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PREFERENTIAL FLOW EFFECTS ON CHEMICAL TRANSPORT AND RETARDATION IN SOILS

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PREFERENTIAL FLOW EFFECTS ON
CHEMICAL TRANSPORT AND RETARDATION IN SOILS

by

Kathleen Economy
Graduate Research Assistant

and

Robert S. Bowman
Associate Professor of Hydrology

Department of Geoscience
New Mexico Institute of Mining and Technology

TECHNICAL COMPLETION REPORT

DISCLAIMER

ACKNOWLEDGEMENTS

ABSTRACT

The study's objective 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 by 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. Comparing 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.

Study results 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 predicators of mildly retarded bromacil movement during the steady state-unsaturated flow regime. For the intermittent ponding flow regime, high R_fs underestimated the bromacil's *initial* appearance for the in situ columns, yet adequately described the movement of bromacil BTC peaks. Underestimating bromacil's initial appearance 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.

This report is based largely upon the Master's thesis of Turney (1991), which may be consulted for further details.

Keywords: Contaminant transport, groundwater recharge, infiltration, model studies, Soil physics, solute transport, unsaturated flow.

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1.INTRODUCTION

Increased world population in the past 100 years has caused industrial growth around urban centers and more intensive agricultural development in rural areas. Consequently, extra stress has been placed on the soil. Industry uses soil to dispose of undesirable waste products and as a recipient of accidental chemical spills. For example, organic chemical production grew from 1 to 300 billion pounds-per-year between 1940 and 1966 and was followed by an equally staggering growth in abandoned and/or improperly designed waste disposal sites. Agribusinesses have increasingly used fertilizers and pesticides, indiscriminately and ignorantly applied in many instances, to insure higher crop yields. This point is illustrated by a British 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. 1987). These pesticides, fertilizers, and chemicals from spills and improperly designed disposal sites are increasingly threatening groundwater quality.

More accurate prediction methods are needed to determine the fate and transport of contaminants through the soil profile to the water table. 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 done in the late 1800s by Lawes et al. (1882) while studying the composition of effluent collected in field tile drains. This analysis led to labeling 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 describes the Green-Ampt theory

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

[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

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

[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

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

[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

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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 than mechanical dispersion in most transport situations, 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

$$R_f = 1 + \frac{\rho_b K_D}{\Theta}$$

[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 hydrodynamic dispersion phenomenon. 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 1960s and early 1970s and is referred to as the classical miscible displacement or convection-dispersion, CD, model.

Numerous soil scientists using this theory found that in many instances predicted

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movement of fluid flow underestimated arrival times of solute free and laden water. 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_fs had been overestimated in many cases, using laboratory derived K_d values. This was due to the misconception that as it moves away from its source point all the solute participates in miscible displacement, 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 describe more adequately fluid flow through a porous medium.

1.2. Preferential Flow - Theoretical Development

In the early 1970s numerous researchers were finding the Green-Ampt (piston flow) and miscible displacement models underestimating solute velocities 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 (1972), and Philip (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 solute "breakthrough" which had been 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 of flow as well as more subtle non-piston type flow processes not satisfactorily described by 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. Fluid flow research on regional, field, and laboratory soils indicated more and more frequently the presence of preferential flow phenomena.

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 1985). These flow paths bypass most of the mitigating, filtering, and adsorption processes that take place in the soil matrix.

Field studies such as those by Steenhuis and Goehring (1990) on effluent collected from subsurface tile drains, called attention to the accelerated movement of conservative and retarded tracers that were not explained adequately 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 field 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 indicated 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 then 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 preferential flow phenomenon needs further investigation. To understand what processes seem to dominate and/or dampen preferential flow, further laboratory and field experiments must be undertaken with controls

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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, and

- aid in predicting variables that might enhance or impede the presence of preferential flow phenomena.

2. MATERIALS AND METHODS

2.1 Soil Characterization

This study used two intact and two repacked columns of the same dimensions. 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 University of Arizona's Maricopa Agricultural Center (MAC). The field from which soil was used for this study had been uncropped for the past four 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 a 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 give a clearer picture of the site's overall physical and chemical processes 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 samples taken for this study relative to the grids created for the concurrently run solute transport study. A complete description of the Casa Grande soil is provided by Post et al. (1988).

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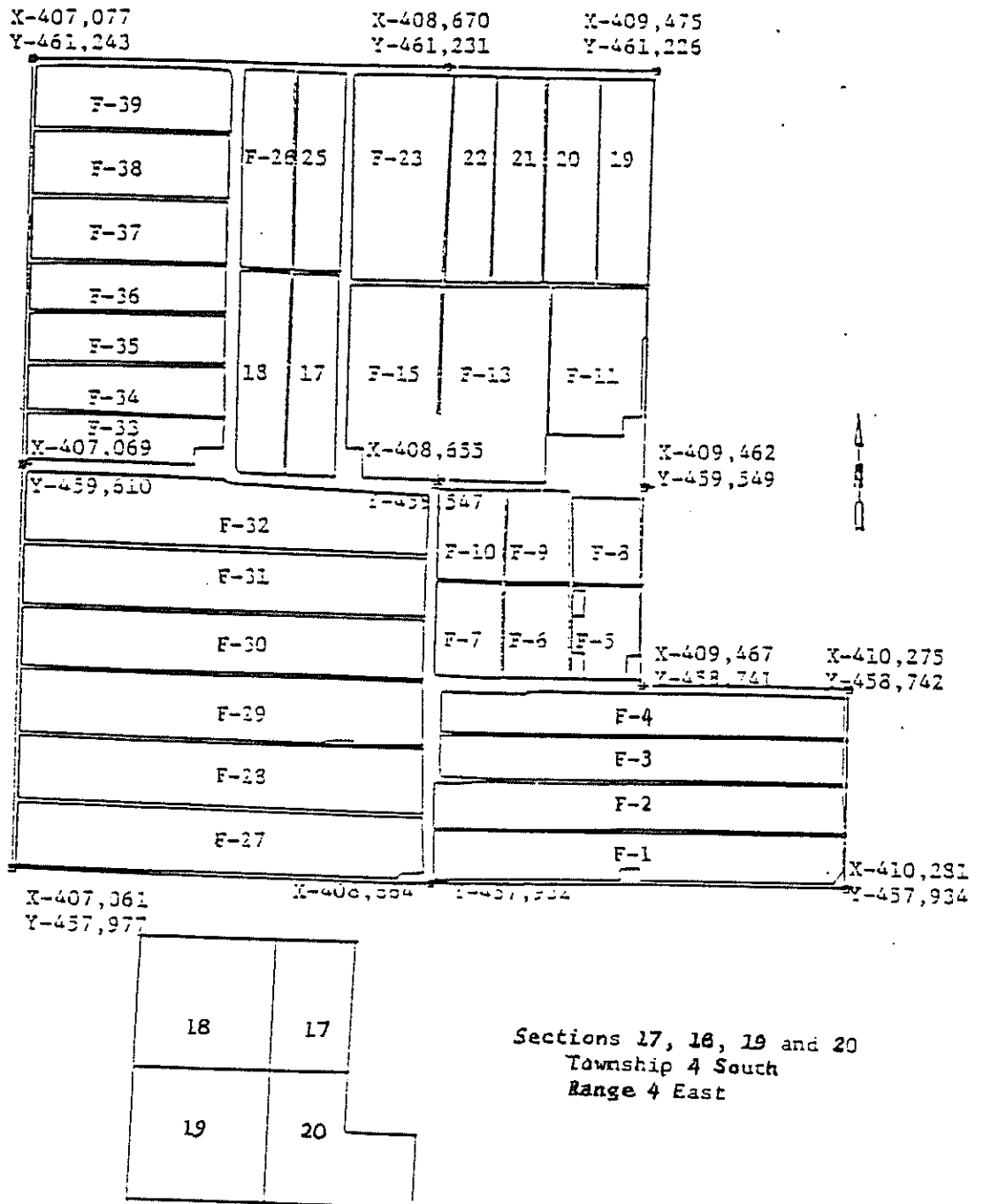
Fig. 1. Map of MAC Farm Located in Central Arizona (Post et al. 1988)

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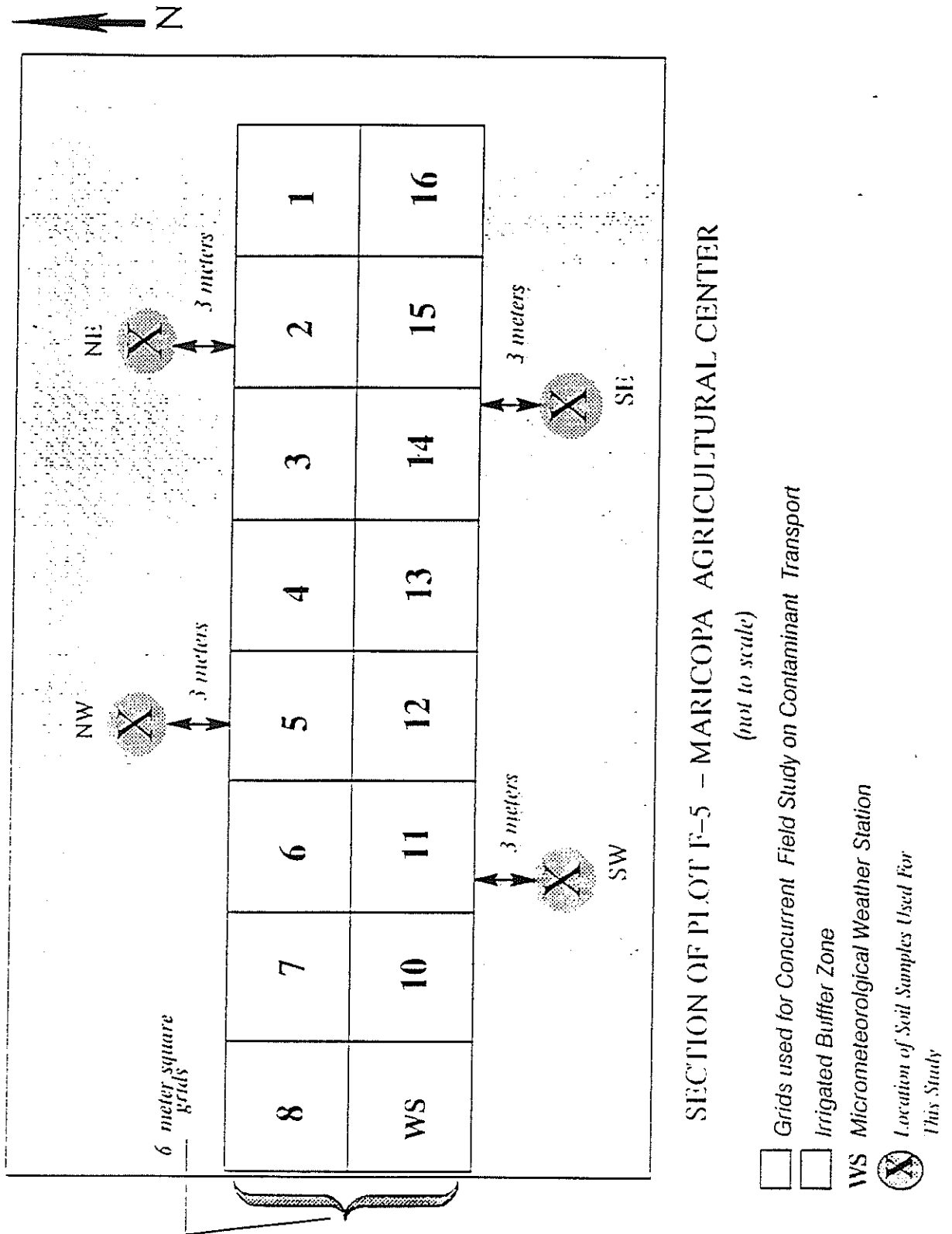
Fig. 2. Layout of a Section of Plot F-5 at MAC Denoting Location of Soil Samples taken for This Study and Concurrent Field Tracer Study.

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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. These parameters and the methods used to obtain them follows.

2.1.1 *Average Soil Bulk Density* $-\rho_{ab}$

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 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 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 had only a small percentage of clay, only one period of oven drying was considered

sufficient. The soil's mass was determined by subtracting the ring weight. Bulk densities, ρ_b, were 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

Depth	71.27 cm³ gr/cm³	Depth	100.0cm³ gr/cm³
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, p,ρ_{ad}, of the soil was calculated with the following equation

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

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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 mixed homogeneously. 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

$$GWC = \frac{\text{weight of soil before drying - weight of soil after drying}}{\text{weight of soil after drying}} \qquad [7]$$

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 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} g/cm^3	1.614	1.614
GWC	0.027	0.0256
ρ_{ad} g/cm^3	1.659	1.656

2.1.3 *Saturated Moisture Contents and Soil Moisture Characteristic Curve*

To determine column moisture contents from tensiometer readings and employ

prewritten programs yielding K_{unsat} values, it was necessary to find 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 Equip-

ment 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

were discarded as the TPC used for these measurements had a cracked porous plate.

Pressures applied to each cell ranged from 14 to 900 mBars. Figure 3 depicts pressure vs.

moisture content found using this procedure.

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 on the surface, indicating complete saturation. 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 room temperature, 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

Depth (cm)	(θ_s)
8	0.294
23	0.291
30	0.308
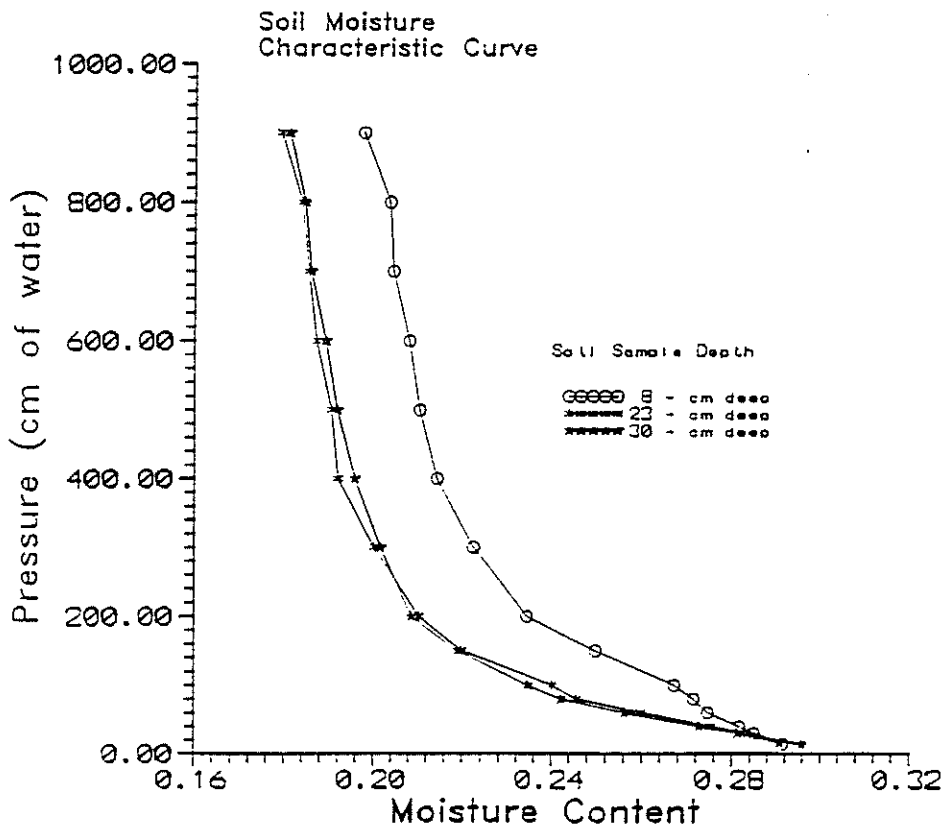
Figure 3. Soil Moisture Characteristic Curve for Casa Grande Soil Samples taken at Maricopa Agircultural Center.

2.1.4 *Porosities* η

Determining porosities, η, was needed to derive the amount of pore volumes, PVs, each column exhibited throughout the experiment's duration and degree of saturation, S_e. These two could be found using soil matric potentials obtained 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

$$\eta = 1 - \frac{\rho_b}{\rho_s} \qquad [8]$$

where ρ_s is the soil particle density, here considered to be 2.60 g/cm^3. Table 4 lists the porosities found for each core.

