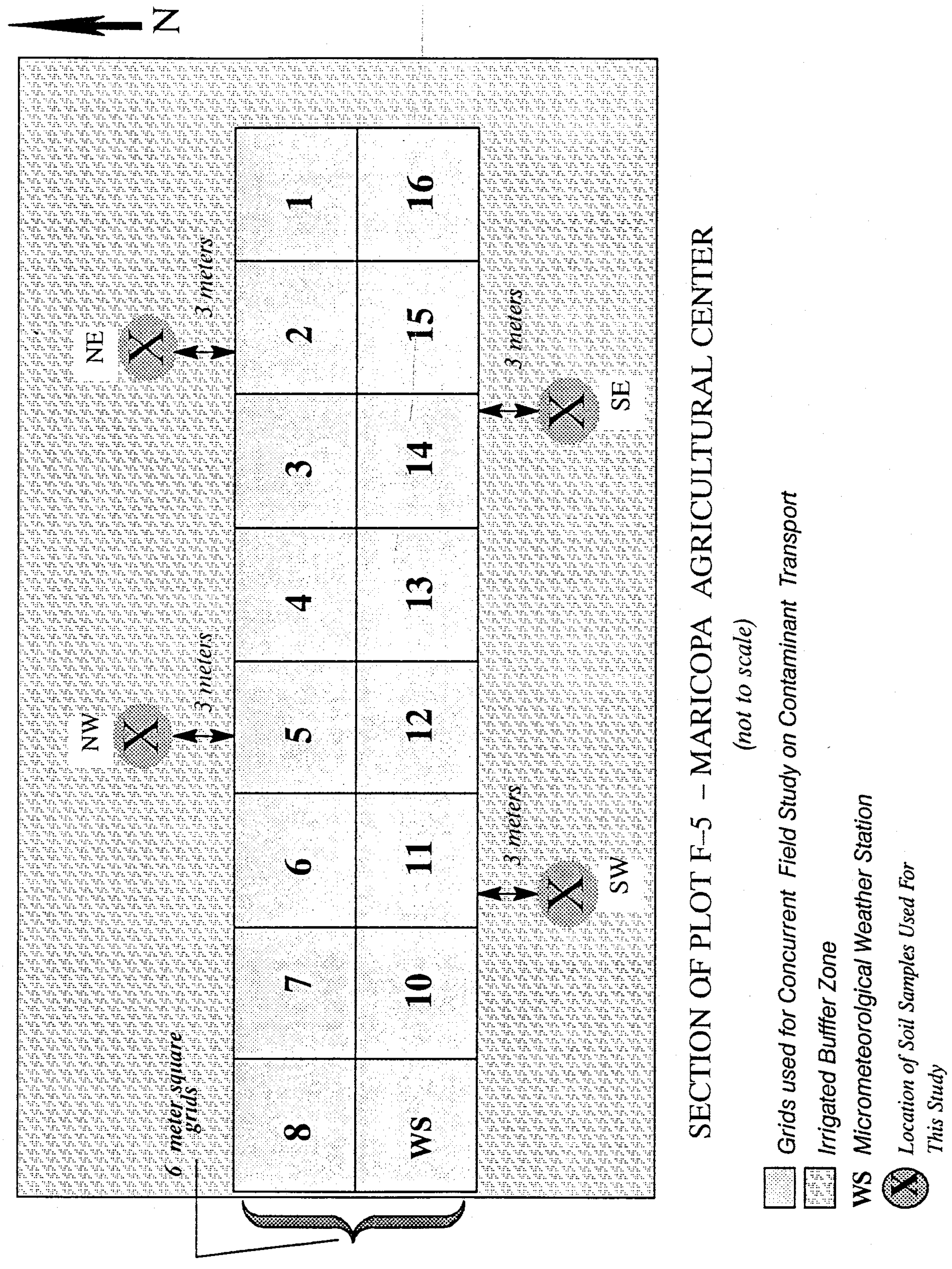


Fig. 2. Layout of a section of Plot F-5 at MAC denoting location of soil samples taken for this study and concurrent field tracer study.

For this study, however, it was necessary to obtain more detailed knowledge of specific soil parameters. These parameters were used to replicate the in situ column bulk densities for the repacked columns and determine column moisture contents using soil matric potentials found with the tensiometers. For steady state and unit gradient conditions the darcy fluxes,q, delivered needed to be equal to the unsaturated hydraulic conductivities, K_{unsat}, throughout the entire length of each column. To arrive at K_{unsat} values with the use of available models, saturated hydraulic conductivities, K_{sat}, and soil moisture characteristic curves, θ-Ψ, needed to be determined. The following lists these parameters and the methods used to obtain them.

2.1.1 *Average Soil Bulk Density -ρ_{ab}*

In order to replicate the same soil density of the in situ columns in the repacked columns an air dried bulk density, ρ_{ad}, of the soil taken from each location needed to be determined. An average bulk density, ρ_{ab}, was needed in order to calculate ρ_{ad}. Soil samples were taken with ring samplers 23.75 cm^2 x 3.0 cm (71.27 cm^3) and 19.63 cm^2 x 5.1 cm (100 cm^3) in size. The 71.27 cm^3 samplers were used to take samples at depths of 8, 15, 23, and 30 cm and were additionally used to derive the soil moisture characteristic curve. The 100 cm^3 samplers were used to take samples at 2, 8, and 30 cm depths and were also used to define K_{sat} values. After the soil moisture characteristic curve and K_{sat} values had been determined the soil samples were oven dried at 105°C for 48 hours, while still in their respective rings, and weighed. Because the soil was considered to have only a small percentage of clay (See Appendix A, Table 16) only one period of oven drying was considered sufficient. The mass of the soil was determined when subtracting the ring weight. Bulk densities, ρ_b, was determined using the following formula.

$$\rho_b = \frac{\text{mass of dry soil}}{\text{volume of soil}}$$

Table 1 lists the ρ_b found using the above procedure. Note that ρ_b decreases with depth.

Table 1. Bulk Densities, ρ_b, of Casa Grande Soil

	71.27 cm^3		100.0cm^3
Depth	gr/cm^3	Depth	gr/cm^3
8	1.648	2	1.744
15	1.642	8	1.642
23	1.639	30	1.577
30	1.555		
Avg. ρ_b	1.614	Avg. ρ_b	1.654

2.1.2 *Air Dried Bulk Densities ρ_{ad}*

Each repacked column used air dried, sieved, and mixed soil taken from the same pit as that of the in situ column to be replicated. The amount of soil needed for each column was determined by the equation

$$\text{Soil Wt}_{\text{repacked column}} = (\rho_{ad})(\text{Volume}_{\text{column}}) \qquad [5]$$

where ρ_{ad}, is average air dried bulk density of the soil taken at each location. The air dried density ,ρ_{ad}, of the soil was calculated with the following equation

$$\rho_{ad} = \rho_{ab} + (\rho_{ab})(\text{GWC}) \qquad [6]$$

where ρ_{ab} is the average bulk densities (found from the soil cores when determining the soil moisture characteristic curve) and GWC is the gravimetric water content of the air dried soil.

It was necessary to determine the GWC of the air dried soil used for the repacked columns. Soil taken from each location was first air dried in pyrex dishes, sieved with a

No. 10 (2.0 mm screen opening) sieve and homogeneously mixed. Soil samples from each sieved and mixed batch were oven dried at 105°C for 24 hours and weighed. The GWC was found using the equation

$$\text{GWC} = \frac{\text{weight of soil before drying - weight of soil after drying}}{\text{weight of soil after drying}}$$

The ρ_{ad}s for each location were calculated using equation 6, ρ_{ab} derived from the 71.27 cm^3 ring samplers, and calculated GWC. These are listed below in Table 2.

Table 2. ρ_{ab}, GWC, and Air Dried Bulk Densities, ρ_{ad} of Soil Used for Repacked Columns

	Location	
	NW	SW
ρ_{ab} gm/cm^3	1.614	1.614
GWC	.0279	.0256
ρ_{ad} gm/cm^3	1.659	1.656

2.1.3 *Saturated Moisture Contents and Soil Moisture Characteristic Curve*

In order to determine column moisture contents from tensiometer readings and employ prewritten programs yielding K_{unsat} values it was necessary to determine a soil moisture characteristic curve, θ-Ψ, and saturated moisture contents, θ_s, for soil used in this study. (The column dimensions and instrumentation prohibited periodic weighing to determine moisture uptake.) A Tempe Pressure Cell (TPC) soil moisture extractor (Soilmoisture Equipment Corp., P.O. Box 30025, Santa Barbara, CA) was employed to determine θ-Ψ. Soil cores were obtained using a ring sampler and a soil core extractor. Samples were taken from depths of 8, 15, 23, and 30 centimeters of the southeast, SE, corner of plot F-5. Time and logistics prohibited the use of more than one soil core taken from each depth. The ring samplers, each containing an intact soil core, were transported to the lab for moisture vs. pressure analysis. Soil moisture measurements from the sample taken at the 15-cm depth had to be discarded as the TPC used for these measurements had a cracked porous plate. Pressures applied to each cell ranged from 14 to 900 mBars. The following plot, Figure 3, is pressure vs. moisture content found using this procedure. A more detailed description of this procedure and results found are in Appendix B.

After each TPC with porous plate was saturated, the ring sampler with soil core was placed on the porous plate and saturated from the bottom up until the soil sample showed a saturated sheen, indicating complete saturation, on the surface. The soil sample with TPC was weighed. The saturated moisture content, θ_s, for each cell was determined using the following equation

$$\theta_s = \frac{\text{volume water}}{\text{volume total}}$$

where the volume of water was determined using the density of water at the temperature of the room, and the total volume was the volume of the ring sampler. The θ_s for each cell is given in Table 3.

Table 3. Saturated Moisture Content, θ_s, for Casa Grande Soil Samples

Sample Depth -cm	θ_s
8	.294
23	.291
30	.308

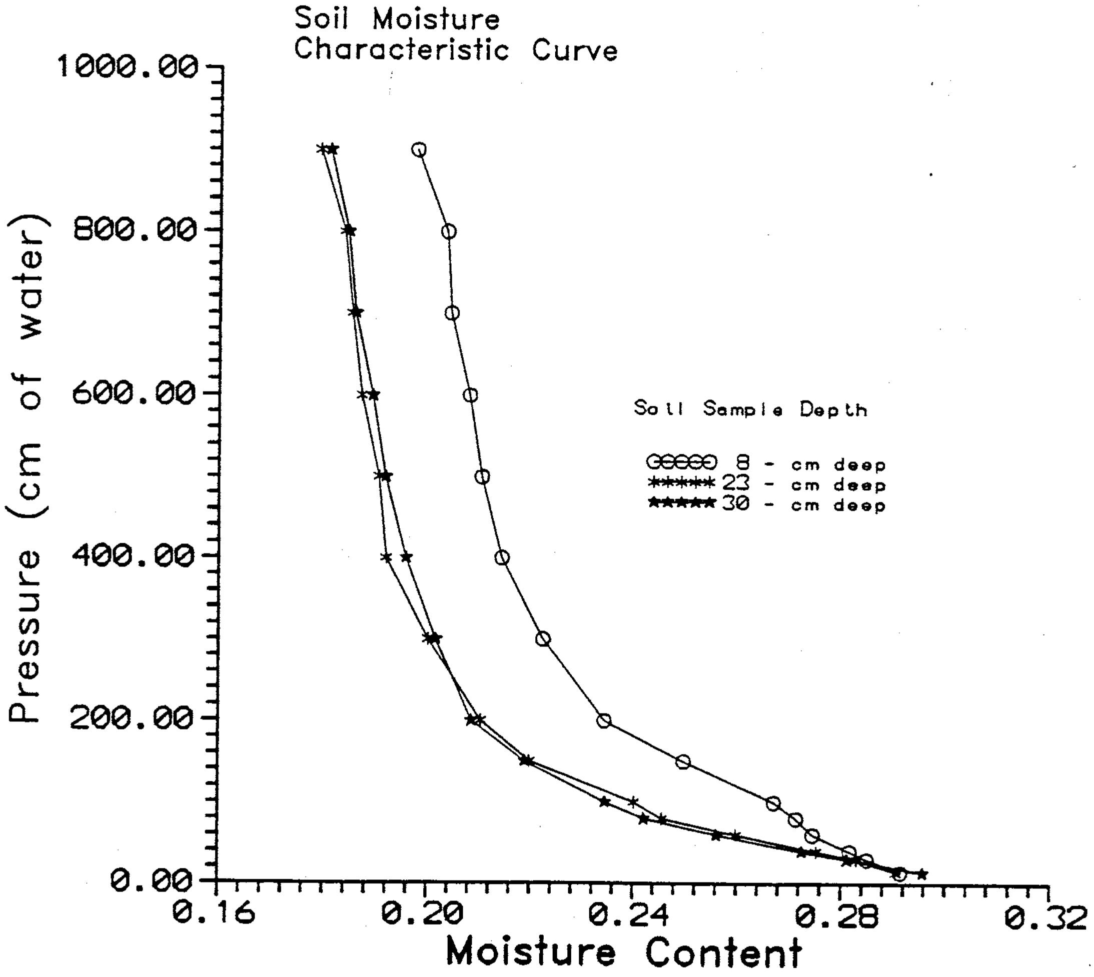


Fig. 3. Soil moisture characteristic curve for Casa Grande soil samples taken at Maricopa Experimental Farm

2.1.4 *Porosities η*

Determination of porosities, η, was needed in order to derive the amount of pore volumes, PVs, each column exhibited throughout the duration of the experiment and degree of saturation, S_e. These two could be found using soil matric potentials gotten from tensiometer readings and the θ-Ψ curve. Soil samples used for the soil moisture characteristic curve and K_{sat} values were also used to determine porosities. Each soil sample was carefully removed from the TPC or K_{sat} testing apparatus and oven dried at 105°C for 24 hours. Samples were removed from the oven and weighed. The soil was then removed from the ring to determine the ring weight. The ring weight was subtracted from the initial oven dried weight, thus giving rise to the oven-dried soil weight. Porosity from each sample was determined using the formula

$$\eta = 1 - \frac{\rho_b}{\rho_s}$$

where ρ_s is the soil particle density, here considered to be 2.60 grm/cm^3. Table 5 lists the porosities found for each core.

Table 4. Porosities, η, of Casa Grande Soil Samples from Maricopa Experimental Farm

Ring Size			
71.27 cm^3		100.0 cm^3	
Depth cm	η	Depth cm	η
8	.3661	2	.3292
15	.3685	8	.3684
23	.3692	30	.3934
30	.4019		
Avg. η	.371	Avg. η	.371

2.1.5 *Saturated Hydraulic Conductivities K_{sat}*

The saturated hydraulic conductivity of intact soil and repacked soil samples was done using samples placed in 100 cm^3 rings and positioned in a constant head tank. The intact soil samples were taken from a large in situ soil cylinder obtained at the SE corner of the test site and transported back to the lab. The repacked soil samples used air dried, sieved, and homogeneously mixed soil from the SW and NW location of the test site. To remove any entrapped air each sample was presaturated for several days before being placed in the constant head tank. Several saturated conductivity values were taken over a five day period. Average K_{sat} values for each sample over the five day period are given in Table 5. Note that conductivity values increase with depth.

Table 5. Saturated Hydraulic Conductivity of Casa Grande In Situ, IS, and repacked, RP, soil samples taken from Maricopa Experimental Farm

			K_{sat} cm/sec	
Location	Depth - cm	Type	Room Temp($\simeq 23^{\circ}$C)	20°C
SE	2	IS	1.7×10^{-5}	1.6×10^{-5}
SE	8	IS	3.2×10^{-4}	2.9×10^{-4}
SE	30	IS	8.6×10^{-4}	7.8×10^{-4}
SW		RP	3.1×10^{-4}	2.8×10^{-4}
SW		RP	1.1×10^{-4}	9.5×10^{-4}
NW		RP	2.1×10^{-4}	1.9×10^{-4}
NW		RP	7.4×10^{-5}	6.7×10^{-5}

2.1.6 *Unsaturated Hydraulic Conductivities K_{unsat}*

Determination of unsaturated hydraulic conductivity values was used employing the analytical models developed by Mualem (1976)

$$K_{unsat} = K_{sat} S_e^{\lambda} \left[\frac{(f(S_e))}{(f(1))} \right]^2$$

where the function $f(S_e)$ is defined as

$$f(S_e) = \int_0^{S_e} \frac{1}{(\psi(S_e^*))} dS_e^*$$

and

θ_r = residual moisture content

θ_s = saturated moisture content

S_e = effective saturation - $(\theta - \theta_r)/(\theta_s - \theta_r)$

λ = is an empirical constant $\simeq$ to .5

The model determines the relationship between unsaturated conductivity, K_{unsat}, soil moisture vs pressure head, θ-Ψ, and effective saturation, S_e. Mualem's model has been translated into a Fortran 77 code developed van Genuchten (1980). The code fits the θ-Ψ curve to

$$\theta = \theta_r + \frac{(\theta_s - \theta_r)}{[1 + (\alpha\psi)^n]^m} \qquad \text{(a)}$$

or

$$\theta = \theta_r + \frac{(\theta_s - \theta_r)}{(\alpha\psi)^n} \qquad \text{(b)}$$

where α, n, and m are empirical constants determined by the program. The model is run with the user choosing equation a or b that will yield the best fit (n is fitted or m = 1 -1/n). K_{unsat} values using soil samples for this experiment were determined with equation a, m = 1 -1/n. Input parameters employed to run the program are; θ-Ψ curve, K_{sat}, θ_r, and θ_s. Appendix C lists K(θ) vs. pressure head for each sample. Figure 2 is plot of K(θ) vs. pressure head for the soil samples taken at different soil depths using the aforementioned model.

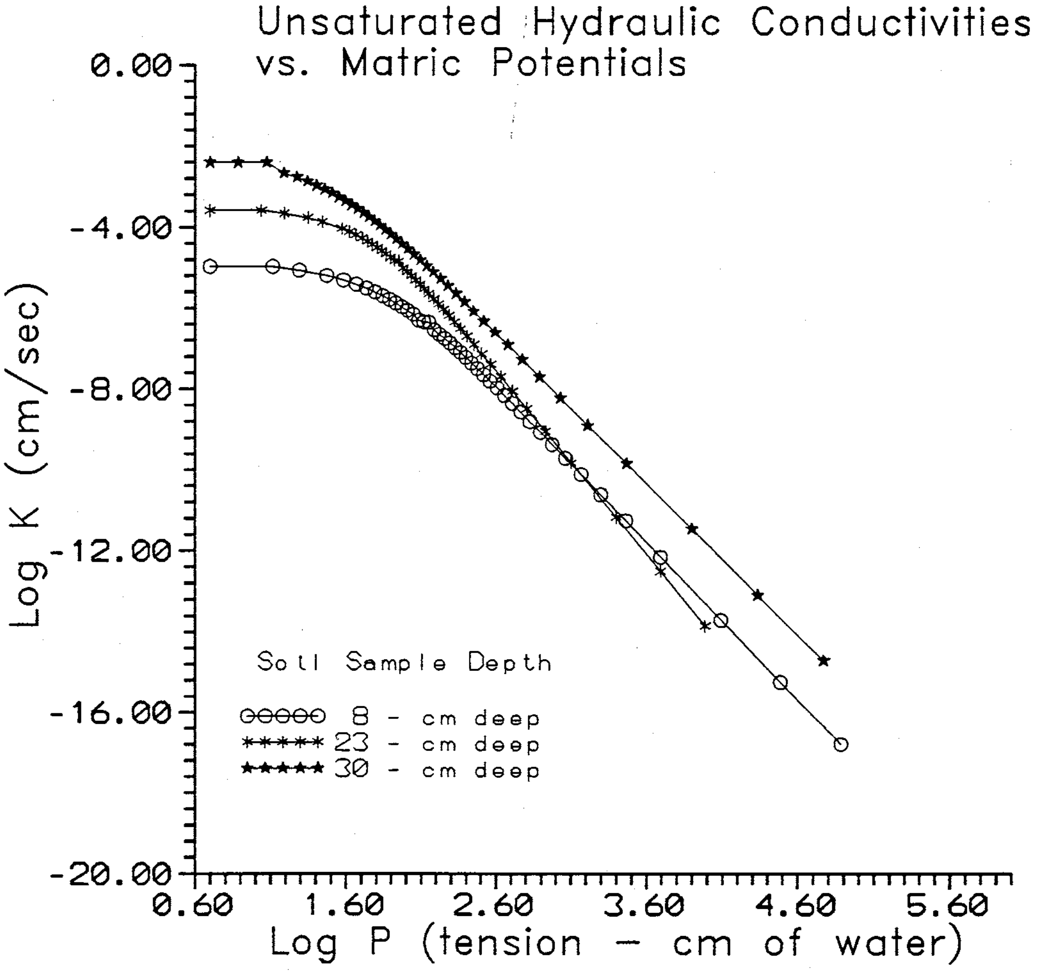


Fig. 4. K(θ) vs. Ψ for Casa Grande soil samples taken at Maricopa Experimental Farm.

2.2 Experimental Apparatus

2.2.1 *Intact Soil Columns*

Two intact soil columns 15-cm in diameter and 30-cm in length were obtained at the Maricopa Agricultural Center, plot F-5, in Central Arizona. (Figure 1, Section 2.1, is a map of the site.) The intact soil columns were hand carved and taken from the soil surface to a depth of approximately 40 cm.

The first step to acquire the intact column was to embed the non-fluted edge of a 16-cm diameter steel chimney flange roughly .5 cm into the soil surface. The surface outlined by this ring was painted with liquid rubber latex. The latex sealed the surface and subsequently prevented cracking or chipping during the digging process.

A 2 m diameter pit with a 0.75 m diameter soil pedestal in the center was dug to a depth of approximately 1-m. The pedestal was whittled to roughly 30 cm in diameter using a tempered steel butcher knife. A flat vertical plane was then carved on one side of this pedestal using a torpedo level and the steel butcher knife. This plane was used as a guide to insure formation of a straight column. The chimney flange and butcher knife were then used to carve the pedestal into a cylinder by rotating the flange down the pedestal side. The flange was turned slowly down the core length while the knife was used to chisel away the soil just underneath the flange bottom. A torpedo level was placed on the flange lip during this operation to insure formation of a straight column. Fine roots were cut with nail clippers and tin snips. After the pedestal trimming was complete, the flange remained at the core bottom until the sample was removed from the pit.

As described by Murphy et al. (1981), a commercially available polyester resin (Evercoat Marine Resin, Fibre Glass-Evercoat., Inc., 660 Cornell Road, Cincinnati, OH) was used to encase the soil core. The resin hardened when mixed with a methyl ethyl ketone peroxide (MEKP) catalyst. A full face mask, latex gloves and full length cotton apparel were worn to protect the eyes, lungs, and skin.

The resin/catalyst ratio used was 50:1. Set up time on sunny days using this ratio was about 1 hour. During overcast or cool days the ratio was reduced, as lack of exposure to the sunlight or a temperature drop increased the set up time.

The soil core was coated with the resin mixture using a 5-cm natural-bristle brush. After the core became tacky, precut strips of fiberglass cloth were wrapped around the column perimeter. A 25 x 45-cm strip was applied to the column center. 5 x 45-cm strips were applied to the column top and bottom . Each strip overlapped its end by about 2 cm. The top and bottom strips overlapped the center strip by roughly 3 cm. A second coat of the catalyzed resin was then applied. During this application the fiberglass was pressed to the core with the bristle brush causing any bubbles to be eliminated. A third coat of catalyzed resin was applied to the core after the second coat became tacky.

After the resin had hardened (approximately 1 hour on a sunny day) the column was detached from the pit bottom by cutting the soil with a piece of baling wire. While the wire was held taut it was slid between the pit bottom and lower flange edge. This resulted in a clean cut. The core was lifted from the pit with the flange still attached. During the coating process a small pool of resin had collected in the flange well. This was scooped out of the flange well, while still tacky, immediately after the core was removed from the pit. The flange was then gently detached from the core bottom using the butcher knife. The column bottom ends were sealed with the liquid rubber latex after all resin coated surfaces had thoroughly hardened. Altogether four soil columns were obtained from the NW, SW, NE, and SE corner of the field (see Figure 2).

The soil columns were then transported to the laboratory where the best two of the four intact columns taken from the site were trimmed up and instrumented for this experiment. The latex caps were removed from the column ends by carefully hand peeling. Because the latex minimally penetrates the soil, only a small amount of soil became detached upon removal. The column bottoms were trimmed to a flat, horizontal cross sectional surface. 9.0 and 3.5-cm sections of 15-cm I.D. poly vinyl chloride, PVC, pipe were glued to the column top and bottom respectively, using the catalyzed resin mixture. The top collar served as a stand to mount the trickle flow irrigator and receptacle for water during ponding conditions. The bottom collar served as a coupling between the column and an endplate assemblage which was attached to each column bottom.

Each collar was slipped approximately 1.5 cm down the column side. A piece of fiberglass rope, the length of the column outer circumference, was wedged between the PVC collar and column side. This allowed the collar to be leveled and formed the bottom of a 1.0-cm deep by .5-cm wide trough between the collar and column side. The collars were attached to each column by pouring approximately 20 mL of the catalyzed resin in the trough and allowing to harden. This was repeated several times until all voids were filled between the collar and column side.

Each column had a 14.5-cm diameter endplate assemblage attached to its bottom. The assemblage consisted of a 1 Bar, high flow porous ceramic plate (Soilmoisture Equipment Corp., P.O. Box 30025, Santa Barbara, CA) and a Plexiglass drain plate bonded together with catalyzed polyester resin. The end plate assemblage was placed on the column bottom after a thick slurry of silica flour, a few mm deep, had been poured on the bottom soil surface. This slurry insured elimination of all voids between the column bottom and the porous plate. After the moisture from the slurry had evaporated, the end plate assemblage was attached to the column bottom. The catalyzed resin was poured in the void space between the PVC collar and the drain plate assemblage and allowed to harden. This was repeated several times to insure an interfacial seal between the porous plate and the column encasing material. The bottom collars were put on first followed by the top collars and bottom assemblage.

During the carving process small voids created by roots and pebbles along the perimeter of the column length had to be either filled with encasing material or soil. This resulted in a final product that had a slight irregular diameter that varied ± a few millimeters, therefore calculation of column volumes were approximations. At the end of the experiment all soil was removed from the intact columns to determine the exact volumes and void ratios. The volumes of in situ columns were determined by placing each column on a scale, taring, then filling with water and recording the weight of the water. These dimensions are given in Table 6.

Table 6. In Situ **Column Dimensions**

Site Location	NW	SW
Column #	1	2
Diameter - cm (average)	14.2	14.2
Length - cm	32.5	32.3
Volume - cm^3		
- calculated	5216.6	5187.6
- measured	5145.8	5135.9

2.2.2 *Repacked Soil Columns*

Two columns, 32.5 and 32.3 cm in length, were designed and repacked with soil to replicate the same dimensions and densities as the NW and SW in situ columns. The repacked columns were made of clear acrylic tubing (Regal Plastics, Albuquerque, NM) 14.6 cm I.D. diameter. On one end of the column a 3.5-cm section of 15-cm I.D. PVC tubing was slid approximately 1-cm down the column edge and glued with the catalyzed resin, thus forming the column bottom. The collar served as a coupling between the acrylic tubing and base endplate. (The base endplates were made in the same way as those used for the in situ columns.) The endplate unit was placed on the acrylic tubing "bottom". Catalyzed polyester resin was then poured between the PVC collar and the end plate assemblage to bond the two to the acrylic tubing. Several layers of the resin were poured around the inside perimeter of the acrylic tubing to seal the interface between the porous endplate and the acrylic tubing.

A horizontal line was drawn around the outside perimeter of each tubing side to indicate the desired soil filled length. This length was the same as that of the in situ soil column to be replicated. The soil was to be filled to this line and packed at the same estimated bulk density as the in situ column. The volumes of the repacked columns were determined by placing the columns on a scale, taring, then filling with water and recording the weight of the water.

Each repacked column used air dried, sieved, and mixed soil taken from the same pit as that of the in situ column to be replicated. The amount of soil needed for each column was determined by the equation

$$\text{Soil Wt}_{\text{repacked column}} = \rho_{ad}\text{Volume}_{\text{column}},$$

where ρ_{ad}, is average air dried bulk density of the soil taken at each location.

A 300-mL glass beaker was used to gently scoop the soil from a plastic bucket and transferred to the acrylic column. The beaker was held inside the column at the depth the soil was to be placed and gently emptied. Care was taken to minimized any sorting as a result of soil particles falling or rolling from any height. Three beakers full of soil, about 900 cm^3, were placed in the column at a time, then mixed. The column was visually inspected for any layering or heterogeneities that might develop. These were eliminated by mixing the soil within the column with a hand held 4-cm spatula. The spatula was positioned vertically and repeatedly rotated approximately 90° until all heterogeneities were gone. After mixing, a hand held vibrator was moved up and down the column side to settle the soil particles. The column was weighed periodically and soil height measured to insure the bulk density of the column was uniform. This was repeated until the prescribed mass of soil had been placed inside the column. When all the soil had been placed in the column it was necessary to further settle the soil to the premarked line by repeatedly hand slapping the column along its sides. Volumes, column lengths, and ρ_{ad} for each soil location and the total prescribed soil weight used for each column are given in Table 7.

Table 7. Repacked Column Dimensions, Soil Bulk Densities, and Mass of Soil Used

	Column # and Soil Location	
Dimensions - cm	NW 3	SW 4
Diameter	14.6	14.6
Length	32.5	32.3
Volume -cm^3	5309.6	5280.1
Soil Densities and Total Mass used per Column		
ρ_{ad} gr cm^{-3}	1.659	1.656
Total Mass of Soil - gr	8811.7	8743.9

2.2.3 *Column Instrumentation and Peripherals*

A stand was made for each column to give support, and maintain a vertical and steady position. The stand was fabricated out of a 20-cm wagon tire that had four, 1-cm diameter, equally spaced holes drilled through the tire sides (perpendicular to the tire treads). The tire was then cut in half. Legs for the stand were made of four, 15-cm long, threaded brass rods which were pushed through each 1-cm tire hole. To position the height of each leg a, threaded nut was screwed up the brass rod until it was tightly wedged against the tire side. The tire halves with legs were placed around the lower 3 cm of the column. A 27-cm diameter metal hose clamp was slipped over the tire and tightened, pressing the tire securely to the column side. The stand could be raised or lowered along the column side, as needed, by loosening the hose clamp. Leveling the column was achieved by gently tapping the rods in or out of the holes drilled in the tire. The leg positions could be secured by tightening the threaded nuts against the tire.

All columns had 4, evenly spaced, 18 gauge hypodermic needles inserted through the base and into approximately 2.5 cm of the soil matrix. This was intended to vent any entrapped air that might ensue during a ponding event.The needles were inserted after the steady state flow regime was completed and before the first pond was applied.

Five, horizontal, .6-cm in diameter by 4-cm deep, holes were drilled through the column sides at 5, 10, 15, 20, and 25 cm from the column bottom. The holes were placed a peripheral distance of 7.5 cm from one another thus encircling about three-quarters of the column. Tensiometers were placed in these holes and pushed about 4.5 cm into the column interior to insure good contact between the soil and the tensiometer porous cup. The tensiometers were glued to the column wall with Hardman A-85 04024 urethane adhesive (Hardman, Inc., Belleville, NJ). This adhesive was selected because of its compatibility with the epoxy used to make the tensiometers (see Appendix D for tensiometer construction) and the column encasement materials. Figures 5 and 6 are a diagrams of the instrumented in situ and repacked soil columns.

2.2.4 *Vacuum Chambers*

Subatmospheric pressures (vacuums) were applied to each column when mounted and attached to a steel cylindrical vacuum chamber (Soil Measurement Systems, Tucson, AZ). The chamber diameter and height were 46 and 30 cm, respectively. The chamber lid was constructed of clear Plexiglas. These pressures insured steady state fluxes throughout each column and increased the hydraulic conductivity of the column porous plate. Vacuums were supplied with an in-house vacuum source regulated with a Moore Model Series 44 pneumatic null-balance pressure regulator (Moore Products Co. Spring House, PA). In order to maintain the prescribed output pressures, an in-house supply of regulated and filtered positive air pressure was used as a counter balance to the vacuum regulator . Positive air pressures were regulated and filtered with a Victor Equipment Company (Thermodyne Industries Inc., Denton, TX) pressure regulator and Moore Air Filter (Moore Products Co. Spring House, PA), respectively.

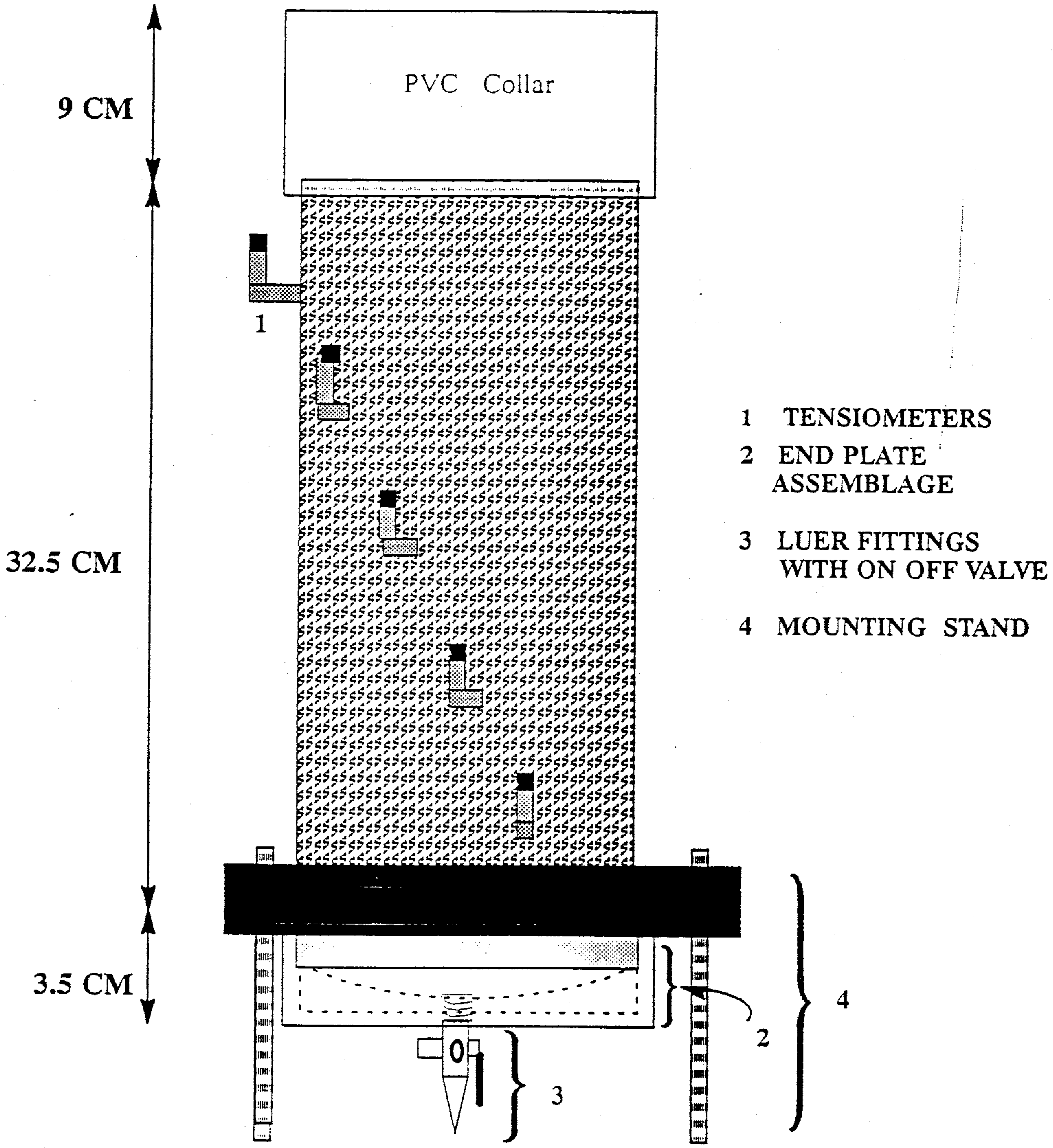


Fig. 5. Schematic of Instrumented in situ column taken from Maricopa Experimental Farm.

