



Comparative evaluation of solute transport using suction lysimeters, ion-exchange resin capsules and soil cores

by James Michael Mulcahy

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Soils
Montana State University

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Abstract:

Transport of agricultural chemicals and naturally occurring elements beyond the rooting zone of plants is a potential problem for producers and groundwater users. This study was conducted to compare PVC column and trench lysimeters, ion-exchange resin capsules and soil core methodologies in monitoring Br transport under three irrigation regimes (high, medium and low water application). A line-source irrigation system was used in a field experiment near Manhattan, MT to apply differential water regimes on a fallow Brocko silt loam. Four replications of each sampling methodology and neutron access tubes were included in each water regime. The Smirnov Maximum Deviation test for similar populations was used for statistical analysis. All Br concentrations were expressed as a proportion of the total observed amount for each specific water regime, depth and sampling methodology to allow comparisons between samples having different concentration units. Samples were assayed using a Br ion-specific electrode. In 1992, a dry summer with limited irrigation water, vacuum extraction in the low water regime was not possible because of low levels of soil water. Comparisons between three methodologies showed significant differences ($P < .05$) for PVC and trench lysimeters and PVC lysimeters and resin capsules in the high water regime at 0.3 m. No significant differences occurred between the sampling methodologies below 0.3 m in 1992. PVC lysimeter breakthrough curves (BTCs) peaked earlier and showed a higher proportion of Br than other methodologies. During the 1993 field season all methodologies were compared over three water regimes. Significant differences occurred between PVC lysimeters and resin capsules in the high water regime at 0.6 m and in the medium water regime at 0.3 and 0.6 m. Significant differences between trench lysimeters and soil cores occurred in the high and medium water regimes at 0.3 m. Comparisons between resin capsules and soil cores were significantly different in all water regimes at 0.3 m. In general, PVC lysimeter BTCs occurred earlier and showed a higher proportion of Br than other methodologies. Results may have been affected by suspected greater water infiltration in the PVC columns. Soil core BTCs were variable reflecting the broad range of soil profile sampling technique. Trench lysimeter and resin capsule methodologies peaked later suggesting reduced transport with less manipulation. All methodologies tested proved useful in monitoring solute transport.

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21 November 1964

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ABSTRACT

Transport of agricultural chemicals and naturally occurring elements beyond the rooting zone of plants is a potential problem for producers and groundwater users. This study was conducted to compare PVC column and trench lysimeters, ion-exchange resin capsules and soil core methodologies in monitoring Br transport under three irrigation regimes (high, medium and low water application). A line-source irrigation system was used in a field experiment near Manhattan, MT to apply differential water regimes on a fallow Brocko silt loam. Four replications of each sampling methodology and neutron access tubes were included in each water regime. The Smirnov Maximum Deviation test for similar populations was used for statistical analysis. All Br concentrations were expressed as a proportion of the total observed amount for each specific water regime, depth and sampling methodology to allow comparisons between samples having different concentration units. Samples were assayed using a Br ion-specific electrode. In 1992, a dry summer with limited irrigation water, vacuum extraction in the low water regime was not possible because of low levels of soil water. Comparisons between three methodologies showed significant differences ($P \leq 0.05$) for PVC and trench lysimeters and PVC lysimeters and resin capsules in the high water regime at 0.3 m. No significant differences occurred between the sampling methodologies below 0.3 m in 1992. PVC lysimeter breakthrough curves (BTCs) peaked earlier and showed a higher proportion of Br than other methodologies. During the 1993 field season all methodologies were compared over three water regimes. Significant differences occurred between PVC lysimeters and resin capsules in the high water regime at 0.6 m and in the medium water regime at 0.3 and 0.6 m. Significant differences between trench lysimeters and soil cores occurred in the high and medium water regimes at 0.3 m. Comparisons between resin capsules and soil cores were significantly different in all water regimes at 0.3 m. In general, PVC lysimeter BTCs occurred earlier and showed a higher proportion of Br than other methodologies. Results may have been affected by suspected greater water infiltration in the PVC columns. Soil core BTCs were variable reflecting the broad range of soil profile sampling technique. Trench lysimeter and resin capsule methodologies peaked later suggesting reduced transport with less manipulation. All methodologies tested proved useful in monitoring solute transport.