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 areas of the test site. To remove any entrapped air, each sample was presaturated for several days before being placed in the

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

Ring Samples			
71.27 cm³		100.0 cm³	
Depth cm	η	Depth cm	η
8	0.3661	2	0.3292
15	0.3685	8	0.3684
23	0.3692	30	0.3934
30	0.4019		
Avg. η	0.371	Avg. η	0.371

Table 5. Saturated Hydraulic Conductivity of Casa Grande In Situ, IS, and Repacked, RP, Soil Samples taken from Maricopa Experimental Farm

Location	Depth (cm)	Type	K_{sat} cm/sec	
			Room Temp($\sim$23°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}

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

$$K_{unsat} = K_{sat} S_e^{\lambda} \left[\frac{f(S_e)}{f(1)} \right]^2 \qquad [9]$$

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

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

and

θ_r = residual moisture content

θ_s = saturated moisture content

S_c = 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

$$\theta = \theta_r + \frac{(\theta_s - \theta_r)}{[1 + (\alpha\psi)^n]^m} \qquad \text{or} \qquad \theta = \theta_r + \frac{(\theta_s - \theta_r)}{(\alpha\psi)^n} \qquad [10]$$

(a)   (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. Figure 4 is plot of K(θ) vs. pressure head for the soil samples taken at different soil depths using the aforementioned model.
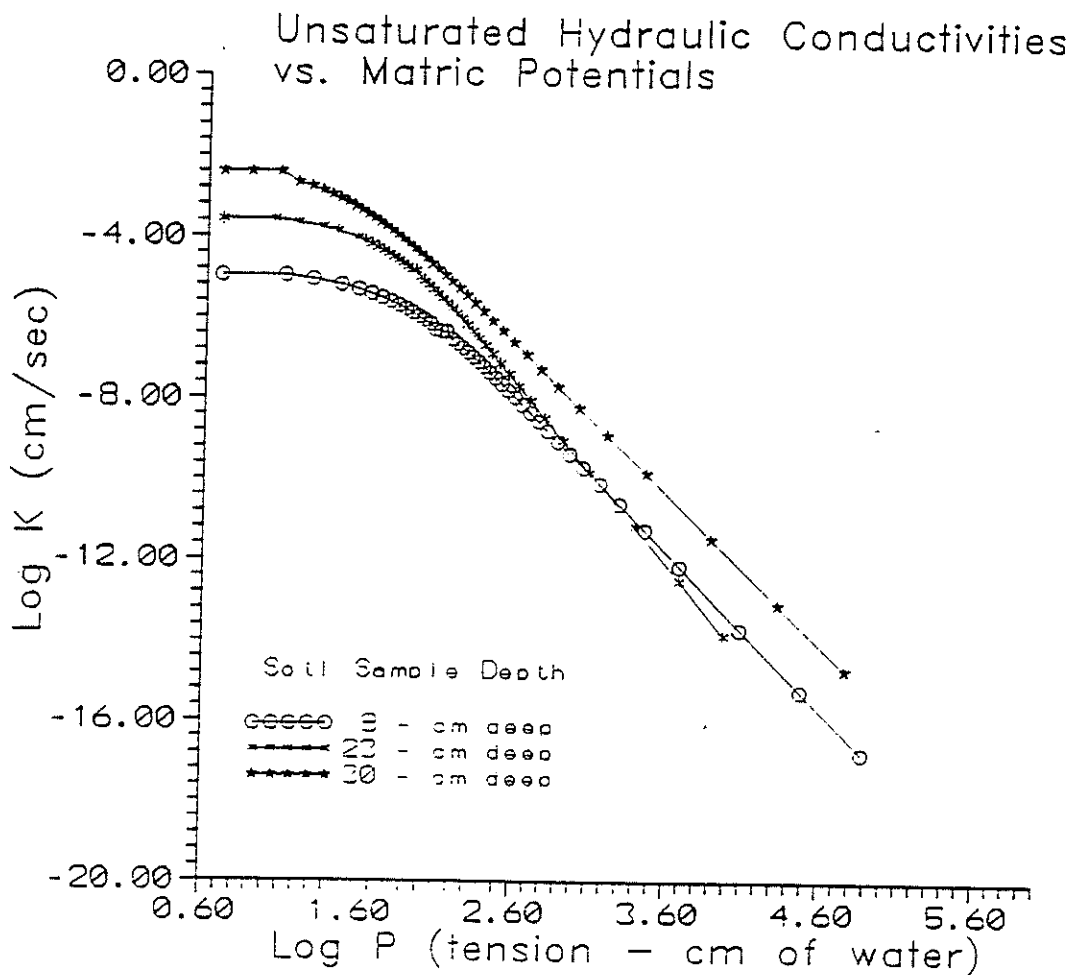
Fig. 4. K(θ) vs. Ψ for Casa Grande Soil Samples taken at Maricopa Agricultural Center.

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). 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. Setup time on sunny days using this ratio was about one hour. During overcast or cool days the ratio was reduced, as lack of exposure to the sunlight or a temperature drop increased the setup 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 and 5 x 45-cm strips 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 one 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,

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NE, and SE corners of the field (figure 2).

The soil columns were then transported to the laboratory where the best two of the four intact columns were trimmed 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. Nine-cm 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's 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 it 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 endplate assemblage was placed on the column bottom after a thick slurry of silica flour, a few mm deep, had been poured on the bottom

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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 endplate 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 filled with encasing material or soil. This resulted in a final product that had a slightly irregular diameter that varied $\pm$ 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

Location	NW	SW
Column #	1	2
Diameter - (cm)	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 re-packed columns were made of clear acrylic tubing (Regal Plastics, Albuquerque, NM) 14.6-cm inside diameter (I.D.). 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 endplate 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 de-termined by placing the columns on a scale, taring, then filling with water and recording the water's weight.

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

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

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

A 300-mL glass beaker was used to scoop the soil gently from a plastic bucket and transfer it 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 minimize 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 inspected visually 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 settle the soil further 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	
Location	NW	SW
Column	3	4
Diameter (cm)	14.6	14.6
Length (cm)	32.5	32.3
Volume (cm^3)	5309.6	5280.1
Soil Densities and Total Mass used per Column		
ρ_{bd} (g/cm^3)	1.659	1.656
Total Mass of Soil (g)	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 from a 20-cm wagon tire that had four, equally spaced holes 1 cm in diameter, 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 threaded brass rods, 15-cm long, 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 wedged tightly 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 four, evenly spaced, 18-gauge hypodermic needles inserted through the base and into approximately 2.5 çm 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 but before the first pond was applied.

Five, horizontal holes, 0.6 cm in diameter by 4-cm deep, 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 and the column encasement materials. Figures 5 and 6 are 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). 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.

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 together tightly 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. Male luer fittings were glued in these holes. Twenty-two-gage hypodermic needles were later attached. The other Plexiglas piece had two predrilled ports with appropriate couplings attached. One port was attached to a supply line and 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

9 CM

PVC Collar

32.5 CM

1

3.5 CM

1   TENSIOMETERS

2   END PLATE
    ASSEMBLAGE

3   LUER FITTINGS
    WITH ON OFF VALVE

4   MOUNTING STAND

2

3

4
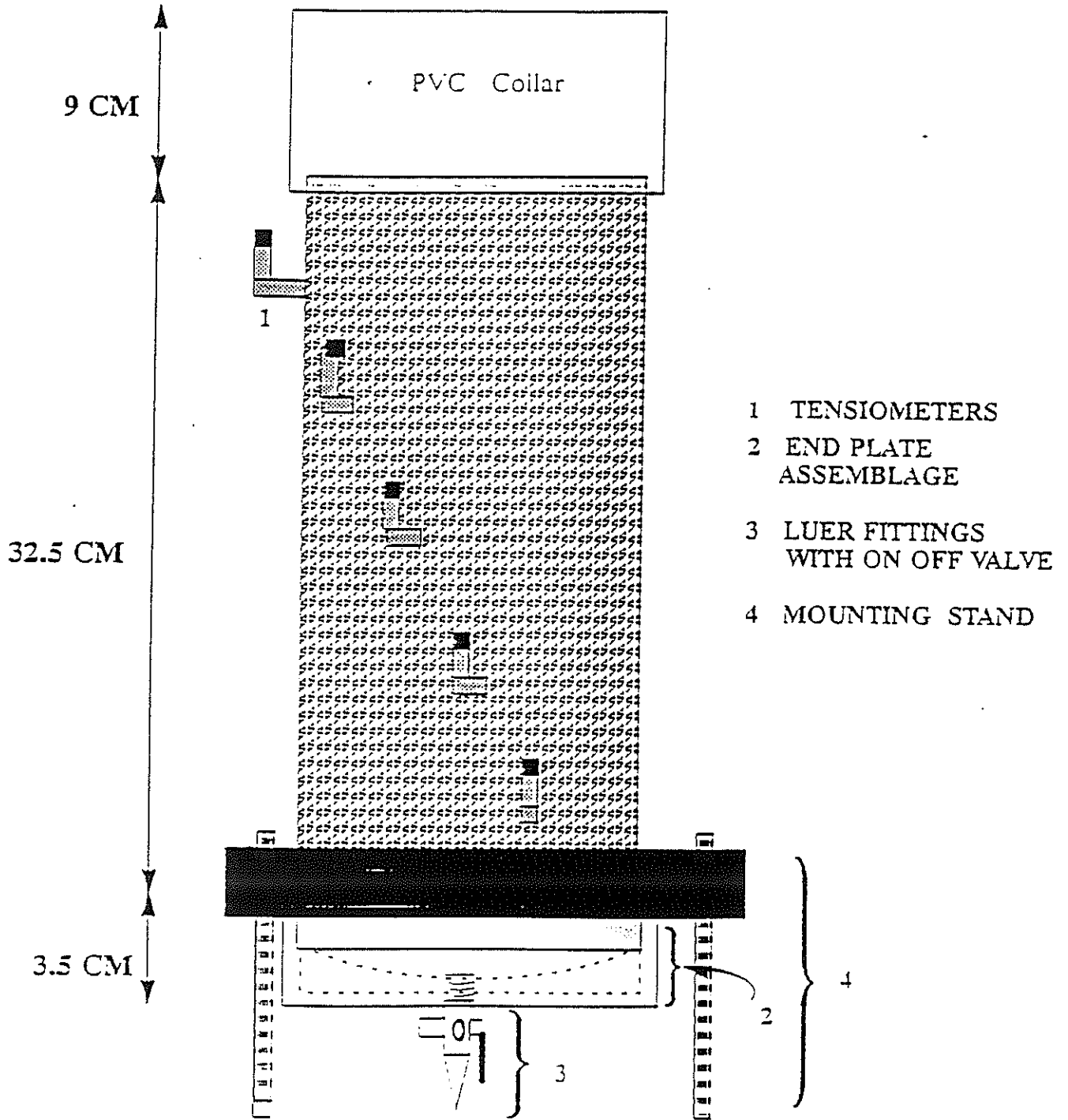
Fig. 5. Schematic of Instrumented In Situ Column taken from Maricopa Agricultural Center.

30
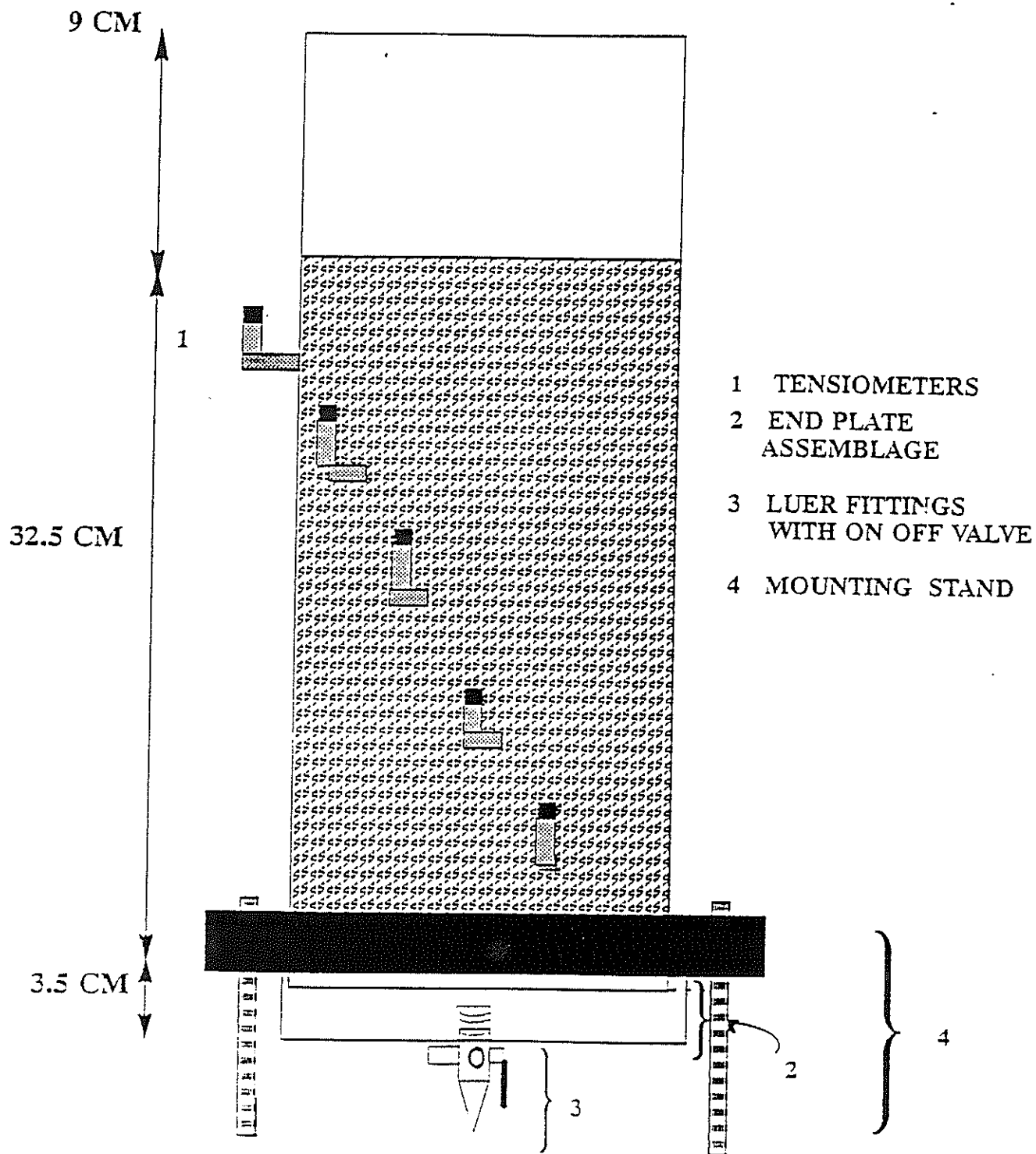
Fig. 6. Schematic of Instrumented Repacked Column using Soil taken from Maricopa Agricultural Center.

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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 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 CTRL1-0P/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.

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.