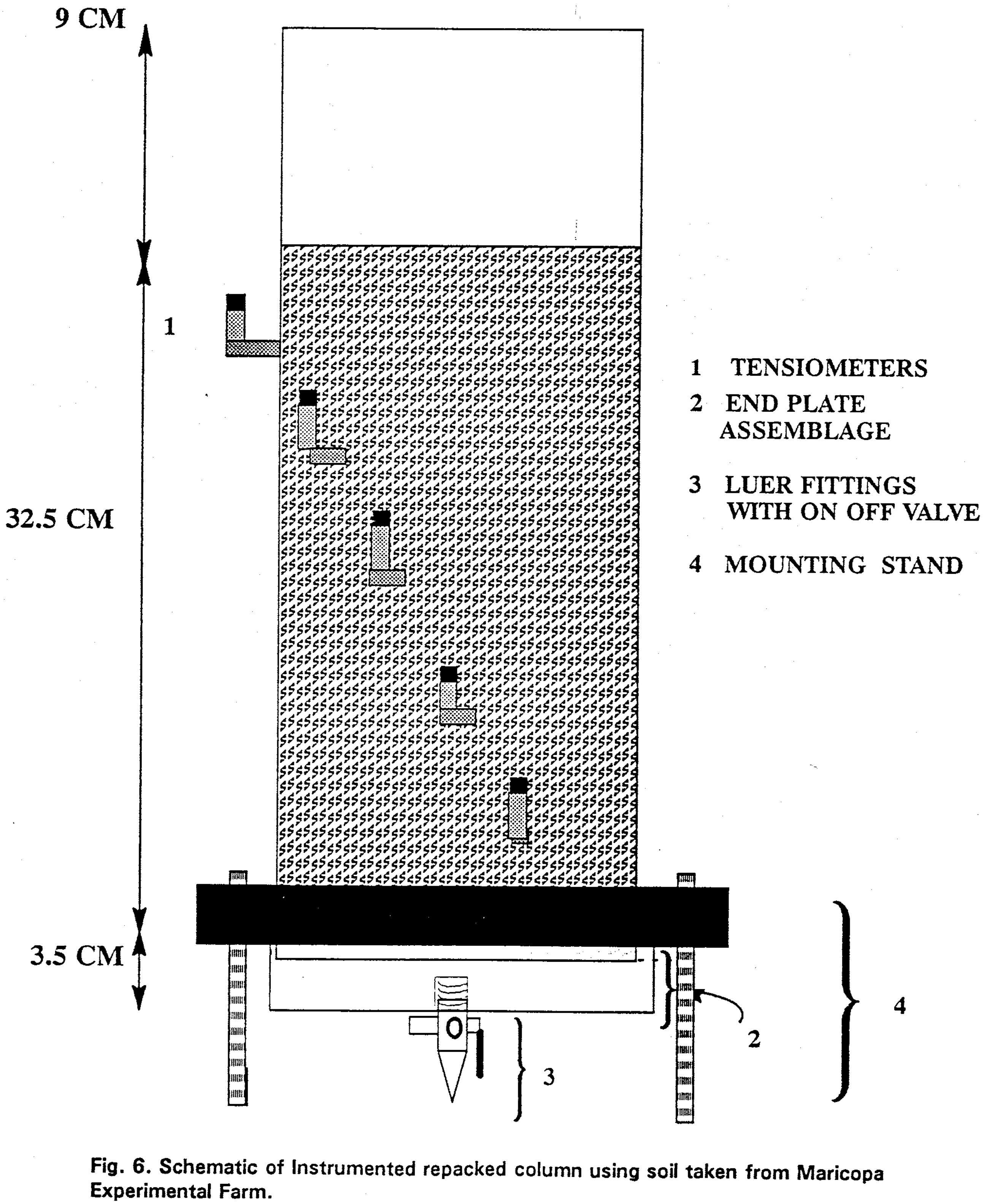


Fig. 6. Schematic of Instrumented repacked column using soil taken from Maricopa Experimental Farm.

2.2.5 *Syringe Pump*

Infiltration fluxes for the unsaturated flow experiment were maintained with a multichannel syringe pump (Soil Measurement Systems, Tucson, Az). Pumping volumes and rates were controlled by changing syringe sizes, changing the time interval between pump strokes, and altering the length of each pump stroke.

2.2.6 *Drip Emitters*

Drip emitters were manufactured to maximize uniform water application for the unsaturated flow experiment. The emitters were constructed of two 21-cm square and .6-cm thick Plexiglas pieces. A 16.5 -cm diameter rubber ring was sandwiched between the Plexiglas pieces to form a manifold. The three pieces were held tightly together by eight nuts and bolts that were inserted through predrilled holes located around the outer perimeter of the Plexiglas pieces. The bottom Plexiglas plate had 45 evenly spaced holes predrilled within a 16 cm diameter center circular space. In these holes male luer fittings were glued. 22 gauge hypodermic needles were later attached. The other Plexiglas piece had a two predrilled ports with appropriate couplings attached. One port was attached to a supply line the other served as a purge valve. A drip emitter was placed on each column collar. Leaching solution was pulsed through the manifold, via the supply line, and evenly distributed to the soil surface via the syringe needles.

2.2.7 *Fraction Collectors*

Effluent was collected from each column with an ISCO Retriever II (Isco, INC. Lincoln, NB) fraction collector placed in each vacuum chamber. The collector is capable of holding vials ranging in size from 12 to 28 -mL. Effluent collection may be set for either time units or volume units.

2.2.8 *Data Acquisition System*

Each column had 5 tensiometers positioned every 5 cm along the column length to measure soil tensions. Tensiometer pressures were transmitted through water-filled urethane tubing attached to one of 24 ports on a scanning fluid switch wafer (Scanivalve model # W0602/1P-24T 303 S.S., San Diego, CA). A Druck PDCR 22 differential, strain gauge pressure transducer (Druck Incorporated, New Fairfield, CN) measured the pressures of each tensiometer as the scanning valve rotated through each fluid switch wafer port. The fluid switch wafer was automatically rotated with a solenoid drive controller (Scanivalve CTRL10P/S2-S6). One complete rotation took approximately 2.5 minutes. The transducer output, in mVolts, was recorded and converted to digital units with an A/D converter (RTD A/D500, State College, PA). The A/D board was mounted in a IBM XT personal computer which also served as the data acquisition system (see Appendix F).

Figure 7 illustrates the overall lab set up for the unsaturated flow experiment. The ponded flow regime (see below) employed the same apparatus minus the drip emitters.

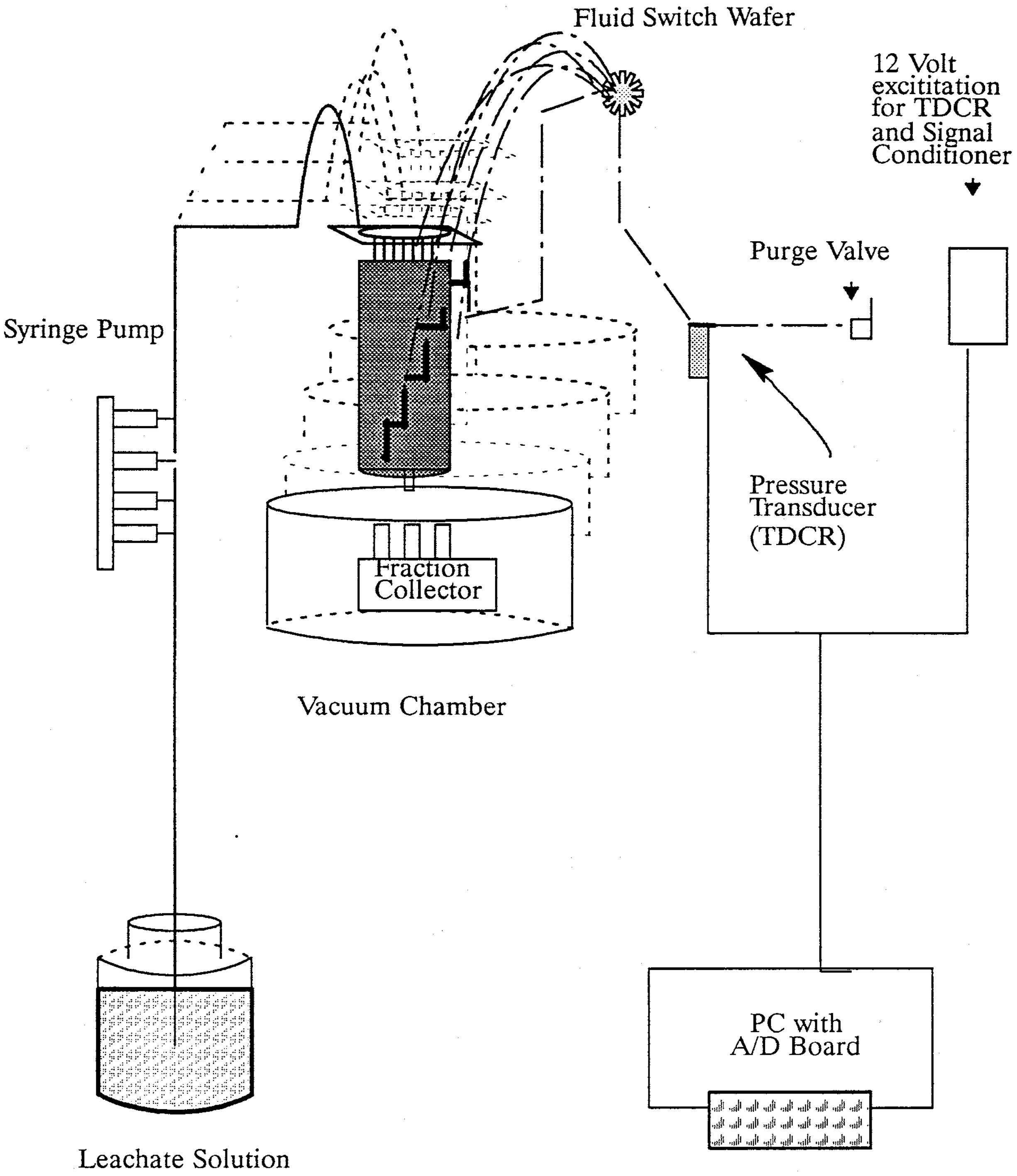


Fig. 7. Schematic of Laboratory Set Up.

2.3 Experimental Design

Two flow experiments were performed on the two intact and two repacked soil columns. A steady state-unsaturated flow experiment was performed first followed by an intermittent ponding experiment. The volume of water applied, per pond, to each column for the ponding experiment was the same as that delivered per week for each column during the unsaturated flow experiment. The two intact soil columns were obtained from the northwest, NW, and southwest, SW, corners of Plot F-5 (see Figure 2) at the Maricopa Experimental Station located in Central Arizona. The NW and SW intact columns were labeled Columns 1 and 2, respectively. The repacked columns used air dried, sieved, and homogeneously mixed soil taken from the same NW and SW corners as the in situ columns. These were labeled columns 3, using soil from NW corner, and 4, using soil from the SW corner. Each flow regime was performed on all four columns simultaneously.

The leaching solution applied to all columns for both flow regimes was of the same composition as the irrigation water found at the Maricopa station. $CaCl_2$, $MgCl_2$, and Na_2SO_4 salts were used to make the leaching solution. A list of the constituents of the water is given in Table 8.

Table 8. Constituents in Leaching Solution

Constituents	Molarity	mg L^{-1}
Ca^{+2}	.0036	144.28
Mg^{+2}	.0016	40.10
Na^{+}	.0184	423.0
SO_4^{-2}	.0092	883.35
Cl^{-}	.0108	382.28

Two tracers, m-trifluoromethylbenzioc acid (m-TFMBA) and bromacil (5-bromo-3-sec-butyl-6-methyluracil), were applied to all columns for all flow regimes. The m-TFMBA served as a conservative tracer. Its movement was used as an indicator in determining average pore water velocities, dispersion coefficients, and degree of preferential flow exhibited by each column. Bromacil served as a mildly retarded tracer and was used to test the validity of laboratory derived retardation factors, if preferential flow was present, in the solute transport mechanisms.

Soil samples used to determine partitioning coefficients, K_d, were taken from the top 30 cm of soil of a randomly picked location within plot F-5. K_d for bromacil was found to be .094 ml gr^{-1} using batch isotherms. To determine the isotherm, solutions of 2, 5, 20, 50, 200 and 500 mg L^{-1} of C^{14} labeled bromacil were made in a .005 M $CaCl_2$ background solution. 10 grams of soil per 10 mL of $CaCl_2$-bromacil solution per batch were equilibrated for 24 hours to determine the amount of bromacil adsorbed for each solution (H.J. Turin, personal communication, 1990). This K_d was used with equation 4 to determine a R_f that was compared to R_fs derived from a curve fitting program (see Section 3.2)

Recent studies have shown the method of tracer application can significantly affect solute breakthrough, especially if the soil matrix contains significant macropores (Kluitenberg and Horton, 1990). For this reason the tracers were applied to the soil surface as grams per unit cross sectional area, rather than a pore volume or fraction there of. All columns received the same concentration per unit cross sectional area as Bowman and Rice (1986a) used in their Maricopa field study. At this prescribed application the <u>in situ</u> columns, having a cross section area of 160.33 cm^2, required 23.88 mg m-TFMBA and 53.20 mg bromacil to be applied evenly on the soil surface. The repacked columns, with a cross sectional area of 167.41 cm^2, required 24.95 mg m-TFMBA and 55.55 mg bromacil to be in applied in the same manner as the <u>in situ</u> columns.

Uniform application of the tracer on such a small area of soil posed a problem. Spraying the dissolved solute on the soil surface would require a much larger volume of tracer solution to be used than the volume of leaching solution being delivered per hour for the unsaturated experiment. Dribbling the solution from a syringe, while criss-crossing the soil surface, was considered unacceptable as less than uniform application was highly probable. For these reasons, a highly concentrated tracer solution was frozen and applied to the soil surface as a 3-mm thick ice disk of the same diameter as each column. For each in situ and repacked column the prescribed amounts of m-TFMBA and bromacil was dissolved in 47.47 and 49.44 mL of solvent (Maricopa water), respectively. To increase solubility of both tracers in such a small volume of solvent, 3% KOH was added to the solvent. A large batch of the tracer solution (composed of the prescribed amount of Maricopa water, KOH, m-TFMBA and bromacil) was mixed per experiment and could be used to make up to 6 tracer ice disks. From this batch solution 49.53 and 51.81 grams were used to make ice disks for each in situ and repacked column, respectively. The components of each tracer batch solution and amount applied to each column is given in Table 9.

Table 9. Composition of Tracer Batch Solution and Amount Added to Each Column

	Components Added to Tracer Batch Solution		Grams of Each Component Delivered to Each Column Type	
Component	grams	mg/L	In Situ	Repacked
bromacil (.95 pure)	.31636	1049	.050	.052
Inert Components	.01665	NA	.0026	.0027
m-TFMBA	.1490	494	.0236	.0247
KOH (.85 pure)	9.04	29,996	1.43	1.50
Inert Components	1.59	NA	.25	.26
Leaching Solution	301.34	NA	47.76	49.96
Total	312.46	31,513	49.53	51.81

Effluent from each column was collected and analyzed for presence of both tracers. From the analysis, average pore water velocities of the water, dispersion coefficients, retardation factors, and any presence of preferential flow could be found. A comparison was made of these found parameters between the in situ and repacked soil columns and the different flow regimes.

2.3.1 *Unsaturated Flow Experiment*

Each column with stand was vertically placed on a vacuum chamber containing a fraction collector. The vacuum chambers and columns were connected together with luer fittings attached to the chamber lid and a 3-way stopcock connected to the column drain. The distance between the column and vacuum chamber was approximately 5.5 cm. This distance minimized any mixing of the effluent after it left the column yet allowed easy column removal when the chamber was opened and closed to change fraction collector vials.

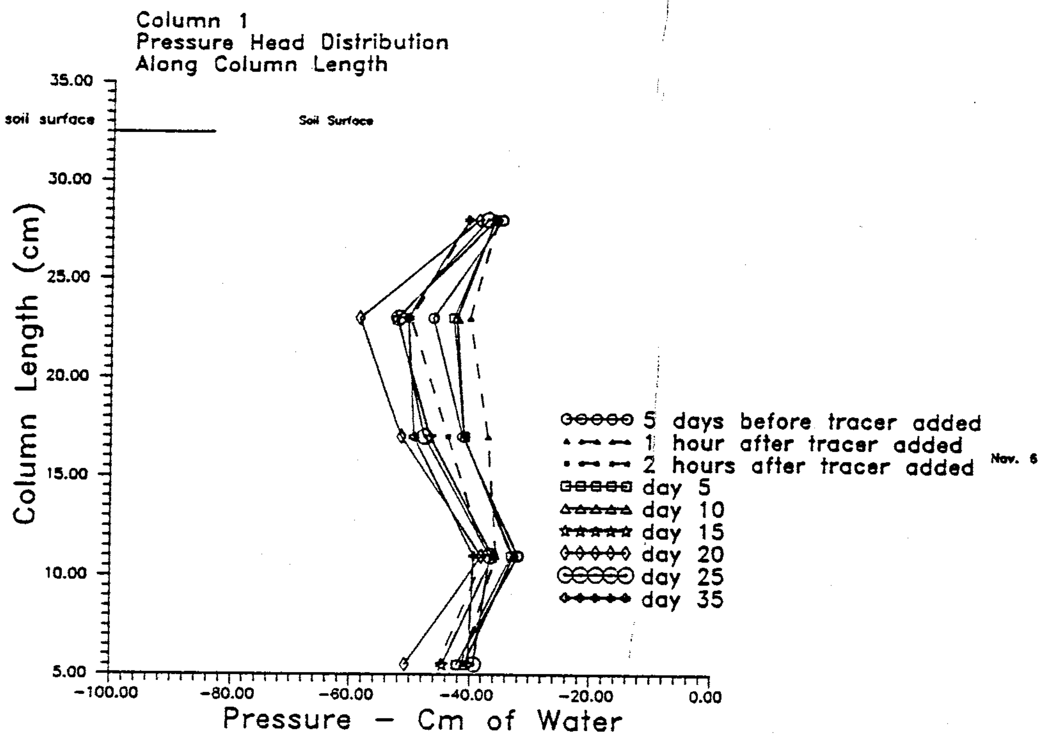
Steady state conditions and unit gradients (where infiltration fluxes, q, equals $K(\theta)$) throughout the length of all columns was desired. To do this it was necessary to find a uniform matric potential, Ψ, that would give rise to uniform $K(\theta)$ values along the column length. Therefore, $K(\theta)$ vs. Ψ values, derived from van Genuchten's code, were used as a guide in setting the infiltration rates delivered to each column.

The syringe pump was set to deliver a .45 cm^3 pulse of leaching solution every 354 sec ($1.3x10^{-4}$ cm/sec) giving fluxes of $7.52x10^{-6}$ cm/sec (approximately .65 cm/day) for the repacked and $7.85x10^{-6}$ cm/sec (approximately .68 cm/day) for the in situ columns. Total volume of water delivered per day was 111.5, 109.0, 109.3, and 110.9 mL for Columns 1,2 3 and 4, respectively.

Soil tensions from each tensiometer were taken every 30 minutes when the PC triggered a command to rotate the fluid switch wafer. Tensiometer pressures were sensed by the transducer and stored in the computer. Tension measurements were monitored every day during the entire experiment. Forty one days of the above described flow rate, with vacuum adjustments applied to the column endplates, were required before near unit gradients and steady state conditions were seen in all columns. Figures 8 and 9 are snapshots of column pressures throughout the steady state-unsaturated flow regime. Each column showed slight tension fluctuations from day to day. Columns 1 and 4 tensions fluctuated every 2 to 3 days between 15 cm of water, and columns 2 and 3 - 10 cm of water. Tension fluctuations were attributed to small air pockets that accumulated within the scanivalve lines every 2 or 3 days, and growth of an unknown microorganism that seemed to make the tensiometers sluggish towards the end of the steady state-unsaturated flow experiment. This required flushing of several tensiometers and scanivalve lines within the data acquisition system every 2 or 3 days. Atmospheric pressures were not checked, but daily fluctuations could have partially caused tensiometer readings to vacillate. A linear regression analysis was employed to determine a time-matric potential relationship (see Figures 10 and 11). A significant linear trend ($P < 0.05$) between time and decreasing tensions (indicating increasing moisture contents) was seen in each column for all depths. Table 10 is a list of r^2 values of the linear regression done for the time-tension relationship for all columns. The lower r^2 values in columns 1, 2, and 4 indicate that other factors may have affected matric potentials. As evident from the matric potential slopes taken along the column lengths in Figures 10 and 11, steady state conditions were roughly, but not

Table 10. Correlation Between Decrease in Column Matric Potentials (increase in θ) and Time

	r^2 for each Column			
Distance from Soil Surface -cm	1	2	3	4
5	.21	.26	NA	NA
10	.06	.37	.81	.12
18	.31	.10	.81	.47
23	.07	.27	.91	.33
28	.26	.47	.92	.14



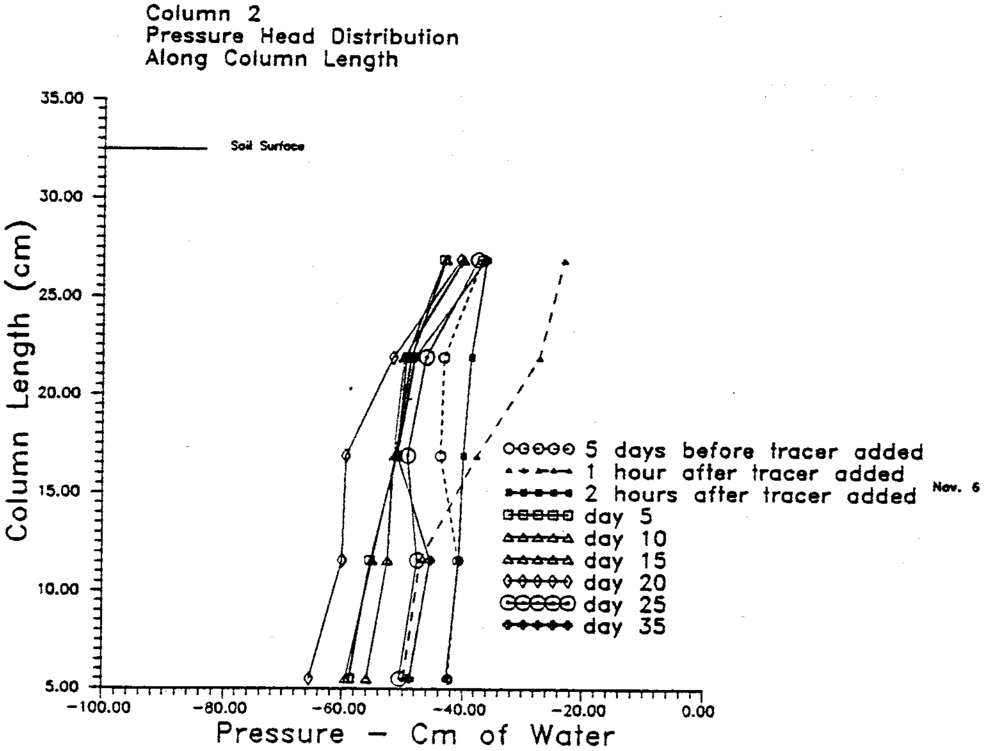


Fig. 8. **Matric Potentials at near steady state and unit gradients conditions for <u>In Situ</u> Column 1 and 2 - Steady State-Unsaturated Flow Regime**

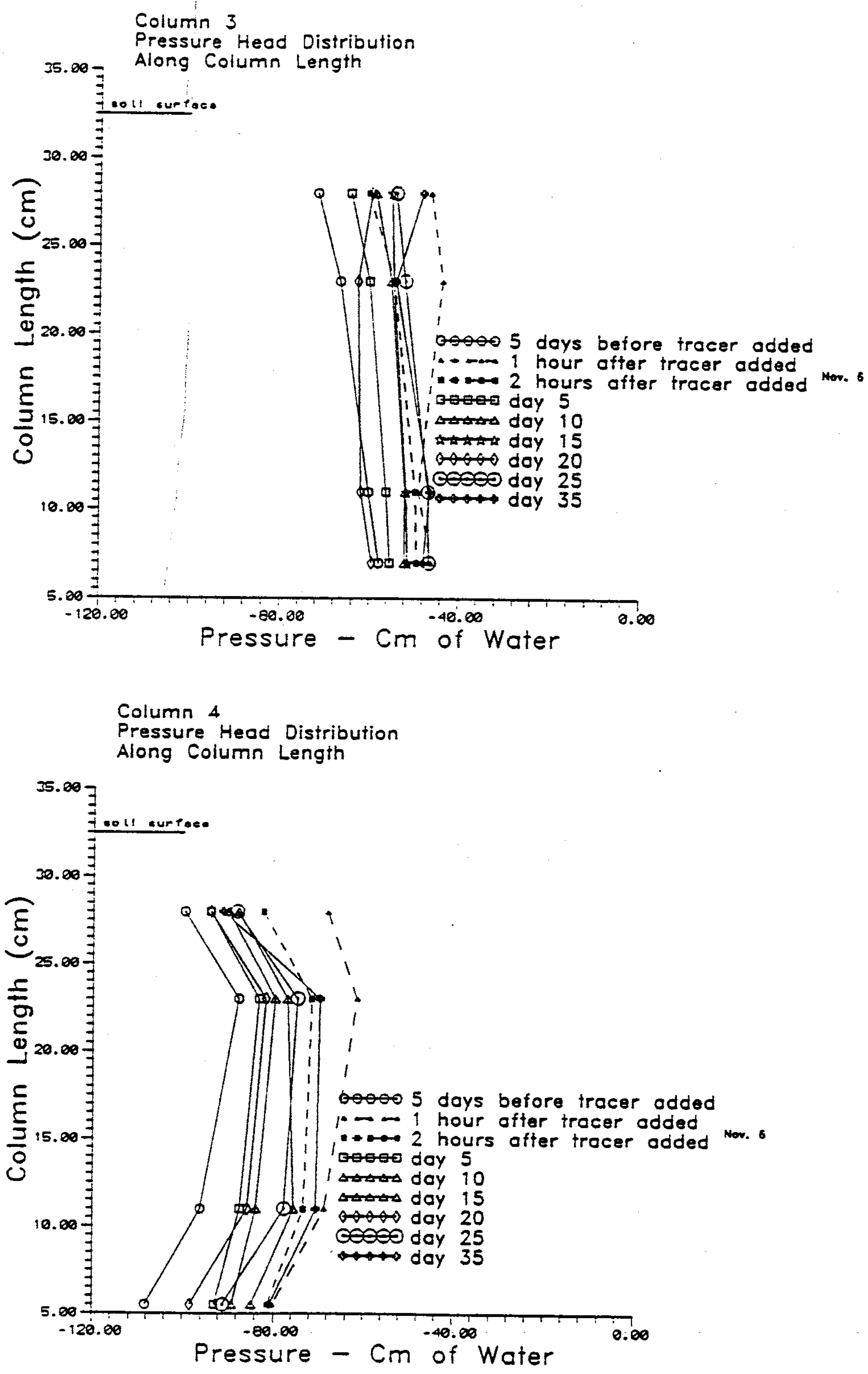


Fig. 9. Matric Potentials at near steady state and unit gradients conditions for Repacked Columns 3 and 4. - Steady State-Unsaturated Flow Regime

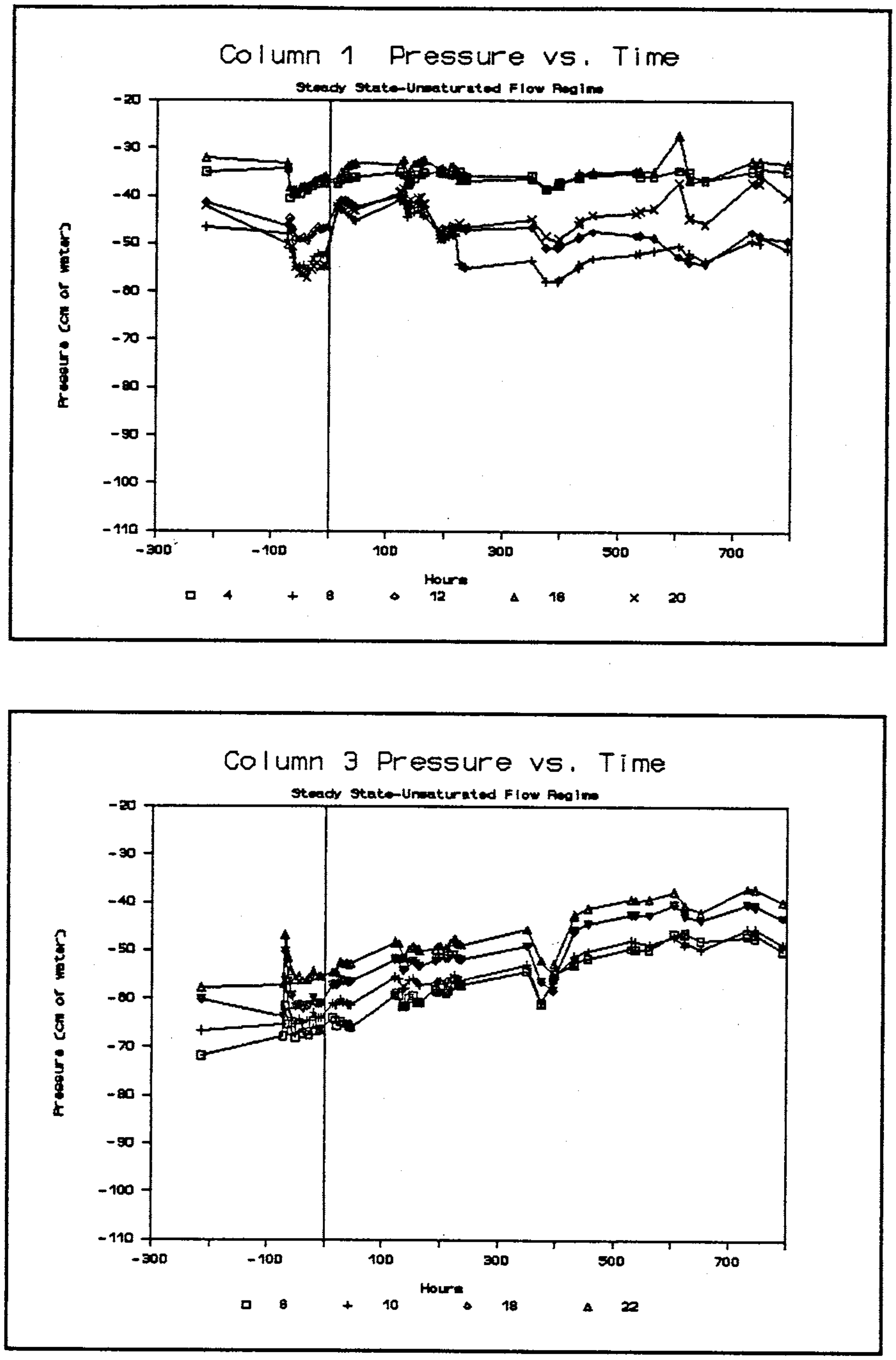


Fig. 10 Pressure changes vs. time for in situ Column 1 and repacked Column 3 during Steady State-Unsaturated Flow Regime.

Symbols on the graphs denote tensiometer numbers for each column. Tensiometer pressures have been adjusted for depth. The dividing line denotes time tracer was added.