Fluid Switch Wafer

12 Volt
excititation
for TDCR
and Signal
Conditioner

Purge Valve

Syringe Pump

Pressure
Transducer
(TDCR)

Fraction
Collector

Vacuum Chamber

PC with
A/D Board

Leachate Solution
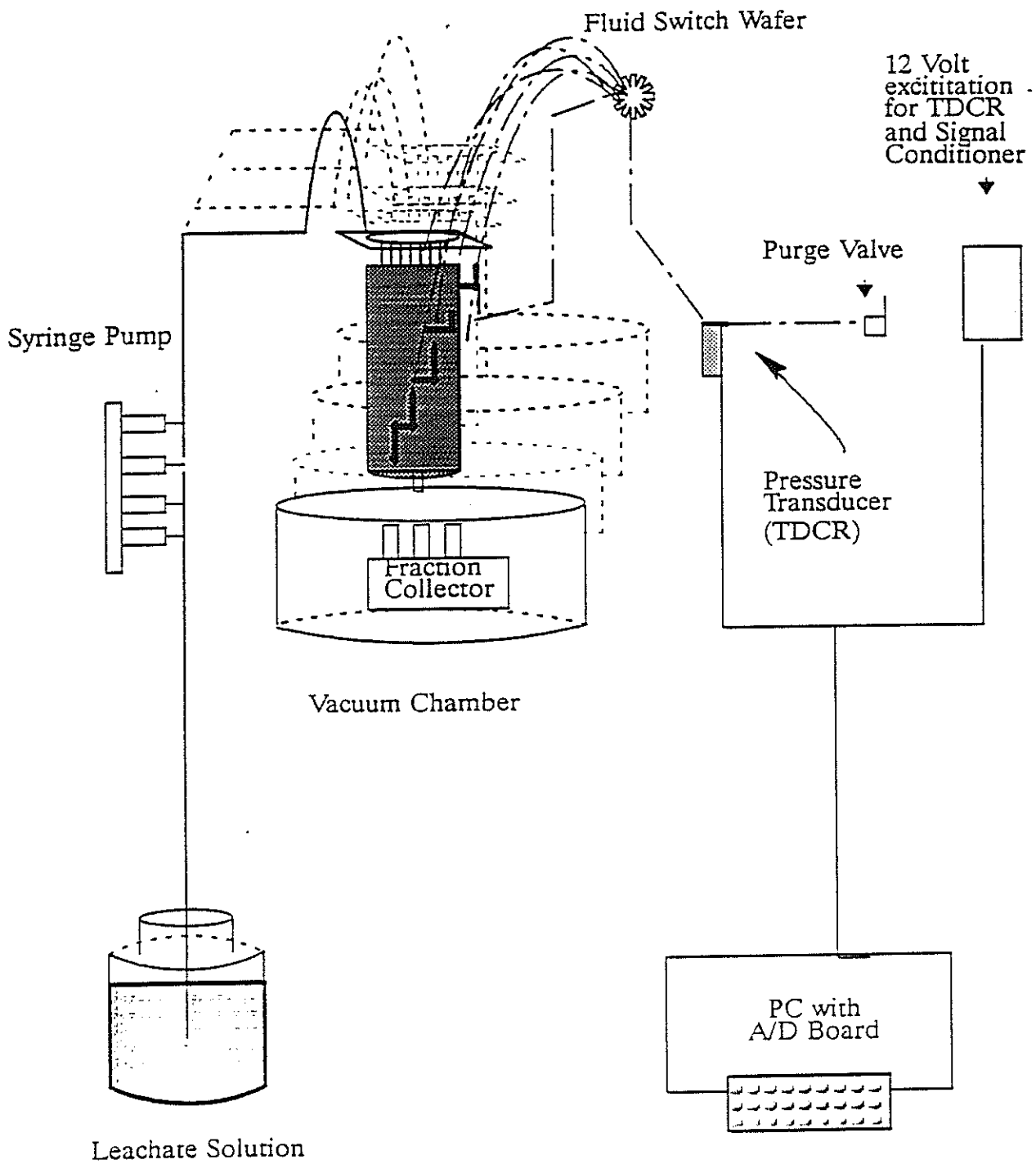
Fig. 7. Schematic of Laboratory Setup

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 (figure 2) at the Maricopa Agricultural Center 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 columns 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
Ca^{+2}	0.0036	144.28
Mg^{+2}	0.0016	40.10
Na^+	0.0184	423.0
SO_4^{-2}	0.0092	883.35
Cl^-	0.0108	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. Ten 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 (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 thereof. 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 in situ columns, having a cross-sectional area of 160.33 cm^2, required 23.88 mg m-TFMBA and 53.20 mg bromacil to be

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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 in situ 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 were 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 are given in Table 9.

Table 9. Composition of Tracer Solution 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 (0.95 pure)	0.31636	1049	0.050	0.052
Inert Components	0.01665	NA	0.0026	0.0027
m-TFMBA	0.1490	494	0.0236	0.0247
KOH (0.85 pure)	9.04	29,996	1.43	1.50
Inert Components	1.59	NA	0.25	0.26
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 was determined. A comparison was made of the identified 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 placed vertically on a vacuum chamber containing a fraction collector. The vacuum chambers and columns were connected together with luer fit-

tings attached to the chamber lid and a three-way stopclock 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 columns' length was desired. This is required finding 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 (1.3×10^{-4} cm/sec) giving fluxes of 7.52×10^{-6} cm/sec (approximately .65 cm/day) for the repacked and 7.85×10^{-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 monitoring 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 two to three days between 15 cm of water, and columns 2 and 3 between 10 cm of water. Tension fluctuations were attributed to small air pockets that accumulated within the scanivalve lines every two or three days, and growth of an unknown microorganism that seemed to make the tensiometers sluggish toward the end of the steady-state unsaturated flow experiment. This required flushing several tensiometers and scanivalve lines within the data acquisition system every two or three days. Atmospheric pressures were not checked, but daily fluctuations partially could have caused tensiometer readings to vacillate. A linear regression analysis determined 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 quite achieved at the time

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

Depth (-cm)	r^2 for each Column			
	1	2	3	4
5	0.21	0.26	NA	NA
10	0.06	0.37	0.81	0.12
18	0.31	0.10	0.81	0.47
23	0.07	0.27	0.91	0.33
28	0.26	0.47	0.92	0.14

Column 1
Pressure Head Distribution
Along Column Length

Soil Surface

Soil Surface

⊙⊙⊙⊙⊙ 5 days before tracer added
•‒‒‒ 1 hour after tracer added   Nov. 6
•‒•‒ 2 hours after tracer added
▯▯▯▯▯ day 5
△△△△△ day 10
∗∗∗∗∗ day 15
◇◇◇◇◇ day 20
⊖⊖⊖⊖⊖ day 25
•‒‒‒• day 35

Column 2
Pressure Head Distribution
Along Column Length

Soil Surface

⊙⊙⊙⊙⊙ 5 days before tracer added
•‒‒‒ 1 hour after tracer added   Nov. 6
▮‒‒‒▮ 2 hours after tracer added
▯▯▯▯▯ day 5
△△△△△ day 10
∗∗∗∗∗ day 15
◇◇◇◇◇ day 20
⊖⊖⊖⊖⊖ day 25
•‒‒‒• day 35

Fig. 8. Matric Potentials at Near Steady State and Unit Gradient Conditions for In Situ Columns 1 and 2 - Steady-State Unsaturated Flow Regime

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Column 3
Pressure Head Distribution
Along Column Length

Pressure — Cm of Water

Column 4
Pressure Head Distribution
Along Column Length

Pressure — Cm of Water
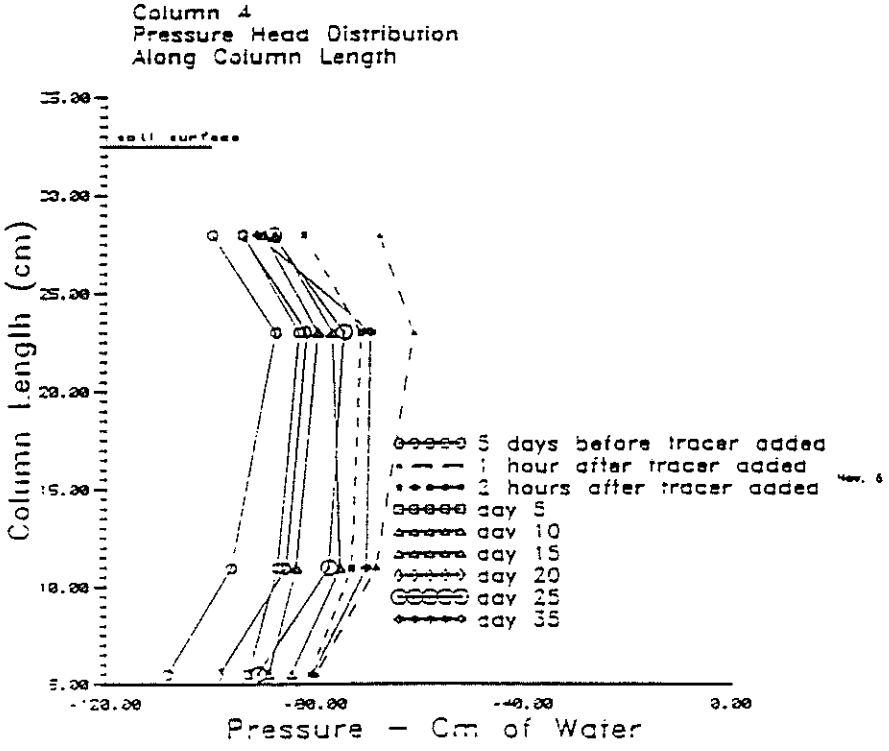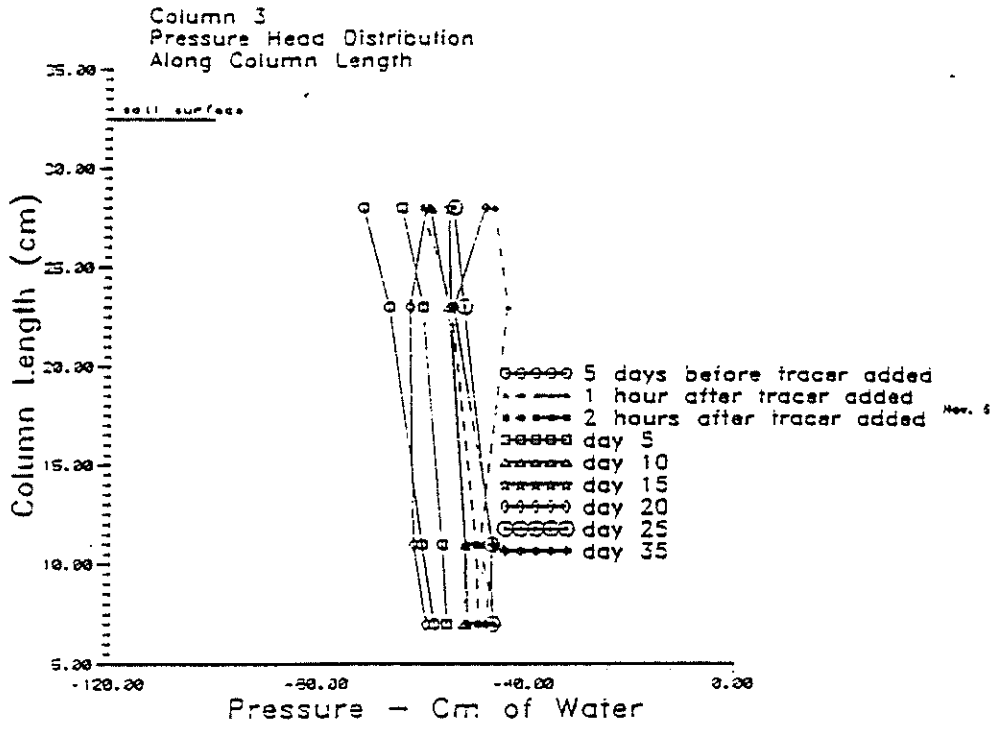
Fig. 9. Matric Potentials at Near Steady State and Unit Gradient Conditions for Repacked Columns 3 and 4. - Steady-State Unsaturated Flow Regime

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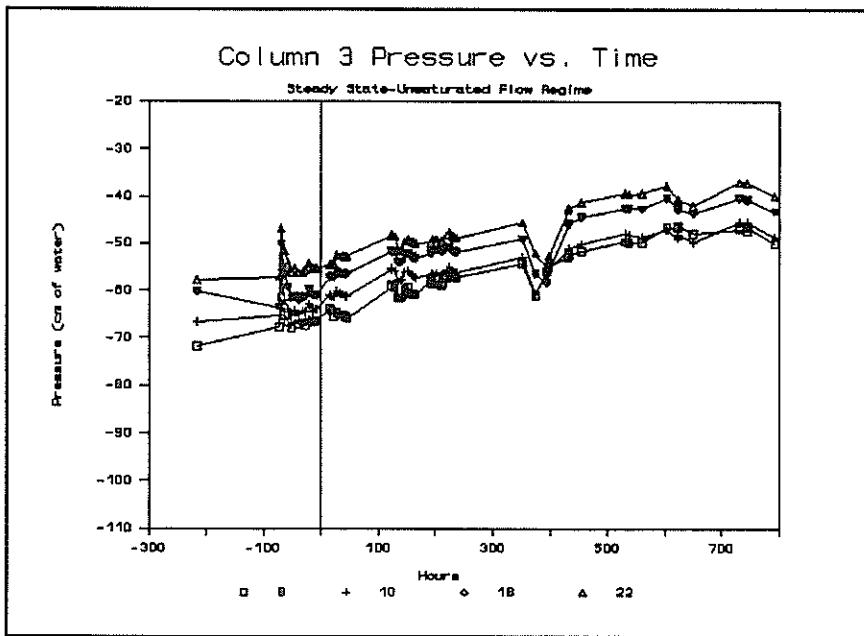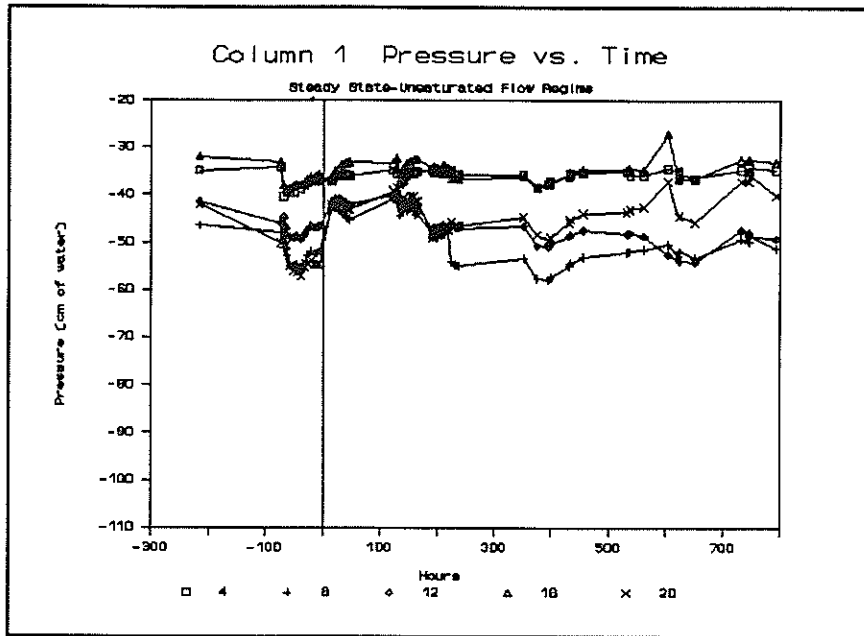
Fig. 10 Pressure Changes vs. Time for In Situ Column 1 and Repacked Column 3 during Steady-State Unsaturated Flow Regime

Symbols on the graphs denote tensiometer numbers for each column. Tensiometer pressures have been adjusted for depth. The dividing line denotes time when tracer was added.
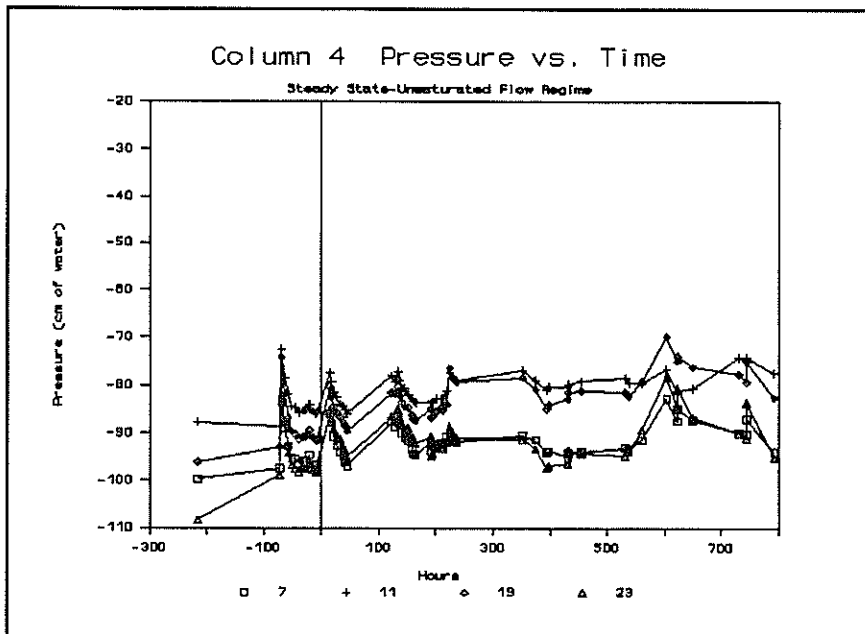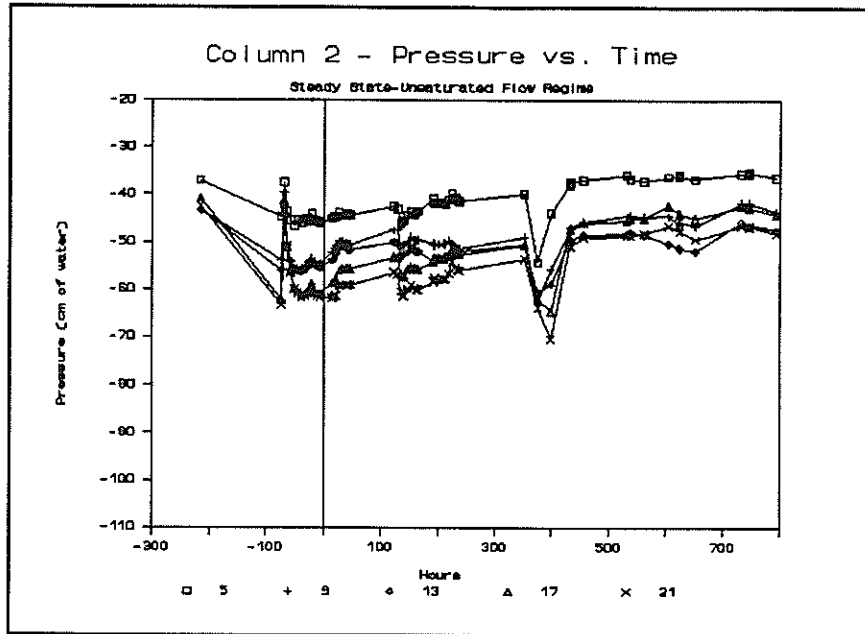
Fig. 11 Pressure Changes vs. Time for In Situ Column 2 and Repacked Column 4 during Steady-State Unsaturated Flow Regime.