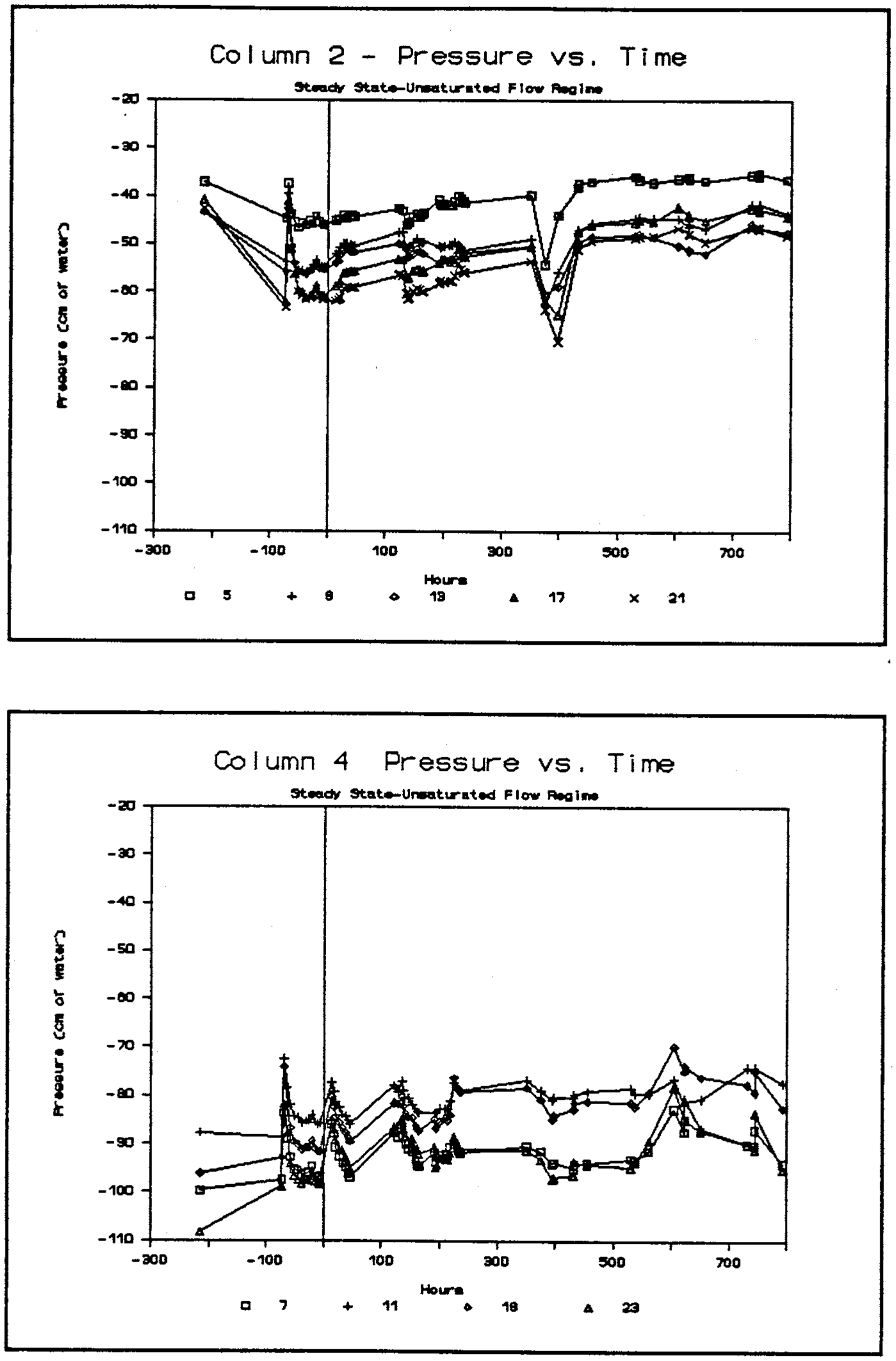


Fig. 11 **Pressure changes vs. time for <u>in situ</u> Column 2 and repacked Column 4 during Steady State-Unsaturated Flow Regime.**

Symbols on the graphs denote tensiometer numbers for each column. Tensiometer pressures have been adjusted for depth. The dividing line denotes time tracer was added.

quite achieved at the time the tracers was added to each column.

The tracer ice disks were applied to each column after near steady state and unit gradient conditions were achieved. Delivery of the leaching solution was suspended just prior to addition of the tracer ice disks. The ice melted within 20 minutes for all columns at a room temperature of 22.7°C. Application of the leaching solution was not resumed for two hours. This allowed all of the tracer solution to infiltrate into the soil. It was noted that on Column 2 ponding of the melted tracer solution existed for approximately 1.5 hours. Entrapped air was suspected as the primary cause.

Effluent from each column was collected in one of 42 labeled, polyethylene, 20-mL scintillation vials placed in the fraction collector. Collection time for each vial was set at three hours resulting in 13.9, 13.636, 13.664, and 13.862 mL of collected effluent from Column 1, 2, 3, and 4, respectively. At this time unit per vial, the fraction collector could be left in the vacuum chamber for five days without resupplying it with empty vials. New vials were put in the collector with each column detached from its respective chamber lid and the lid removed. Each column was removed from its respective vacuum chamber with the stopcock closed to maintain tensions along the column bottom. Sancivalve lines remained attached to all tensiometers during this maneuver. The time to do the entire procedure, per column, was approximately 30 minutes. Vials were weighed and capped, as soon as possible, after removal from the vacuum chamber.

The entire unsaturated flow experiment lasted for 37 days. The degree of saturation, determined gravimetrically, for Column 1 was .798, Column 2 -.8058, Column 3 - .957, and 4 -.932. At the imposed flow rate, the number of pore volumes of effluent collected ranged from a high of 2.683 for Column 2, to a low of 2.020 for Column 3. Pore volumes of effluent collected from Columns 1 and 4 were 2.589 and 2.18, respectively. Equivalent pore volumes from Columns 1,2,3, and 4 collected in each vial were .00707, .0679, .00757, and .00843, respectively.

At the end of the steady state-unsaturated flow experiment all of the columns were ponded with 700 cm^3 of leaching solution and allowed to drain for one week. This was repeated a second time. The purpose of the two ponding events was to flush out any residual bromacil that had not yet been removed from each column during the steady state-unsaturated flow regime. Bromacil concentrations at the end of this flushing process were .65, 1.22, .08, and .02 mg/L for Columns 1, 2, 3 and 4, respectively.

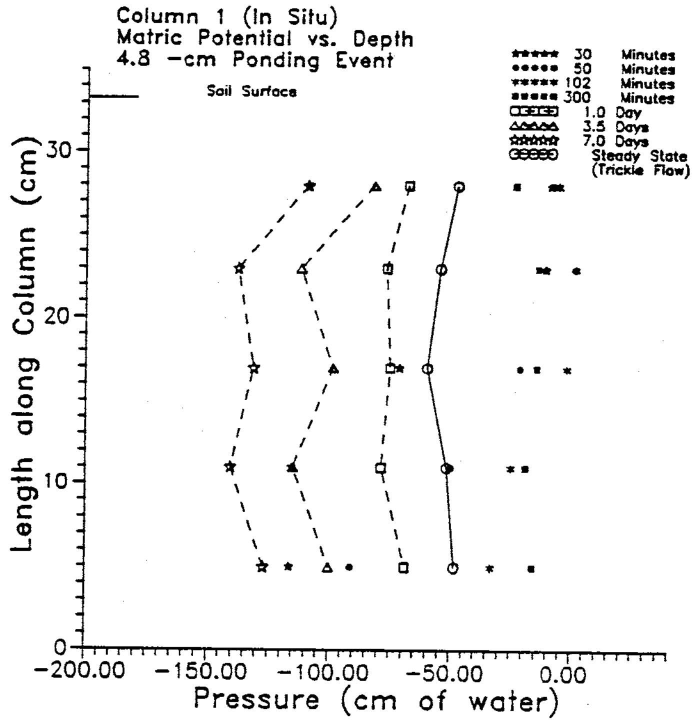
2.3.2 *Intermittent Ponding Experiment*

The intermittent ponding experiment consisted of one 775.0 cm^3 application of leaching solution delivered to each column every seven days for a six week period. The volume of leaching solution per pond was equal to the same amount of leaching solution delivered to each column during a seven day time period for the unsaturated flow experiment.

Each column were brought to the same steady state conditions that existed for the unsaturated flow regime. When this was achieved, one $\simeq$ 4.8 cm (775 cm^3) pond was applied to each column. The columns were allowed to drain for one week before adding both tracers. Tracer ice disks were added to each column in the same manner and of the same concentration as that done for the steady state flow regime.

All columns was placed on their respective vacuum chamber and vacuums applied at the same pressures as that of the unsaturated flow experiment. Effluent was collected with a fraction collector placed inside the vacuum chambers. Collection times were set to 30 minutes per vial for the first 20 hours after ponding. From 20 to approximately 40 hours after ponding collection times per vial were set to 1 hour. From 40 hours to the next ponding event collection times per vial were set to 3 hours. Varying the collection times per vial was necessary as effluent fluxes right after each ponding event were three orders of magnitude greater than those at the end of the ponding event.

Soil tensions were taken from each tensiometer every 30 minutes throughout the entire intermittent ponding experiment. This aided in monitoring the movement of wetting fronts. Figures 12 and 13 are representative matric potentials for one ponding cycle.



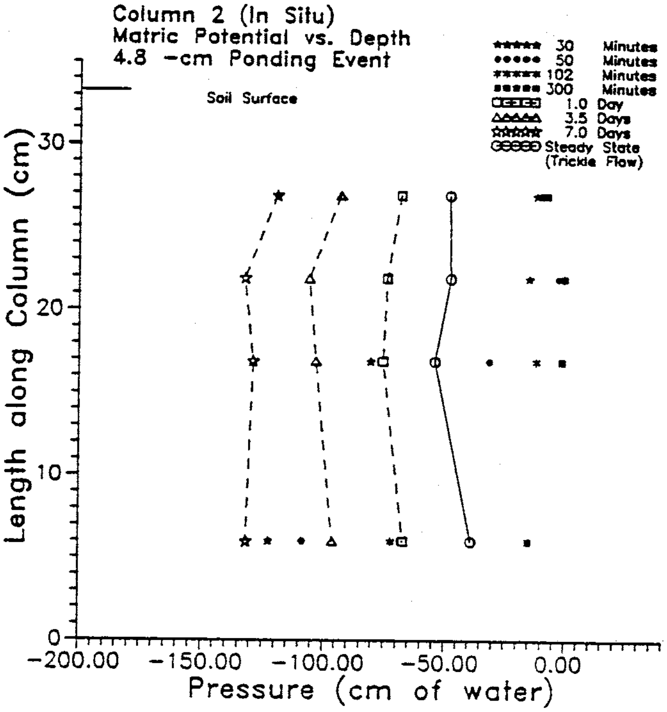


Fig. 12. Matric Potentials for Wetting and Draining Cycle of In Situ Columns 1 and 2 - Intermittent Ponding Flow Regime.

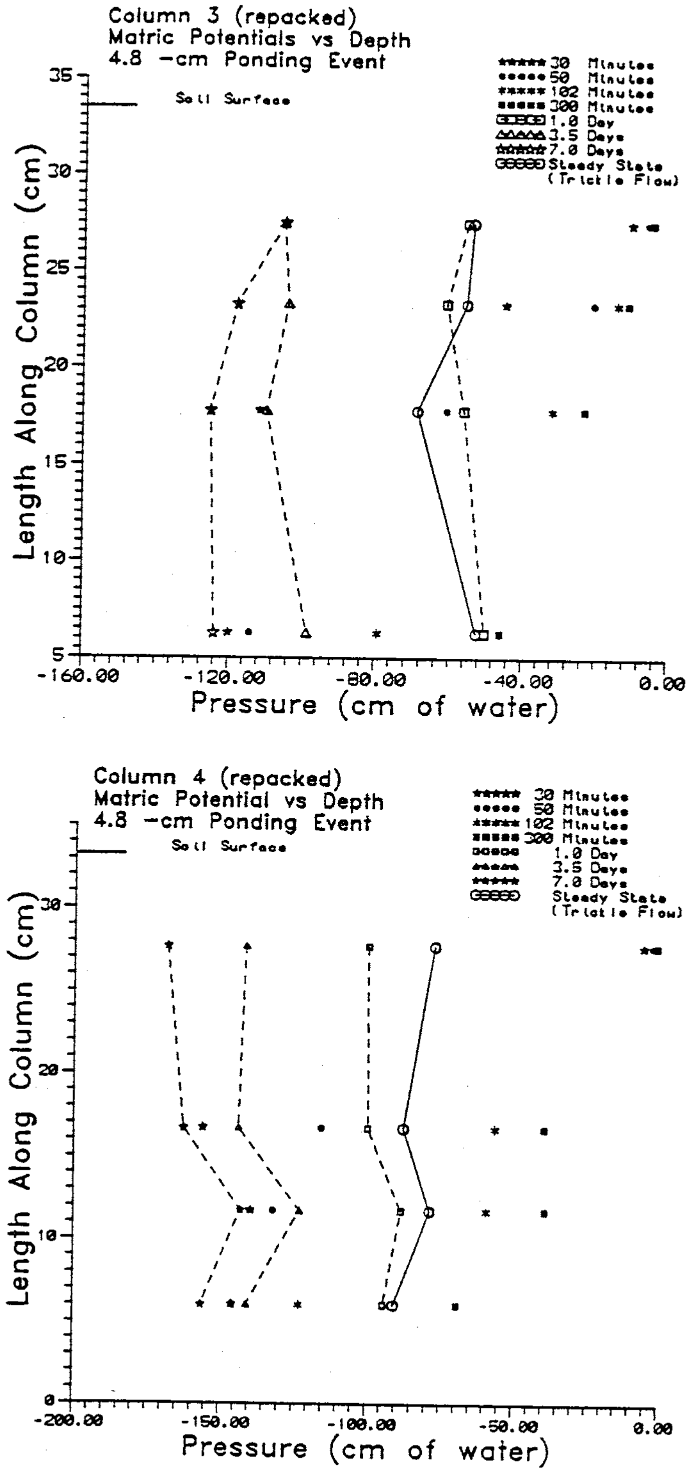


Fig. 13. Matric Potentials for Wetting and Draining Cycle of Repacked Columns 3 and 4 - Intermittent Ponding Flow Regime.

2.4. Chemical Analysis

Chemical analysis of the column effluent from all flow experiments was done using a High Performance Liquid Chromatograph (HPLC). A narrow pore, 15-cm x 4.6-mm I.D., Rex-chrom (Regis Chemical Co., Morton Grove, IL) ODS (C18) anion exchange column packed with 5 micron particles was used. The mobile phase consisted of a 60/40 MeOH/KH_2PO_4 (.02 M) solution with pH adjusted to 3.5 using orthophosphoric acid.

Flow rates were set at 1-mL per minute using a Waters Model 501 Solvent Delivery System pump (Water Associates, Inc., Milford, MA) . A Waters Lamba-Max Model 481 and 745 Data Module served as the spectrophotometer and integrator, respectively. Wavelength detection for the spectrophotometer was set at 220 nm. The integrator was set to calculate relative peak heights on the chromatogram. m-TFMBA and bromacil standard concentrations of 5, 25, and 50 mg L^{-1} were used to determine effluent concentrations of m-TFMBA and bromacil. Effluent injection volumes of 25 μL were done with a Perkin-Elmer ISS-200 (Perkin-Elmer Corp., Analytical Instruments, Norwalk, CT) Advanced Auto Sampler.

Initially, the BTC of m-TFMBA for each column was determined and required approximately twenty vials per column per experiment to be sampled. Care was taken to find peak heights and the rising and falling tails of the tracer breakthrough. Because bromacil is mildly retarded its BTC peak was considered to occur after that of m-TFMBA. Effluent samples for bromacil breakthrough were selected with this in mind.

3.RESULTS

3.1 Mass Balance

Mass balances of both tracers from all columns for the unsaturated-steady state and intermittent ponding flow regimes are listed in Table 11. Mass recoveries were calculated by trapezoidal integration of the raw concentration data with respect to cumulative effluent. Percent mass recovered was less than desirable. Ideally for column studies done in the laboratory mass recovered from m-TFMBA should be close to 100 % (Bowman, 1984). Recoveries significantly less than 100% have been reported in the field. For example, Bowman and Rice (1986b) have reported m-TFMBA recoveries of 84 % from field plots undergoing intermittent flood irrigation. Field studies carried out on the same soil as that used for this study using bromacil as one of the tracers, (Bowman and Rice, 1986a) showed recoveries of 89%. Heterogeneities of a soil profile and less than uniform application of tracers over large areas can easily account for less than 100 % mass recoveries on field sites. Several possible causes leading to the low mass recoveries in this laboratory study were investigated and are listed below.

Table 11. Percent Mass Recovery of m-TFMBA and bromacil for Steady State-Unsaturated and Intermittent Ponding Flow Experiments

	% Recovery			
Flow Regime	Steady State Unsaturated		Intermittent Ponding	
Column #	m-TFMBA	bromacil	m-TFMBA	bromacil
1	41.0	50.0	56.2	51.4
2	62.3	62.8	72.8	55.5
3	96.4	74.4	92.5	74.4
4	90.4	74.7	70.6	74.8

Errors in the amount of tracer solution used for each ice disk were discounted. The mass used to make each ice disk was weighed in a pretared beaker then poured in a cellophane lined mold. Weighing errors and transfer of solution to the mold might have caused a 1 to 5 % difference between the amount of tracers each column was to have received, not the 20 to 50 % differences found.

Degradation of both tracers was considered. m-TFMBA has been reported to have minimal, if any, degradation (Bowman, 1984). Bromacil degradation, under similar conditions as that carried out by this experiment, showed $t_{1/2}$ ranging from 421 to 758 days (Gerstl and Yaron, 1983). These rates were considered as much too low to account for such large losses.

Nonlinear desorption kinetics (hysterisis) has been reported by Gerstl and Yaron (1983). Low recovery of bromacil was partially attributed to this desorption hysterisis as indicated by the long tail on the falling limb of bromacil BTCs. Time limitations of the experiment prevented the steady state-unsaturated flow experiment to continue until all traces of bromacil were flushed from each column.

Errors in BTC concentrations indicated by the HPLC chromatogram were considered. It was noted that the time of chromatogram peaks for both tracers seemed to wander. To resolve the problem the pH of the mobile phase and the concentration of the buffer solution were varied. Ratios of the buffer solution to MeOH were also changed. These did stabilize, somewhat, peak breakthrough times, but not completely. A sample of a typical chromatogram illustrating this problem is given in Appendix G.

Less than complete dissolution of both tracers in solution was suspected as a primary cause of low recoveries, as the tracer batch solution showed a grayish cloudy precipitate. It was later observed that the batch solution, after refrigerator storage, showed distinct layering. A solid precipitate had settled on the bottom of the storage flask. A check was done to see if any tracer concentration differences existed between the top and bottom layers of the tracer batch solution. One mL samples were taken from the top, middle, and bottom layers of the remaining batch solution and diluted. This solution was then mixed thoroughly and approximately 15 mL was drawn off and centrifuged. One mL samples were then taken from the mixed tracer batch and the supernatant of the centrifuged tracer batch. It was found that samples taken from the bottom of the original tracer batch had up to 30 % more m-TFMBA than expected. Samples taken from the top of each tracer batch varied widely in concentration levels, with most showing significantly less m-TFMBA concentration than expected. Samples from the mixed batch was very close to the prescribed concentration of the original tracer batch (see Section 2.3, Table 10). These results imply that possibly each tracer was not totally dissolved in each tracer batch solution, therefore less than the prescribed amount of each tracer was applied to each column.

To check if varying KOH and pHs concentrations might affect chromatogram peaks four additional tracer batches were then made using 3, 2, 1, and .5 % KOH. Each test batch had the same concentrations of m-TFMBA and bromacil as that used for the initial tracer batch solution. One mL samples were withdrawn from each test solution and diluted in the same manner as that of the original batch solution. All of these samples were then run through the HPLC. Each test batch, with varying concentrations of KOH, was again run through the HPLC with the pH of the injected sample adjusted from 10 to 6.0. Slight changes in pH, especially in the range between 6.0 to 6.5 gave marked differences in chromatogram peak breakthrough times. HPLC chromatograms from the column effluent also seemed to have varying peak breakthrough times. These variations in chromatogram peak times could have caused miscalculations of detected concentration levels in the column effluent.

The problem could not be resolved within the time limits of this experiment and the resulting tracer BTCs, producing less than desirable mass balance, especially from the in situ columns, were considered adequate in defining the needed parameters.

3.2. Analytical Model

Tracer concentrations in the effluent collected from the two flow regimes and all columns were used to compare and contrast average pore water velocities,v, dispersion coefficients, D, and retardation factors, R_f. CXTFIT, a nonlinear least-squares inversion model, developed by Parker and van Genuchten (1984), was employed to determine the aforementioned parameters. Average pore water velocities, v, are defined as the darcy flux per unit cross sectional area (q) divided by the soil moisture content (θ), q/θ. CXTFIT is used to fit the parameters of equation 3, given earlier, to concentrations exiting the lower boundary of the columns. Concentrations were considered flux averaged. Initial and boundary conditions using a flux average solution are

$$C(x,0) = 0 \qquad \text{- with no solute initially present}$$

$$C(0,t) = \left| \begin{array}{ll} C_0, & 0 < t \leq t_o \\ & \\ 0, & t > t_0 \end{array} \right. \qquad \text{- at the upper boundary}$$

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

where C_o is the input concentration and t_o is the duration of the of the input concentration. For both flow regimes a continuum model, labeled Mode 2, of CXTFIT was used. Initially BTCs of m-TFMBA were used to derive fitted D coefficients and v values. Because m-TFMBA is a conservative tracer (nonadsorbing) R_f was fixed at 1. Parameters for the bromacil BTCs used m-TFMBA derived D coefficients and average pore water velocities, v, as fixed values. R_f was then curve fitted.

Modeling the transient flow regime using a steady state model has been justified by Wierenga (1977) and Cassel et al. (1975) when concentration vs. cumulative drainage are used. Therefore, it was necessary to reduce cumulative effluent values into dimensionless pore volumes, PV. PV is defined as the volume that is taken up by the fluid within the column or (vt)/L, where v is the average pore water velocity, t is time, and L is the length of the column. PV's for the transient flow regime were calculated by numerically integrating the volume of effluent over a one week ponding cycle. One ponding cycle was sliced into 3 hour intervals. The volume of effluent was measured for each 3 hour interval and divided by the column cross sectional area to yield a darcy flux, q, at that time t, at the exit boundary. The average pore water velocity, v, for each three hour interval was found by dividing q, at time t, by the average moisture content of the entire column at time t. The cumulative pore volumes of fluid exiting the column since the tracer was introduced at the column upper boundary, was the sum of all the PVs for each 3 hour interval.

Resulting D coefficients were looked at closely as they indicate the amount of variation between the derived CXTFIT average pore water velocities and the velocities calculated using the delivered fluxes divided by the column moisture content. Velocity variations are induced by varying pore sizes, shapes, and directions. It is also a measure of the amount of spreading of the infiltrating solute laden fluid around its peak concentration, or center of mass, as it moves through the soil profile. Small D values imply that solute or displacing fluid flows through less varied pore sizes and has fewer variations in flow velocities. Large D values indicate the opposite. Presence of preferential flow can result in high D coefficients.

It was important to find the D/v ratio, from CXTFIT derived parameters, which yielded the dispersivity, α, of the porous medium. α values close to, or equal to 1-cm, indicated that the porous medium is considered to be of uniform density, pore size, and thus induces less varied flow velocities, and is expected in repacked columns (van Genuchten and Wierenga, 1986). If an appreciable amount of solute is transmitted through preferential flow paths than the α of the soil matrix will diverge, to a lesser or greater extent, from 1. Therefore, the relationship between D and v values is an indication of media induced variabilities in flow velocities between conducting pores, and hence, an indication of preferential flow.

3.3. Steady State Flow Experiment

BTCs for each tracer are shown in the Figures 14 thru 17 with CXTFIT derived parameters. Average pore water velocities (q/θ), dispersion coefficients, retardation factors and moisture contents using the CXTFIT model and measured values are listed in Table 12. Moisture contents, θ, to determine average pore water velocities were found gravimetrically by weighing each column at the end of the experiment. Pore Volumes, PV, are defined as the amount of moisture present in each column. For total miscible displacement PV should equal the gravimetric moisture content, θ_{grv}. θ inversely derived from CXTFIT parameters should also equal θ_{grv}.

Table 12. Average Pore Water Velocities, Moisture Contents, Dispersion Coefficients, α, and R_f for the Steady State-Unsaturated Flow Regime

	Column			
	In Situ		Repacked	
Parameters	1	2	3	4
v-CXTFIT -cm/day	3.13	3.11	2.41	2.35
v-derived -cm/day	2.28	2.31	1.83	2.64
θ-CXTFIT	.222	.219	.271	.282
θ-gravimetric	.305	.2949	.357	.311
$\frac{\theta\text{-CXTFIT}}{\theta\text{-gravimetric}}$	.720	.742	.760	.907
$PV_{bypassed}$	.280	.258	.240	.093
D-CXTFIT -cm^2/day	1.46	2.46	2.86	3.53
α CXTFIT -cm	.467	.793	1.188	1.502
R_f-CXTFIT	1.577	1.518	1.515	1.618
R_f-derived	1.505	1.512	1.446	1.474

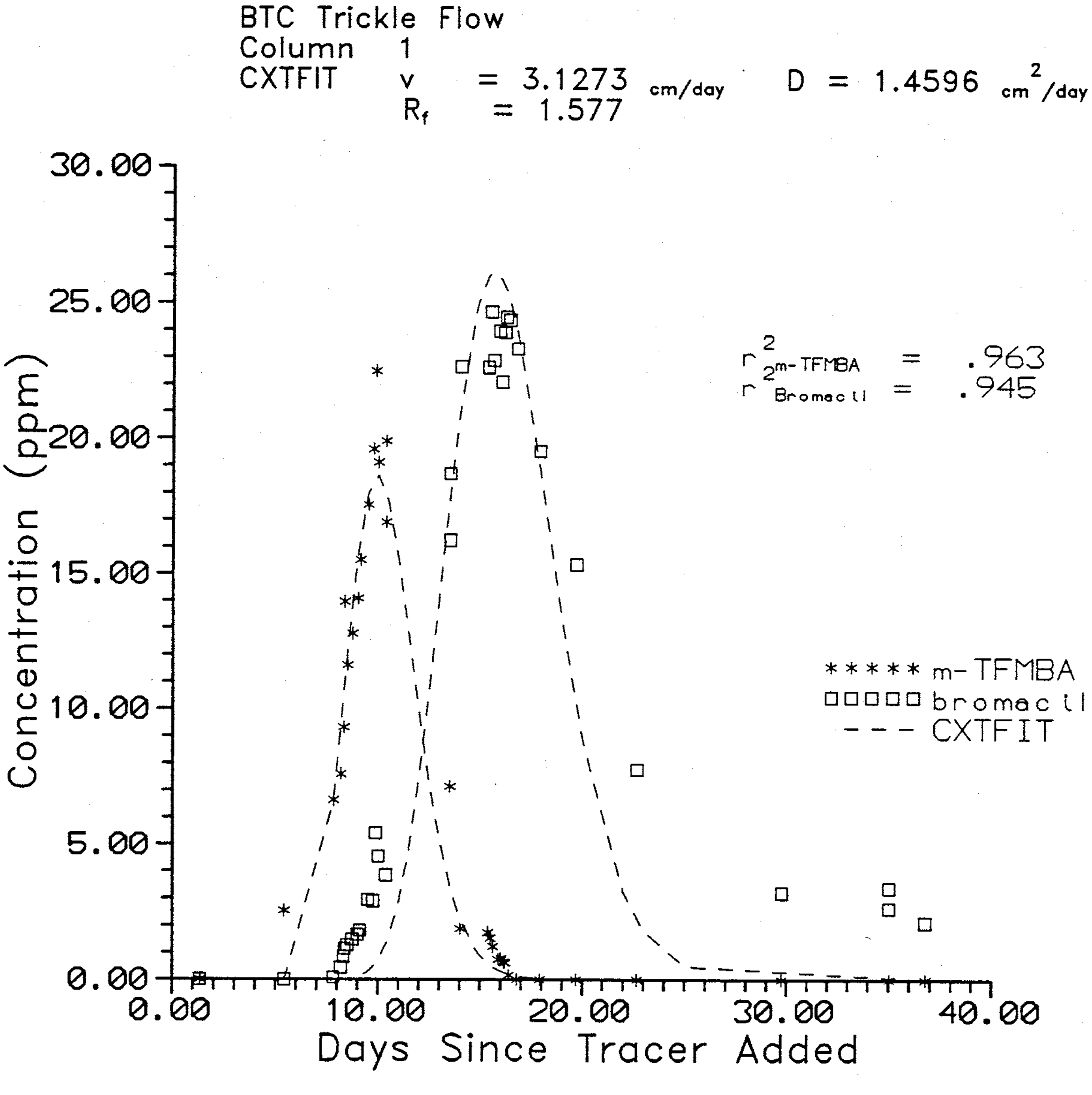


Fig. 14. m-TFBMA and bromacil BTCs for in situ Column 1 - Steady State-Unsaturated Flow Regime.

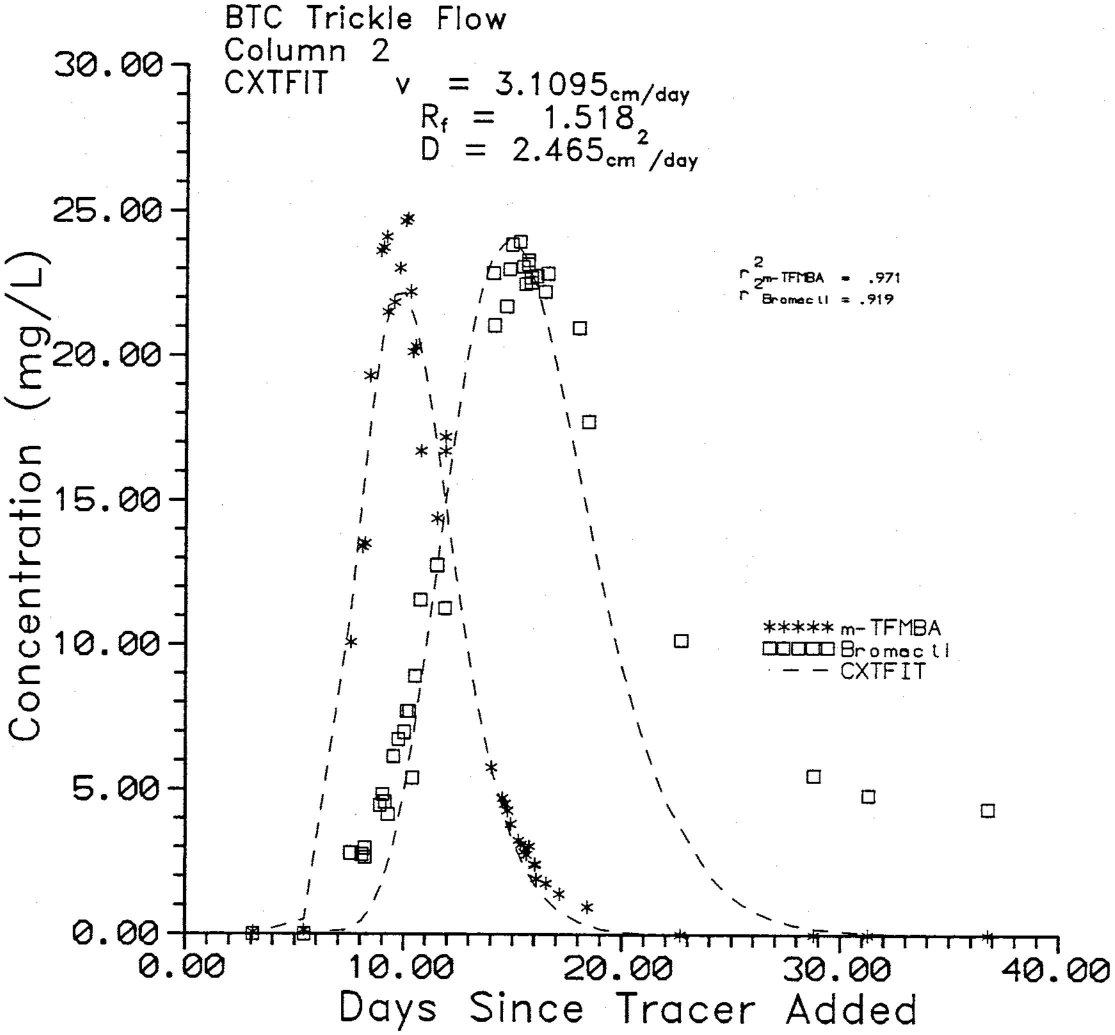


Fig. 15. m-TFBMA and bromacil BTC's for *in situ* Column 2 - Steady State-Unsaturated Flow Regime.

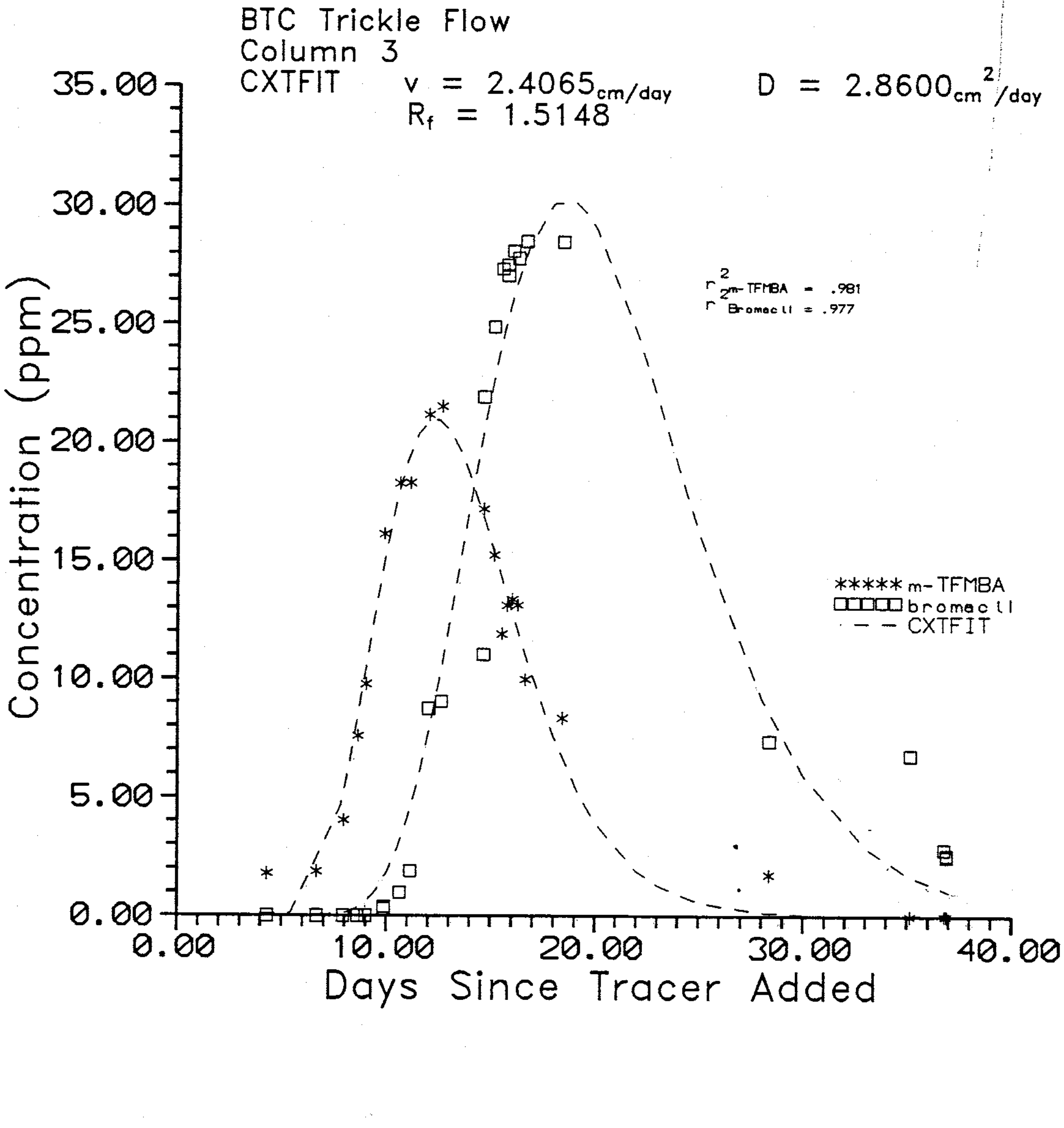


Fig. 16. m-TFBMA and bromacil BTC's for Repacked Column 3 - Steady State-Unsaturated Flow Regime.