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

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the tracers were 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 entire procedure, per column, took 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, was 0.798, for Column 1, 0.806 for Column 2, 0.975 for Column 3, and 0.932 for column 4. 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 0.00707, 0.00679, 0.00757, and 0.00843, respectively.

At the end of the steady-state unsaturated flow experiment, all columns were ponded with 700 cm^3 of leaching solution and allowed to drain for one week. This was repeated a second time. Two ponding events were conducted to flush out any residual bromacil that had not yet been removed from each column during the steady-state unsaturated flow regime. Bromacil concentrations after this process were 0.65, 1.22, 0.08, and 0.02 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 de-livered to each column during a seven-day time period for the unsaturated flow experiment.

Each column was brought to the same steady-state conditions as 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 for as the steady-state flow regime.

All columns were placed on their respective vacuum chambers and vacuums applied at the same pressures as for 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 one hour. From 40 hours to the next ponding event, collection times per vial were set to three 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 intermittent ponding experiment. This aided in monitoring the movement of wetting fronts. Figures 12 and 13 are representative matric potentials for one ponding cycle.

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 five 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.

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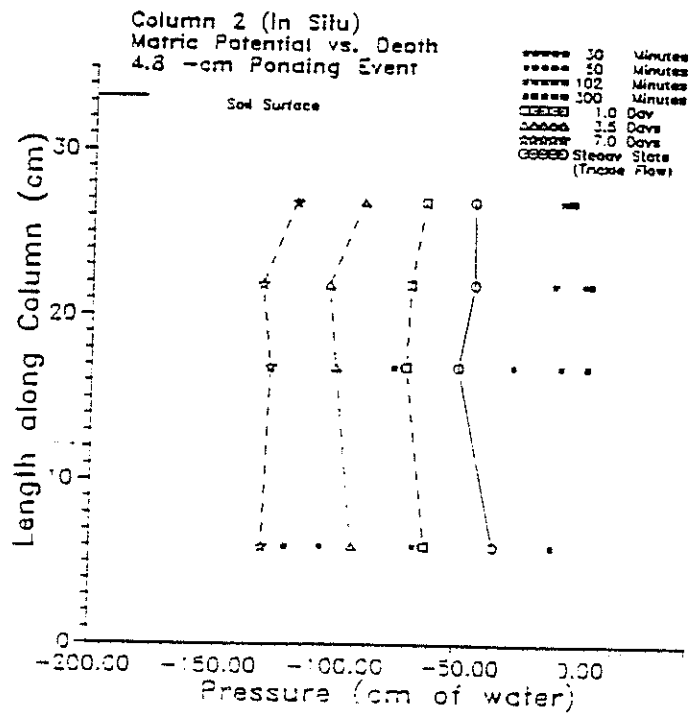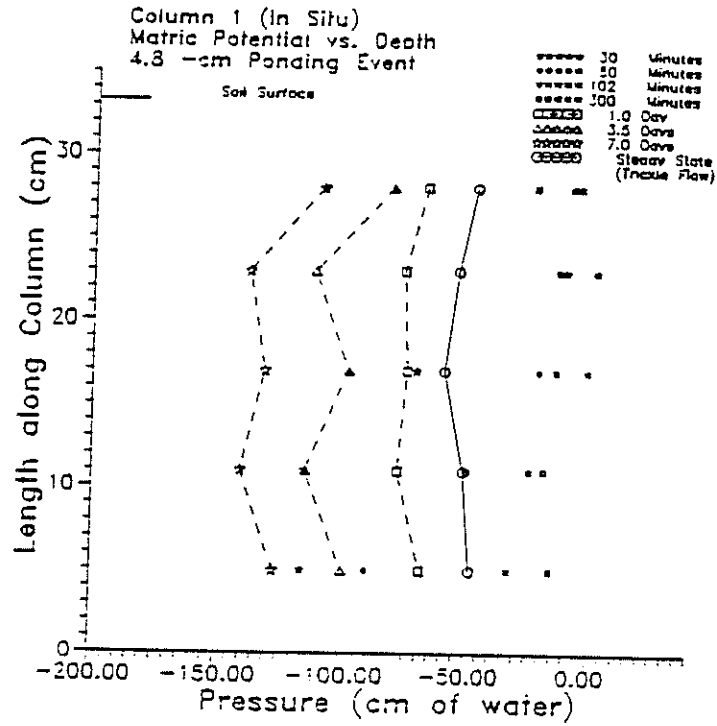
Fig. 12. Matric Potentials for Wetting and Draining Cycle of In Situ Columns 1 and 2 - Intermittent Ponding Flow Regime

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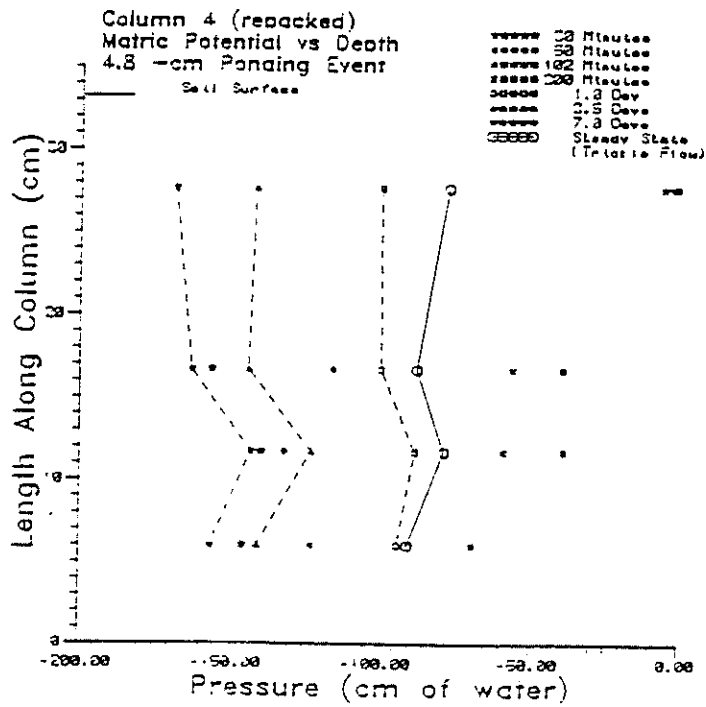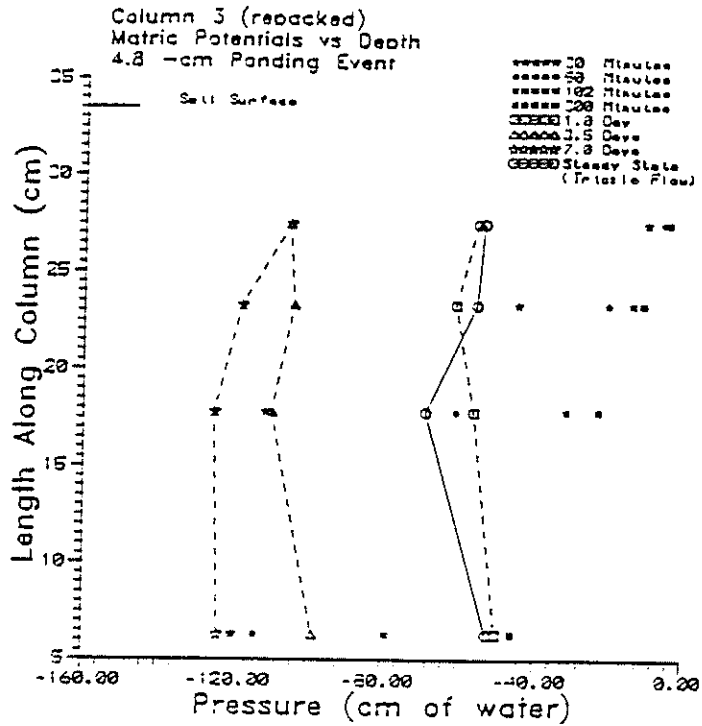
Fig. 13. Matric Potentials for Wetting and Draining Cycle of Repacked Columns 3 and 4 - Intermittent Ponding Flow Regime.

Initially, the BTC of m-TFMBA for each column was determined and required approximately 20 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 occurred 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

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

Flow Regime	% Recovery			
	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

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 using the same soil as in this study and bromacil as one of the tracers, (Bowman and Rice 1986a) showed recoveries of 89%. Soil profile heterogeneities and less than uniform tracer application 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.

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.

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

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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 were 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 0.5% 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 columns lower boundary. Concentrations were considered flux averaged. Initial and boundary conditions using a flux average solution are

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

$$C(0,t) \quad = \quad \begin{cases} C_0, & 0 < t \leq t_o \\ \\ 0, & t > t_o \end{cases} \qquad \text{- at the upper boundary}$$

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

where C_o is the input concentration and t_o is the duration 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 column length. PVs for the transient flow regime were calculated by integrating numerically the volume of effluent over a one-week ponding cycle. One ponding cycle was sliced into three-hour intervals. The volume of effluent was measured for each three-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 three-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 dis-

placing 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 induced 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, the α of the soil matrix will diverge, to a lesser or greater extent, from one. 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	0.222	0.219	0.271	0.282
θ-gravimetric	0.305	0.2949	0.357	0.311
$\dfrac{\theta\text{-CXTFIT}}{\theta\text{-gravimetric}}$	0.720	0.742	0.760	0.907
$PV_{bypassed}$	0.280	.258	0.240	0.093
D-CXTFIT -cm²/day	1.46	2.46	2.86	3.53
α CXTFIT -cm	0.467	0.793	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

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 0.907, respectively from $v_{derived}$. A comparison of v_{cxt} between the two column 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

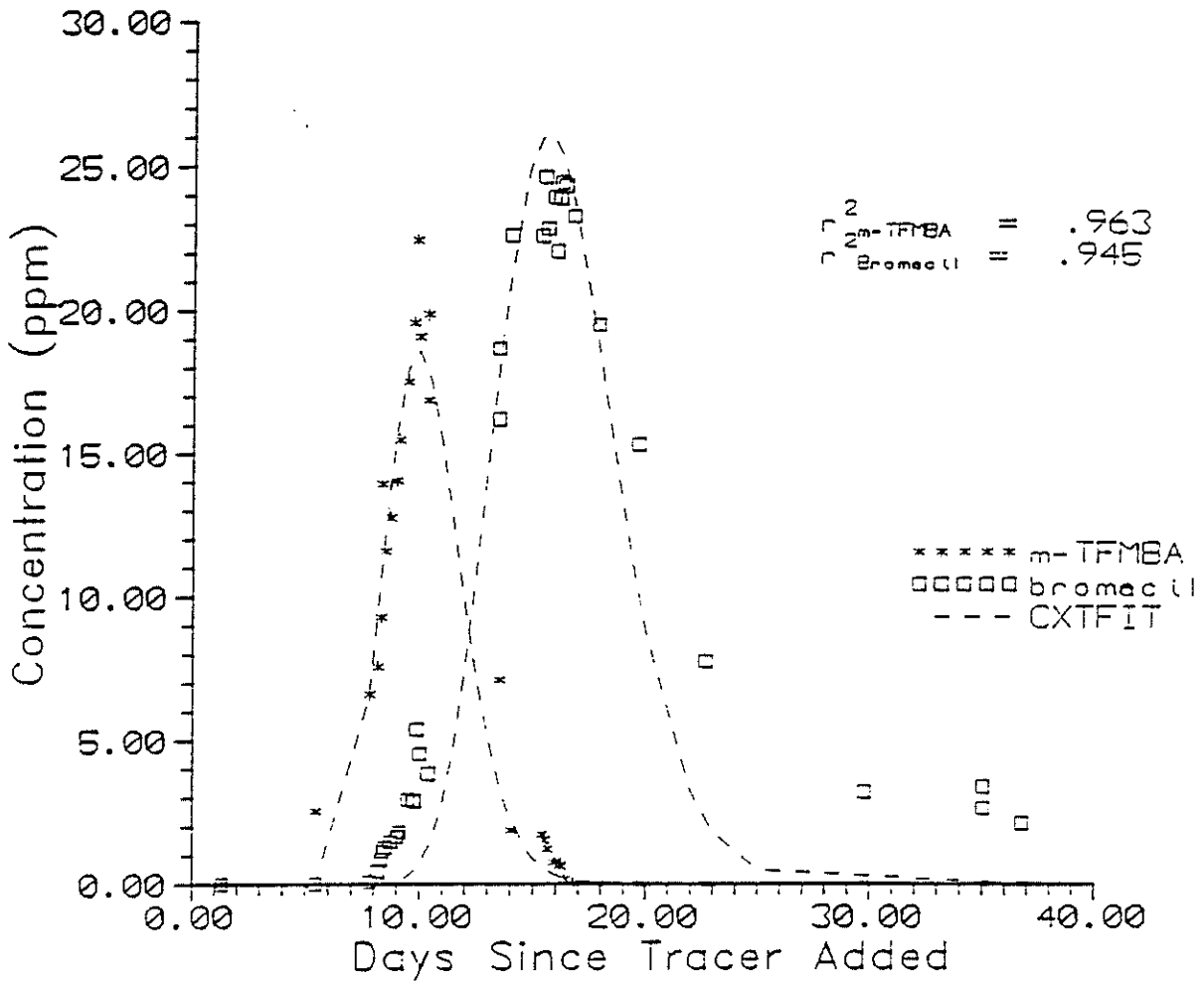Fig. 14. m-TFBMA and Bromacil BTCs for In Situ Column 1 - Steady-State
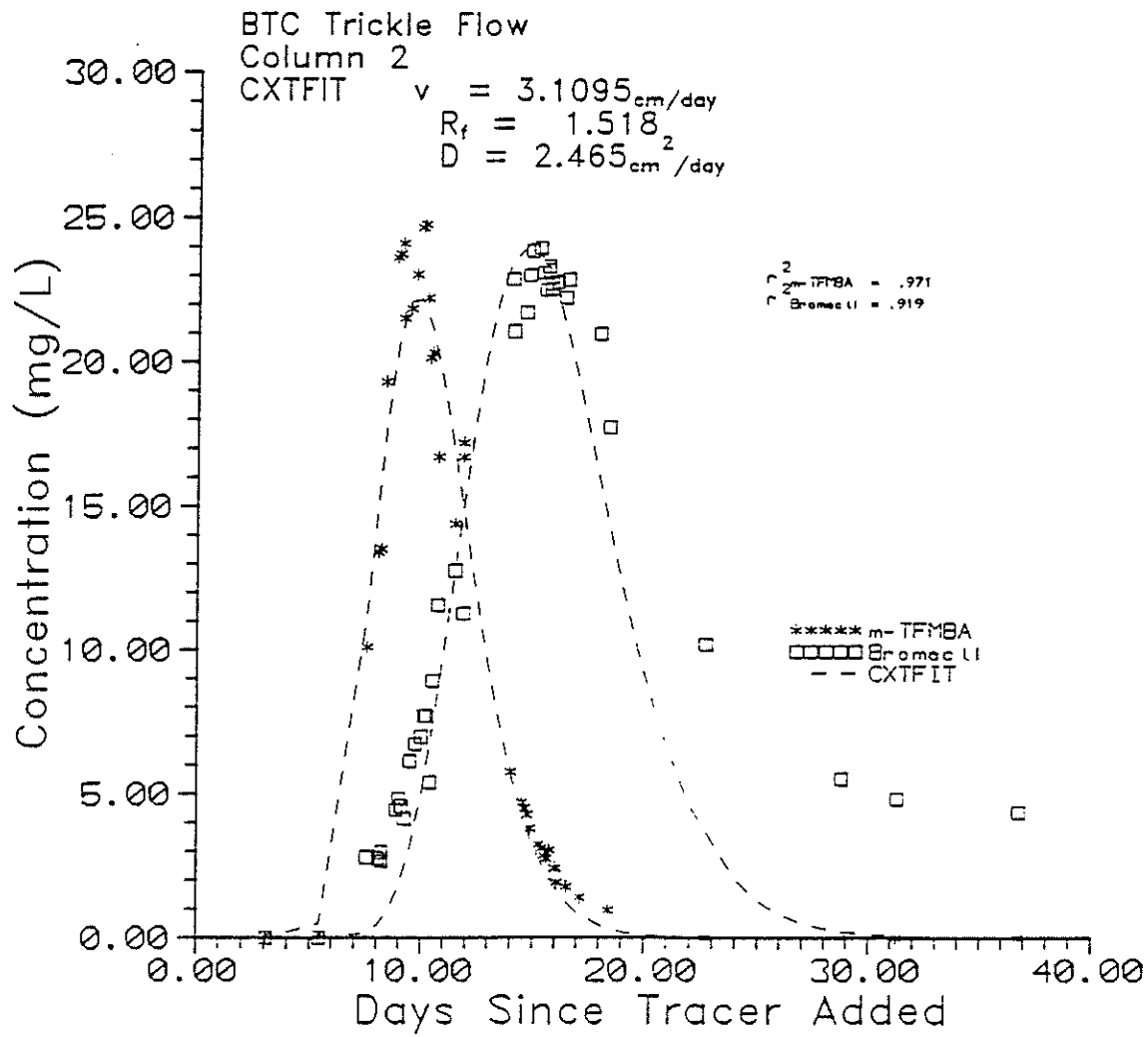Unsaturated Flow Regime.