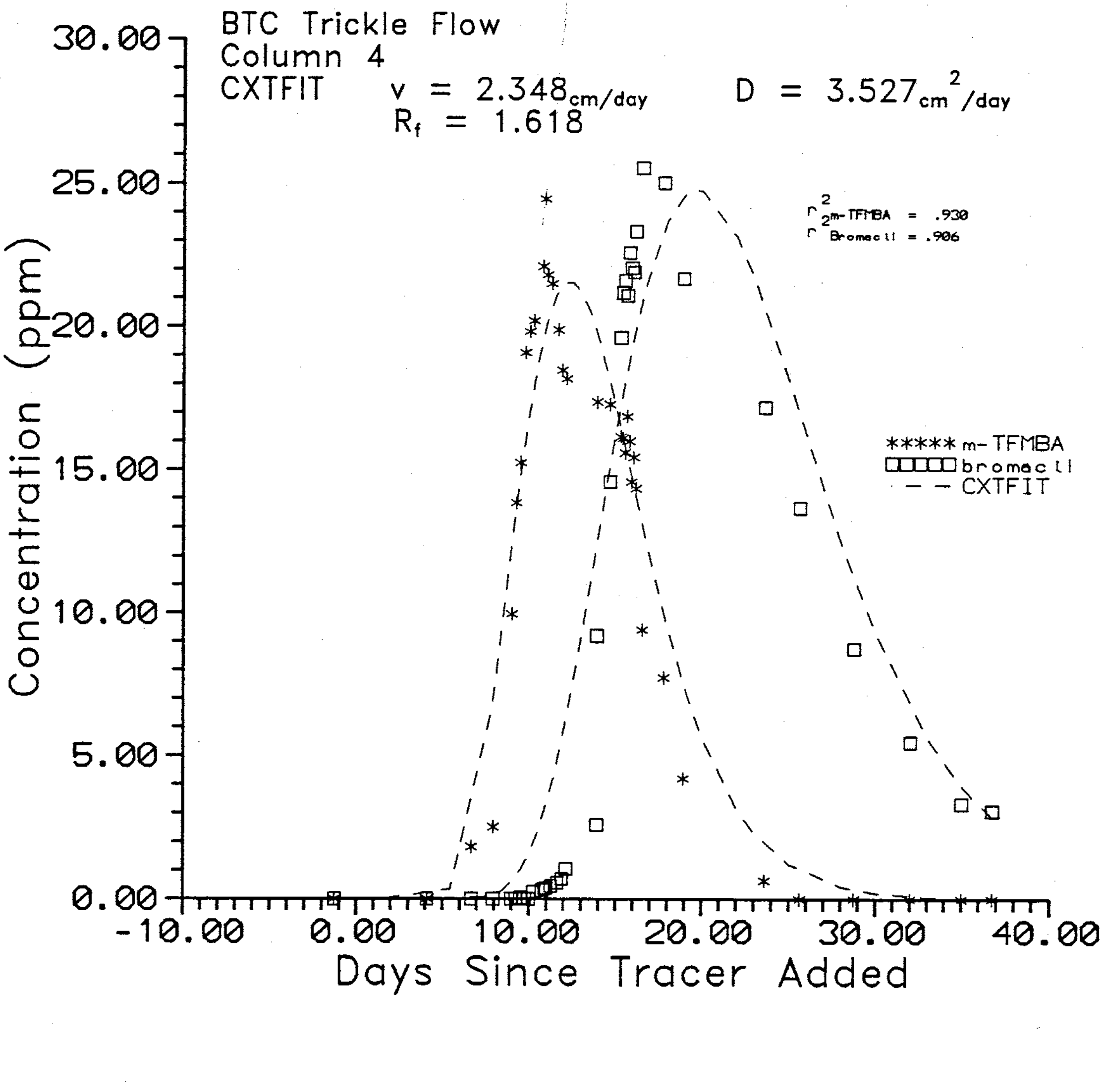


Fig. 17. m-TFMBA and bromacil BTC's for Repacked Column 4 - Steady State-Unsaturated Flow Regime.

Average pore water velocities using CXTFIT, v_{cxt}, were 1.372 and 1.393 times faster in Columns 1 and 2, respectively, than those calculated using fluxes delivered and divided by the column moisture content (q/θ_{grav}), defined here as $v_{derived}$. The repacked Columns 3 and 4 had v_{cxt} that varied by 1.315 and .907, respectively from $v_{derived}$. A comparison of v_{cxt} between the two columns types give in situ Columns 1 and 2 velocities 1.299 and 1.324 times greater than those found in their respective repacked Columns 3 and 4. This was expected as any soil structure that existed in the in situ columns, destroyed in the repacked columns, would promote preferential movement of the tracers. Soil taken from the SW corner of the site (Columns 2 and 4) showed the greatest difference in flow velocities between the in situ and repacked columns. Repacked Column 3 had $v_{derived}$ values that were greater than v_{cxt}, Column 4 had v_{cxt} values smaller than $v_{derived}$. Differences between $v_{derived}$ and v_{cxt} for Column 3 were probably due to this column showing an increase in moisture content. This column showed a very strong correlation between time and moisture increase during this part of the experiment as described in Section 2.3.1.

From the CXTFIT paramaterized v values the effective or fluid transporting moisture content, θ_{cxt}, was found for all columns. These values were compared to the gravimetrically derived volumetric moisture content measurements for each column measured upon completion of the steady state flow experiment, defined as θ_{grv}. All columns had θ_{grv} larger than θ_{cxt} by factors of 1.388, 1.348, 1.315, and 1.104 for Columns 1,2,3, and 4, respectively. Ideally these should be close to 1 if total miscible displacement occurs, especially in the repacked columns. However, the above indicates that a portion of the moisture filled pores in all columns did not participate in the transmission of solute, θ_{nt}, with the in situ columns having more nontransmitting fluid filled pores than their replicated repacked columns, as expected.

Column 3 had a much larger θ_{nt} than that of repacked Column 4. This may be due to a greater clay fraction existing in the soil taken at the NW location and used in this column. Column 3 had slower infiltration rates during each ponding event, exhibited more swelling, and initially, the soil used to repack the column had a larger GWC. All three of these characteristics indicate a higher clay content than the soil taken from the SW corner. An appreciably high correlation between uptake of water with respect to time was seen on Column 3. This would explain somewhat the large value of θ_{m}. Examination of matric potentials monitored over the entire steady state flow period indicate a large change in storage occurred in this column relative to the other columns (Section 2.3.1 Figures 6, 7, and 8).

The lower D coefficients for the in situ columns, compared to the repacked columns, are intriguing. These low values may indicate tracer flow paths were dominated by a narrow range in pore sizes. Therefore solute spreading, induced by varying pore sizes, was minimized. This is supported by the lower dispersivities, αs, for the in situ columns. Low αs indicate flow velocities were affected by pore sizes or pore network geometry that was less varied in size, angle and tortuosity than that of the repacked columns. Because no visible macropores were evident in the columns, flow through discrete pore networks, causing a micro flow path, seems more likely. Column 1 had the lowest α and highest v values, therefore it can be assumed, a greater degree of delineated conducting pore networks existed in that column. Because α and v values are much lower for Column 3 (using soil from the NW location as in Column 1) it can be assumed the more conductive pore networks found in the NW soil were destroyed during the sieving, mixing and packing process. Lower α for in situ Column 2, as compared to in situ Column 1, indicate less discrete, highly conductive, pore networks existed in soil taken at the SW location. The α differences between Column 2 and its replicated repacked Column 4 indicate soil structure was significantly altered when used to repack Column 4.

R_f derived from the CXTFIT model were compared with those found using, θ_{grv}, equation 4, and K_d (.094 ml/gr) derived from batch isotherms. As a comparison, measured and CXTFIT moisture contents were employed in the equation. R_f derived from CXTFIT, θ_{grv}, and θ_{cxtfit} are listed in Table 13.

Table 13. Retardation factors derived from CXTFIT and those found using measured moisture contents

	Column # and Soil Location			
R_f	NW 1	NW 2	SW 3	SW 4
From CXTFIT	1.577	1.518	1.515	1.618
From θ_{grv}	1.505	1.512	1.422	1.493
From θ_{CXTFIT}	1.679	1.708	1.555	1.543
Mean	1.587	1.578	1.497	1.551
Standard Deviation	.087	.111	.0682	.0629

For all columns, R_fs derived from θ_{grv} are lower than that produced by CXTFIT model. Discrepancies between R_f derived from θ_{grv} and θ_{CXTFIT} seem to follow no obvious or clear trend that can be explained. Irregularities between CXTFIT values, and those defined by equation 4 may be due to less than uniform distribution or pockets of varying soil components, lenses, and other heterogeneities within each column not picked up in batch isotherms.

3.4. Intermittent Ponding Flow Regime

Reduced concentrations, C/Co, of both tracers vs. reduced time, PV, were input into the CXTFIT model for all columns. Along with C/Co and PV, an average pore water velocity, v_a, was required as a constant to run the program. An estimation of v_a was found by dividing the average column moisture content during the time interval between ponds (7 days) into the ponded height. This value was divided by 7 to get v_a per day. To determine the best fit, the program was executed several times, with v_a values varying slightly per run. All other input values remained constant. Fitted D values varied linearly with each v_a input value, hence dispersivity, α, remained constant. Correlation coefficients, r^2, and D coefficients did not differ significantly from each execution. D coefficients were initially determined using reduced m-TFMBA concentrations and subsequently used to define the R_f of bromacil. If r^2 for bromacil derived parameters fell below .85, then D was allowed to vary until the best fit was achieved. Table 14 lists CXTFIT fitted parameters using the v_a value that the yielded the highest r^2 factor.

A striking difference occurred between D coefficients for the in situ and repacked columns. High D coefficients for the in situ columns is an indication that soil structure, coupled with the ponding event, had induced pore water velocities which widely varied from one another, Column 1 having the largest variation. The reason for these high values seems intuitively obvious. The act of ponding a 4.8 cm pressure head at the soil surface was enough to overcome the air entry pressures of any relatively larger pores or channels. These larger fluid filled channels served as conduits or coupled clusters of more conductive pore networks within the soil profile and facilitated preferential movement of surface applied leaching solution through the column length. The influent bypassed a major portion of the fluid filled pores. As the pressure head at the soil surface decreased, the larger channels drained and/or pore networking became disconnected. Effluent flow was then

Table 14. Average Pore Water Velocities, Dispersion Coefficients, and Retardation Factors for Intermittent Ponding Flow Regime

Parameters	Column			
	in situ		Repacked	
	1	2	3	4
.V_{avg} -cm/day	2.79	2.79	2.27	2.29
$V_{m\text{-}TFMBA}$	4.59	2.56	2.48	3.36
$\theta_{\text{average from trans meas.}}$	.246	.248	.265	.260
θ_{CXTFIT}	.163	.150	.194	.253
$\theta_{\text{gravimetric at end of pond}}$	.213	.258	.2817	.262
$\theta_{m\text{-}TFMBA}$	.224	.296	.253	.253
$\frac{\theta_{\text{-CXTFIT}}}{\theta_{\text{-gravimetric}}}$	.7635	.582	.689	.973
$PV_{\text{bypassed using}}$ θcxt and θ grav	.236	.419	.307	.027
D_{CXTFIT} m-TFMBA cm^2/day	11.948	8.155	2.998	2.469
α-cm	4.282	2.922	1.320	1.078
r^2	.944	.919	.935	.947
D bromacil cm_2/day	19.660	15.358	2.998	2.460
α-cm	4.282	2.922	1.320	1.078
r^2	.921	.845	.900	.942
$R_{f\text{-}CXTFIT}$	1.921	2.035	1.775	1.599
$R_{f\theta\ grv}$	1.714	1.606	1.530	1.591

dominated by smaller pores and/or pore networks as the spread of BTCs data imply (see Figures 18 and 21). Immediately after a ponding event BTCs show tracer concentration in the effluent changes dramatically. Effluent tracer concentrations fell for a period than slowly rose again. More dramatic concentration differences were seen for the <u>in situ</u>

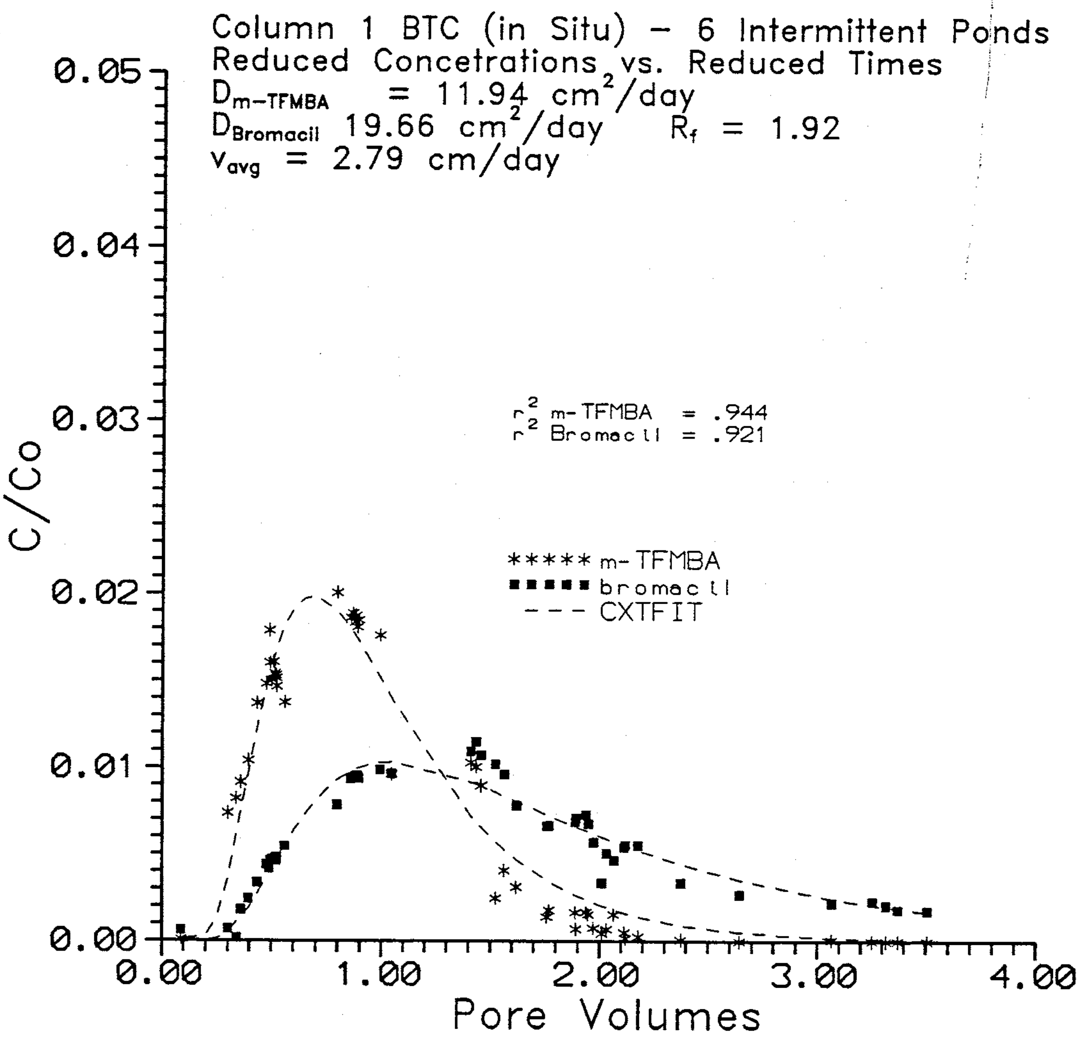


Fig. 18. m-TFMBA and bromacil BTCs for in situ Column 1 - Intermittent Ponding Flow Regime.

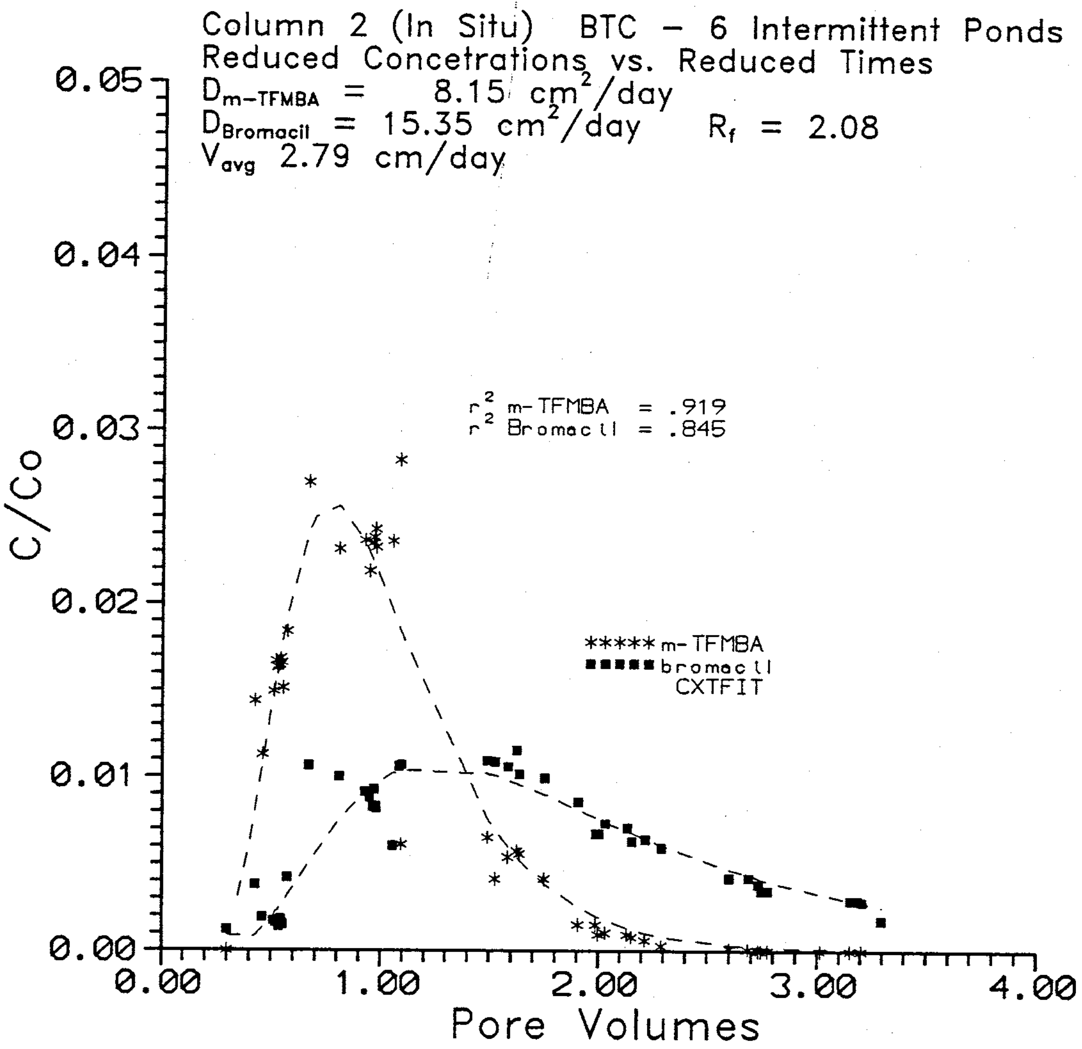


Fig. 19. m-TFMBA and bromacil BTCs for <u>in situ</u> Column 2 - Intermittent Ponding Regime.

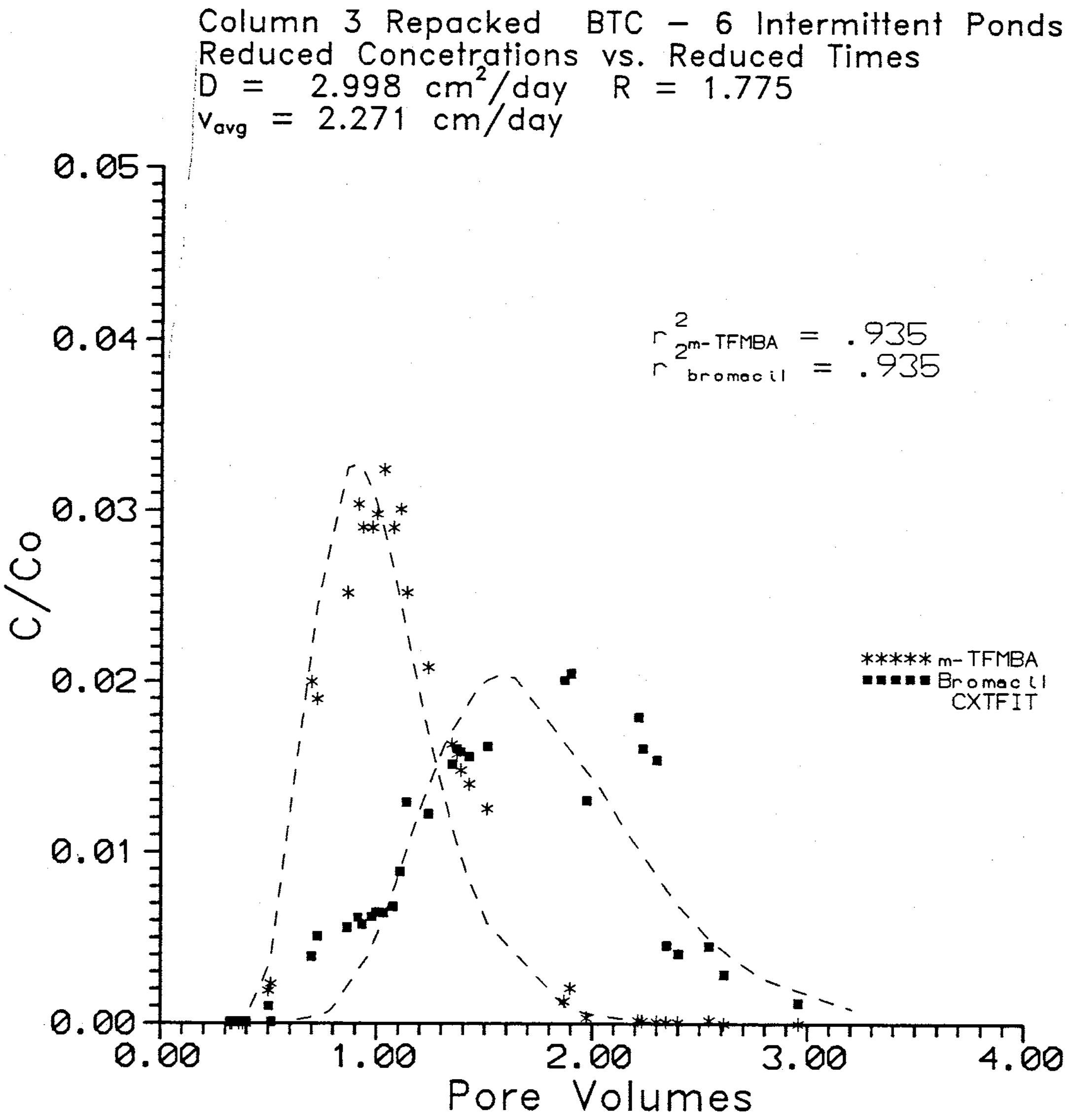


Fig. 20. m-TFMBA and bromacil BTCs of repacked Column 3 - Intermittent Ponding Flow Regime.

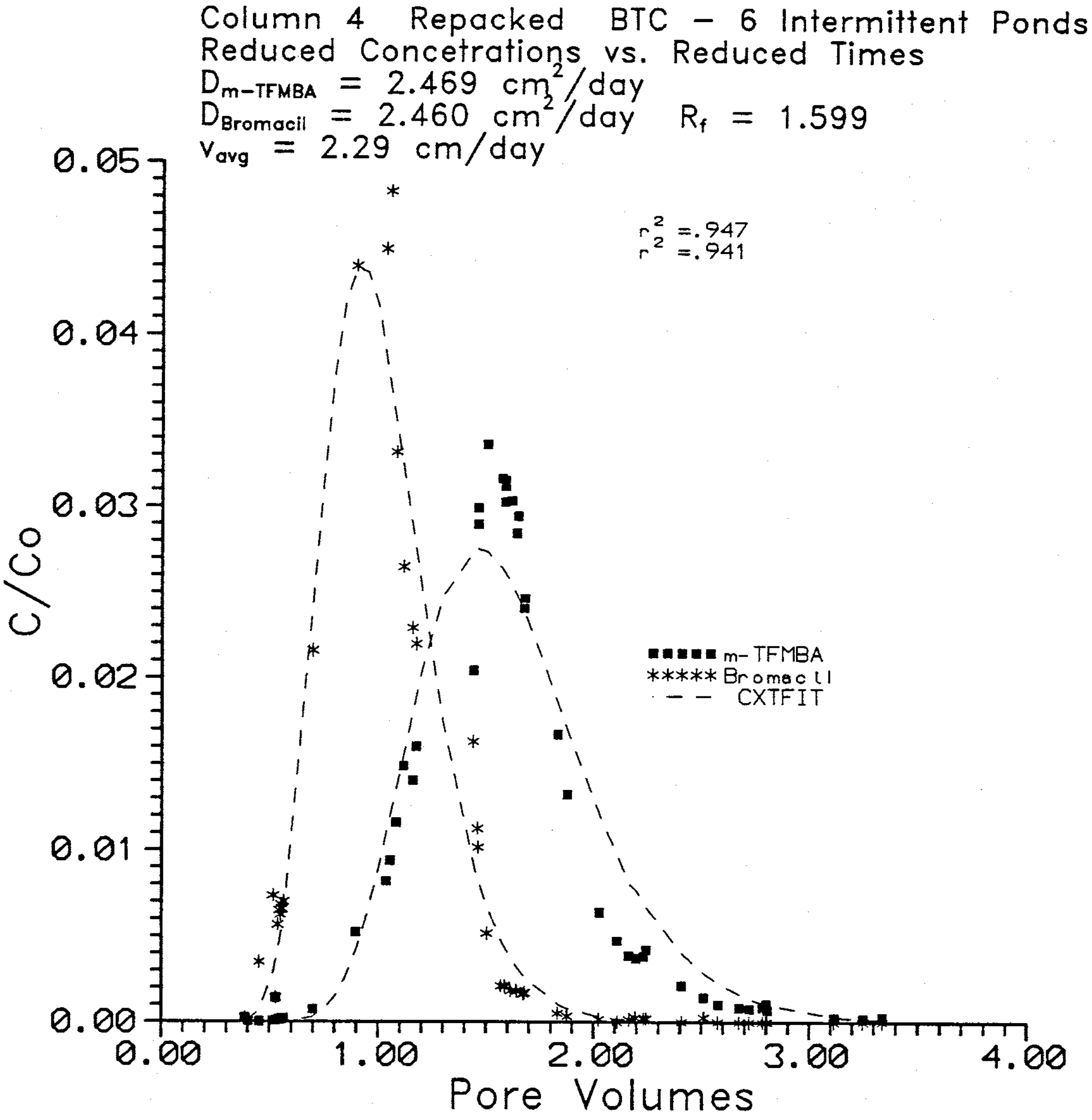


Fig. 21. m-TFMBA and bromacil BTCs of repacked Column 4 - Intermittent Ponding Flow Regime.

columns. This is further supported by the fluctuating nature of effluent pHs. Immediately after each ponding event pHs seemed to be representative of the surface applied waters rather than the soil matrix solution. pHs again changed after the majority of the volume of surface applied water had drained from the column. These changes indicated that column drainage, at this later time (especially for the in situ columns), was more representative of solution that had been residing in the less mobile fluid filled pores of the soil matrix.

The extent that the effluent concentration was composed primarily of surface applied and/or soil matrix water is more clearly seen when examining plots of tracer concentrations against cumulative effluent. This plot was superimposed over a plot of the volume of effluent drainage per 3 hours as shown in Figures 22 and 23. For the in situ columns, approximately 50 percent of the volume of surface applied water was expelled at the column exit boundary within the first 20 hours of the 168 hour interval between ponds. A major portion of effluent collected within this first 20 hours seemed to be water that was applied at the surface, as indicated by the spiky nature of the in situ BTCs .

During the intermittent ponding regime tracer transport seemed to be affected by both vertical and lateral transport mechanisms. The time each mechanism was dominant depended on the elapsed time between each ponding event. For example, both tracers were seen within a few hours after the first ponding event, signifying a large volume of solute laden influent, applied at the surface, was transported by advective processes and thus short circuited or bypassed a major portion of the soil profile just after the onset of the first ponding event. Each ponded event was separated by a long length of quiescent time (for this experiment 120 to 150 hours), relative to the amount of time that was required for the volume of ponded leaching solution to infiltrate into the soil matrix (approximately 12 hours for the in situ and 24 hours for the repacked columns). During this 120 to 150 hour quiescent period, BTCs indicate vertical movement of the solute was actually retarded as it infiltrated laterally into smaller, less mobile fluid filled pores. Molecular diffusion and

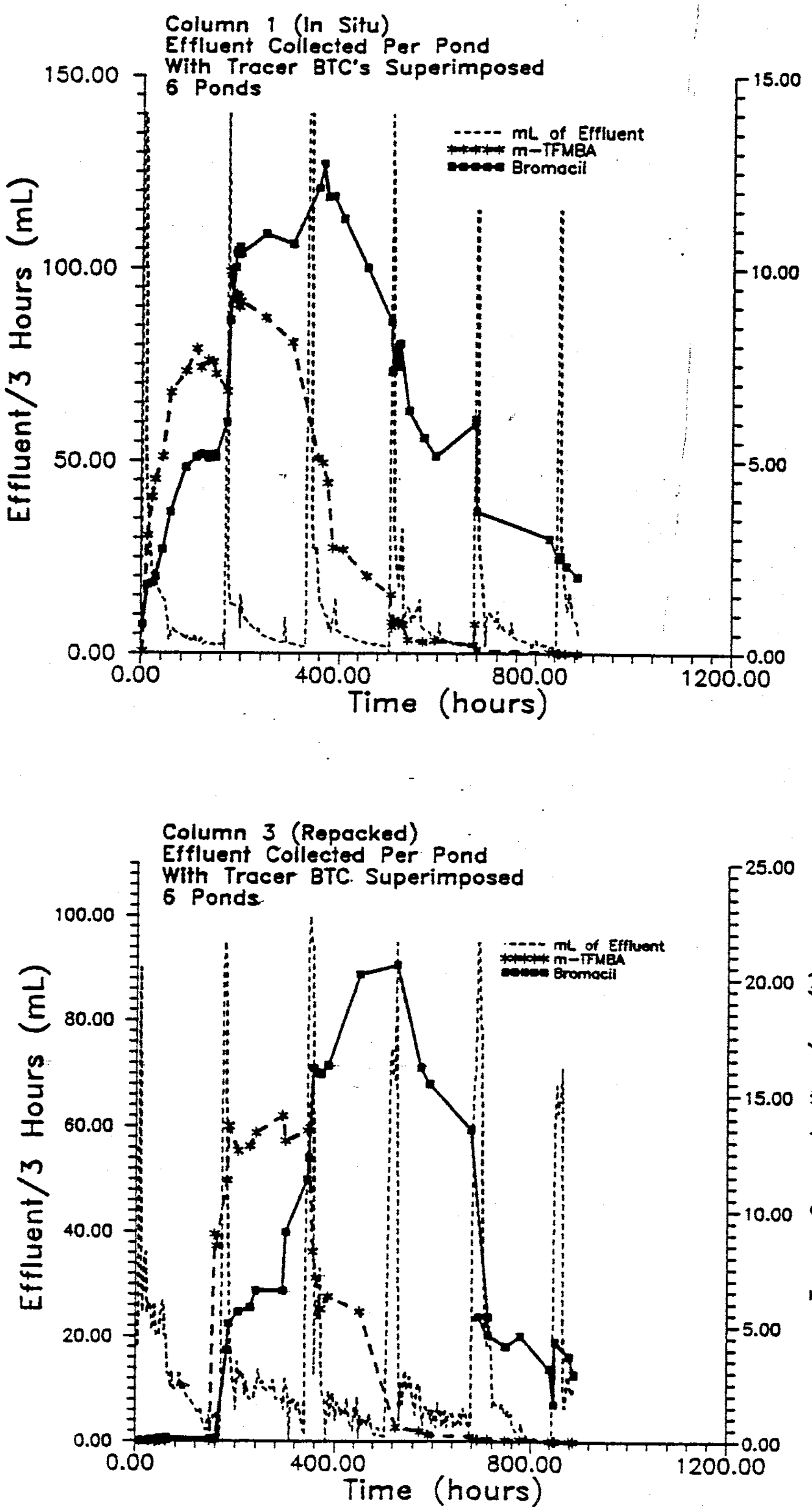
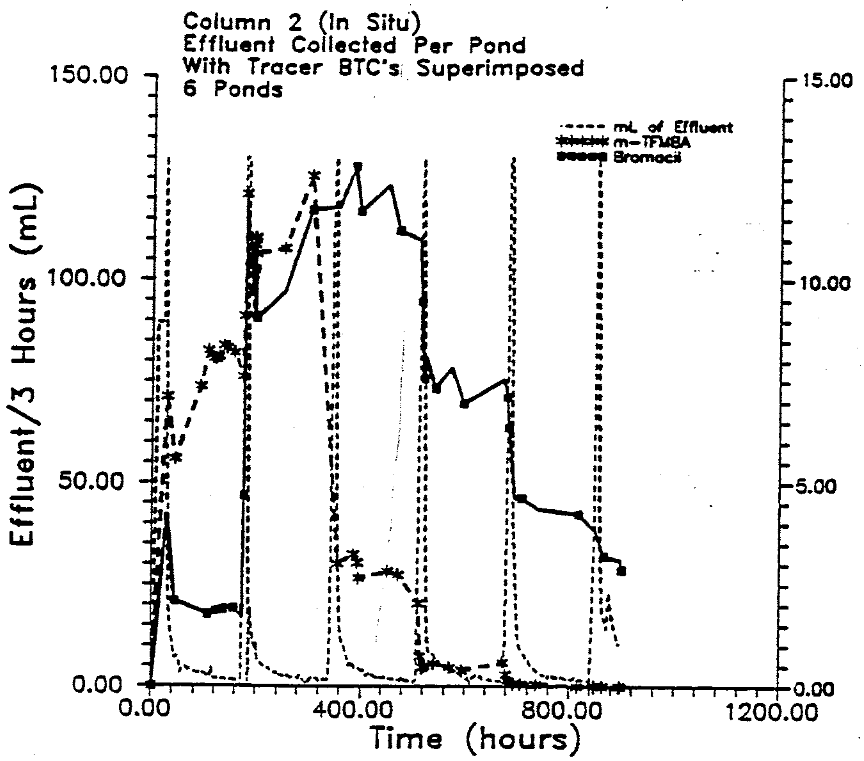


Fig. 22. Concentration vs. Cumulative Effluent for <u>in situ</u> Column 1 and repacked Column 3 during Intermittent Ponding Flow Regime.



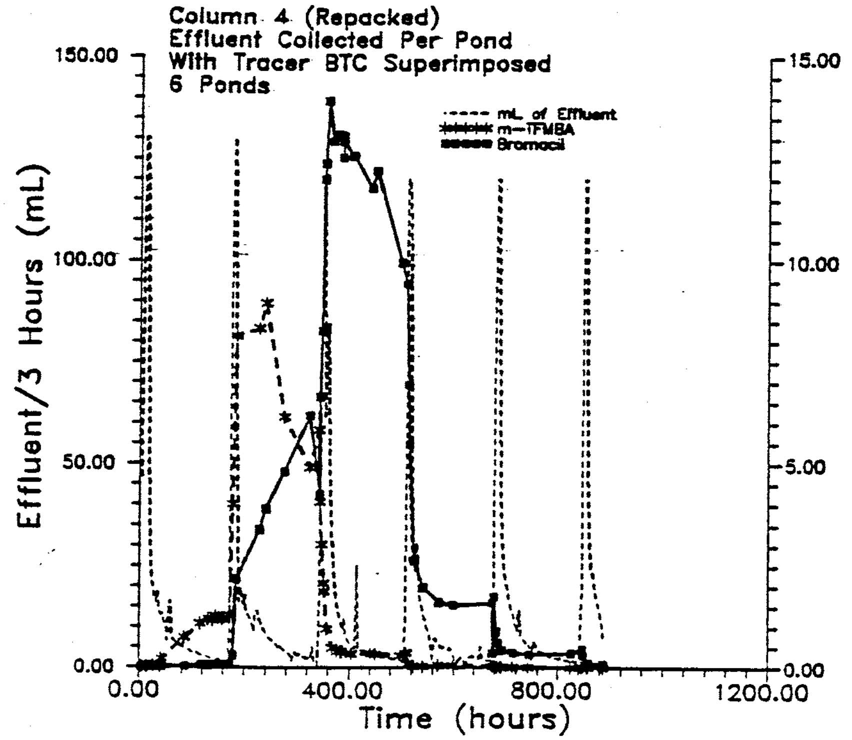


Fig. 23. Concentration vs. Cumulative Effluent for in situ Column 2 and repacked Column 4 during Intermittent Ponding Flow Regime.

concentration gradients appeared to be the mechanism that moved the tracer laden solute laterally into these smaller, less mobile fluid filled pores. At the onset of the next pond, concentration gradients were reversed and mechanical dispersion (as opposed to molecular diffusion) became dominant. The rapid transport of the incoming leaching solution bypassed the smaller, less mobile and tracer filled pores. BTCs show effluent concentrations were less concentrated immediately after each subsequent ponding event. This was especially pronounced for the in situ columns where tracer peaks are broad and stretch through 3 ponding events as compared to the narrower, more concise and sharper BTCs of the repacked columns. The implication is, preferential flow, as well as lateral spreading, was exacerbated by the intermittent ponding, especially in the in situ columns.

The repacked columns had D coefficients that indicated soil structure, coupled with ponding, did not induce a wide range in average pore water velocities. Similar to the in situ columns, effluent released immediately after the pond (40 hours) was equivalent to about 50 percent the total ponded volume. Tracer breakthrough for the repacked soil columns suggested little short circuiting or bypass flow was induced at the onset of each ponding event. Both tracers moved through these columns in a more piston like fashion, pushing antecedent moisture ahead of the wetting front. The result, BTC peaks spanned only 1 to 1.5 ponding events.

The moisture content of each column at the end of the last ponding interval was determined gravimetrically and denoted as θ_{grv}. θ_{grv} was considered to represent the most conservative column PV as measurements were taken at the end of a 7 day drainage period. Using equation 4 and R_f from CXTFIT, θ_{cxt} was inversely derived and considered to conservatively represent the column PV that transmitted both conservative and retarded tracers. The ratio $\theta_{cxt}/\theta_{grv}$, suggested a major portion of the fluid filled pores for the in situ column did not come in contact with the retarded tracer. This is misleading, as bromacil movement was not always retarded to the extent that R_f indicate, relative to the m-TFMBA. Investigation of in situ column BTCs find the initial appearance of both tracers with very similar relative concentrations , C/C_o, at the exit boundary within 20 hours of the initial ponding event. Presumably, during the initial pond, short circuiting created such rapid transport of both solutes that bromacil adsorption kinetics had not come to equilibrium. (A similar phenomenon has been reported by White et al., 1986.) θ_{cxt} seems to be a measure of those fluid filled pores that had come to equilibrium with bromacil adsorption kinetics sometime after the pond, and is still significantly less than θ_{grv}. Therefore, θ_{cxt} is used as more of qualitative measurement of the transmitting fraction of PV for both tracers. For the <u>in situ</u> Column 2, over 40 percent of the column PVs was bypassed, or out of equilibrium with the bromacil adsorption kinetics, for the repacked column 4 - less than 1 percent. Column 3 $\theta_{cxt}/\theta_{grv}$ indicated large bypass flow occurring relative to the other repacked column. Entrapped air, coupled with significant swelling, and an increasing moisture content (change in storage) were suspected to be a contributing factors. (During each ponding event leaching solution took 10 to 12 hours longer to infiltrate in Column 3 than in the other columns.) The column integrity was also suspected, as effluent emitted from the bottom drain port exhibited intermittent bubbling, indicating less than air tight seals existed between the various column parts.

Breakthrough times of m-TFMBA, $v_{m\text{-}TFMBA}$, were compared to v_a derived values. A qualitative estimation of $v_{m\text{-}TFMBA}$ was done by evaluating BTCs of m-TFMBA concentration vs. cumulative effluent over the entire intermittent ponding experiment. This proved to be an arbitrary task, as there were several elevated tracer peaks separated by relatively low points for the <u>in situ</u> columns BTCs. These peaks and valleys corresponded to the transient nature of effluent drainage affected by the onset of each ponding event, and denoted that a significant mass of tracer was bypassing the soil profile due to induced preferential flow. $v_{m\text{-}TFMBA}$ from the <u>in situ</u> columns had the largest divergence from v_a values and signify preferential flow was a primary mode of transport in these columns for the first few hours after the initial pond.

A comparison of the moisture contents derived from $v_{m\text{-TFMBA}}$, denoted as $\theta_{m\text{-TFMBA}}$, and those derived from θ_{ext}, show large discrepancies exist. This discrepancy <u>seems</u> to support the notion that, initially, advective precesses dominated transport of both tracers and inhibited adsorption equilibrium. The time interval between additional ponds enabled diffusion and concentration gradients to laterally transport tracers into smaller fluid filled pores, where adsorption kinetics equilibrated.

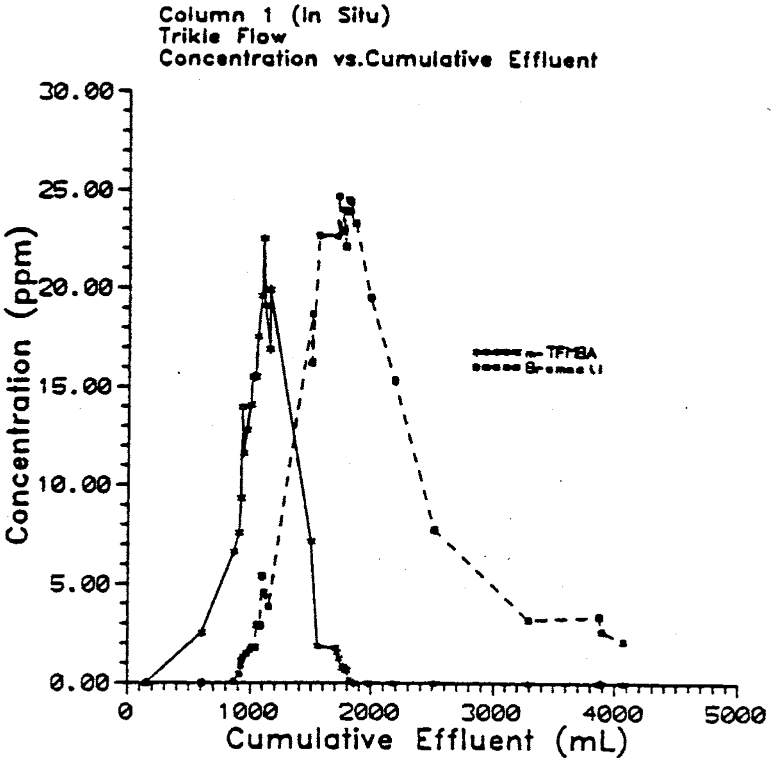
3.5. Comparison of Steady State Unsaturated and Intermittent Ponding Flow Regimes.

The most dramatic differences that existed between the steady state and intermittent ponding flow regimes were seen in D coefficients and α parameters. The in situ columns had the highest D and α values during intermittent ponding and the lowest during the steady state regime. Large α and D coefficients for the in situ columns during the intermittent ponding flow regime indicate average pore water velocities were extremely varied and soil structure, coupled with the mode of leachate application, induced spreading of tracer laden solute from its center of mass. Because D coefficients for the repacked columns did not differ much between the steady state and intermittent ponding flow regime, it can be assumed that the presence of macropores, or delineated, highly conductive pore networks, was minimal. Therefore an increase in pressure head, given a ponded condition, did not induce significant preferential movement.

A plot of tracer concentration vs. cumulative effluent (see Figures 24 thru 27) reveals that tracer peak breakthrough during the steady state-unsaturated flow regime for all columns required less cumulative leaching solution than that for the ponded regime (see Table 15) especially in the in situ columns. Reasons for this seem intuitively obvious. During the first ponded event a significant volume of the ponded leaching solution mixed

Table 15. Cumulative Effluent Used for Breakthrough of Tracer Peaks during Steady State-Unsaturated, SS, and Intermittent Ponding, IP

	Column							
mL of Effluent	1		2		3		4	
	SS	IP	SS	IP	SS	IP	SS	IP
m-TFMBA	1092	1217	1105	1531	1381	1415	1207	1422
bromacil	1799	2123	1663	2228	1820	2710	1777	1887



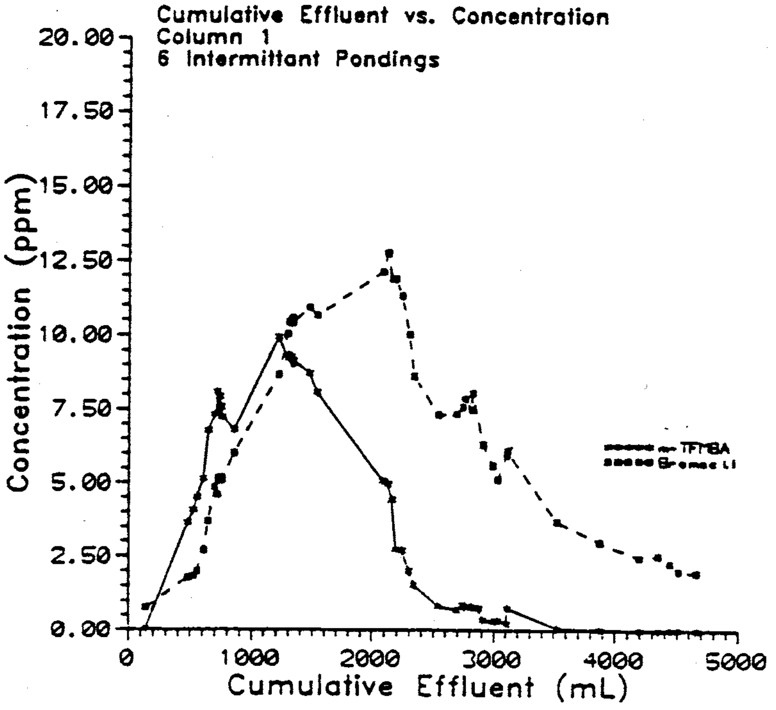


Fig. 24. Concentration vs. Cumulative Effluent for in situ Column 1 During Steady State-Unsaturated and Intermittent Ponding Flow Regimes.

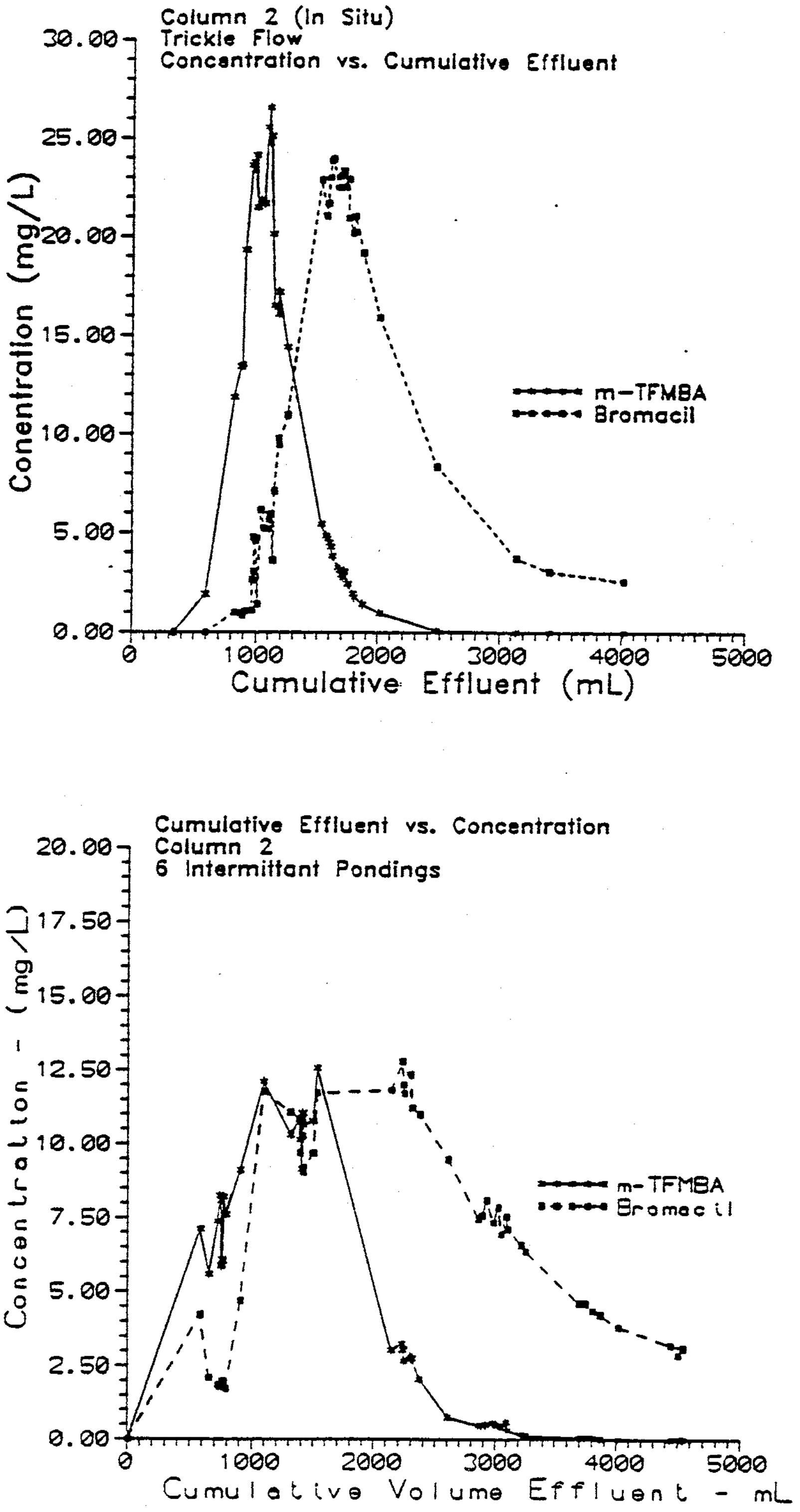


Fig. 25. Concentration vs. Cumulative Effluent for <u>in situ</u> Column 2 During Steady State-Unsaturated and Intermittent Ponding Flow Regimes.

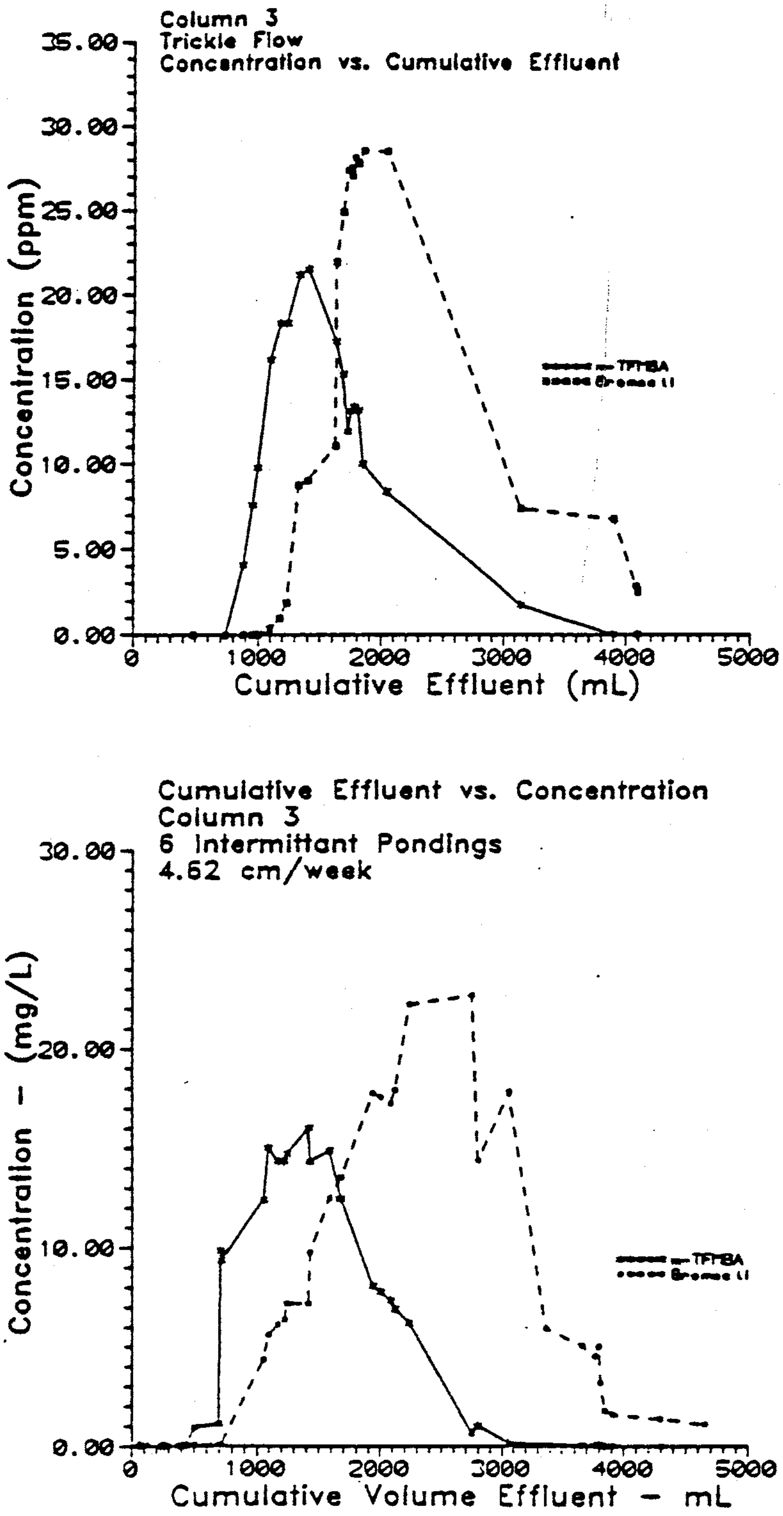


Fig. 26. Concentration vs. Cumulative Effluent for repacked Column 3 During Steady State-Unsaturated and Intermittent Ponding Flow Regimes.

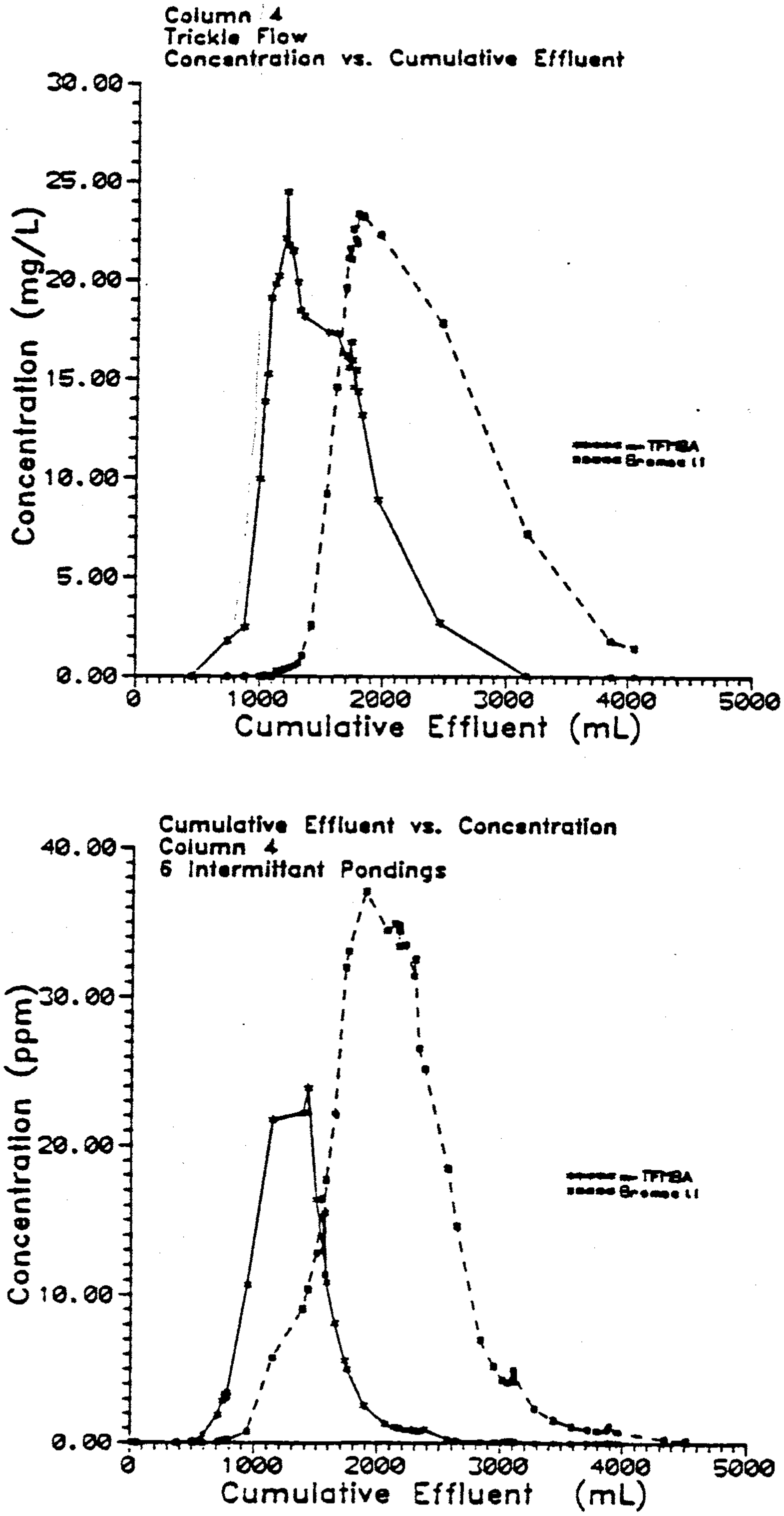


Fig. 27. Concentration vs. Cumulative Effluent for repacked Column 4 During Steady State-Unsaturated and Intermittent Ponding Flow Regimes.

with the surface applied tracers at the column upper boundary. Within the first 25 hours after the ponding event 78, 75, 68 and 58 % of the volume of surface applied water had been collected as effluent for Columns 1, 2, 3, and 4, respectively. The initial appearance of both tracers was seen in the in situ column effluent collected during this period. The implication is that a portion of surface applied leaching solution rapidly bypassed the less conductive fluid filled pores of the in situ columns. During the time interval between the first pond, after the bulk of effluent had drained, concentration gradients and molecular diffusion came into play, driving any tracer laden solute laterally into less conductive pores.

Subsequent leachings were less effective in flushing out tracers that had recently infiltrated into the less conductive pores prior to the ponding event. This is indicated by the marked peaks and valley of the in situ column BTCs during the intermittent ponding flow regime. These peaks and valleys indicate effluent concentrations were markedly effected by the onset of each ponding event (the repacked columns showing less BTC fluctuation). Effluent collected during the first 25 or so hours of each ponding event had concentrations more like the surface applied water. During the remaining 140 hours between ponding intervals, effluent collected had concentrations that primarily reflected that of the soil matrix. This statement is additionally supported when examining plots of effluent pH values vs. time (see Figures 28 thru 31) with the dashed lines denoting the time of each ponding event. pH values from each in situ column were plotted with those of the repacked column using soil taken from the same location. (In situ Column 1 corresponded with repacked Column 3, and likewise, Column 2 with Column 4.) It should be noted the rise and fall in pH values initially before and after each ponding event. The marked increase in pH values immediately *after the first* ponding, especially for the in situ columns, is a consequence of preferential flow bypassing a major portion of the soil matrix (which would act as a buffer) and hence reflected the high pH of the tracer solution. Note that pH does not change as drastically before and after each ponding event for the repacked columns.

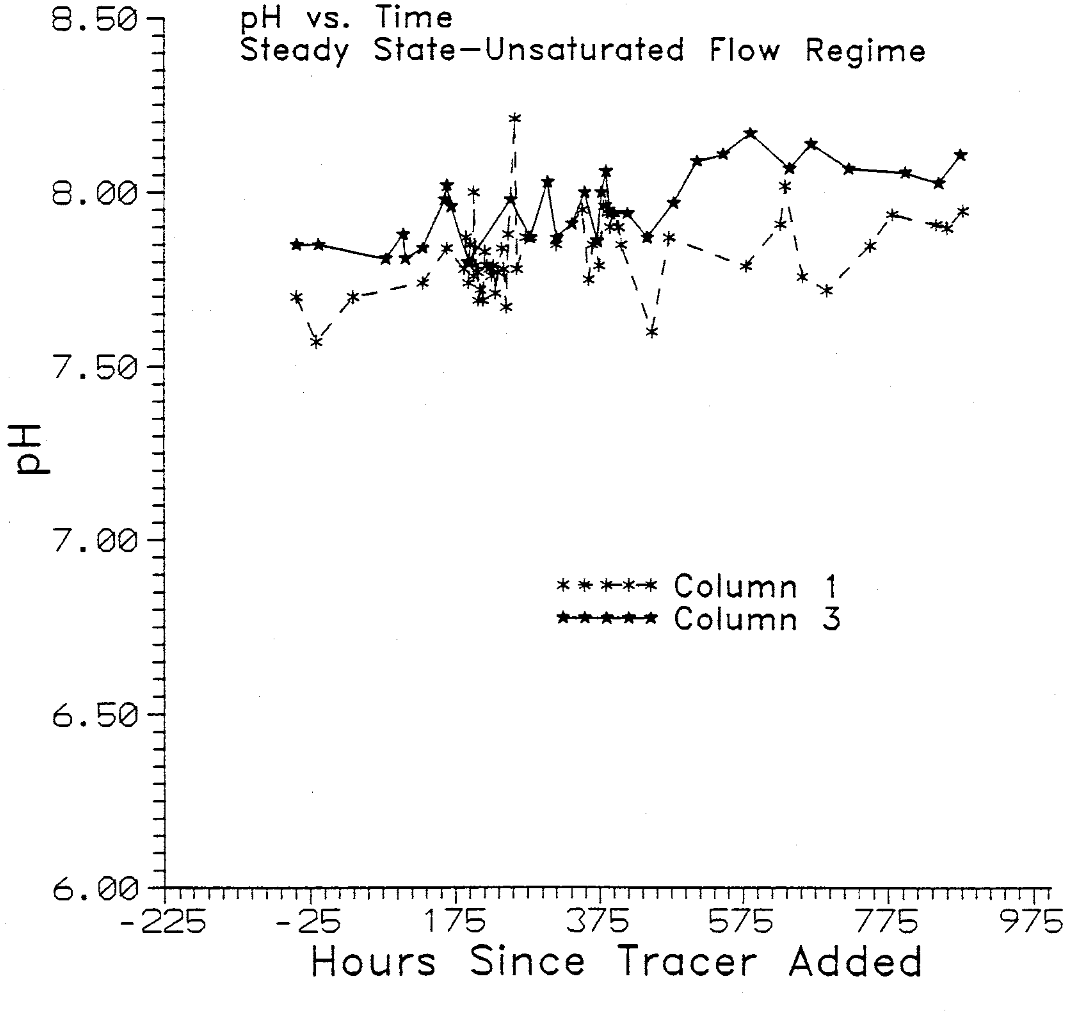


Fig. 28. **pH values for in situ Column 1 and repacked Column 3 during Steady State-Unsaturated Flow Regime.**

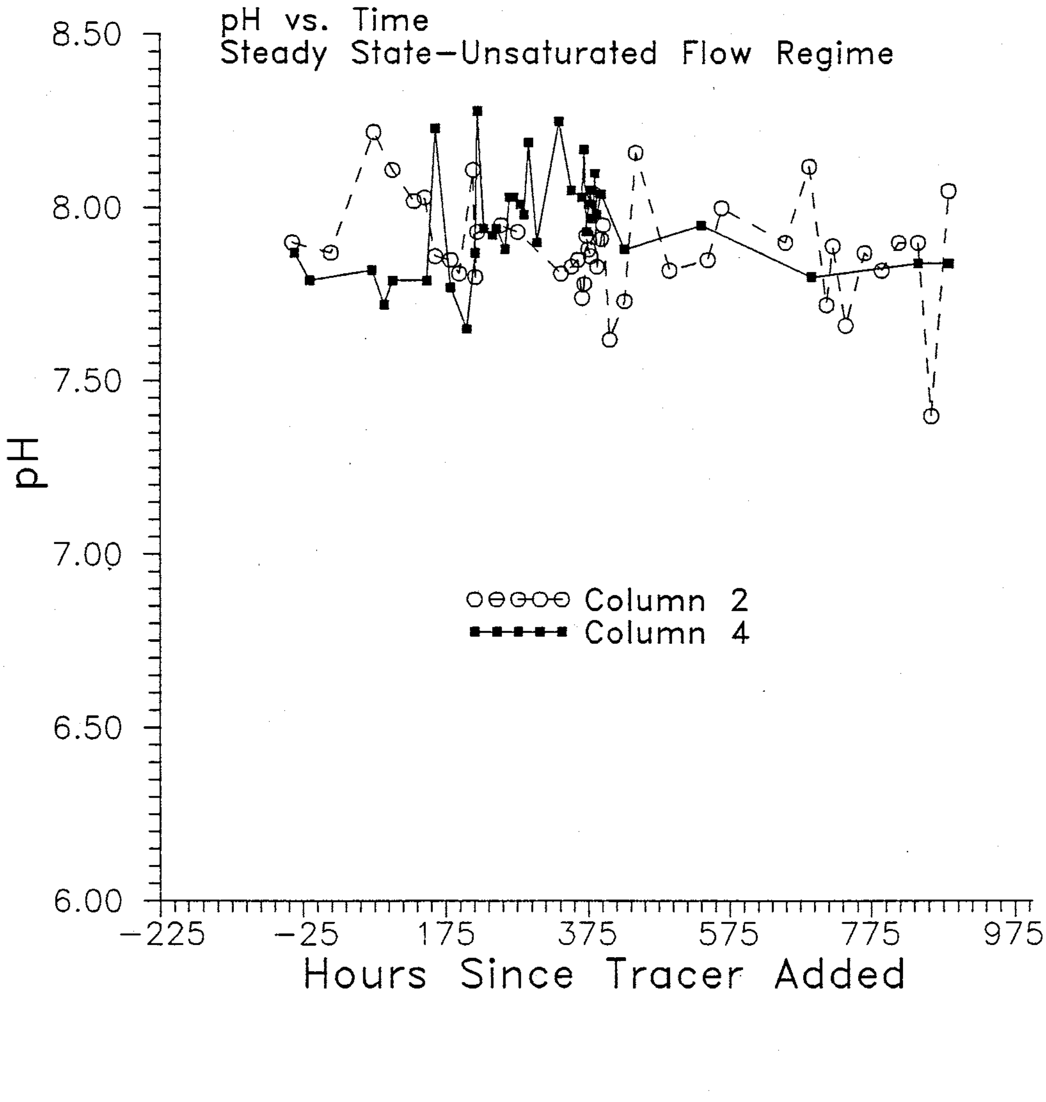


Fig. 29. pH values for in situ Column 2 and repacked Column 4 during Steady State-Unsaturated Flow Regime.