Fig. 15. m-TFBMA and Bromacil BTCs for In Situ Column 2 - Steady-State Unsaturated Flow Regime.
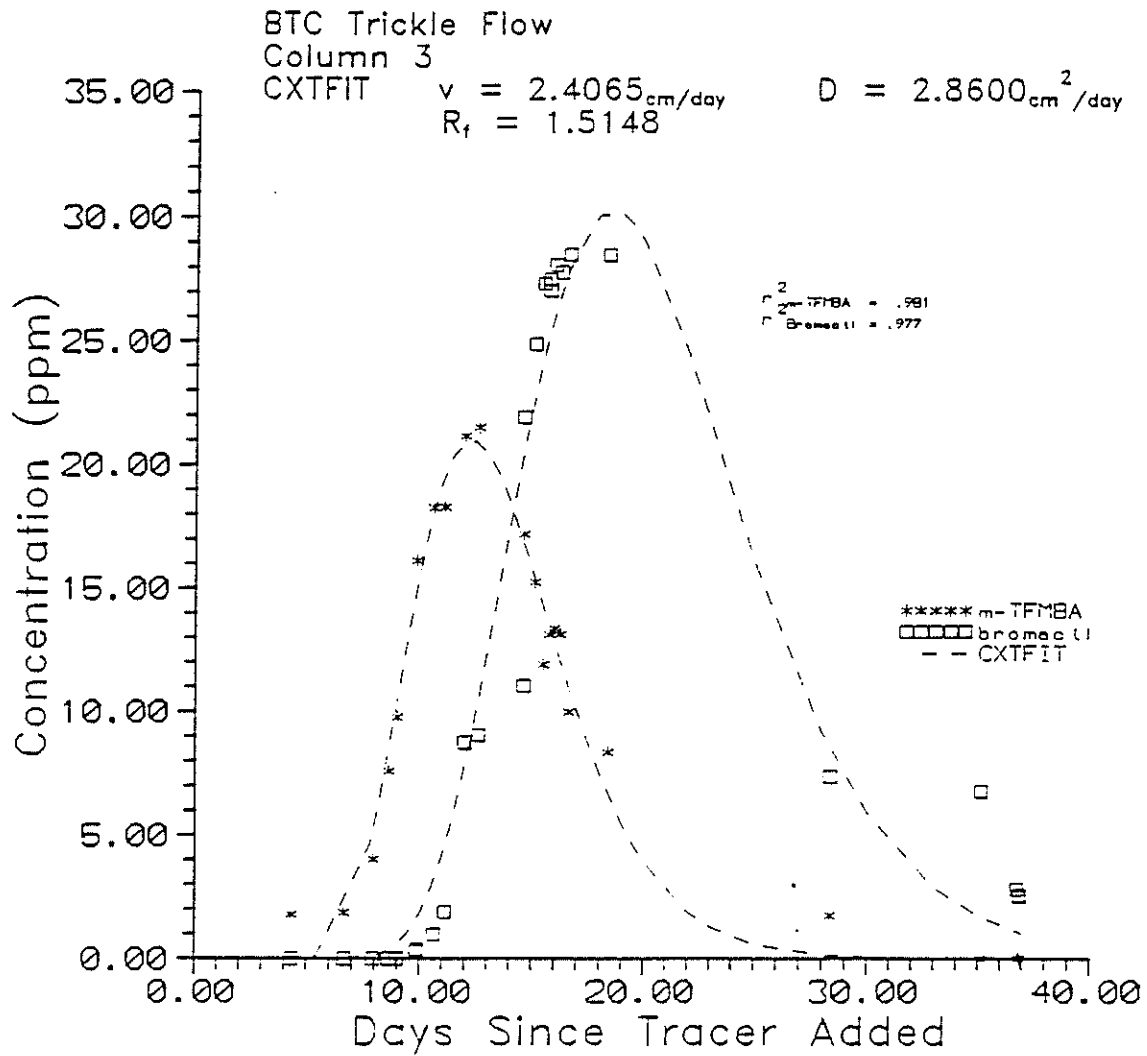
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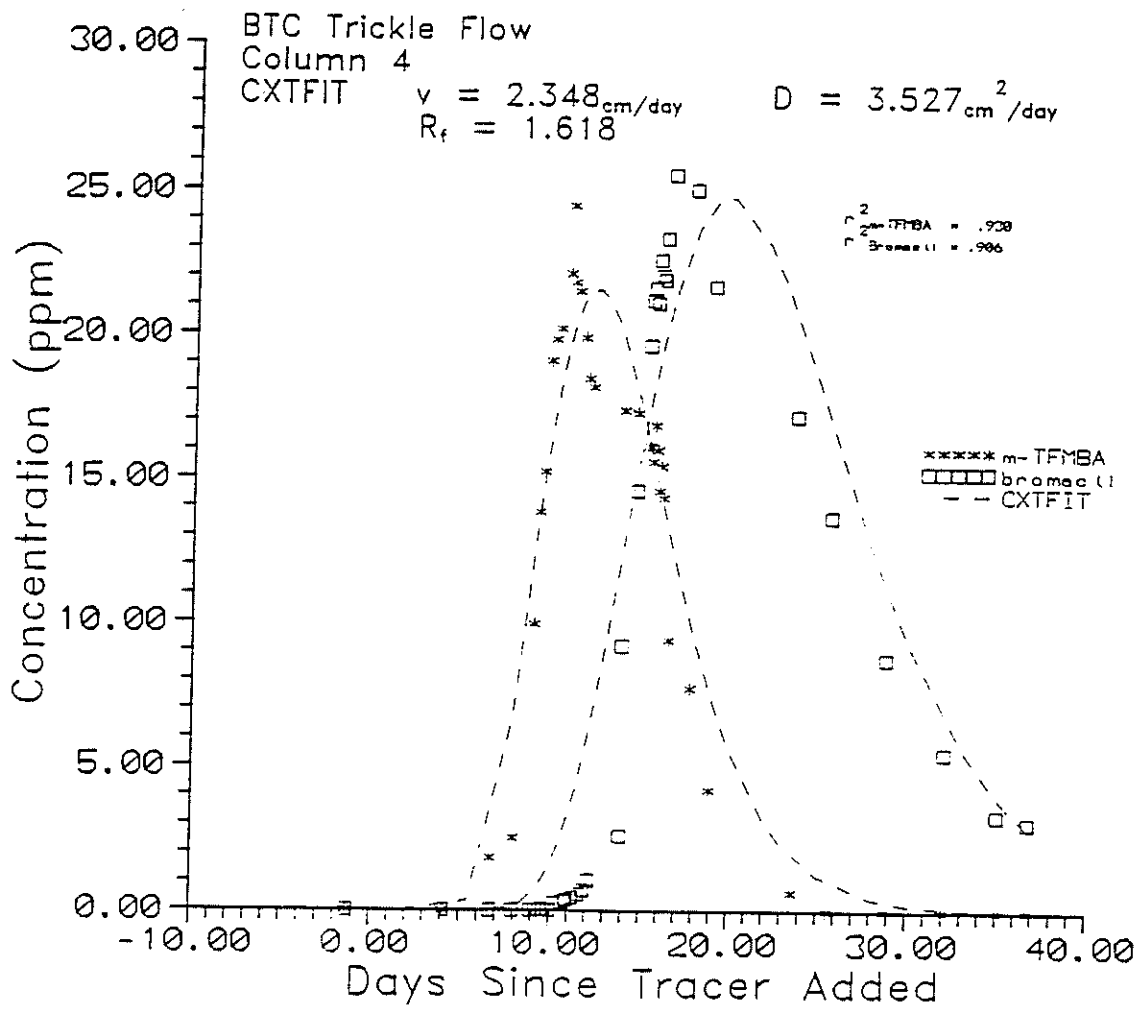**Fig. 16. m-TFBMA and Bromacil BTCs for Repacked Column 3 - Steady-State Unsaturated Flow Regime**

Fig. 17. m-TFMBA and Bromacil BTCs for Repacked Column 4 - Steady-State Unsaturated Flow Regime.

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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. Column 3 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 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_{nt}. Examination of matric potentials monitored over the entire steady-state flow period indicate a large change in storage occurred in this column

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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, indicates 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 altered significantly 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 (0.094 mL/g) 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

R_f	NW 1	NW 2	SW 3	SW 4
	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	0.087	0.111	0.0682	0.0629

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 varied widely from one another, Column 1 having the largest variation. The reason for these high values seems obvious intuitively. 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 dominated by smaller pores and/or pore networks as the spread of BTCs data imply (see Figure 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 in situ columns. This is supported further by the fluctuating nature of effluent pHs. Immediately after each ponding event, pHs

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

Parameters	in situ 1	in situ 2	Repacked 3	Repacked 4
$.V_{avg}$ -cm/day	2.79	2.79	2.27	2.29
$V_{m-TFMBA}$	4.59	2.56	2.48	3.36
$\theta_{average\ from\ trans\ meas.}$	0.246	0.248	0.265	0.260
θ_{CXTFIT}	0.163	0.150	0.194	0.253
$\theta_{gravimetric\ at\ end\ of\ pond}$	0.213	0.258	0.2817	0.262
$\theta_{m-TFMBA}$	0.224	0.296	0.253	0.253
$\dfrac{\theta_{-CXTFIT}}{\theta_{-gravimetric}}$	0.7635	0.582	0.689	0.973
$PV_{bypassed\ using\ \theta cxt\ and\ \theta\ grav}$	0.236	0.419	0.307	0.027
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	0.944	0.919	0.935	0.947
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	0.921	0.845	0.900	0.942
$R_{f-CXTFIT}$	1.921	2.035	1.775	1.599
$R_{f\theta\ grv}$	1.714	1.606	1.530	1.591