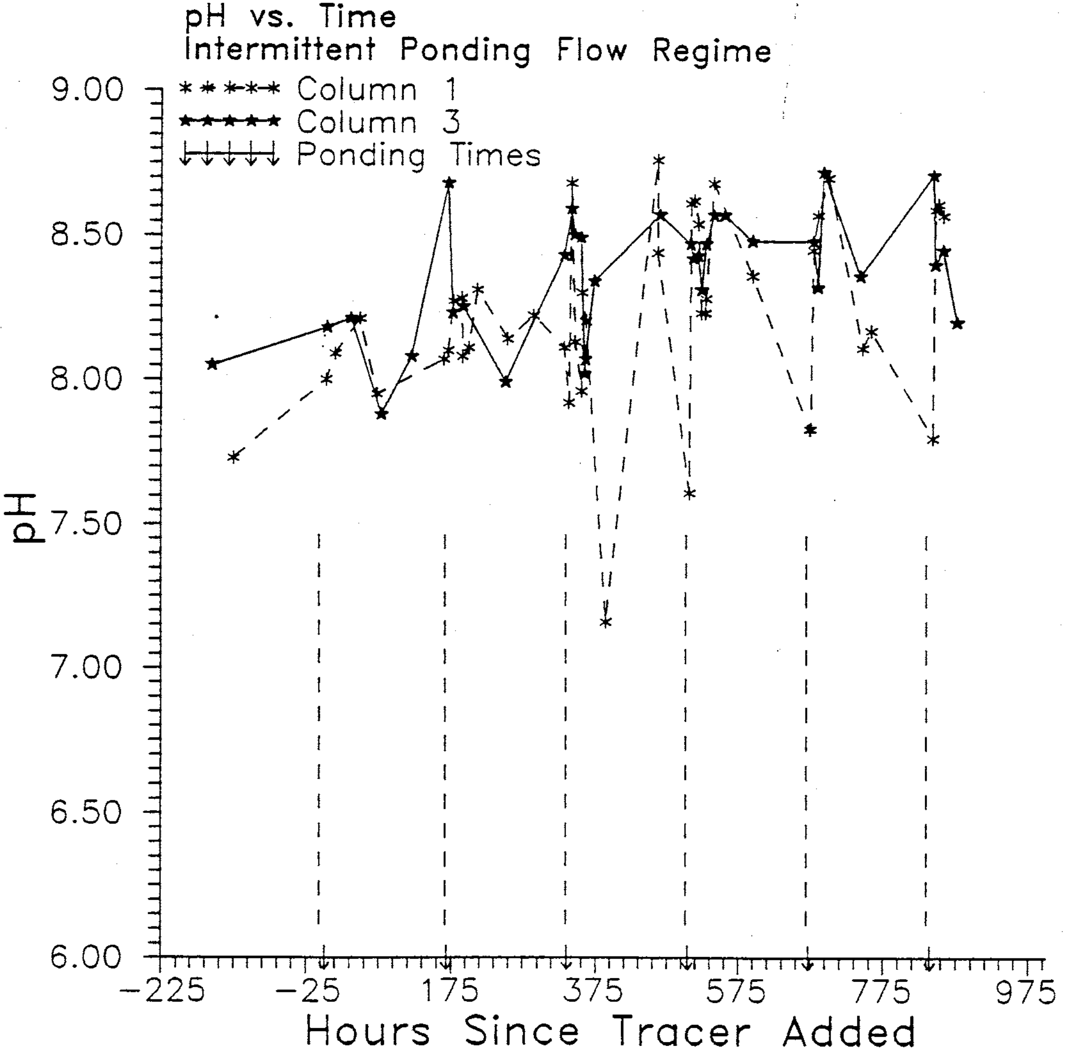


Fig. 30. pH values for in situ Column 1 and repacked Column 3 during Intermittent Ponding Flow Regime.

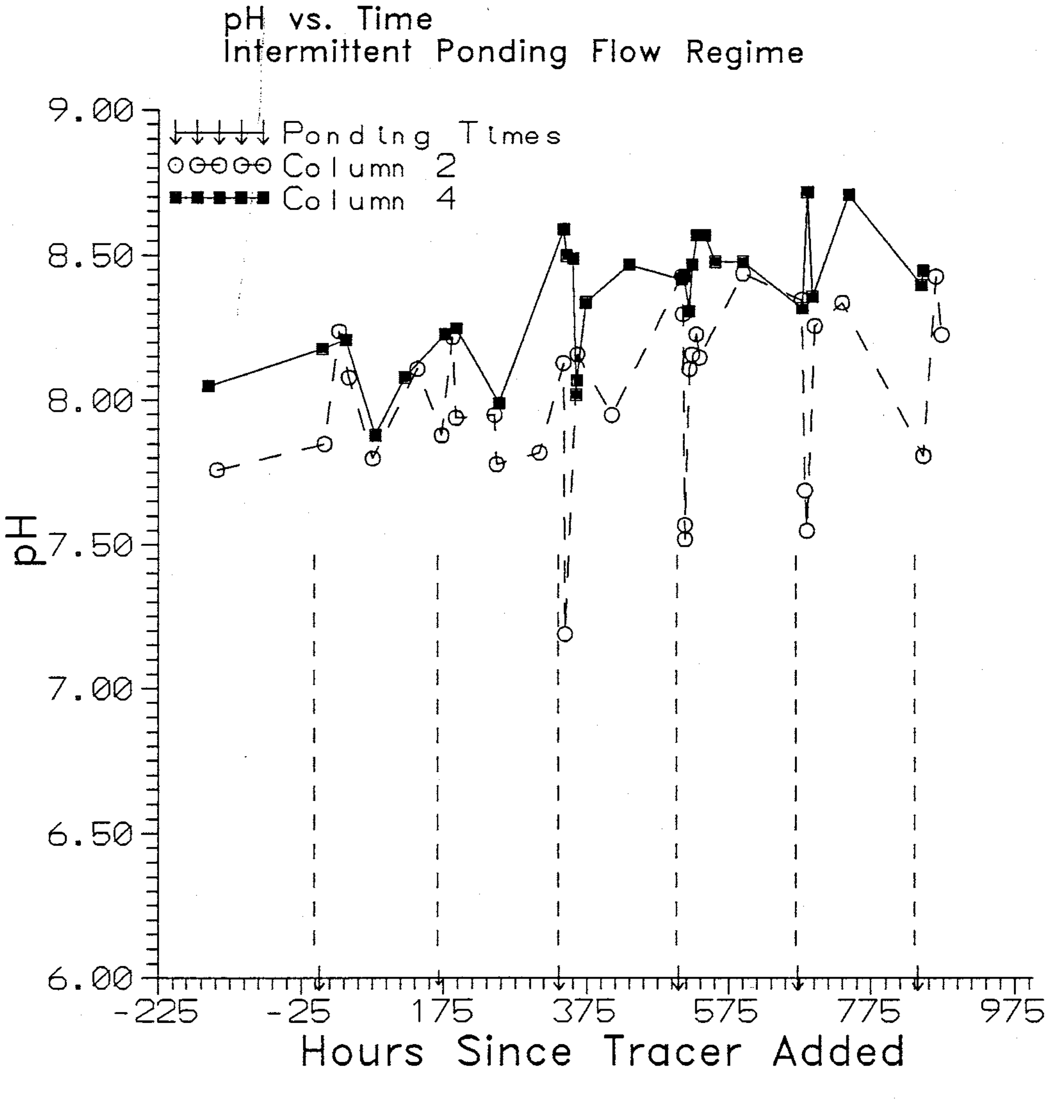


Fig. 31. pH values for in situ Column 2 and repacked Column 4 during Intermittent Ponding Flow Regime.

After a majority of the *volume* of ponded leaching solution had been collected in the effluent, pH values again changed and reflected the concentration residing in the soil matrix. As pH plots and BTCs imply, both tracers were more resistant to influent flushing in the <u>in situ</u> columns when residing in the less mobile water of the soil matrix. Because a major portion of influent was rapidly transmitted through the larger pore networks, more cumulative effluent was required to reverse concentration gradients and remove tracers from these less conductive pores.

Similar findings have been reported by Thomas and Phillips (1979) while investigating NO_3 and Cl^- movement through soil profiles given a sudden input of surface applied water. Effluent concentrations collected immediately after the flushing event signify the incoming water "skimmed off" only a portion of the surface applied salts. Salt concentrations in the effluent rose in an unsteady manner that coincided with each subsequent surface irrigation, indicating effluent concentrations were effected by two distinct bodies of water, that residing in the soil matrix or that of surface applied (ponded) waters. The composition of the effluent was highly correlated to the infiltration period of the surface applied waters. White et al. (1986) also reported a similar occurrence when investigating variations in the transport of napropamide and bromacil in <u>in situ</u> columns given different soil moisture contents and different modes of leaching applications. A continuous leaching regime was compared to an intermittent regime. Each water irrigation for the intermittent regime was separated by a 24 hour interval. The study found both herbicides were flushed through the soil profile to a greater extent during the continuous leaching regime. The authors concluded that diffusion of both herbicides from more to less conductive pores occurred during the 24 hour time interval between irrigations. Salts residing in the less conductive pores were more resistant to the flushing action of subsequent irrigations.

The intermittent ponding regime implemented in this study may have been less efficient in flushing out both tracers due to the short time length of the pond infiltration period relative to the much longer time length of the quiescent period. Flushing efficiency may have also been related to the amount of leaching solution used relative to the saturated porosity of the soil. Both tracers were initially seen the in situ column effluent within the first 24 hours of the first pond. It took a relatively short time for a major portion of ponded water to drain from each column. During the long quiescent period that followed high drainage rates, molecular diffusion along concentration gradients, drove both tracers into the less conductive pores. Therefore, subsequent flushings of tracers through the less mobile regions of the columns took more cumulative effluent than that of the steady state-unsaturated flow regime.

Differences in flushing efficiency between the two column types were also seen. Soil for the repacked columns was homogeneously mixed and uniformly packed (ideally). As a result, pore spaces in the repacked columns should not have varied as much in size as that of the in situ columns and tracer movement in these columns should have behaved as classical miscible displacement. BTCs did indicate close to ideal miscible displacement existed in these columns during the intermittent ponding regime. In contrast, advection with minimum molecular diffusion, seems to have dominated tracer movement in the repacked columns *and* the in situ columns during steady state flow. This is evident in the taller and narrower BTC peaks for the steady state regime.

Retardation factors were deceptively larger for intermittent ponding than for the steady state flow regime. This conclusion came about when measuring in situ column effluent taken after the onset of the first pond. Bromacil and m-TFMBA had similar C/C_o values. Thus, a significant amount of bromacil was not retarded to the extent that high R_fs portend. This indicates rapid advective transport of bromacil, during the first pond, did not allow adsorption equilibrium to occur. For the intermittent ponded flow regime the long time intervals between subsequent ponds (120 to 150 hours) of low column drainage enabled both tracers to diffuse laterally into smaller pores. Column PVs (moisture contents) during the low drainage phase (quiescent period) were less than that of the steady state-unsaturated flow regime. These low column moisture contents, during the quiescent period, gave rise to comparatively larger bromacil R_fs. Lateral molecular diffusion of both tracers into the less conductive pores between ponding events, and rapid bypass flow of subsequent water applications, made ponding less effective in flushing or moving both tracers vertically. Bypass flow of the less conductive pores gave rise to wide, jagged BTCs of both tracers and high R_fs for bromacil. Retardation factors for all columns during steady state flow conditions was smaller than that for the ponded conditions. Using these values, and equation 4 to derive an effective θ_t (or effective PV), it can be assumed that for the transient flow conditions a significant portion of the wetted soil profile was bypassed due to preferential flow induced by the ponding condition.

4.0 SUMMARY AND CONCLUSIONS

Two intact and two repacked soil columns, of the same dimensions and bulk densities, were used to study preferential flow phenomena given steady state-unsaturated and intermittent ponding flow regimes. All columns used a sandy clay loam soil taken from the Maricopa Agricultural Center located in Central Arizona. Soil used for the in situ columns was structureless and showed no visible cracks or macropores commonly associated with preferential flow. Soil used in the repacked columns was taken from the same location as that for the in situ columns and was air dried, sieved and homogeneously mixed before repacking. A conservative tracer, m-TFMBA, and a mildly retarded tracer, bromacil, were used to investigate the degree of preferential flow through the two column types and under the two flow regimes. Average pore water water velocities for m-TFMBA were calculated using a nonlinear least squares curve fitting program. Retardation factors for bromacil were then found by applying the same curve fitting program to bromacil BTCs. These R_fs were compared to R_fs derived using bromacil batch isotherm partitioning coefficients, average soil bulk densities, and gravimetrically-derived moisture contents.

Analysis of solute BTCs indicated that preferential flow occurred in all columns for both flow regimes. Preferential flow was most pronounced during the intermittent ponding regime in the in situ columns. Presumably the soil in the in situ columns had subtle structural characteristics, not found in the repacked soil columns, which promoted preferential flow. These structural characteristics were destroyed during the sieving and repacking process.

Under intermittent ponding, rapid bypass flow caused an early appearance of both surface-applied tracers in the in situ column effluent within the first 24 hours of the experiment. This initial rapid movement of the tracers can be misleading if used to predict the overall bulk movement of the tracers. The appearance of the tracer peaks required more cumulative effluent under the intermittent ponding flow regime than that of the steady state-unsaturated flow regime. This may be due to the particular characteristics of the intermittent ponding conditions. During the relatively short infiltration period tracer solution was rapidly transmitted through the more conductive pore networks. During the longer quiescent period, molecular diffusion along concentration gradients drove the tracers into the less conductive pores. Consequently, the influent from subsequent ponds was less efficient in flushing both tracers through the column lengths. This resulted in jagged and wide BTCs peaks for both tracers in the in situ soil columns.

Retardation factors derived from batch isotherms were reasonably good predictors of transport of the mildly adsorbed bromacil through the presumably homogenous soil profile of both column types during unsaturated steady state flow. Under intermittent ponding conditions, the transient flow conditions may have prevented bromacil adsorption to reach equilibrium. Therefore bromacil may have been less retarded than expected, especially during the first few hours after the initial pond was applied. At the onset of the first ponding event transport was dominated by rapid advective processes preventing adsorption equilibrium. Molecular diffusion and concentration gradients were dominant during the long time intervals between ponds, when column drainage was minimal. During minimal drainage, when both tracers were transmitted into the relatively smaller pores, bromacil adsorption was able to come to equilibrium. This gave rise to high R_fs that underestimated initial arrival times of the bromacil, yet still described adequately the movement of the bromacil peak.

In conclusion, preferential flow processes must be considered when predicting the fate and transport of chemical spills or fertilizers and pesticides, applied on the surface of seemingly homogeneous soils. Given the existence of preferential flow, a steady state-unsaturated flow regime is more efficient than intermittent ponding at transporting the bulk of a surface applied miscible solute deep and uniformly within a soil profile. Under intermittent ponding, rapid vertical movement of the ponded water during the infiltration period is followed by lateral movement during the quiescent period into the less conductive regions of the soil. Under these conditions, preferential flow can cause an accelerated first appearance of a small portion of the surface applied miscible solute deep in the soil profile. Because a large portion of the water bypasses the less conductive regions, subsequent ponds are less efficient in flushing newly-introduced solute from these areas. As a result, under intermittent ponding, transport of the bulk of the chemical may significantly lag behind its leading edge.

The results of this study are;

+ a homogeneous soil profile may have significant structural characteristics that promote preferential flow under steady state-unsaturated and intermittent ponding irrigations, with preferential flow most pronounced for intermittent ponding,
+ adsorption equilibria along preferential flow paths may not be reached during a rapid infiltration phase, therefore, retardation factors used to predict solute transport may be inaccurate,
+ under certain conditions, preferential flow processes make intermittent ponding less efficient in moving a surface applied chemical through a soil profile.

5. RECOMMENDATIONS

It is speculated that entrapped air affected, to some extent, the infiltrating properties of these columns. This was first suspected when the small amount of tracer solution added to each column during the steady state-unsaturated flow experiment caused an immediate increase in matric potentials throughout the entire length of all columns. Because only a small amount of fluid was added at that time, 49 to 51 mL depending on the column type, entrapped air was the only reasonable explanation. The slow infiltration rates during the intermittent ponding flow regimes of the repacked columns was considered to be partially caused by air entrapment. Therefore, venting of the columns, done between the two flow regimes, as an afterthought, was later considered inadequate. McWhorter (1971) and Peck (1965) have reported the dramatic affects of entrapped air when undertaking columns studies. It is suggested that further experiments employ their recommendations in order to alleviate this problem.

Infiltration times of the ponded leaching solution into each column should be carefully recorded. These times are necessary in order to use more sophisticated and appropriate models (for example HYDRUS, Hydrogeolic Inc., Herndon, VA) for the transient ponding condition.

The 3 percent KOH added to increase the solubility of m-TFMBA and bromacil in the tracer batch solution resulted in a pH of $\simeq$ 13. These high pHs may have altered the soil chemistry enough at the surface to cause possible release of colloidal material, dissolution and desorption of other chemicals. These could have interacted with the applied tracers causing less than adequate mass balances. It is recommended that the percentage of KOH used to dissolve both tracers be lowered from 3 to less than .5 percent. The lower KOH is still effective in causing both tracers to be easily dissolved, yet will be within the range of the soil buffering capacity when applied at the surface.

APPENDICES

A. Soil Characteristics of Casa Grande Sandy Clay Loam

The soil used for this study was a Casa Grande deep sandy clay loam (fine-loamy, mixed, hyperthermic Typic Natrargrids) well drained, and slowly permeable located at the Maricopa Agricultural Center of the University of Arizona in Central Arizona. From 0-30 cm depths it is a brown to reddish brown sandy loam to sandy clay loam. From 30-60 cm depths the soil is considered to be a reddish brown sandy clay loam. Calcium carbonate is found in this horizon and increases with depth. It is one of three soil series found at this site (sandy loam, sandy clay loam, and clay loam suites). These soils were formed on Holocene age alluvium overlying a Pleistocene age basin floor. Prior to land-leveling and agricultural reclamation this soil was strongly saline and sodic which probably resulted from a fluctuating water table during the mid-Holocene. Soils in this suite were affected in development by low energy, depositional water flowing near braided channels of the Santa Cruz Wash. This wash has been channelized into one large channel which serves as a drain for overland flow and irrigation tail waters on the farm and surrounding lands (Post, et al. 1988). The following is an abbreviated table of soil parameters found by Post et al. that were pertinent to this study.

Table 16. Soil Characterization of Casa Grande Soil from Maricopa Experimental Farm, Arizona (Post, 1988)

	Textural Class			
	SL, SCL	SL, SCL	SCL	SCL
Depth - cm	0 - 30	30 - 70	0 - 30	30-70
Sand - %	55-65	55-65	45-55	45-55
Clay - %	15-22	15-22	22-27	22-27
Total Pore Space - %	7.0 to 9.0	7.0 to 9.0	10.0 to 10.5	1.45 to 1.55
%Water				
-.1 Bar	16.0 to 22.0	16.0 to 22.0	18.0 to 23.0	18.0 to 23.0
-.15 Bars	12.0 to 18.0	12.0 to 18.0	16.0 to 19.0	16.0 to 19.0
-.33 Bars	7.0 to 9.0	7.0 to 9.0	10.0 to 10.5	10.0 to 10.5
Organic Matter %	.5 - .7	.1 - .3	.8 - 1.2	.2 - .4
$CaCO_3$ - %	3-5	4-20	3-5	5-20
CEC meq/100 gr	9-13	8-12	13-16	12-15

B. Determination of Soil Moisture Characteristic Curve for Casa Grande Soil Samples

Determination of the soil moisture characteristic curve for the soil used in this study employed a Tempe Pressure Cell (TPC) soil moisture extractor (Soilmoisture Equipment Corp. P.O. Box 30025, Santa Barbara, CA). The soil cores were obtained using a ring sampler and soil core extractor. Samples were taken from depths of 7.62, 15.24, 22.86, and 30.48 centimeters along the irrigated buffer zone of plot F-5 (see Section 2.1, Figure 2). The ring samplers, each containing an intact soil core, were transported to the lab for moisture vs pressure analysis. (Soil moisture measurements from the sample taken at the 15.24-cm depth had to be thrown out as the TPC used for these measurements had a cracked porous plate.) Each ring with soil core was placed on a presaturated porous plate located at the bottom half of the TPC. The soil within each ring was saturated with deaired water from the bottom up through the lower drain tube of the TPC. Each sample was considered saturated when a very slight water wet sheen was observed on the upper surface of the soil sample. The TPC cover was then put on, the bottom drain tube filled with deaired water, and the entire assemblage weighed on a Mettler balance.

A positive pressure potential was applied to each cell through the top pressure inlet tube. Pressures were regulated using two nullmatic pressure regulators connected in a series. A Victor Equipment Co. model no. 4TS-450-D positive pressure regulator (Moore Products Co., Spring House, PA) was used to regulate the supply pressure to a Wilkerson (Soilmoisture Equipment Corp, Santa Barbara, CA) regulator. This second regulator supplied the prescribed pressure, via a manifold, to each cell. Pressures were measured using a Soil Moisture System pressure gauge (Soilmoisture Equipment Corp, Santa Barbara, CA) coupled with a transducer interfaced to a Tensicorder signal conditioner (Soil Measurement Systems, Tuscon, AZ).

Prescribed pressures applied were 14, 30, 40, 60, 80, 100, 150, 200, 300, 400, 500, 600, 700, 800, and 900 mBars. The cells were weighed 24 to 36 hours after each pressure application. Before each weighing the bottom drain tube was filled with deaired water. Equilibrium between pressure applied and soil moisture was considered to have been achieved when there was a constant weight between two consecutive readings. Pressure applied to the cells were then raised to the next prescribed value. The same procedure was followed to determine the water loss that occurred at that given pressure. This process was continued up to pressures of 900 mBars. The moisture content of the soil for each applied pressure was determined using the pressure vs. equilibrium weight values. The positive pressures applied were correlated to soil moisture tensions (negative pressures) that would exist in a draining soil. Pressure (as tensions) vs moisture contents are given in the Table 17.

Table 17. Moisture Content vs. Applied Pressure of Casa Grande Soil Samples

	θ		
		Cell # Sample depth	
Pressure mBars (cm of water)	# 2 7.62	# 3 22.84	# 4 30.48
0 (0.0)	.2941	.2913	.3075
14.0 (14.28)	.2915	.2906	.2958
30.0 (30.60)	.2850	.2803	.2912
40.0 (40.80)	.2817	.2754	.2726
60.0 (61.20)	.2747	.2599	.2562
80.0 (81.60)	.2715	.2457	.2422
100.0 (102.0	.2672	.2402	.2345
150.0 (153.0)	.2499	.2200	.2190
200.0 (204.0)	.2344	.2105	.2087
300.0 (306.0)	.2225	.2002	.2017
400.0 (408.0)	.2145	.1921	.1959
500.0 (510.0)	.2106	.1907	.1920
600.0 (612.0)	.2086	.1872	.1894
700.0 (714.0)	.2045	.1855	.1861
800.0 (816.0)	.2037	.1840	.1847
900.0 (918.0)	.1957	.1793	.1812

C. Saturated and Unsaturated Hydraulic Conductivity Values

Saturated hydraulic conductivities, K_{sat}, were determined using a constant head tank. These values were later used as input parameters in order to determine unsaturated hydraulic conductivities, K_{unsat}. In situ and repacked soil samples were used. The in situ samples were taken at the SE portion of the site. K_{sat} values for the repacked samples were done and used as a general comparison between those found from the in situ soil samples. The repacked samples used soil that was taken from the SW and NW corner of the site and were packed to the same bulk density as the repacked columns used for this experiment. Tables 12 thru 24 lists these values.

Table 18. Saturated Hydraulic Conductivity Values, K_{sat}, from Constant Head Tank for SE In Situ Soil Sample taken at 3.0 -cm Depth

Temp Water (C)	Tank Head (-cm)	Sample Head (-cm)	Flow Volume (cm^3)	Flow Time (seconds)	K_{sat} (cm/sec)	Corrected K_{sat} 20°C (cm/sec)
23.5	2.7	5.7	3.1	11208	2.40E-5	2.19E-5
24.0	2.7	5.4	1.8	9684	1.79E-5	1.61E-5
24.0	2.7	5.4	1.2	6378	1.81E-5	1.63E-5
23.5	2.6	5.4	1.0	5452	1.70E-5	1.55E-5
23.5	2.7	5.5	1.2	5951	1.84E-5	1.68E-5
23.0	2.6	5.6	.5	3083	1.40E-5	1.30E-5
23.5	2.7	2.5	1.1	6692	1.53E-5	1.39E-5
23.5	2.5	5.5	.6	3353	1.55E-5	1.41E-5

K_{unsat} values were determined using van Genuchten's FORTAN 77 code and the θ-Ψ curve from the soil samples used to determine the soil moisture characteristic curve as described in Appendix B. These are listed in Table 25.

Table 19. Saturated Hydraulic Conductivity Values, K_{sat}, from Constant Tank for SE In Situ Soil Sample taken at 8.0 -cm Depth

Temp Water (C)	Tank Head -cm	Sample Head (-cm)	Flow Volume (cm^3)	Flow Time (seconds)	K_{sat} (cm/sec)	Corrected K_{sat} 2°C (cm/sec)
24.5	2.7	5.6	13.1	3851	3.14E-4	2.83E-4
24.0	2.7	5.5	8.5	2506	3.15E-4	2.83E-4
23.5	2.7	5.5	10.2	2593	3.63E-4	3.31E-4
23.5	2.6	5.3	16.8	3874	4.25E-4	3.88E-4
23.0	2.7	5.4	14.9	3135	4.41E-4	4.08E-4
23.5	2.6	5.4	16.1	4061	3.75E-4	3.42E-4
23.5	2.7	2.5	9.92	2440	3.53E-4	3.22E-4

Table 20. Saturated Hydraulic Conductivity Values, K_{sat}, from Constant Tank for SE In Situ Soil Sample taken at 32 -cm Depth

Temp Water (C)	Tank Head -cm	Sample Head (-cm)	Flow Volume (cm^3)	Flow Time (seconds)	K_{sat} (cm/sec)	Corrected K_{sat} 20°C (cm/sec)
23.5	2.7	5.4	35.9	3541	9.76E-4	8.90E-4
24.0	2.7	5.4	37.8	3702	9.83E-4	8.84E-4
24.0	2.7	5.5	23.0	2359	9.05E-4	8.14E-4
23.5	2.6	5.3	22.4	2515	8.57E-4	7.82E-4
23.5	2.7	5.4	32.5	4802	6.39E-4	5.84E-4
23.0	2.6	5.0	14.4	1891	8.24E-4	7.63E-4
23.5	2.7	4.8	30.6	4097	9.24E-4	8.43E-4
23.5	2.5	5.5	20.4	2293	7.84E-4	7.15E-4

Table 21. Saturated Hydraulic Conductivity Values, K_{sat}, from Constant Tank for Repacked Soil Samples taken at NW Location

Temp Water (C)	Tank Head -cm	Sample Head (-cm)	Flow Volume (cm^3)	Flow Time (seconds)	K_{sat} (cm/sec)	Corrected K_{sat} 2°C (cm/sec)
23.5	2.7	5.4	12.1	5733	2.03E-4	1.85E-4
24.0	2.7	5.2	18.5	9481	2.03E-4	1.83E-4
24.0	2.7	5.15	12.3	6451	2.02E-4	1.82E-4
23.5	2.6	5.2	10.3	5414	1.90E-4	1.74E-4
23.5	2.7	5.1	7.4	3819	2.05E-4	1.88E-4
23.0	2.6	5.05	5.9	3043	2.06E-4	1.90E-4
23.5	2.7	5.0	13.6	6599	2.33E-4	2.12E-4
23.5	2.5	5.2	6.9	3265	2.03E-4	1.86E-4

Table 22. Saturated Hydraulic Conductivity Values, K_{sat}, from Constant Tank for Repacked Soil Samples taken at NW Location

Temp Water (C)	Tank Head -cm	Sample Head (-cm)	Flow Volume (cm^3)	Flow Time (seconds)	K_{sat} (cm/sec)	Corrected K_{sat} 20°C (cm/sec)
23.5	2.7	5.4	23.4	5814	3.84E-4	3.50E-4
24.0	2.7	5.55	6.8	9541	6.50E-5	5.85E-5
24.0	2.7	5.4	4.7	6419	7.05E-5	6.34E-5
23.5	2.6	5.4	4.2	5468	7.107-5	6.54E-5
23.5	2.7	5.5	3.2	3785	7.71E-5	7.05E-5
23.0	2.6	5.5	2.5	3058	7.32E-5	6.78E-5
23.5	2.7	5.4	5.6	6622	8.14E-5	7.43E-5
23.5	2.5	5.4	2.9	3339	7.78E-5	7.10E-5

Table 23. Saturated Hydraulic Conductivity Values, K_{sat}, from Constant Tank for Repacked Soil Samples taken at SW Location

Temp Water (C)	Tank Head -cm	Sample Head (-cm)	Flow Volume (cm^3)	Flow Time (seconds)	K_{sat} (cm/sec)	Corrected K_{sat} 20°C (cm/sec)
23.5	2.7	5.5	11.5	4446	2.40E-4	2.19E-4
24.0	2.7	5.6	33.5	9456	2.92E-4	2.63E-4
24.0	2.7	5.25	22.7	6489	3.08E-4	2.77E-4
23.5	2.6	5.4	19.8	5392	2.947-4	2.68E-4
23.5	2.7	5.5	14.9	3785	3.34E-4	3.05E-4
23.0	2.6	5.5	11.3	3015	3.14E-4	2.91E-4
23.5	2.5	5.5	24.7	6540	3.38E-4	3.09E-4
23.5	2.7	5.5	8.4	2291	3.18E-4	2.90E-4

Table 24. Saturated Hydraulic Conductivity Values, K_{sat}, from Constant Tank for Repacked Soil Samples taken at SW Location

Temp Water (C)	Tank Head -cm	Sample Head (-cm)	Flow Volume (cm^3)	Flow Time (seconds)	K_{sat} (cm/sec)	Corrected K_{sat} 2°C (cm/sec)
23.5	2.7	5.35	31.8	3693	8.60E-4	7.85E-4
24.0	2.7	5.6	36.5	3748	8.72E-4	7.85E-4
24.0	2.7	5.25	25.0	2410	1.06E-4	9.51E-4
23.5	2.6	5.4	26.3	2490	9.80E-4	8.94E-4
23.5	2.7	5.5	27.4	2110	1.148-3	1.03E-3
23.0	2.6	5.5	25.0	1912	1.17E-3	1.08E-3
23.5	2.5	5.5	28.5	2306	1.07E-3	9.77E-3
23.5	2.7	5.5	33.0	2627	1.17E-3	2.90E-3

Table 25. Unsaturated Hydraulic Conductivities for In Situ Soil Samples using van Genuchten code.

Depth from Soil Surface					
8 -cm		23 -cm		30 - cm	
log Tension (cm of water)	log K (cm sec^{-1})	log Tension (cm of water)	log K (cm sec^{-1})	log Pressure (cm of water)	log K (cm sec^{-1})
4.883	-16.796	3.988	-13.854	4.768	-14.707
4.487	-15.251	3.693	-12.511	4.334	-13.086
4.091	-13.707	3.398	-11.169	3.9	-11.465
3.694	-12.162	3.103	-9.826	3.466	-9.844
3.462	-11.258	2.93	-9.04	3.212	-8.896
3.297	-10.616	2.806	-8.482	3.031	-8.223
3.169	-10.118	2.71	-8.049	2.89	-7.7
3.064	-9.711	2.631	-7.694	2.775	-7.273
2.975	-9.366	2.564	-7.394	2.678	-6.911
2.897	-9.067	2.505	-7.133	2.593	-6.598
2.827	-8.802	2.452	-6.902	2.517	-6.32
2.765	-8.565	2.405	-6.696	2.449	-6.072
2.708	-8.35	2.361	-6.508	2.387	-5.847
2.655	-8.154	2.32	-6.336	2.33	-5.641
2.606	-7.972	2.283	-6.177	2.277	-5.45
2.56	-7.803	2.247	-6.03	2.227	-5.274
2.517	-7.645	2.213	-5.892	2.179	-5.108
2.475	-7.497	2.181	-5.762	2.135	-4.953
2.435	-7.357	2.149	-5.64	2.092	-4.807
2.397	-7.224	2.119	-5.523	2.05	-4.668
2.36	-7.098	2.09	-5.413	2.01	-4.535
2.324	-6.977	2.061	-5.307	1.972	-4.409
2.288	-6.861	2.033	-5.205	1.934	-4.288
2.254	-6.75	2.005	-5.108	1.896	-4.171
2.219	-6.642	1.977	-5.014	1.859	-4.059
2.185	-6.538	1.949	-4.834	1.823	-3.95
2.15	-6.347	1.921	-4.834	1.786	-3.845
2.116	-6.339	1.893	-4.748	1.749	-3.742
2.081	-6.343	1.864	-4.665	1.712	-3.641
2.045	-6.149	1.835	-4.582	1.674	-3.543
2.008	-6.056	1.804	-4.501	1.635	-3.446
1.97	-5.965	1.772	-4.421	1.594	-3.35
1.929	-5.874	1.739	-4.343	1.552	-3.256
1.887	-5.784	1.703	-4.264	1.507	-3.161
1.841	-5.693	1.64	-4.186	1.458	-3.066
1.79	-5.601	1.621	-4.106	1.405	-2.97
1.733	-5.508	1.572	-4.026	1.345	-2.872
1.666	-5.411	1.444	-3.943	1.275	-2.77
1.583	-5.308	1.348	-3.856	1.189	-2.662
1.472	-5.195	1.191	-3.761	1.073	-2.399
1.291	-5.06	1.038	-3.651	0.884	-2.399
1.114	-4.971		-3.58	0.7	-2.303

D. Tensiometer Construction

The tensiometers used in each column were constructed of three parts; a 8-cm long by .5-cm diameter, 1 Bar high flow, straight walled porous cup (Soilmoisture Equipment Corp., Santa Barbara, CA), a .952-cm nylon barbed elbow (Cole-Parmer, Chicago, IL) and a .5-cm diameter by 4-cm long clear acrylic tube. The interior of one end of the acrylic tubing had been threaded a distance of 1-cm from the edge using a tap. This screwed over one end of the nylon barb, which had been threaded on the outside perimeter, a distance of 1-cm from the edge, with a dye. The junction between the tubing and the elbow was coated with Two-Ton epoxy (Devcon Corp., Danvers, MA). The elbow was placed so that the epoxy flowed down filling and sealing the overlapping edges of the two pieces. The epoxy was allowed to dry for 24 hours.

The porous straight walled cup was coated from the noncupped end toward the cup end with the Two-Ton epoxy, leaving the last 2 cm epoxy free. The open end of the porous cup was inserted 1.5-cm into the free end of the elbow. The three piece unit was allowed to dry for 48 hours with the porous cup end vertically positioned. This allowed the glue to flow down the shaft of the straight wall cup, filling and sealing the gap connecting the two. The acrylic tubing end of the assembled unit was capped with a small rubber septum (Soil Measurement Systems, Tucson, AZ).

After all parts were dry the unit was soaked and filled with deaired water as prescribed by Cassel and Klute (1986). The tensiometer was checked for sluggishness and/or leaks by applying a positive or negative pressure, with the porous cup submerged in deaired water. Pressures of up to +400 mBars and -750 mBars were applied using a syringe with attached needle inserted through the septum. The procedure was repeated with the entire unit submerged in deaired water. Air bubbles entering or exiting the tensiometer were checked for and indicated leaks. Appropriate repairs were made on any suspected leaking joints.

During the period of the steady state-unsaturated flow experiment a pinkish slimy mass was noted as developing inside several of the tensiometers and lines of urethane tubing. It was suspected that the slime was the product of some unknown microorganism growing in the system (T. L. Kieft, 1990, personnel communication). Attempts to flush this from the system were futile while the first flow regime was in progress (steady state-unsaturated flow). The entire system was thoroughly flushed, at the end of the first flow regime, to rid it of this foreign substance. This flushing process eventually clogged the tiny channels of the fluid switch wafer, thus requiring cleaning. To prevent this from occurring during the second flow regime the tensiometers and urethane lines were filled with a 10 mg/L NaN3 concentration of deaired water which served as a mild antiseptic. This mild concentration seemed to eliminate the problem.

E. Calibration of Druck Pressure Transducer

The Druck PDCR22 (Druck Incorporated, New Fairfield, CN) is a high quality, strain gauge, differential, pressure transducer using a single silicon crystal diaphragm as the pressure sensor. The diaphragm is mounted on the transducer nose which minimizes the traveling volume of the rotary pressure collector used on the fluid switch wafer. The operating range of the transducer is +/- 5 psi corresponding to a 50 millivolt (mV) output.

Calibration of the transducer was done using the following equipment: a water manometer, variably placed hanging water column, Tensicorder pressure transducer and accompanying signal conditioner (Soilmeasurement Systems, Tuscon, AZ), Duragauge pressure gauge, Moore vacuum pressure regulator model series 44-2, Moore air filter (Moore Products Co., Spring House, PA), Victor Equipment Co. positive pressure regulator model no. 4TS-450-D, (Thermodyne Industries Inc., Denton, TX) RTD Series 500 A/D Converter board (Real Time Devices, State College, PN), and an IBM XT personal computer. mV output on the A/D converter board was cross-checked using a Fluke (John Fluke Mfg. Co. Inc., Everett, WS) multimeter.

Separate calibrations were done against the Tensicorder, hanging water column, and the water manometer. Pressures created using a pressurized in house air line were measured and cross checked using the water manometer and Tensicorder. These were compared with the mV output generated by the transducer. The hanging water column was positioned at several elevations above and below the transducer thus inducing a specific mV output corresponding to each elevation. Calibrations against the Tensicorder were thrown out because a strong hysterisis was seen. It was necessary to determine which instrument, if not both, produced this hysterisis. A hysterisis check for the Druck transducer was done against the water manometer. Pressure sequences going from positive pressures stepping down incrementally to atmospheric, then going from negative pressures and incremental stepping up to atmospheric pressure, were compared to mV output. A similar sequence was done going from atmospheric pressure to positive and negative pressures. Linear regressions were done on all data points. These are listed in table 26.

As a monitor of the transducer accuracy and continual calibration during the experiment, three hanging columns were positioned so that the menisci were 158.8 and 38.4-cm above and 71.4 below the center line of the pressure transducer. One water column was positioned with its meniscus at the same elevation as that of the transducer center. Urethane lines emanating from the bottom of each column were hooked up to the fluid switch wafer. These columns were used as continual calibrations of the mV output for every revolution of the scanning fluid switch wafer. A liner regression was done on the four elevations of the water columns and is also listed in table .

There was approximately a 3 mV zero offset difference (y-intercept) between the previously done calibrations and those using the water columns attached to the fluid switch wafer. The differences was attributed to some idiosyncracies, causing slight change in mVolt output, arising when the transducer was attached to all 24 water filled lines hooked up to the fluid switch wafer, giving a slight constant background pressure applied to the transducer.

Table 26. Calibration and Hysterisis Check for Druck Pressure Transducer

Pressure Applied to Manometer	Slope	Y-int	Correlation
atm to "-"	6.959	7.794	.999
atm to "+"	6.938	6.552	1.0
"-" to atm	6.946	6.629	1.0
"+" to atm	6.916	7.095	1.0
Elevated Water Column of Varying Heights	6.692	7.735	.995
Stationary Hanging Water Columns Attached to Scanivalve	7.145	3.42	.999

F. Data Acquisition System

Each tensiometer was retrofitted to a data acquisition system in order to facilitate accumulation of pressure readings every 30 minutes. All tensiometers had a 1.59-mm O.D. urethane tubing inserted through its septum and glued in place with Hardman urethane glue (Hardman Inc. Belleville, NJ). The other end of the tubing was connected to one of 24 ports of a scanning fluid switch wafer (Scanivalve, San Diego, CA). The tensiometers and tubing were filled with deaired water with care taken to eliminate any air bubbles or pockets. Each tensiometer septum had an 18 gauge hypodermic needle inserted through its septum. A 1-way stopcock was connected to the top of each needle using a luer fitting. This stopcock facilitated purging the tensiometer and scanivalve lines of any bubbles that might accumulate.

The fluid switch wafer is equipped with a water filled collection port (attached to a collection line), that when rotated from port to port on command, equilibrates with the pressure within that port. The equilibrated pressure of the collection line is sensed by a Druck PDCR22 strain gage pressure transducer (see Appendix E) referenced to ambient air pressure. The transducer uses a 12 V DC excitation power supply which causes it to emit output voltages ranging from ± 50 mV. The transducer was mounted to a zero volume pressure transducer adapter (Scanivalve Corp.. San Diego, CA). The adapter enables mounting of the 1.59-mm collector tube to the transducer with a minimum volume between the two. It is equipped with a bleed valve which enables purging of air from the water filled lines.

Small voltage outputs from the transducer are sensitive and proportional to pressure changes within the collection line (see Table 26, Appendix E). The voltage output is transmitted to a IBM PC where it is digitized using a RTD A/D 500 12-BIT analog input board (Real Time Device, INC., Sate College, PN). The A/D 500 board served as a signal conditioner and amplifier as well.

Control of the board, rotation of the fluid switch wafer, and data storage within the computer was done using a Turbo Pascal program (given at the end of this appendix). The program is loaded in the computer and activated by typing the word "Kathy" at the C:\ prompt. After which the computer asks the user to insert a floppy disk (on which data is collected), name of the new data file, time between one complete rotation of the fluid switch wafer, and number of ports to be read. The output file, in mVolts, for each rotation is written to the screen. Data is stored on the floppy disk and is of the following format.

	mV Output From Each Port			
(yearmonthday.time)	1	2	3	24

The data file set up so that it can be manipulated when imported into LOTUS 123.

A schematic of the connections between the computer, transducer, Scanivalve and controller are given in Figure 32. Connections 5, 8, and 9 transmit signals from the computer to the Scanivalve controller. Signals for the fluid switch wafer to advance one port at a time and/or to the home port (port 3) are transmitted through connections 8 and 9, respectively. Ground is connection 5. Connections 7 transmits the home and step signal from the Scanivalve controller to the fluid switch wafer. Connections 3 and 4 are power supply connections, 5 serves as a ground for the fluid switch wafer. Two nonpolarized, tantalum 50 V capacitors had to be mounted between connection 5-8, and 5-9. This attenuated any unwanted electrical pulses generated from the syringe pump, fraction collectors, and other appliances within the lab from triggering an unwanted signal (through the controller) causing the fluid switch wafer to advance.

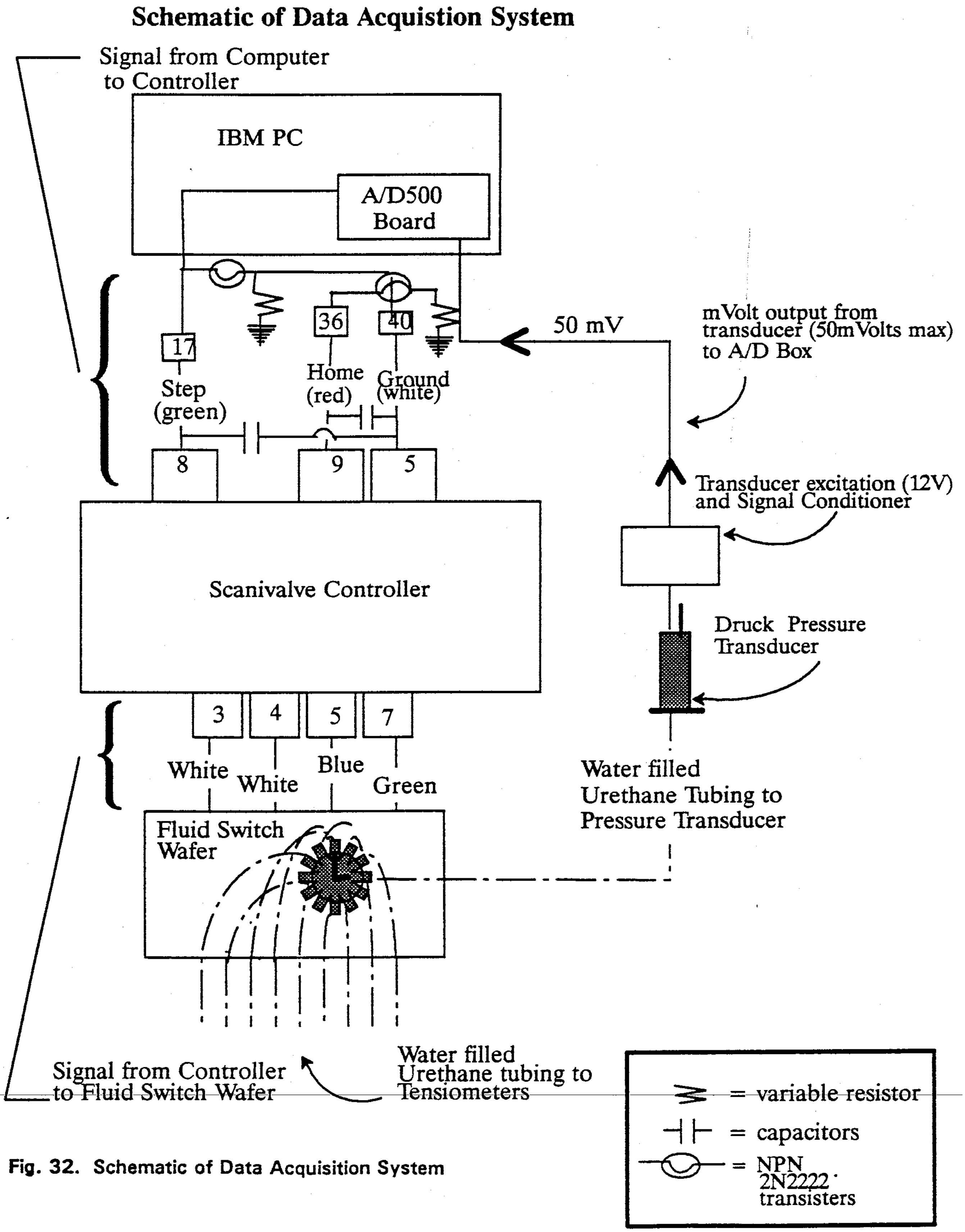


Fig. 32. Schematic of Data Acquisition System

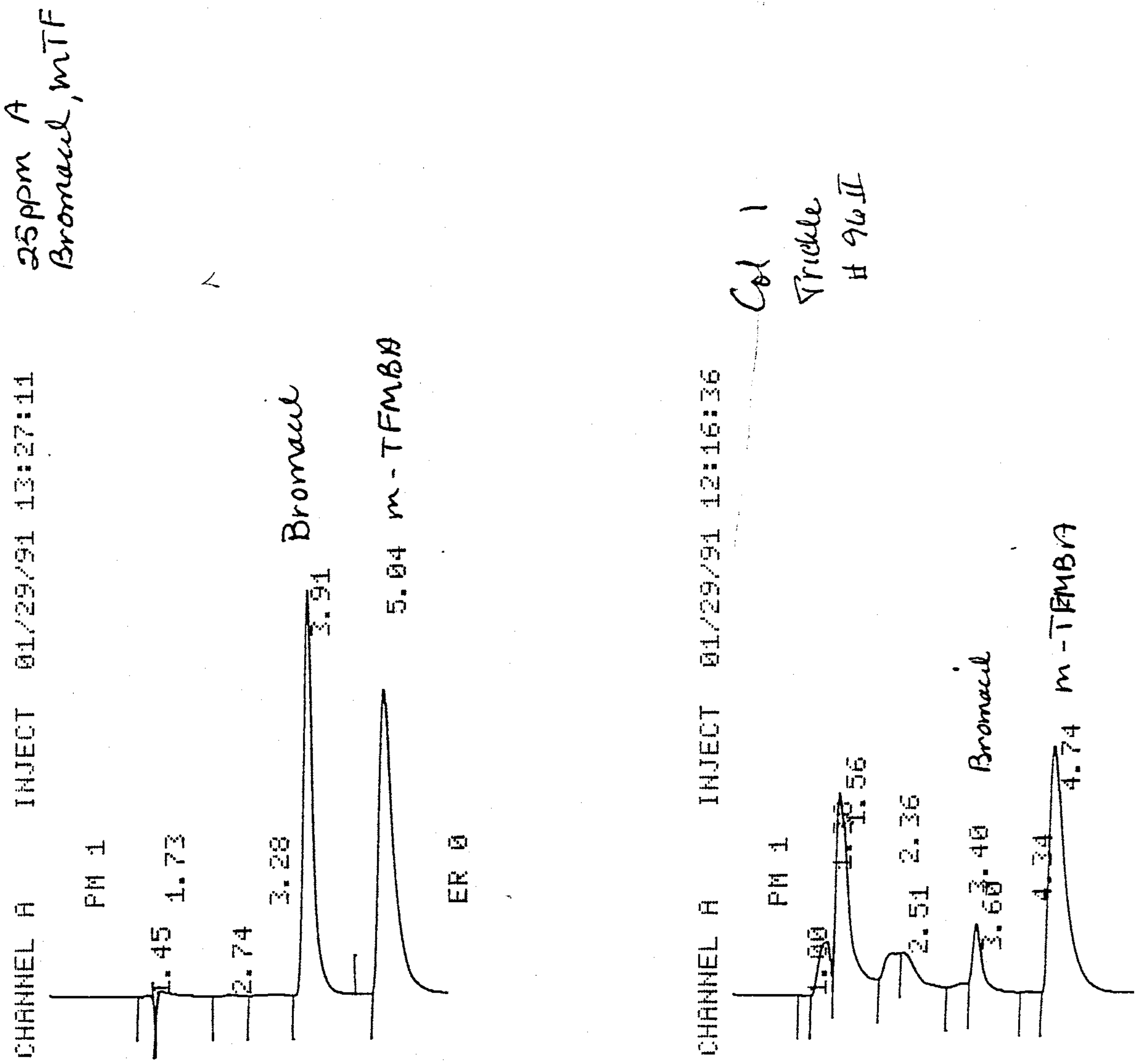
```
{  THIS PROGRAM CONTROLS AN AD500 I/O BOARD OPERATING A
{  SCANIVALVE STEPPING VALVE READING A PRESSURE XDUCER.
{  THE USER IS ASKED FOR NUMBER OF CHANNELS TO READ AND
{  TIEM TO WAIT BETWEEN READINGS.
{  DATA IS RECORDED TO DISK.
{   }
{   }
{            Jim Ruff - 7.15.90          }

PROGRAM kathy(input,output);
USES DOS,CRT,DTIME;
{$I VOLTS.PSL}      {adc(addr,reading:integer) takes a readi
{$I INIT.PSL}       {init(addr:integer) initializes a/d}
{$I MUX.PSL}        {Selects an A/D Channel}
{$I PGA.PSL}        {Sets Programmable Gain}
{$I AINIT.PSL}      {Starts data conversions}
{$I ADONE.PSL}      {Stops data conversions}

{N-}
const base = $280;                                   {AD500 addre
      Gain = 100;                                    {AD500 Gain}
      waittime: array[1..24] of word = (2000,2000,2000,10000
                                        2000,2000,2000,10000
                                        2000,2000,2000,10000
                                        2000,2000,2000,10000
                                        2000,2000,2000,10000
                                        2000,2000,2000,10000
VAR
   OUT                      : STRING[20];           {Output file
   F                        : TEXT;
   t,d                      : REAL;                 {Time & Dela
   V                        : REAL;                 {Voltage}
   numch,i                  : Byte;                 {Number of G
   p                        : Byte;                 {Register in
   x,ss                     : string;               {Operator In
   code                     : integer;
   dirinfo                  : searchrec;

PROCEDURE STEP;
BEGIN
     p := port[base+1];                        {Read port B register
{     writeln(#7);     writeln(#7);  }                       {BEEP}
     Port[base+1] := (p or $20);               {Set PB3 High to trig
     delay(100);                               {Wait 100 msec}
{     writeln(#7);    }                        {BEEP}
     Port[base+1] := (p and $DF);              {Restore PB3}
END;

PROCEDURE HOME;
BEGIN
     p := port[base+1];                        {Read port B register
     Port[base+1] := (p or $10);               {Set PB4 High to trig
     delay(100);                               {Wait 100 msec}
{     writeln(#7);         }
     Port[base+1] := (p and $EF);              {Restore PB4}
     delay(5000);                              {Homing Time}
END;
```

```
{    THIS UNIT READS THE SYSTEM CLOCK AND RETURNS    }
{    THE DECIMAL DAY OF THE YEAR.                    }
{    TO USE IN PROGRAMS, USE FUNCTION "TIME".        }
{    JIM RUFF    10/26/88                            }

UNIT DTIME;
INTERFACE
USES DOS;
function time   :  real;
function tstamp:  string;

IMPLEMENTATION
VAR
   YR,MO,DT,DOW,HR,MIN,SEC,SEC100:word;

function time   :  real;
BEGIN
     GETDATE(YR,MO,DT,DOW);
     GETTIME(HR,MIN,SEC,SEC100);
     if (mo = 1) or (mo = 2) then
        time := dt + (mo-1)*31 + (hr + min/60.0 + sec/3600.0
     if (mo = 3) or (mo = 4) then
        time := dt - 3 + (mo-1)*31 + (hr + min/60.0 + sec/36
     if (mo = 5) or (mo = 6) then
        time := dt - 4 + (mo-1)*31 + (hr + min/60.0 + sec/36
     if (mo = 7) or (mo = 8) or (mo = 9) then
        time := dt - 5 + (mo-1)*31 + (hr + min/60.0 + sec/36
     if (mo = 10) or (mo = 11) then
        time := dt - 6 + (mo-1)*31 + (hr + min/60.0 + sec/36
     if (mo = 12) then
        time := dt - 7 + (mo-1)*31 + (hr + min/60.0 + sec/36
end;

function tstamp:  string;
var y,m,d,h,mi,s : string;
begin
     GETDATE(YR,MO,DT,DOW);
     GETTIME(HR,MIN,SEC,SEC100);
     str(yr,y);
     str(mo,m);  if length(m) < 2 then m := '0'+m;
     str(dt,d);  if length(d) < 2 then d := '0'+d;
     str(hr,h);  if length(h) < 2 then h := '0'+h;
     str(min,mi);  if length(mi) < 2 then mi := '0'+mi;
     str(sec,s);  if length(s) < 2 then s := '0'+s;
     tstamp := y+m+d+'.'+h+mi+s;
END;
END.
```

```
PROCEDURE SAMPLE;
BEGIN
     t := time + d;                   {Set timer for next re
     home;                            {Home the Scanivalve}
     append(f);                       {Open disk file for ap
     write(f,tstamp);              {Write timestamp to disk}
     write(tstamp);                {Write timestamp to CRT}
     for i := 1 to numch do           {Step thru all pressur
     begin
          Step;                        {Steps scanivalve}
          delay(2500);                 {waits for prs. to se
          Volts(Base,Gain,V) ;         {Read Voltage}
          delay(200);
          write(f,V:9:3);            {Write Voltage to disk}
          write(V:9:3);              {Write Voltage to scree
          if (i mod 4 = 0) then writeln;  {New Line}

          delay(waittime[i]);                        {Settlin
     end;
     writeln(f,'');                   {Linefeed}
     writeln('');                     {Linefeed}
     close(f);
END;

PROCEDURE WAIT;
BEGIN
     repeat                           {Hang around until rea
     until (time > t) or keypressed;
END;

BEGIN
     textattr := $0F;
     CLRSCR;
     gotoxy(2,1);     write('Insert Data Disk Now! ',#7);
     gotoxy(2,2);     write('Enter Time Between Readings <15
     gotoxy(44,2);    readln(x);
     if x = '' then d := 15 else val(x,d,code);
     d := d/60/24;                                  {Convert

     repeat
      gotoxy(2,3);     clreol;
      write('Enter Data File Name <test.fil>:');
      gotoxy(36,3);    readln(x);
        if x = '' then x := 'test.fil';
        findfirst(x,anyfile,dirinfo);
        if doserror = 0 then begin
           writeln(#7);
           ss := 'N';
           gotoxy(2,3);    clreol;
           write(x,' already exists. OK to overwrite?');
           readln(ss);    if ss = 'y' then ss := 'Y';
        end;
        gotoxy(2,3);    clreol;
        writeln('FileName: ',x,', ErrorCode: ',doserror);
     until (doserror = 2) or (doserror = 18) or (ss = 'Y');
     assign(f,x);
```

```
     rewrite(f);

     gotoxy(2,4);      write('Enter Number of Ports <1>:');
     gotoxy(36,4);     readln(x);
     if x = '' then numch := 1 else val(x,numch,code)    ;

     gotoxy(2,24);     writeln('Press any key to abort test')
     textattr := $0F;
     window(2,6,79,23);
     clrscr;

     Init(base);            {Initialize the D/A.}
     Ainit(base);           {Start Conversion}
     Mux(base,1);           {Select Channel 1.}
     PGA(base,Gain);        {Select gain.}

     repeat
       Sample;                {Read all pressures.}
       Wait;                  {Delay till next read.}
     until keypressed;
     Adone(base);             {Stop Conversion}
end.
```

H. HPLC Sample Chromatograms for Bromacil and m-TFMBA



Chromatograms were done within 45 minutes of one another.

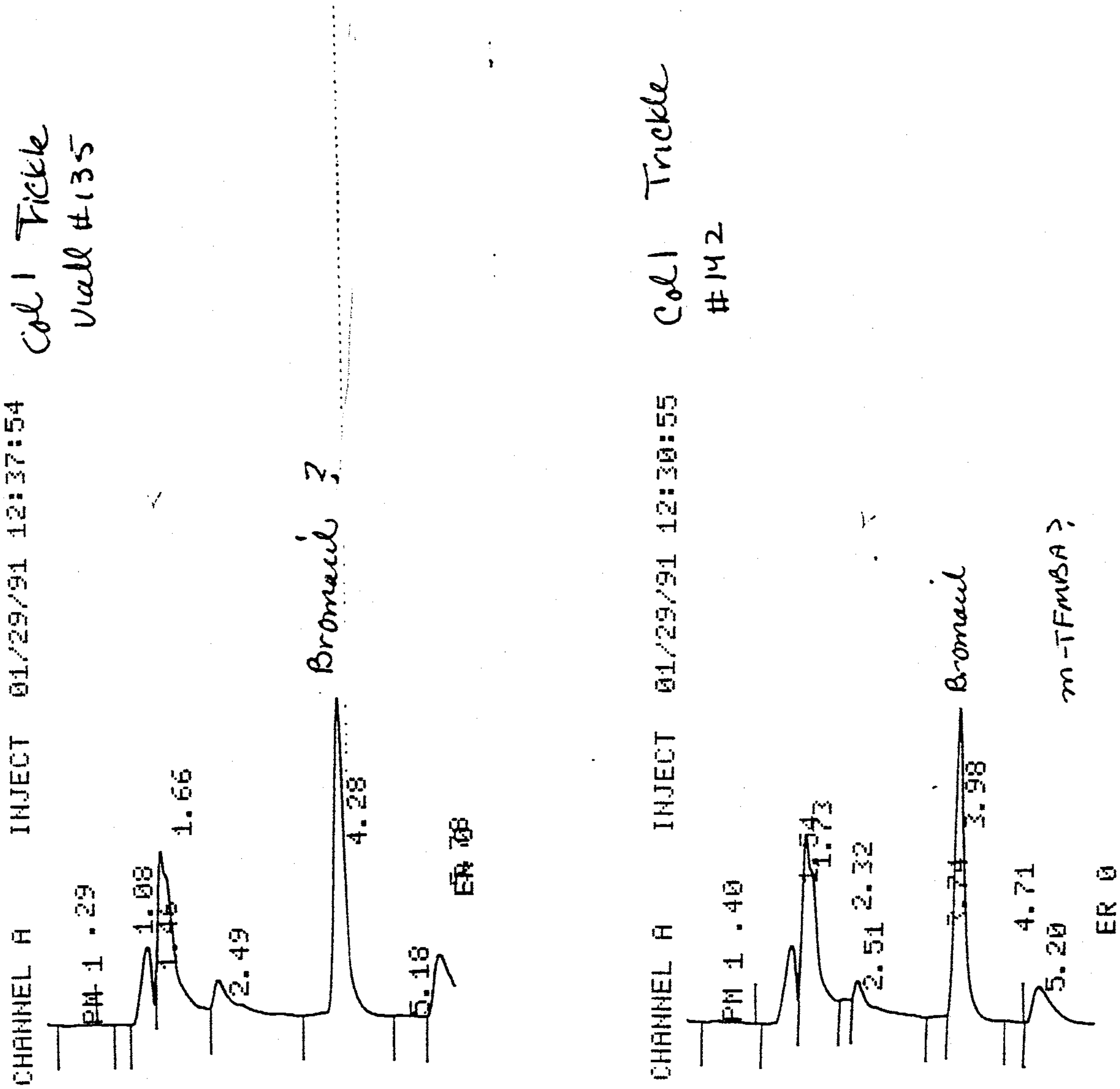
(a)

25 ppm standard for bromacil and m-TFMBA. Bromacil and m-TFMBA peaks are marked. Notice the time that each peak leaves the column.

(b)

Chromatogram of effluent from Column 1. Notice how both the bromacil and m-TFMBA peaks have the same time separating the two, but both times are delayed by approximately .25 minutes

Fig. 33. Sample Chromatograms - 25ppm bromacil and m-TFMBA standard and Effluent from Column 1 (Steady State-Unsaturated Flow)



(a)

Chromatograms from Column 1 effluent. Bromacil peak time off from standard peak (Fig. 33a) by 30 seconds. m-TFMBA peak has been truncated.

(b)

This chromatogram shows good agreement with standard chromatograph given in Fig 33a. Both bromacil and m-TFMBA peaks are within the expected elapsed time of the run.

Fig. 34. Sample Chromatograms - Effluent from Column 1 (Steady State-Unsaturated Flow).

H. <u>BTC Data for Steady State-Unsaturated Flow Regime</u>

Table 27. <u>In Situ</u> Column 1 BTC Values for Steady State-Unsatuated Flow Regime

Days Since Tracer Added (mL)	Cumulative Effluent (mL)	Concentration (mg/L) Observed	
		m-TFMBA	bromacil
1.34	148.202	0	0
5.42	602.388	2.54	0
7.825	864.388	6.64266	0.0812
8.2	906.346	7.6	0.4459
8.325	920.646	9.32356	0.842
8.3854	926.84	13.9506	1.1415
8.5104	940.162	11.6147	1.2868
8.7604	968.288	12.7745	1.474
9.0104	995.921	14.0772	1.6495
9.1354	1009.74	15.511	1.81
9.1354	1023.55	15.511	1.81
9.1354	1037.37	15.51	1.81
9.5104	1051.19	17.5389	2.933
9.7605	1078.82	19.6057	2.8886
9.8854	1092.64	22.4909	5.4058
10.0104	1106.45	19.1133	4.5488
10.3854	1147.9	16.8988	3.8423
10.3854	1147.9	19.8988	3.8423
13.5104	1493.31	7.1404	18.6942
13.5104	1493.31	7.1404	16.2265
14.0313	1550.87	1.8788	22.6457
15.3854	1700.55	1.7354	22.625
15.5104	1714.37	1.5326	24.6554
15.6363	1730.48	1.22	22.8804
15.9000	1758.12	0.7455	23.95
16.0313	1771.93	0.7903	22.0913
16.1600	1785.75	0.6383	23.8967
16.2313	1799.57	0.623	24.4632
16.4063	1813.38	0.1656	24.3499
16.7813	1854.83	0	23.288
17.9063	1979.18	0	19.5268
19.6866	2175.97	0	15.3369
22.6860	2507.56	0	7.7579
29.77	3291.31	0	3.1993
35.0275	3871.59	0	3.3767
35.0275	3891.59	0	2.6297
36.775	4065.02	0	2.1077

Table 28. In Situ Column 2 BTC Values for Steady State-Unsatuated Flow Regime

		Concentration (mg/L) Observed	
Days Since Tracer Added	Cumulative Effluent (mL)	m-TFMBA	Bromacil
3.0908	344.7203	0.0628	0
5.4500	607.8385	0.1458	0
7.5750	844.8398	10.1058	2.7935
8.0750	900.6048	13.4272	2.7525
8.2000	914.546	13.5376	2.6625
8.3854	935.2237	19.3102	2.9808
8.8845	990.9887	23.0318	4.4559
9.0096	1004.439	23.7638	4.8353
9.1345	1018.871	24.1274	4.5794
9.2060	1026.79	21.5130	4.1406
9.5104	1060.695	21.8522	6.1493
9.7604	1064.767	23.041	6.7221
10.0104	1092.034	24.669	6.9771
10.1354	1105.631	24.7728	7.700
10.2596	1119.219	22.2176	7.7016
10.3854	1149.804	20.1458	5.4109
10.5104	1146.579	20.3288	8.9251
10.7600	1193.803	16.722	11.5701
11.8854	1296.579	17.2024	11.2856
11.8854	1296.579	16.7220	
11.5104	1255.669	14.397	12.7809
14.0313	1530.646	5.7760	22.885
14.1060	1620.676	4.7174	21.0628
14.6563	1598.855	4.5052	21.7128
14.7813	1612.492	4.2910	23.0062

Table 28. (continued)

		Concentration (mg/L) Observed	
Days Since Tracer Added	Cumulative Effluent (mL)	m-TFMBA	Bromacil
14.7813	1612.492	4.2910	23.0062
14.9063	1626.128	3.8206	23.8702
15.2513	1663.766	3.2592	23.9602
15.5313	1694.309	2.853	22.4960
15.4033	1680.346	3.1064	23.0956
15.6563	1707.947	2.7610	23.1794
15.6563	1707.947	2.7610	23.3323
15.7813	1721.582	3.0534	22.5372
15.7813	1721.582		22.7256
16.0313	1748.856		22.7744
16.1063	1789.766	2.4346	
16.4063	1803.396	1.9136	22.237
16.5313	1869.392		22.86
17.1563	1962.804	1.7678	20.9925
17.9925	2011.259	1.4038	
18.4367	2530.236	0.9552	7.7423
22.6866	2474.88	0	10.1818
28.7775	3139.064	0	5.5204
31.2775	3412.062	0	4.8403
36.775	4011.780	0	4.3700

Table 29. Repacked Column 3 BTC Values for Steady State-Unsatuated Flow Regime

		Concentration (mg/L) Observed	
Days Since Tracer Added	Cumulative Effluent (mL)	m-TFMBA	Bromacil
4.325	472.35	0.000	0.000
6.660	728.20	1.864	0.000
7.950	869.25	4.034	0.000
8.635	944.20	7.577	0.000
9.010	985.20	9.774	0.001
9.885	1080.87	16.134	0.371
9.885	1094.54	16.134	0.289
10.635	1162.88	18.281	0.972
11.135	1217.55	18.299	1.871
12.010	1313.22	21.176	8.741
12.635	1381.56	21.526	9.036
14.656	1602.51	17.205	11.024
14.656	1602.51	17.205	21.914
15.156	1657.18	15.240	24.887
15.531	1698.19	11.905	27.348
15.781	1725.52	13.110	27.050
15.781	1725.52	13.110	27.504
16.031	1752.86	13.375	28.096
16.281	1780.19	13.137	27.789
16.656	1821.19	9.981	28.509
18.406	2012.54	8.346	28.471
28.373	3102.29	1.732	7.369
35.153	3843.57	0.000	6.773
36.903	4034.92	0.000	2.501
36.882	4032.45	0.000	2.583
36.778	4021.52	0.000	2.814

Table 30. Repacked Column 4 BTC Values for Steady State-Unsatuated Flow Regime

		Concentration (mg/L) Observed	
Days Since Tracer Added	Cumulative Effluent (mL)	m-TFMBA	Bromacil
4.1166	456.5309	0	0
6.7	743.03	1.82684	0
7.95	881.655	2.51733	0
9.01042	999.2556	9.95889	0
9.26042	1026.981	13.855	.004
9.51042	1054.706	15.2508	.047
9.76042	1082.431	19.0955	.006
10.0104	1110.153	19.837	0
10.2604	1137.878	20.214	.254
10.7604	1193.328	22.1141	.308
10.8854	1207.191	24.4776	.365
11.0104	1221.053	21.81	.385
11.2604	1248.778	21.4996	.460
11.6354	1290.366	19.8908	.556
11.8854	1318.091	18.4874	.693
12.1354	1345.816	18.1846	1.046
13.9063	1542.209	17.3721	2.579
13.9063	1542.209	17.3721	9.198
14.6563	1625.384	17.2873	14.594
15.2813	1694.696	16.1581	19.604
15.4063	1708.559	16.1059	21.174
15.5212	1721.301	15.5974	21.598
15.6563	1736.284	16.875	21.086
15.7813	1750.146	15.995	22.579
15.9063	1764.009	14.5883	22.064
16.0313	1777.871	15.4338	23.336
16.1563	1791.734	14.3589	23.237
16.5313	1833.321	9.4121	22.291
17.7813	1971.946	7.734	
18.9366	2100.069	4.2041	17.841
22.3117	2619.78	0.6445	
25.6229 *	2841.58	0	10.390
28.7775	3191.425	0	7.139
32.0275 *	3551.85	0	3.344
35.0275	3884.55	0	1.811
36.7775	4078.625	0	1.430