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 dominated by
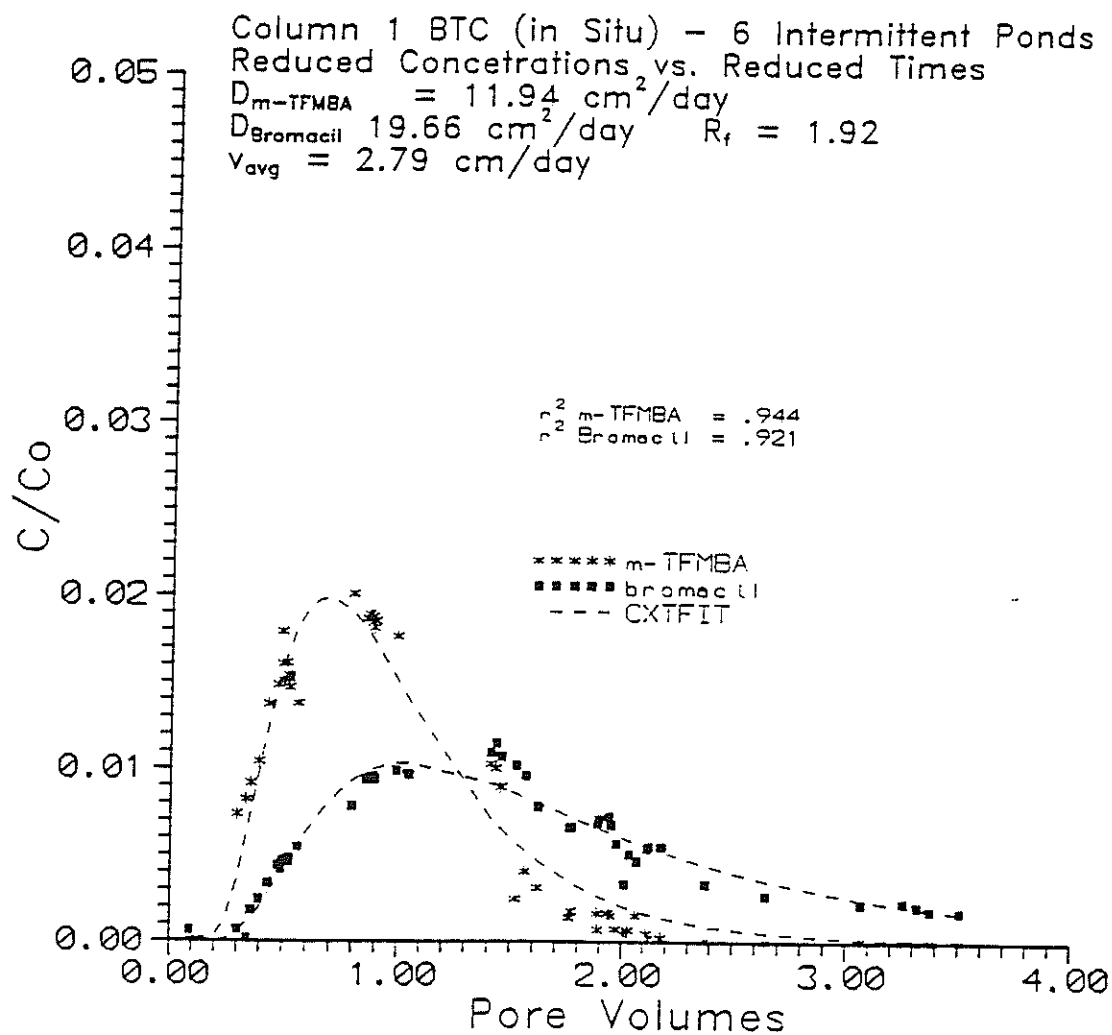
Fig. 18. m-TFMBA and Bromacil BTCs for In Situ Column 1 - Intermittent Ponding Flow Regime.
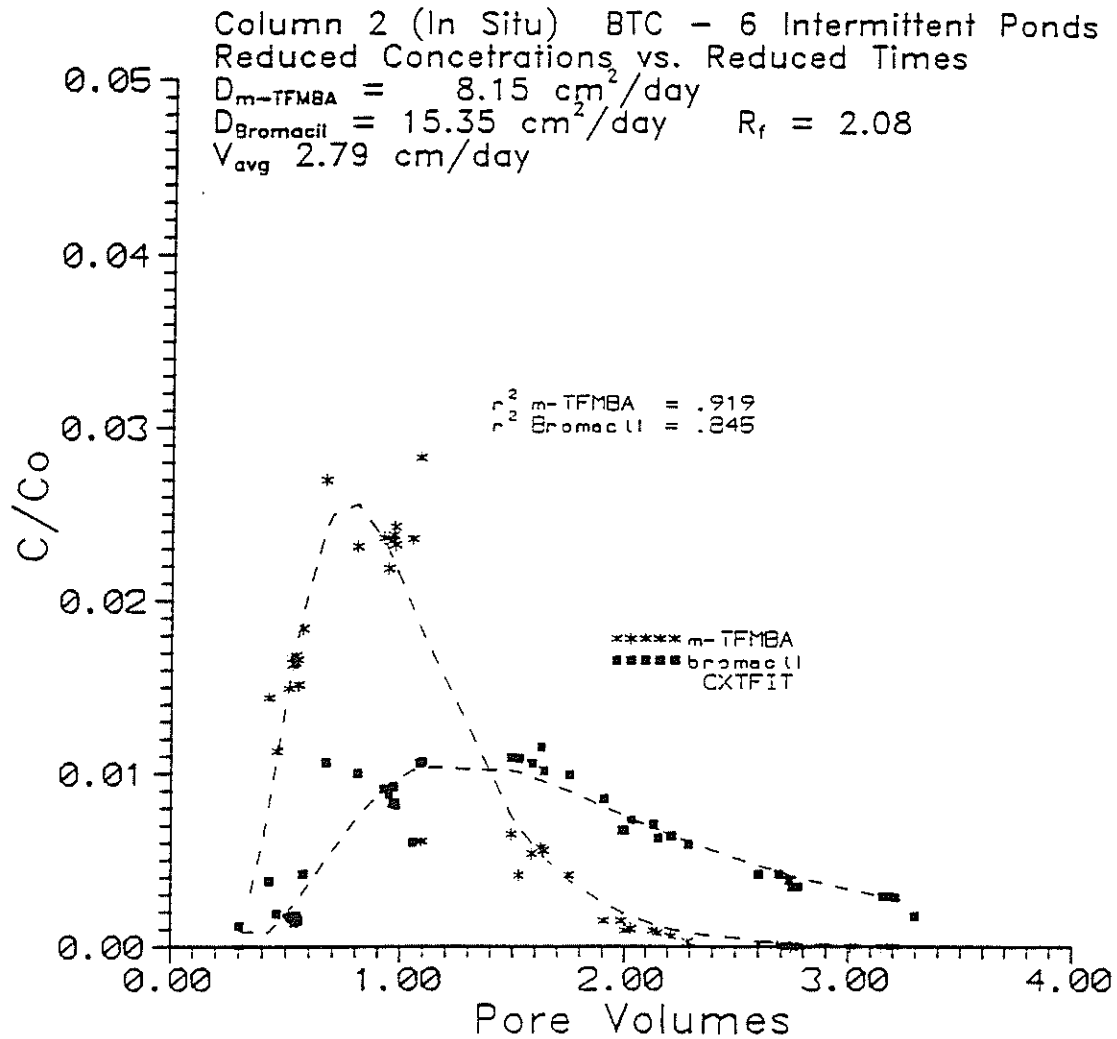
Fig. 19. m-TFMBA and Bromacil BTCs for In Situ Column 2 - Intermittent Ponding Flow Regime.
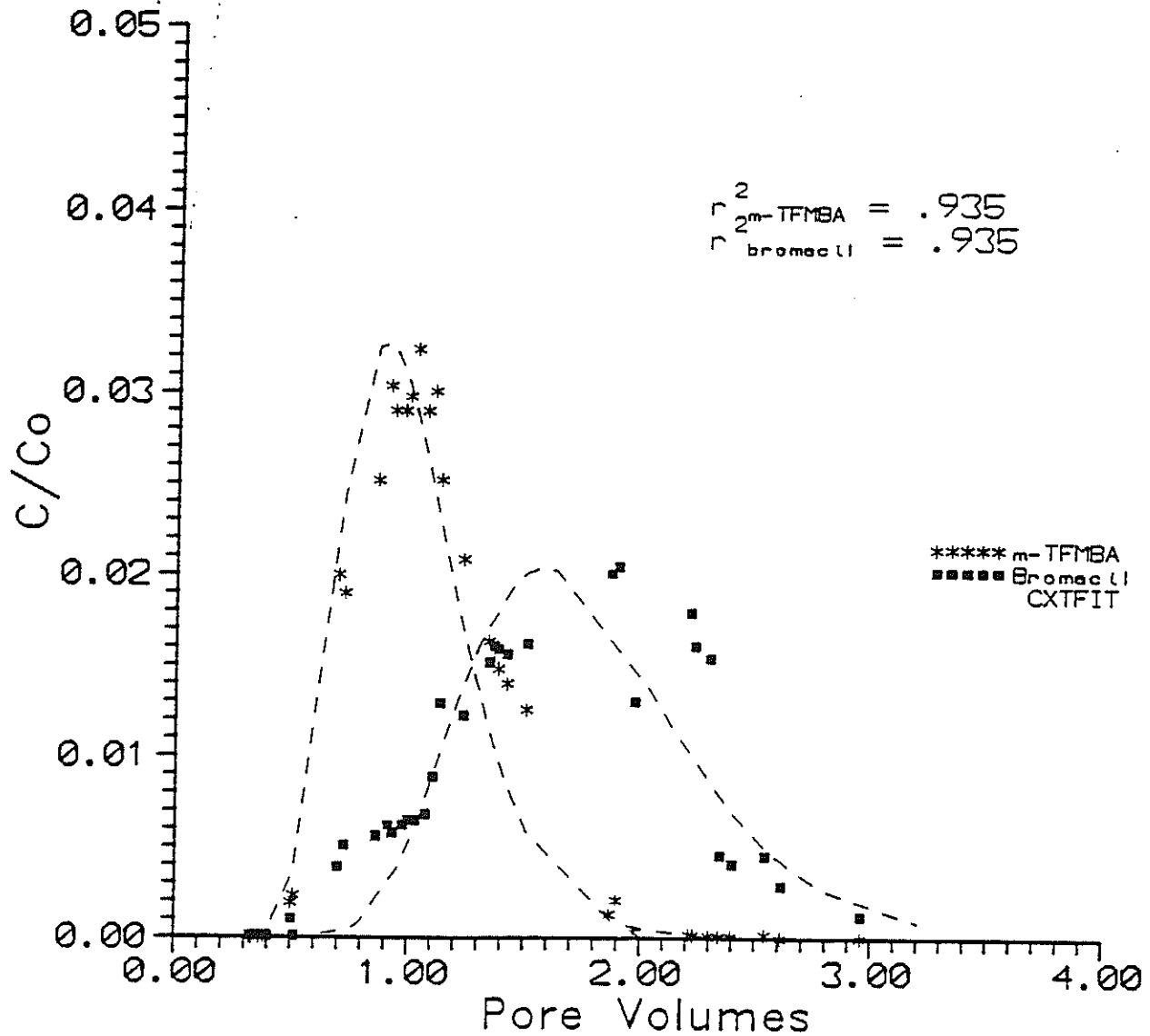
Fig. 20. m-TFMBA and Bromacil BTCs of Repacked Column 3 - Intermittent Ponding Flow Regime.
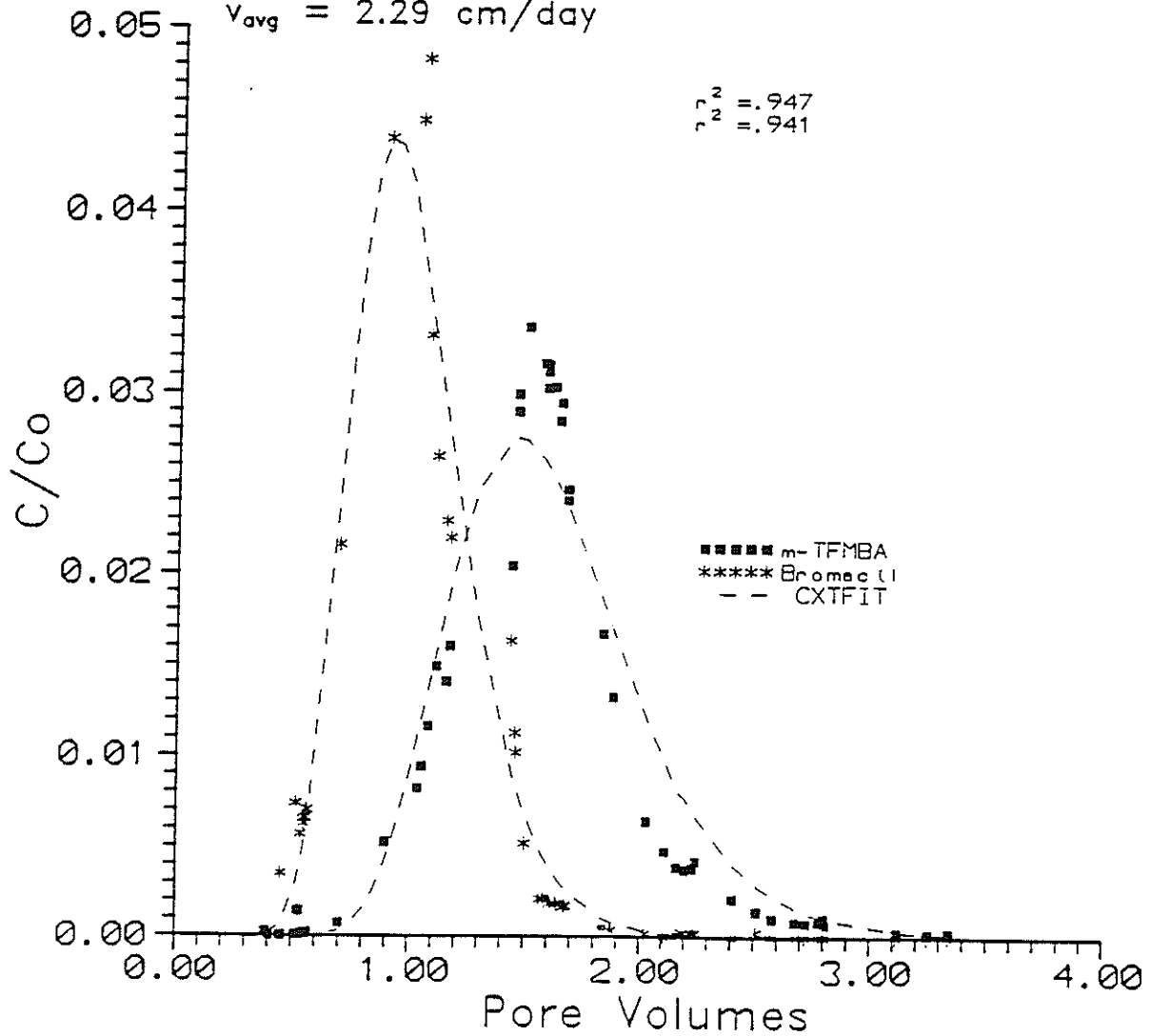
Fig. 21. m-TFMBA and Bromacil BTCs of Repacked Column 4 - Intermittent Ponding
Flow Regime.

smaller pores and/or pore networks as the spread of BTCs data imply (see Figure 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 in situ columns. This is supported further 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 to which 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 ponding events. 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. The tracer thus short circuited or bypassed a major portion of the soil profile just after the onset of the first ponding event.
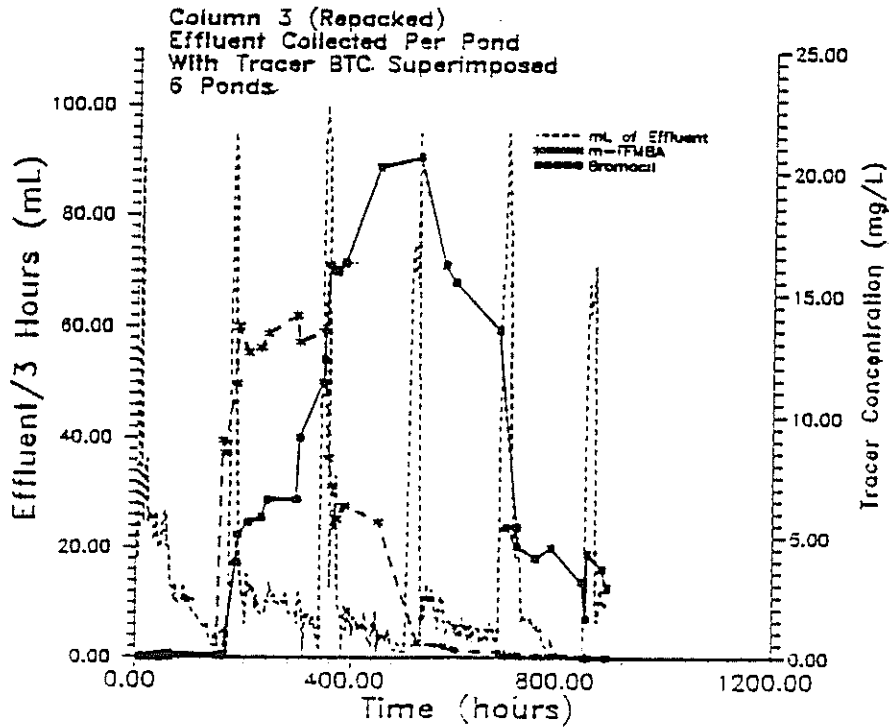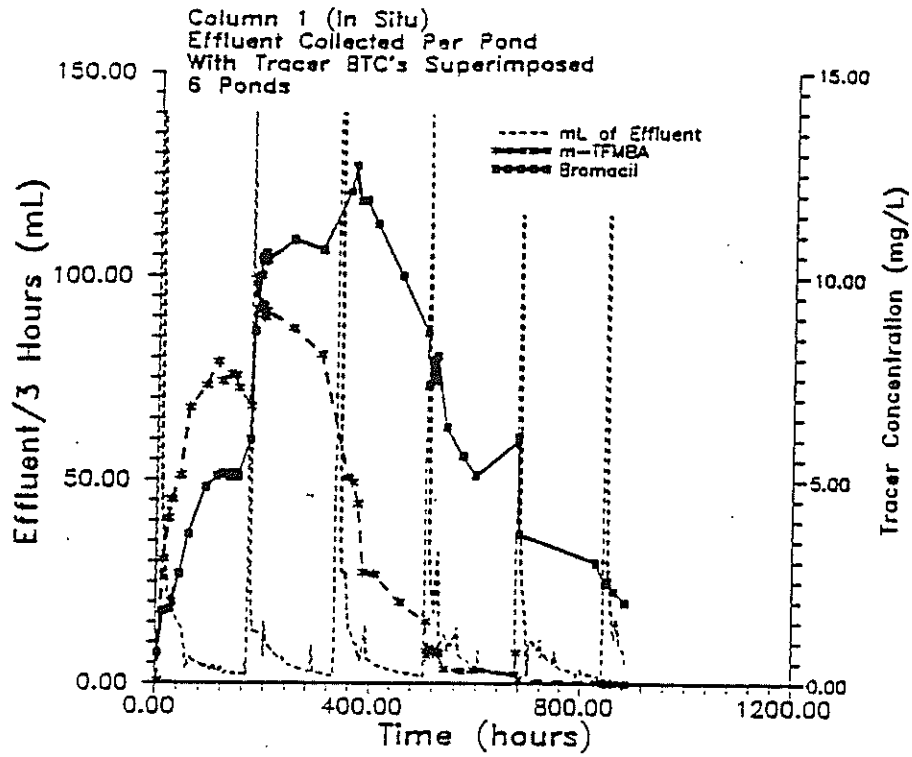
70

Fig. 22. Concentration vs. Cumulative Effluent for In Situ Column 1 and Repacked Column 3 during Intermittent Ponding Flow Regime.
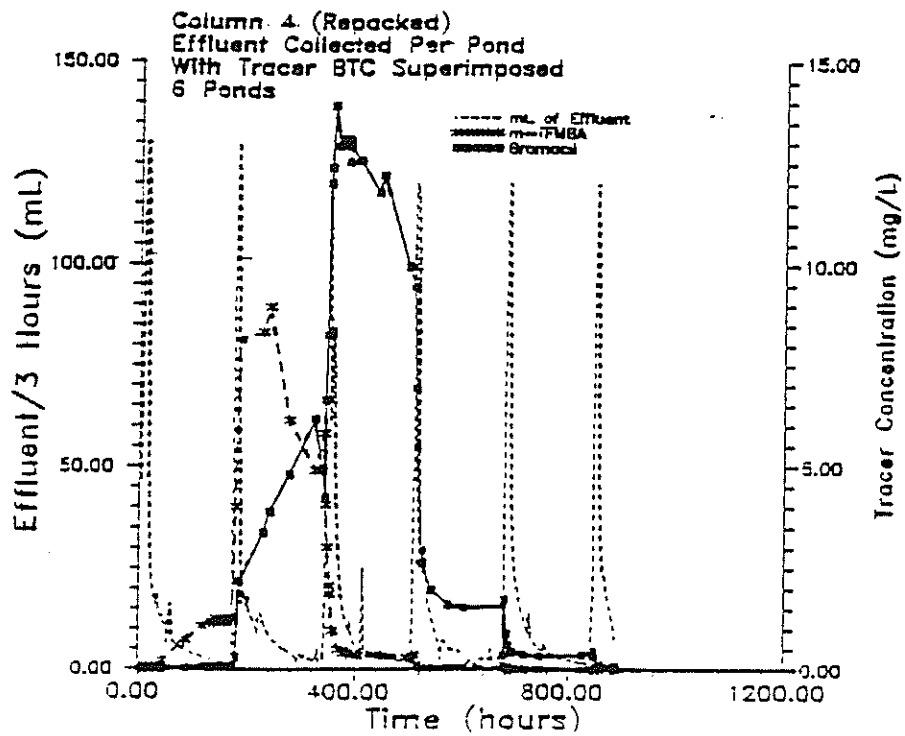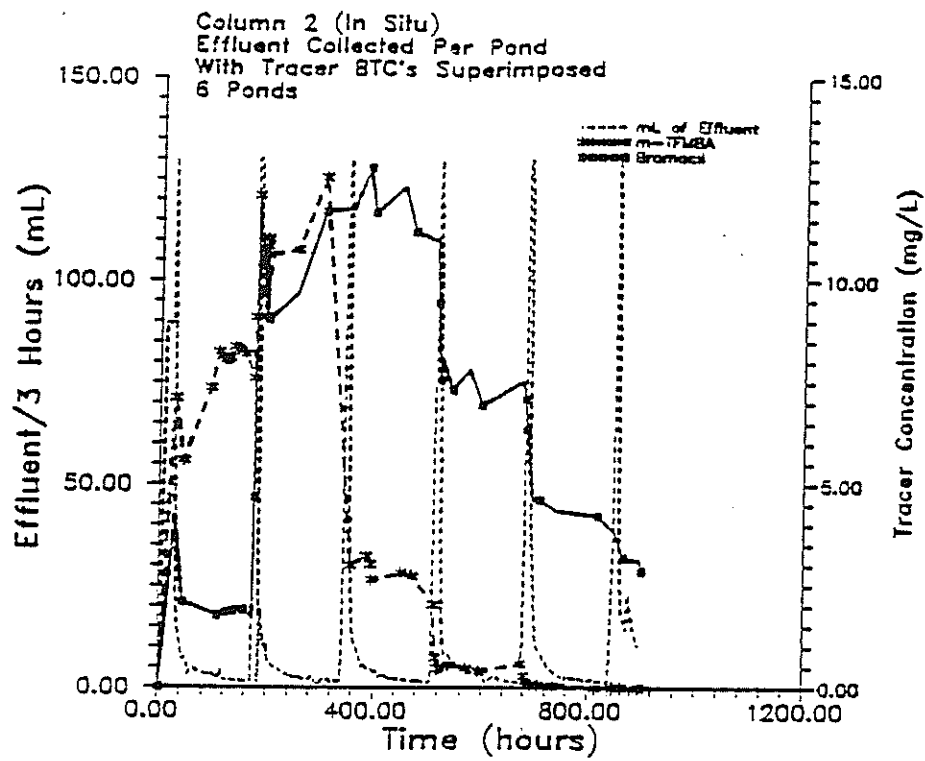
Fig. 23. Concentration vs. Cumulative Effluent for In Situ Column 2 and Repacked Column 4 during Intermittent Ponding Flow Regime.

Each ponding event was separated by a long length of quiescent time (for this experiment 120 to 150 hours), relative to the time that was required for the volume of ponded leaching solution to infiltrate into the soil conmatrix (approximately 12 hours for the in situ and 24 hours for the repacked columns). During this 120 to 150 hour quiescent period, BTCs indicated vertical movement of the solute was actually retarded as it infiltrated laterally into smaller, less mobile fluid-filled pores. Molecular diffusion and 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 three ponding events as compared to the narrower, more concise and sharper BTCs of the repacked columns. This implies that preferential and lateral spreading were 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 seven-day drainage period. Using equation 4 and R_f from CXTFIT, θ_{cxt} was inversely derived and considered to represent conservatively 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 indicated, 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 a qualitative measurement of the transmitting fraction of PV for both tracers. For the in situ 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 columns. Entrapped air, coupled with significant swelling, and an increasing moisture content (change in storage) were suspected to be 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 airtight seals existed between the various column

parts.

Breakthrough times of m-TFMBA, $v_{m-TFMBA}$, were compared to v_a derived values. A qualitative estimation of $v_{m-TFMBA}$ 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 in situ 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. $v_{m-TFMBA}$ from the in situ 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.

Comparing the moisture contents derived from $v_{m-TFMBA}$, denoted as $\theta_{m-TFMBA}$, and those derived from θ_{cxt}, show large discrepancies exist. This discrepancy seems to support the notion that, initially, advective processes dominated transport of both tracers and inhibited adsorption equilibrium. The time interval between additional ponds enabled diffusion and concentration gradients to transport tracers laterally 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 existing 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**

mL of Effluent	Column							
	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

with the surface-applied tracers at the column's upper boundary. Within the first 25 hours

after the ponding event, 78, 75, 68 and 58 percent of the volume of surface-applied water

had been collected as effluent for columns 1, 2, 3, and 4, respectively. The initial appear-

ance 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

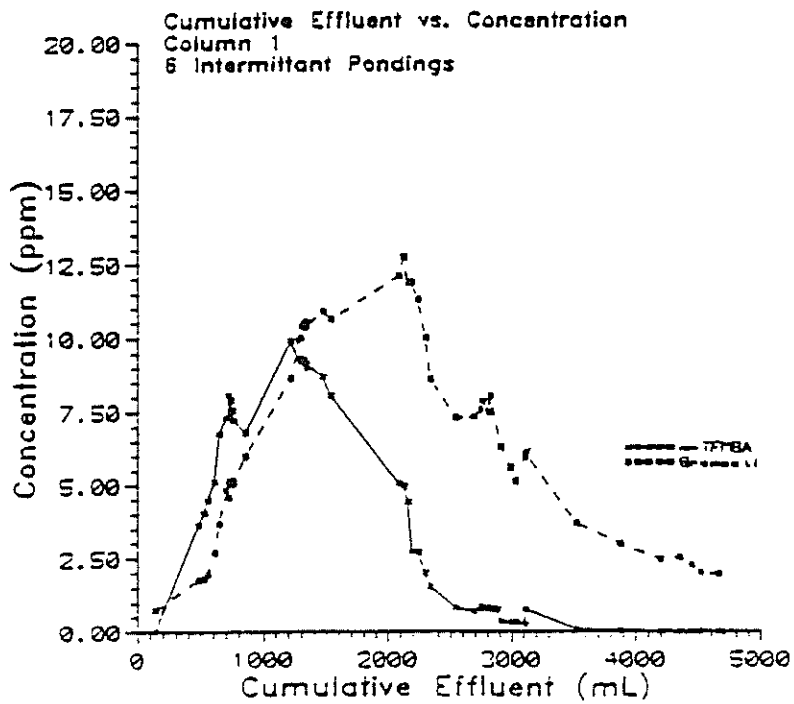conductive fluid-filled pores of the in situ columns. During the time interval between the
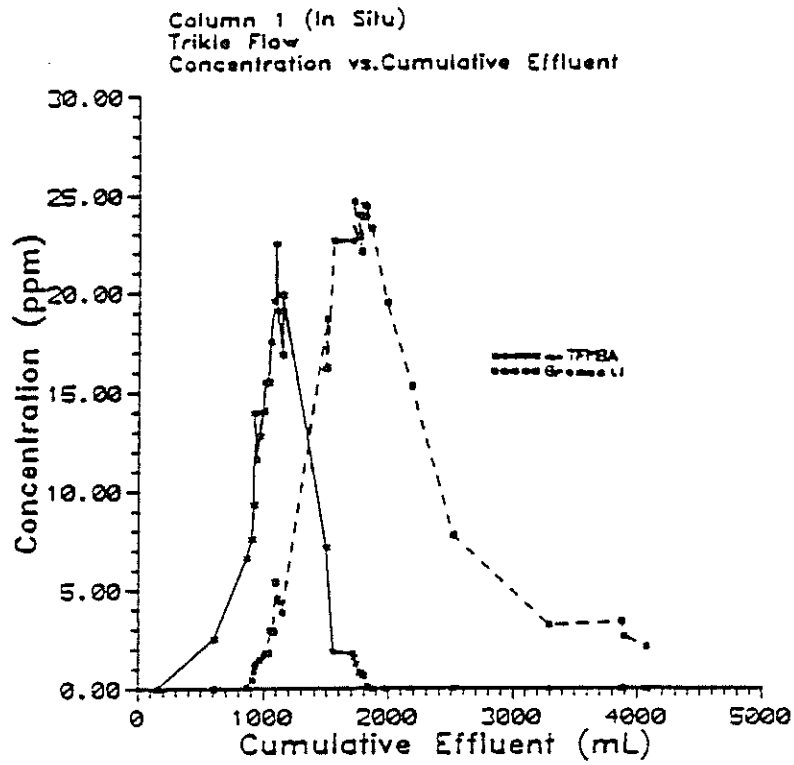
Fig. 24. Concentration vs. Cumulative Effluent for In Situ Column 1 during Steady-State Unsaturated and Intermittent Ponding Flow Regimes.

Fig. 25. Concentration vs. Cumulative Effluent for In Situ 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.
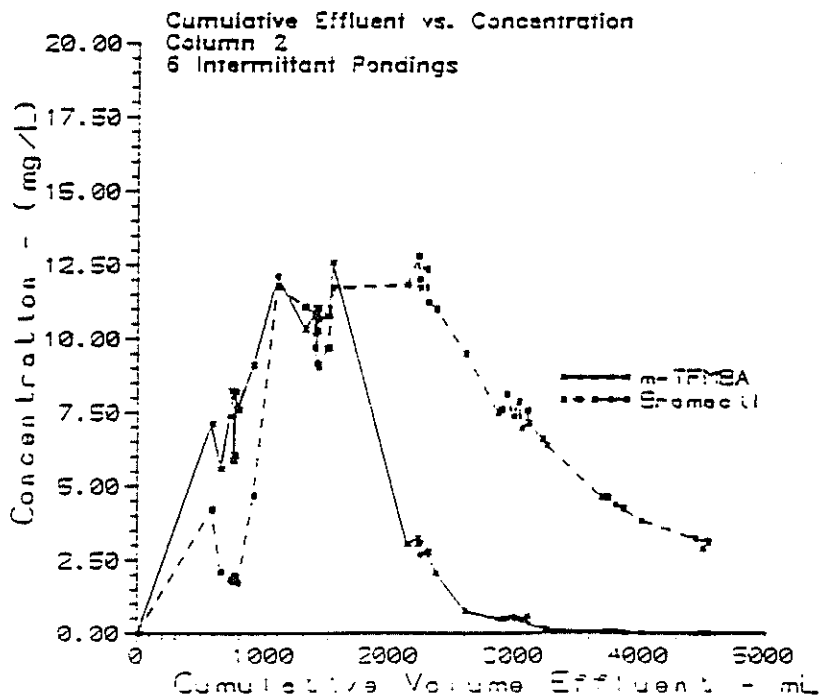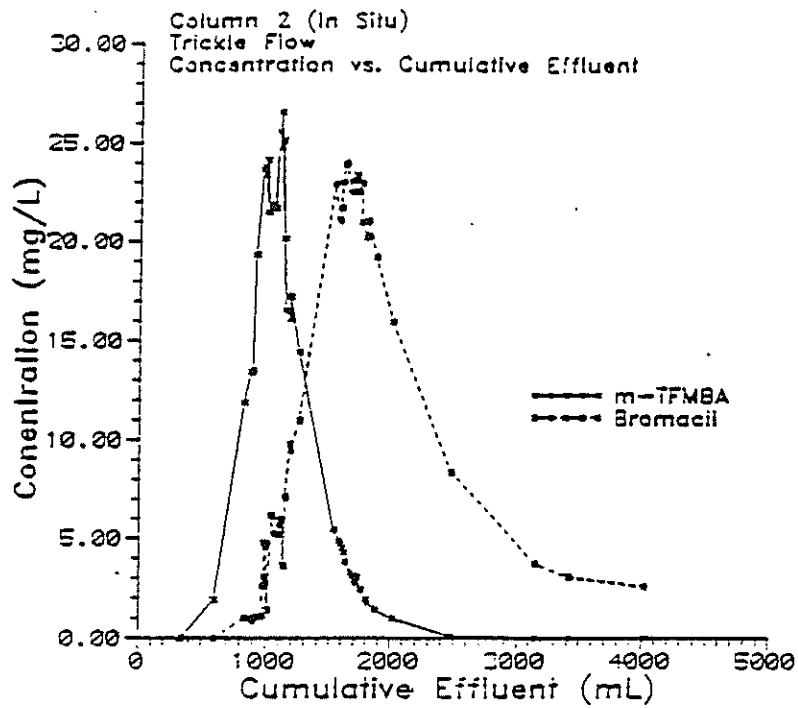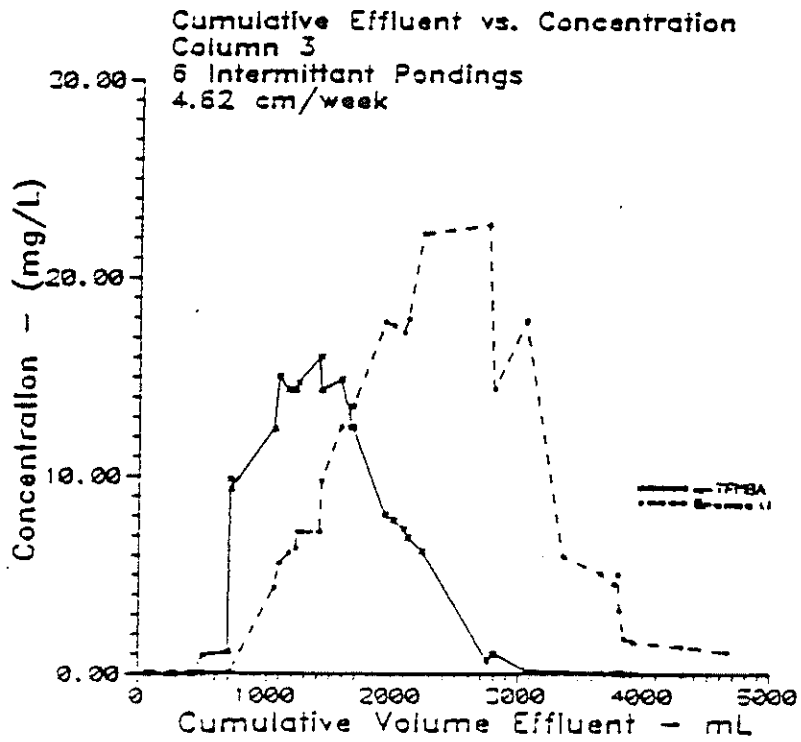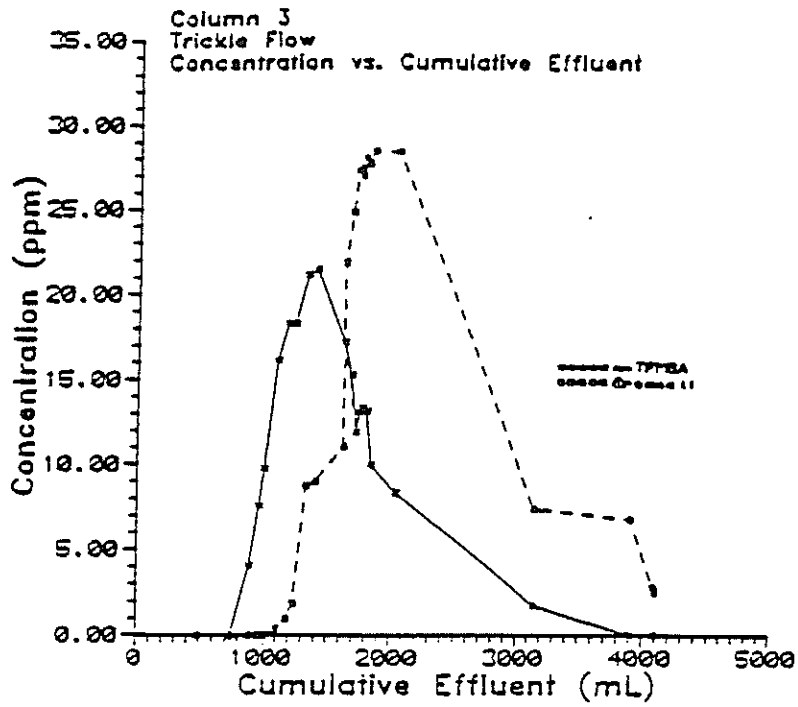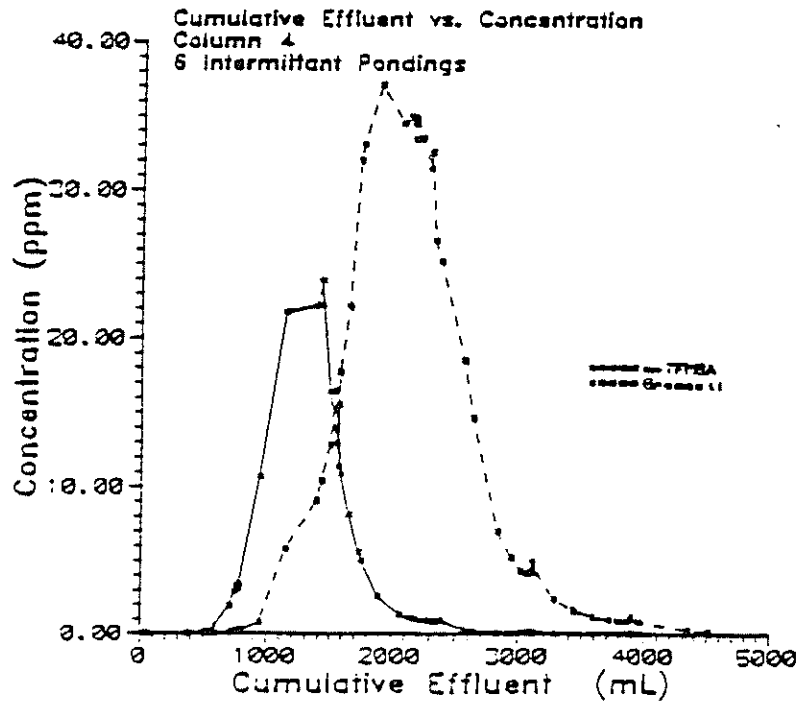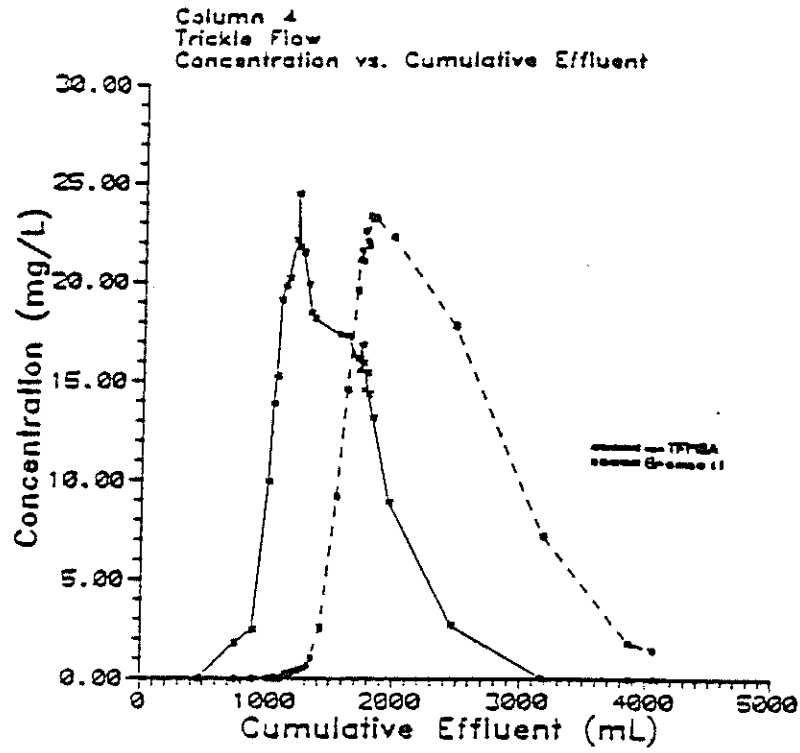
Fig. 27. Concentration vs. Cumulative Effluent for Repacked Column 4 during Steady-State Unsaturated and Intermittent Ponding Flow Regimes.