I. <u>BTC Data for Intermittent Ponding Flow Regime</u>

Table 31. <u>In Situ</u> Column 1 BTC Values for Intermittent Ponding Flow Regme m-TFMBA

		m-TFMBA		
Days Since Since Tracer Added	**Cumulative Effluent**	**Concentration (mg/L)**	**PV**	**C/C_o Observed**
0.104	136	0.0494	0.087	0.0001
0.541	478.35	3.64078	0.3005	0.00737
0.792	516.4	4.05574	0.3403	0.00821
1.145	551.15	4.5201	0.3604	0.00915
1.729	604.92	5.1376	0.395	0.0104
2.416	642.65	6.77274	0.4352	0.01371
3.634	696.4	7.31614	0.4761	0.01481
4.259	714.5	8.83766	0.49008	0.01789
4.509	723.5	7.91388	0.4949	0.01602
4.884	731.38	7.42482	0.5002	0.01503
5.134	737.24	7.93858	0.50947	0.01607
5.509	745.12	7.6076	0.5151	0.0154
5.509	745.12	7.6076	0.5151	0.0154
5.759	749.63	7.5582	0.5189	0.0153
6.0095	754.35	7.47916	0.52233	0.01514
6.1345	756.53	7.24698	0.52396	0.01467
7.083	794.44	6.79744	0.5604	0.01376
7.298	1217.02	9.91952	0.7984	0.02008
7.756	1291.75	9.20816	0.8607	0.01864
7.8402	1301.69	9.32672	0.8695	0.01888
7.881	1306.45	9.23286	0.8739	0.01869
7.965	1315.44	9.06984	0.8802	0.01836
8.006	1319.69	9.25262	0.8834	0.01873
8.132	1332	8.9414	0.8891	0.0181
8.215	1339.28	9.139	0.8952	0.0185
10.34	1467.48	8.70428	0.9946	0.01762
12.59	1532.09	4.75722	1.0465	0.00963
14.812	2085.02	5.07832	1.4122	0.01028
15.187	2123.24	4.95976	1.4344	0.01004
15.604	2157.57	4.43118	1.4578	0.00897
16.979	2237.39	1.22018	1.5232	0.00247

Table 31. continued

		m-TFMBA		
Days Since Since Tracer Added	Cumulative Effluent	Concentration (mg/L)	PV	C/C_o Observed
16.979	2237.39	1.22018	1.5232	0.00247
19.001	2295.02	2.0007	1.56486	0.00405
21.062	2329.94	1.5314	1.62063	0.0031
21.229	2704.319	0.68172	1.76007	0.00138
21.291	2711.5	0.87438	1.76926	0.00177
21.437	2759.6	0.8151	1.88865	0.00165
21.52	2776	0.3458	1.89263	0.0007
21.895	2840.269	0.82004	1.93885	0.00166
22.145	2874.959	0.75582	1.94932	0.00153
22.52	2905.739	0.37544	1.97344	0.00076
23.145	2954.389	0.21736	2.00986	0.00044
23.645	2980.509	0.33592	2.03156	0.00068
24.645	3024.519	0.76076	2.06479	0.00154
27.77	3099.441	0.24206	2.11393	0.00049
27.77	3099.441	0.08398	2.11994	0.00017
28.1041	3107.541	0.1235	2.17847	0.00025
28.25	3522.481	0.03458	2.3759	0.00007
34.458	3871.9	0	2.64439	0
34.864	3877.131	0.03952	3.06629	0.00008
35.052	3877.6	0	3.2531	0
35.572	4376.121	0	3.3173	0

Table 32. In Situ Column 1 BTC Values for Intermittent Ponding Flow Regime - bromacil

		bromacil		
Days Since Since Tracer Added	Cumulative Effluent	Concentration (mg/L)	PV	C/C_o Observed
0.104	136	0.663	0.087	0.0006
0.541	478.35	0.74035	0.3005	0.00067
0.792	516.4	0.1768	0.3403	0.00016
1.145	551.15	1.989	0.3604	0.0018
1.729	604.92	2.6962	0.395	0.00244
2.416	642.65	3.67965	0.4352	0.00333
3.634	696.4	4.8399	0.4761	0.00438
4.259	714.5	4.5968	0.49008	0.00416
4.509	723.5	5.1051	0.4949	0.00462
4.884	731.38	5.18245	0.5002	0.00469
5.134	737.24	5.16035	0.50947	0.00467
5.509	745.12	5.07195	0.5151	0.00459
5.509	745.12	5.1714	0.5151	0.00468
5.759	749.63	5.2819	0.5189	0.00478
6.0095	754.35	5.1051	0.52233	0.00462
6.1345	756.53	5.2819	0.52396	0.00478
7.083	794.44	6.0112	0.5604	0.00544
7.298	1217.02	8.65215	0.7984	0.00783
7.756	1291.75	10.33175	0.8607	0.00935
7.8402	1301.69	10.4091	0.8695	0.00942
7.881	1306.45	10.37595	0.8739	0.00939
7.965	1315.44	10.4754	0.8802	0.00948
8.006	1319.69	10.35385	0.8834	0.00937
8.132	1332	10.55275	0.8891	0.00955
8.215	1339.28	10.387	0.8952	0.0094
10.34	1467.48	10.8953	0.9946	0.00986
12.59	1532.09	10.64115	1.0465	0.00963
14.812	2085.02	12.09975	1.4122	0.01095
15.187	2123.24	12.71855	1.4344	0.01151
15.604	2157.57	11.8677	1.4578	0.01074
16.979	2237.39	11.2931	1.5232	0.01022

Table 32. continued

		bromacil		
Days Since Since Tracer Added	Cumulative Effluent	Concentration (mg/L)	PV	C/C_o Observed
19.001	2295.02	10.6190	1.56486	0.00961
21.062	2329.94	8.619	1.62063	0.0078
21.229	2704.319	7.3040	1.76007	0.00661
21.291	2711.50	7.3480	1.76926	0.00665
21.437	2759.60	7.569	1.88865	0.00685
21.52	2776.00	7.845	1.89263	0.0071
21.895	2840.269	8.044	1.93885	0.00728
22.145	2874.959	7.458	1.94932	0.00675
22.52	2905.739	6.298	1.97344	0.0057
23.145	2954.389	3.697	2.00986	0.00334
23.645	2980.509	5.593	2.03156	0.00506
24.645	3024.519	5.122	2.06479	0.00464
27.77	3099.441	5.955	2.11393	0.00539
27.77	3099.441	6.077	2.11994	0.0055
28.104	3107.541	6.077	2.17847	0.0055
28.250	3522.481	3.690	2.3759	0.00334
34.458	3871.9	2.972	2.64439	0.00269
34.864	3877.131	2.431	3.06629	0.0022
35.052	3877.6	2.530	3.2531	0.00229
35.572	4376.121	2.276	3.3173	0.00206
	**	2.000		0.00181
42.000	4500.00	1.948		0.00176

Table 33. In situ **Column 2 BTC Values for Intermittent Ponding Flow Regime m-TFMBA**

		m-TFMBA		
Days Since Since Tracer Added	Cumulative Effluent	Concentration (mg/L)	PV	C/C$_o$ Observed
	0.62	0		0
1.145833	583.18	7.109448	0.425	0.014392
1.791667	654.44	5.58312	0.459	0.011302
3.759583	723.73	7.378026	0.51	0.014935
4.384583	739.35	8.250582	0.519	0.016702
4.759583	748.5	8.064822	0.5268	0.016326
5.009583	752.26	5.838888	0.5297	0.01182
5.259583	756.08	5.887321	0.533	0.011918
5.634583	761.44	6.075256	0.5379	0.012298
5.884583	764.79	6.032807	0.5405	0.012212
6.509583	772.4	8.206464	0.5469	0.016612
7.173613	788.12	7.61487	0.552	0.015415
7.256946	908.82	9.1074	0.5705	0.018436
7.381946	1090.66	12.11116	0.6691	0.024517
7.548613	1313.22	10.30398	0.8086	0.020858
7.840279	1380.46	10.793	0.9268	0.021848
7.923613	1390.2	10.11932	0.9482	0.020484
8.048613	1402.26	9.148184	0.9632	0.018519
8.131946	1409.37	10.85821	0.9686	0.02198
8.173613	1412.67	11.03683	0.9747	0.02234
8.215279	1415.77	10.63778	0.977	0.021534
10.46528	1497.68	10.7722	1.0547	0.021806
12.59028	1531.12	12.56683	1.0852	0.025439
14.79861	2142.44	3.029952	1.095	0.006134
16.04861	2228.43	3.262926	1.4919	0.006605
16.34028	2238.9	3.047754	1.4919	0.00617
16.46528	2243.49	2.672106	1.5257	0.005409
18.75	2294.08	2.840064	1.5845	0.005749
19.625	2306.33	2.754924	1.6256	0.005577
21.25	2368.43	2.049294	1.6366	0.004148
21.41667	2601.94	0.745662	1.75	0.001509
21.58333	2858.62	0.468528	1.905	0.000948
21.64583	2889.29	0.463626	1.9868	0.000939
21.77083	2924.84	0.513678	1.999	0.00104
22.52083	2983.62	0.566568	2.03	0.01147
23.77083	3024.23	0.463626	2.133	0.00093
24.77083	3050.61	0.394224	2.153	.000798

Table 33. continued

		m-TFMBA		
Days Since Since Tracer Added	**Cumulative Effluent**	**Concentration (mg/L)**	**PV**	**C/C_o Observed**
28.0208	3095.95	0.593658	2.2159	0.001202
28.250	3105.74	0.29928	2.2906	0.000606
28.375	3218.25	0.144738	2.5989	0.000293
28.39583	3254.253	0.125646	2.686	0.000254
28.91667	3690.627	0.063726	2.7336	0.000129
29.45833	3741.067	0.057534	2.7451	0.000116
30.70833	3800.797	0.051084	2.7737	0.000103 0
33.95833	3860.647	0	3.1527	0
35.3333	4009.917	0	3.1527	0
36.000	4438.917	0	3.206	0
37.29167	4538.447	0	3.29447	0
37.41667	4500.427	0	3.29447	

Table 34. *In situ* Column 2 BTC Values for Intermittent Ponding Flow Regime - bromacil

		bromacil		
Days Since Since Tracer Added	**Cumulative Effluent**	**Concentration (mg/L)**	**PV**	**C/C_o Observed**
	0.62	0	0.425	0
1.145833	583.18	4.220081	0.459	0.014392
1.791667	654.44	2.086496	0.51	0.011302
3.759583	723.73	1.857463	0.519	0.014935
4.384583	739.35	1.776764	0.5268	0.016702
4.759583	748.5	1.861578	0.5297	0.016326
5.009583	752.26	1.858657	0.533	0.01182
5.259583	756.08	1.84008	0.5379	0.011918
5.634583	761.44	1.89808	0.540	0.012298
5.884583	764.79	1.975867	0.5469	0.012212
6.509583	772.4	1.911858	0.552	0.016612
7.173613	788.12	1.699108	0.5705	0.015415
7.256946	908.82	4.683695	0.6691	0.018436
7.381946	1090.66	11.76331	0.8086	0.024517
7.548613	1313.22	11.06458	0.9268	0.020858
7.840279	1380.46	10.8314	0.9482	0.021848
7.923613	1390.2	9.699158	0.9632	0.020484
8.048613	1402.26	10.7578	0.9686	0.018519
8.131946	1409.37	10.25706	0.9747	0.02198
8.173613	1412.67	9.174171	0.977	0.022342
8.215279	1415.77	9.05035	1.0547	0.021534
10.46528	1497.68	9.688959	1.0852	0.021806
12.59028	1531.12	11.72681	1.095	0.025439
14.79861	2142.44	11.82755	1.4919	0.006134
16.04861	2228.43	12.80219	1.4919	0.006605
16.34028	2238.9	12.01274	1.5257	0.00617
16.46528	2243.49	11.70963	1.5845	0.005409
18.75	2294.08	12.34341	1.6256	0.005749
19.625	2306.33	11.2233	1.6366	0.005577
21.25	2368.43	10.98657	1.75	0.004148
21.41667	2601.94	9.472272	1.905	0.001509
21.58333	2858.62	7.473244	1.9868	0.000948
21.64583	2889.29	7.579529	1.999	0.000939
21.77083	2924.84	8.100221	2.03	0.00104
22.52083	2983.62	7.335108	2.133	0.001147
23.77083	3024.23	7.853116	2.153	0.0009390.
24.77083	3050.61	6.964898		000798

Table 34. continued

			bromacil	
Days Since Since Tracer Added	Cumulative Effluent	Concentration (mg/L)	PV	C/C_o Observed
28.0208	3095.950	7.555	2.215	0.006838
28.2500	3105.740	7.117	2.290	0.006442
28.3750	3218.250	6.581	2.598	0.005956
28.3958	3254.253	6.369	2.686	0.005764
28.9166	3690.627	4.628	2.733	0.004189
29.4583	3741.067	4.630	2.745	0.00419
30.7083	3800.797	4.368	2.773	0.003954
33.9583	3860.647	4.238	3.152	0.003836
35.3333	4009.917	3.822	3.152	0.00346
36.0000	4438.917	3.202	3.206	0.002899
37.2916	4538.447	3.112	3.294	0.002817
37.4166	4500.427	2.873	3.294	0.0026

Table 35. Repacked Column 3 BTC Values for Intermittent Ponding Flow Regime - m-TFMBA

			m-TFMBA	
Days Since Since Tracer Added	Cumulative Effluent (mL)	Concentration (mg/L)	PV	C/C_o Observed
1.041	236	0	.3240	0
1.229	273	0	.3343	0
1.791	383	0	.3666	0
1.979	404	0	.3841	0
2.479	501	0	.3970	0
6.134	691	.944	.5009	0
6.509	706	1.140	.5119	0
7.590	1057	1.221	.6987	.0199
7.673	1080	9.896	.7244	.0189
8.465	1161	9.370	.8642	.0252
9.465	1211	12.414	.9137	.0304
9.965	1235	14.630	.9350	.0290
11.465	1364	14.330	.9795	.0290
12.215	1405	14.710	.9990	.0298
12.965	1445	NA	1.0176	NA
13.465	1474	16.003	1.0324	.0324
14.166	1531	14.320	1.0768	.0290
14.229	1565	14.86	1.1086	.0300
14.312	1617	12.45	1.1388	.0252
14.583	1805	10.28	1.2381	.0208
14.812	1957	8.07	1.3472	.0163
15.020	2000	7.78	1.3691	.0574
15.437	2081	7.31	1.3870	.0148
16.021	2105	6.91	1.4262	.0139
18.750	2220	6.20	1.5104	.0126
21.895	2710	1.10	1.8698	.0013
22.270	2758	1.02	1.8987	.0021
22.520	2787	.52	1.9123	.0010
23.895	2888	.17	1.9741	.0003
24.645	2961	NA	1.9974	0
28.467	3179	1.095	2.2142	0
28.770	3333	.076	2.2343	0
28.875	3403	.060	2.2995	0
29.583	3623	.050	2.3170	0
31.083	3747	.047	2.4000	0
32.333	3781	.091	2.5430	0
34.958	3794	0	2.5430	0
36.516	4272	0	2.6120	0
			2.9573	0

Table 36. Repacked Column 3 BTC Values for Intermittent Ponding Flow Regime - bromacil

bromacil				
Days Since Since Tracer Added	Cumulative Effluent (mL)	Concentration (mg/L)	PV	C/C_o Observed
1.041	236	.082	.3240	.0001
1.229	273	.080	.3343	.0001
1.791	383	.067	.3666	.0001
1.979	404	.126	.3841	.0001
2.479	501	.072	.3970	.0001
6.134	691	.117	.5009	.0001
6.509	706	.125	.5119	.0001
7.590	1057	.122	.6987	.0039
7.673	1080	4.34	.7244	.0050
8.465	1161	5.60	.8642	.0055
9.465	1211	6.138	.9137	.0062
9.965	1235	6.390	.9350	.0058
11.465	1364	6.909	.9795	.0063
12.215	1405	7.181	.9990	.0065
12.965	1445	7.138	1.0176	.0065
13.465	1474	7.580	1.0324	.0068
14.166	1531	9.798	1.0768	.0089
14.229	1565	12.476	1.1086	.0013
14.312	1617	13.529	1.1388	.0129
14.583	1805	16.763	1.2381	.0122
14.812	1957	17.759	1.3472	.0152
15.020	2000	17.549	1.3691	.0161
15.437	2081	17.249	1.3870	.0579
16.021	2105	17.916	1.4262	.0156
18.750	2220	22.216	1.5104	.0162
21.895	2710	14.383	1.8698	.0201
22.270	2758	14.387	1.8987	.0205
22.520	2787	19.816	1.9123	.0130
23.895	2888	17.800	1.9741	.0161
24.645	2961	17.026	1.9974	.0154
28.467	3179	5.816	2.2142	.0053
28.770	3333	5.920	2.2343	.0053
28.875	3403	5.370	2.2995	.0049
29.583	3623	5.051	2.3170	.0046
31.083	3747	4.503	2.4000	.0041
32.333	3781	5.000	2.5430	.0045
34.958	3794	2.770	2.5430	.0045
36.516	4272	1.348	2.6120	.0028
			2.9573	.0012
				0

Table 37. Repacked Column 4 BTC Values for Intermittent Ponding Flow Regime - m-TFMBA

			m-TFMBA	
Days Since Since Tracer Added	Cumulative Effluent	Concentration (mg/L)	PV	C/C_o Observed
1.0410	499.48	0.11856	0.38613	0.00024
1.1450	516.94	0.01482	0.4008	0.00003
1.7291	584.45	1.729	0.4533	0.0035
3.6345	707.7	3.63584	0.51604	0.00736
4.8840	740.54	0.6916	0.5282	0.0014
5.5095	756.2	2.80098	0.5372	0.00567
5.8845	762.77	3.21594	0.5432	0.00651
6.1345	766.68	3.08256	0.5489	0.00624
6.6345	774.14	3.37402	0.552	0.00683
6.6345	774.14	3.25546	0.5546	0.00659
6.7500	774.59	3.2357	0.556	0.00655
7.1319	783.24	3.458	0.5649	0.007
7.3402	939.17	10.6704	0.69919	0.0216
7.6319	1139.58	21.72118	0.8986	0.04397
9.4650	1382.22	22.21024	1.03624	0.04496
9.9650	1422.45	23.87008	1.0552	0.04832
11.4650	1494.76	16.38598	1.0818	0.03317
13.4650	1542.08	13.08606	1.115	0.02649
14.2490	1566.18	11.3126	1.158	0.0229
14.2708	1576.57	10.85318	1.174	0.02197
14.4166	1648.12	8.05714	1.439	0.01631
14.5830	1728.642	5.56738	1.46	0.01127
14.6240	1748.49	5.02398	1.462	0.01017
14.8540	1887.385	2.55398	1.502	0.00517
15.6870	2125.18	1.0374	1.57	0.0021
15.9790	2153.038	1.00776	1.585	0.00204
16.0200	2159.32	1.04234	1.586	0.00211
16.0620	2159.32	1.04234	1.586	0.00211
16.8540	2207.108	0.88426	1.614	0.00179
18.3540	2277.984	0.89908	1.639	0.00182
18.7500	2287.568	0.8645	1.644	0.00175
20.7500	2324.318	0.79534	1.673	0.00161
21.1870	2371.088	0.8398	1.6775	0.0017

Table 37. continued

		m-TFMBA		
Days Since Since Tracer Added	Cumulative Effluent	Concentration (mg/L)	PV	C/C_o Observed
21.3330	2560.188	0.247	1.8316	0.0005
21.3950	2632.768	0.16796	1.8776	0.00034
21.7960	2828.168	0.06916	2.027	0.00014
22.5200	2939.838	0.00494	2.11	0.00001
23.7700	3014.258	0.0741	2.1641	0.00015
25.0200	3057.198	0.1235	2.195	0.00025
28.020	3101.018	0.10374	2.232	0.00021
28.1870	3103.658	0.10374	2.244	0.00021
28.1870	3103.658	0.10374	2.244	0.00021
28.3750	3273.503	0	2.406	0
28.5200	3433.054	0.13832	2.51	0.00028
28.8330	3576.784	0	2.577	0
29.7080	3712.234	0	2.676	0
30.9580	3792.954	0	2.722	0
34.3330	3869.544	0	2.783	0
35.1875	3884.254	0	2.8	0
35.2708	3954.248	0	2.805	0
35.7290	4338.584	0	3.1162	0
36.9160	4506.224	0	3.25	0
42.0000	4650.204	0	3.34	0

Table 38. Repacked Column 4 BTC Values for Intermittent Ponding Flow Regime - bromacil

		bromacil		
Days Since Since Tracer Added	Cumulative Effluent	Concentration (mg/L)	PV	C/C_o Observed
1.0410	499.48	0.0221	0.38613	0.00002
1.1450	516.94	0.01105	0.4008	0.00001
1.7291	584.45	0.0221	0.4533	0.00002
3.6345	707.7	0.05525	0.51604	0.00005
4.8840	740.54	1.547	0.5282	0.0014
5.5095	756.2	0.12155	0.5372	0.00011
5.8845	762.77	0.18785	0.5432	0.00017
6.1345	766.68	0.14365	0.5489	0.00013
6.6345	774.14	0.14365	0.552	0.00013
6.6345	774.14	0.14365	0.5546	0.00013
6.7500	774.59	0.14365	0.556	0.00013
7.1319	783.24	0.20995	0.5649	0.00019
7.3402	939.17	0.78455	0.69919	0.00071
7.6319	1139.58	5.7902	0.8986	0.00524
9.4650	1382.22	9.0389	1.03624	0.00818
9.9650	1422.45	10.37595	1.0552	0.00939
11.4650	1494.76	12.818	1.0818	0.0116
13.4605	1542.08	16.45345	1.115	0.01489
14.2490	1566.18	15.54735	1.158	0.01407
14.2708	1576.57	17.69105	1.174	0.01601
14.4166	1648.12	22.5641	1.439	0.02042
14.5830	1728.642	32.0008	1.46	0.02896
14.6240	1748.49	33.05055	1.462	0.02991
14.8540	1887.385	37.128	1.502	0.0336
15.6870	2125.18	34.92905	1.57	0.03161
15.9790	2153.038	34.81855	1.585	0.03151
16.0200	2159.32	33.4152	1.586	0.03024
16.0620	2159.32	34.4318	1.586	0.03116
16.8540	2207.108	33.5036	1.614	0.03032
18.3540	2277.984	31.4041	1.639	0.02842
18.7500	2287.568	32.5312	1.644	0.02944
20.7500	2324.318	26.55315	1.673	0.02403
21.1870	2371.088	27.21615	1.6775	0.02463

Table 38. continued

bromacil				
Days Since Since Tracer Added	Cumulative Effluent	Concentration (mg/L)	PV	C/C_o Observed
21.3330	2560.188	18.46455	1.8316	0.01671
21.3950	2632.768	14.61915	1.8776	0.01323
21.7960	2828.168	7.0499	2.027	0.00638
22.5200	2939.838	5.2377	2.11	0.00474
23.7700	3014.258	4.27635	2.1641	0.00387
25.0200	3057.198	4.09955	2.195	0.00371
28.0200	3101.018	4.2432	2.232	0.00384
28.1870	3103.658	4.6631	2.244	0.00422
28.1870	3103.658	4.6631	2.244	0.00422
28.3750	3273.503	2.35365	2.406	0.00213
28.5200	3433.054	1.5691	2.51	0.00142
28.8330	3576.784	1.1271	2.577	0.00102
29.7080	3712.234	0.91715	2.676	0.00083
30.9580	3792.954	0.8398	2.722	0.00076
34.3330	3869.544	0.9282	2.783	0.00084
35.1875	3884.254	1.18235	2.8	0.00107
35.2708	3954.248	0.7514	2.805	0.00068
35.7290	4338.584	0.27625	3.1162	0.00025
36.9160	4506.224	0.20995	3.25	0.00019
42.0000	4650.204	0.32045	3.34	0.00029

J. pH Values for Column Effluent During Steady State-Unsaturaed Flow Regime

Table 39. pH Values for *In Situ* Columns 1 and 2 Steady State-Unsaturated Flow Regime

		Column #	
Hours Since Tracer Added	Cumulative Effluent (mL)	1	2
-42.82	-196.54	7.70	
-39.82	-182.77		7.90
-15.82	-72.61	7.57	
14.18	65.08		7.87
35.18	161.47	7.70	
74.18	340.48		8.22
100.8	462.67		8.11
130.8	600.37	7.74	8.02
145.8	669.22		8.03
160.8	738.07		7.86
163.8	751.84	7.84	
181.8	834.46		7.85
187.8	862.00	7.78	
190.8	875.77	7.87	
193.8	889.54	7.74	7.81
196.8	903.31	7.85	
201.25	923.73	.76	
204.25	937.55	7.79	
207.25	951.27	7.77	
213.25	978.81	7.69	811
216.25	992.58	7.83	7.80
219.25	1006.36	7.79	7.93
222.25	1020.13	7.78	
225.25	1033.98	7.76	
228.25	1047.58	7.79	
234.25	1075.20	7.77	
240.25	1102.75	7.84	
243.25	1116.52	7.78	
246.25	1130.29	7.67	
249.25	1144.06	7.88	
252.25	1157.83		7.95
258.25	1185.30	8.21	
261.23	1199.14	7.79	
273.23	1254..22	7.78	
276.25	1267.99	7.91	7.93

Table 39. continued

		Column #	
Hours Since Tracer Added	Cumulative Effluent (mL)	1	2
336.75	1545.68		7.81
351.75	1614.53	7.95	7.83
360.75	1655.84	7.75	7.85
366.75	1683.38	7.85	7.74
369.75	1697.15	7.86	7.78
372.75	1710.92		7.92
375.75	1724.69	7.79	7.88
378.75	1738.46		7.86
381.75	1752.23	7.96	
384.75	1766	7.96	8.04
387.75	1779.77	7.94	7.83
390.75	1793.54	7.9	
393.75	1807.31	7.94	7.91
396.75	1821.08	7.94	7.95
402.75	1848.62	7.9	
405.75	1862.39	7.85	7.62
426.75	1958.78		7.73
442.48	2030.98		8.16
448.48	2058.52	7.6	
472.48	2168.68	7.87	
490.48	2251.3		7.82
544.48	2499.16		7.85
563.95	2588.53		8.0
578.95	2657.38	7.79	
626.95	2877.7	7.91	
632.95	2905.24	8.02	
653.95	3001.63		7.90
656.95	3015.4	7.76	
687.66	3156.36		8.12
690.66	3170.13	7.72	
711.66	3266.52		7.72
720.66	3307.83		7.89
738.66	3390.45		7.66
750.66	3445.53	7.85	
765.66	3514.38		7.87
780.66	3583.23	7.94	

Table 39. continued

		Column #	
Hours Since Tracer Added	Cumulative Effluent (mL)	1	2
789.66	3624.54		7.82
813.66	3734.7		7.9
840.66	3858.63	7.91	7.9
855.66	3927.48	7.9	
858.66	3941.25		7.4
876.66	4023.87	7.95	
882.66	4051.41		8.05

Table 40. pH Values for Repacked Columns 3 and 4 Steady State-Unsaturated Flow Regime

		Column #	
Hours Since Tracer Added	Cumulative Effluent (mL)	1	2
240.25	1102.75		7.92
246.25	1130.29		7.94
258.25	1185.37		7.88
264.25	1212.91		8.03
270.25	1240.45		8.03
279.25	1281.76	7.87	8.01
285.05	1308.38		7.98
291.25	1336.84		8.19
303.25	1391.92	8.03	7.9
315.25	1447	7.87	
333.75	1531.91		8.25
336.75	1545.68	7.91	
351.75	1614.53		8.05
354.75	1628.3	8	
366.75	1683.38		8.03
369.75	1697.15		8.17
372.75	1710.92	7.86	7.93
375.75	1724.69		8.01
378.75	1738.46	8	8.05
381.75	1752.23		7.97
384.75	1766	8.06	8.1
387.75	1779.77		7.98
390.75	1793.54	7.94	
393.75	1807.31		8.04
414.75	1903.7	7.94	
426.75	1958.78		7.88
441.75	2027.63	7.87	
478.48	2196.22	7.97	
511.48	2347.69	8.09	
535.48	2457.85		7.95
547.48	2512.93	8.11	
584.95	2684.92	8.17	
638.95	2932.78	8.07	
668.95	3070.48	8.14	
690.66	3170.13		7.8
711.66	3266.52		
720.66	3307.83	8.07	
798.66	3665.85	8.06	
843.66	3872.4	8.03	
873.66	4010.1	8.11	
882.66	4051.41		7.84

K. pH Values for Column Effluent During Intermittent Ponding Flow Regime

Table 41. pH Values for In Situ Columns 1 Intermittent Ponding Flow Regime

Hours Since Tracer Added	Cumulative Effluent (mL)	Column # 1
-125	0	7.73
3	59	8
16	499.3	8.09
49	627.41	8.21
73	672.66	7.95
165.23	773.78	8.07
170.7	853.48	8.1
174.16	1191.74	8.19
178.16	1244.34	8.27
190.16	1311	8.28
191.16	1315.44	8.08
200.16	1357.53	8.11
212.06	1395.06	8.31
254.16	1475.98	8.14
290.16	1521.71	8.22
332.16	1550.79	8.11
338.49	1695.19	7.92
341.66	1958.13	8.68
346.49	2005.7	8.13
355.49	2085.02	7.96
356.49	2088.81	8.3
361.16	2110.88	8.2
388.49	2195.14	7.86
389.49	2202.48	7.16
395.49	2215.78	8.04
456.00	2295.02	8.17
462.00	2300.24	8.76
462.00	2300.24	8.44
506.50	2469.56	7.61
507.50	2604.9	8.6
509.00	2696.13	8.61
513.50	2750.3	8.62
519.00	2793.83	8.54
523.00	2817.25	8.23
528.50	2871.49	8.23

Table 41. (continued)

Hours Since Tracer Added	Cumulative Effluent (mL)	pH
529.5	2872.51	8.28
540.5	2905.74	8.68
594.5	3028.69	8.36
672.5	3104.32	7.83
675	3182.91	7.83
677.5	3510.34	8.16
678	3522.45	8.45
678.5	3531.7	8.71
684.5	3596.63	8.57
687.5	3619	8.46
699	3662.31	8.7
746	3789.66	8.11
758	3810.41	8.17
844	3958.13	7.8
847	4319.38	8.59

Table 42. pH Values for In Situ Columns 2 Intermittent Ponding Flow Regime

Hours Since Tracer Added	Cumulative Effluent (mL)	pH
-143	0	7.76
7.5	56.57	7.85
28	595.7	8.24
41.5	650.54	8.08
75.23	706.8	7.8
138.23	763.26	8.11
172.16	788.12	7.88
187.16	1374.62	8.22
192.16	1398.6	7.94
245.16	1492.35	7.95
248.16	1494.99	7.78
308.16	1535.11	7.82
341.66	1571.44	8.13
344.16	1681.44	7.19
361.16	2168.19	8.16
410.16	2265	7.95
508.21	2326.62	8.43
510	2386.44	8.3
513	2564.35	7.52
513	2564.35	7.57
519	2827.5	8.11
523.1	2928.95	8.16
528.5	2956.4	8.23
533.5	2969.94	8.15
594.5	3050.61	8.44
677	3099.61	8.35
681.5	3254.25	7.69
684.5	3467.58	7.55
695	3690.6	8.26
734	3797.12	8.34
847	3942.69	7.81
864	4438.9	8.43
872	4438.91	8.23

Table 43. pH Values for Repacked Columns 3 Intermittent Ponding Flow Regime

Hours Since Tracer Added	Cumulative Effluent (mL)	pH
-215	0	7.99
-155	0	7.79
4.5	18.27	8.01
41.5	360.54	8.05
55.5	480.76	8.07
93.23	622.11	8.19
170.33	731.79	8.43
171.16	775.59	8.68
329.16	1487.74	8.02
340.99	1556.86	8.1
344.16	1644.1	7.19
345.16	1673.98	8.2
355.49	1957.81	8.31
356.49	1966.47	8.31
360.49	2000.91	8.29
366.49	2047.27	8.26
384.49	2105.29	8.48
389.48	2119.74	8.09
444	2211.21	8.27
508	2287.1	8.66
512	2407.76	8.47
518.5	2535.03	8.34
523	2641.16	8.1
529.5	2743.13	8.3
555.5	2848.51	8.91
594.5	2926.61	8.63
674	3039.27	8.3
675	3044.31	8.3
678	3072.1	8.58
684.5	3219.02	8.88
692	3360.26	8.2
702	3593.38	8.99
746	3747.63	8.57
752	3758.45	8.2
846	3831.45	8.45
851.5	3962.58	8.47
861.5	4176.7	8.16
873	4256.06	8.21

Table 44. pH Values for Repacked Columns 4 Intermittent Ponding Flow Regime.

Hours Since Tracer Added	Cumulative Effluent (mL)	pH
-155	0	8.05
4.5	46.81	8.18
37	565.43	8.21
78.75	688.18	7.88
120.23	743.44	8.08
171.16	783.24	8.68
177.16	970.2	8.23
192.16	1221.26	8.25
251.16	1452.08	7.99
332.16	1551.01	8.43
341.66	1566.18	8.59
345.99	1648.12	8.5
354.49	1819.82	8.49
359.5	1973.06	8.02
360.49	2109.93	8.07
373.49	2270.98	8.34
465	2301.378	8.57
508	2350.33	8.47
511.5	2526.09	8.42
518.5	2777.34	8.43
523.21	2828.17	8.31
529.5	2880.46	8.47
540.5	2939.84	8.57
555.5	2987.51	8.57
594.5	3051.56	8.48
678	3142.82	8.48
684.5	3433.05	8.32
692	3576.78	8.72
743	3792.95	8.36
844.5	3884.25	8.71
847	3979.91	8.4
858	4343.46	8.45
876	4467.74	8.2

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