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 infiltrated recently 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 affected 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 primarily reflecting that of the soil matrix. This statement is supported additionally 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.) Note the initial rise and fall in pH values 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.

After most ponded leaching solution had been collected in the effluent, pH values again changed and reflected the concentration in the soil matrix. As pH plots and BTCs imply, both tracers were more resistant to influent flushing in the in situ columns when

Fig. 28. pH Values for In Situ Column 1 and Repacked Column 3 during Steady-State Unsaturated Flow Regime.
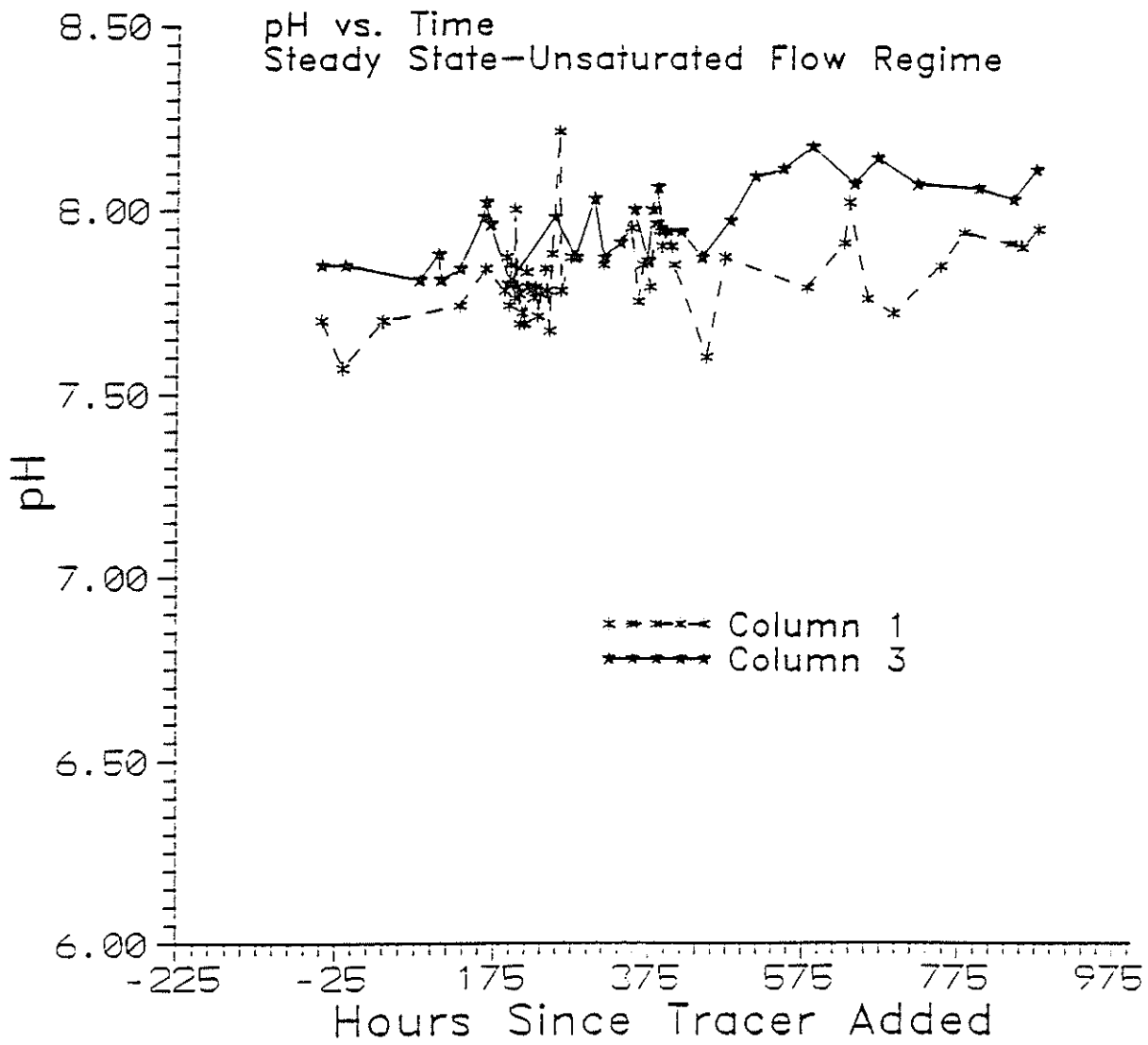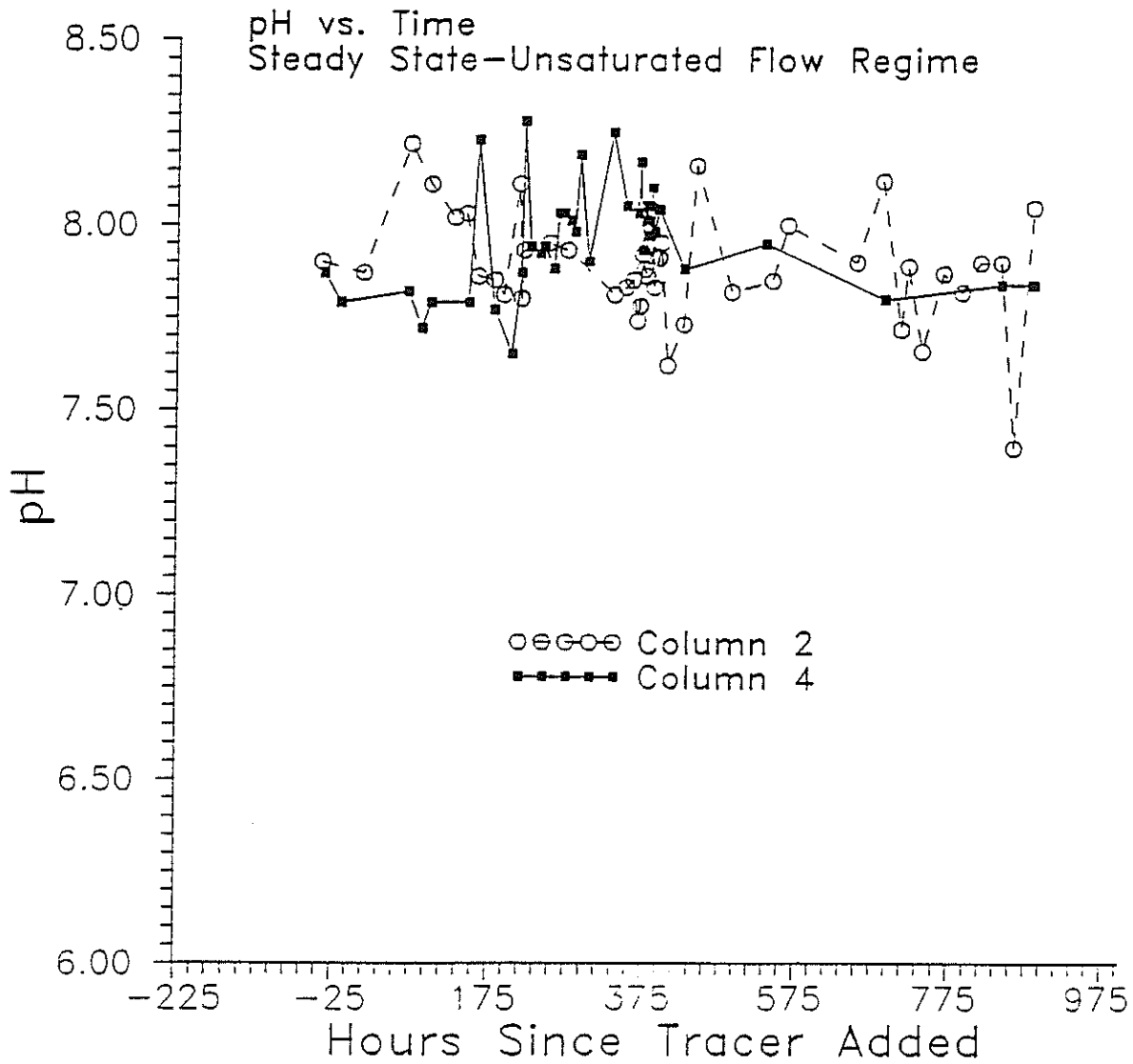
82

Fig. 29. pH Values for In Situ Column 2 and Repacked Column 4 during Steady-State Unsaturated Flow Regime.

83

Fig. 30. pH Values for In Situ Column 1 and Repacked Column 3 during Intermittent Ponding Flow Regime.
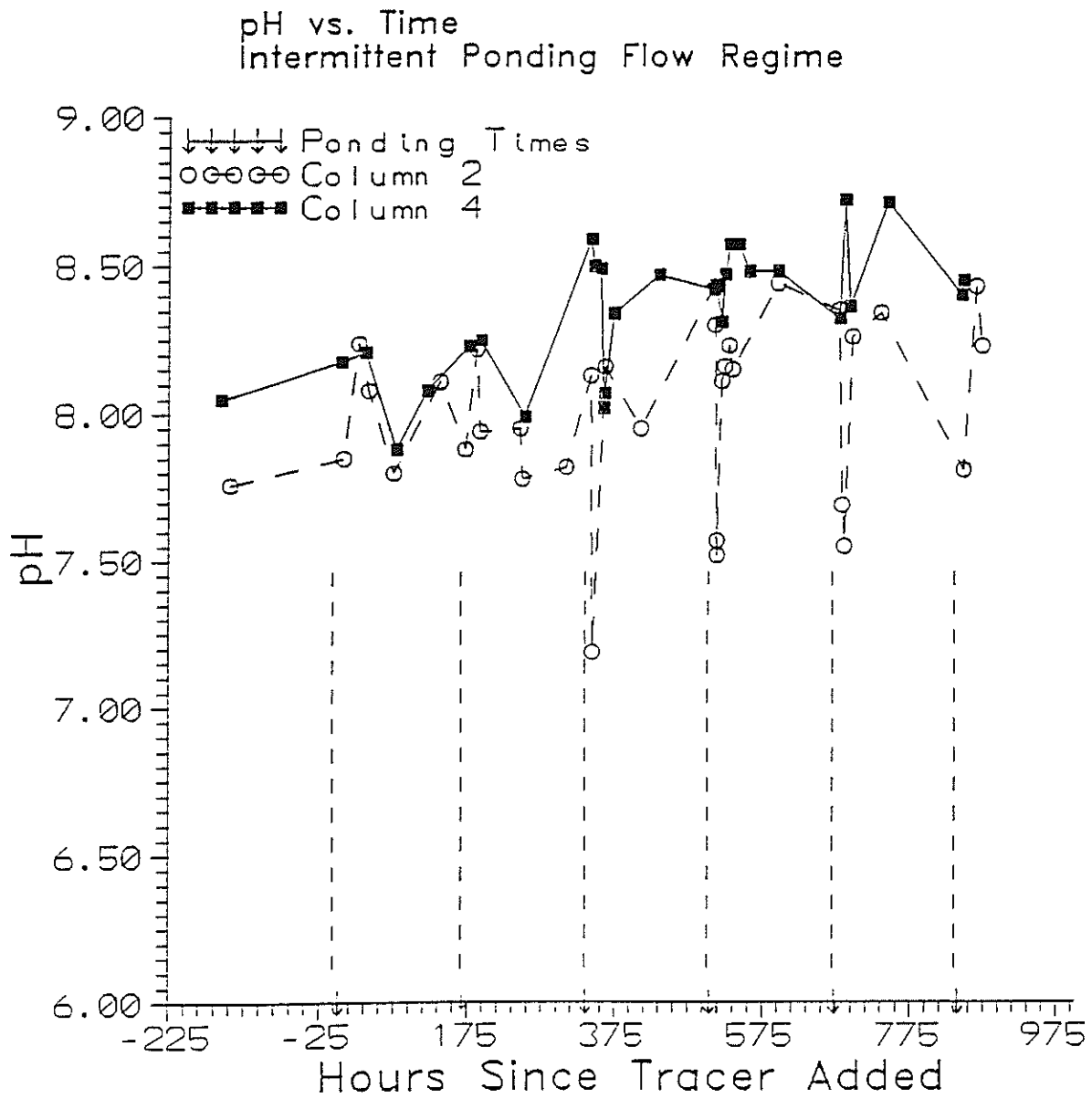
Fig. 31. pH Values for In Situ Column 2 and Repacked Column 4 during Intermittent Ponding Flow Regime.

residing in the less mobile water of the soil matrix. Because most 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 signified the incoming water "skimmed off" only a portion of the surface applied salts. Effluent salt concentrations 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 effluent's composition 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 in situ 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 in the in situ column effluent within the first 24 hours of the first pond. It took relatively little 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 column 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 indicated almost 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 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 tracers initial rapid movement 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 reach 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, and

- 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 to some extent entrapped air affected 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 column venting, done between the two flow regimes as an afterthought, was later considered inadequate. McWhorter (1971) and Peck (1965) have reported the dramatic effects of entrapped air when undertaking column studies. Further experiments should employ their recommendations to alleviate this problem.

Infiltration times of the ponded leaching solution into each column should be recorded carefully. 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% 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 0.5%. 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.

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