INTRODUCTION

Transport of agricultural chemicals and naturally-occurring elements through the soil affects producers, water users and regulatory agencies throughout the world. Not only is water quality affected, but chemical transport beyond the rooting zone affects total production costs. Almost half of the population of the United States and over 90% of the rural population depend on wells as the primary source for drinking water. By the end of the 1980's, 46 pesticides had been detected in ground water in 26 states (Dirgell, 1991). In 1990, the EPA reported that 10% of urban wells and 40% of rural wells had detectable levels of pesticides.

According to Gustafson (1993), reliable detection procedures unavailable prior to 1979 resulted in little quantitative data on pesticides in drinking water. Furthermore, it was often assumed that the soil root zone was able to degrade or adsorb contaminants before they reached ground water. Gustafson detailed some of the more problematic pesticides and geographic areas where drinking water contamination occurred. Aldicarb (2-methyl-2-(methylthio)propanal O-[(methylamino)carbonyl]oxime) is an insecticide used to control insect and nematode pests in many commercial crops. Aldicarb was used in the 1970's to control

pests in potatoes (Solanum tuberosum L.) in Wisconsin and New York and in citrus in Florida. By the early 1980's, contamination of drinking water wells in these areas resulted in application rate reductions and partial use restrictions. The herbicide, atrazine (2-chloro-4-(ethylamino)-6-isopropylamino-s-triazine), has been widely used on sorghum [Sorghum bicolor (L.) Moench] and field corn (Zea mays L.) to control grass and broad-leaf weeds. It is a persistent herbicide, with a carry-over effect that may be detrimental to succeeding crops. Well testing in Kansas, Nebraska and Iowa detected atrazine in water used for human consumption. It was found in 18% of tested municipal wells in western Iowa where corn is extensively grown and well depths are often less than 30 m. In Montana, Clark (1990) reported the detection of aldicarb, atrazine and dicamba (3,6-dichloro-2-methoxybenzoic acid) in wells monitored in agricultural areas.

Nitrate (NO_3) contamination of drinking water, primarily from N applied in agricultural areas may also be a problem. In high nutrient consumptive crops, such as corn, high levels of N are often applied under high irrigation and/or heavy rainfall. High levels of NO_3 -based fertilizers are especially susceptible to leaching during periods of high water application. Increased solute transport of anionic chemicals is most pronounced during the spring and fall when low evapotranspiration (ET), increased precipitation and

minimal plant uptake are common (Magdoff, 1992). Other sources of potential N contamination are feedlots, silos, septic systems, compost containments, and naturally-occurring marine shales.

For many years, lysimeter and soil core methodologies have been used in the field to monitor chemical leaching (Wagner, 1962; Everts and Kanwar, 1988; Phillips, 1992). Recent laboratory research using ion-exchange resins to monitor Br transport in disturbed soil columns indicated a high level of precision in assessing leaching potential (Li et al., 1993). Furthermore, a preliminary study by Skogley (1992) using resin-filled capsules to monitor the movement of picloram (4-amino-3,5,6-trichloropiclonic acid) indicated that resin capsules may be suitable for a broad range of solute transport studies involving applied and indigenous soil chemicals.

Solute transport monitoring using suction lysimeters, soil cores or resin capsules present several potential problems that may occur with any of the methodologies. The non-homogeneous nature of soils can affect chemical concentrations throughout a sampling area resulting in concentration data that may not accurately reflect solutes present in the soil profile. Additionally, large pores may transport some chemicals past the sampling sites. Macropores are formed by factors such as soil fauna, roots, shrink-swell cycles and chemical weathering (Beven and Germann, 1982).

They may transport relatively larger amounts of water of differing chemical concentrations than smaller pores in the soil (Hansen and Harris, 1975).

Water moving through the soil may transport chemicals beyond the root-zone of plants and eventually into ground water. Nitrate-nitrogen ($\text{NO}_3\text{-N}$), other agricultural chemicals and naturally occurring elements can be transported through the soil profile with the movement of water. In recent years, solute transport in the soil has become increasingly important as the effects of potential pollutants on ground water quality have become more fully understood. The objective of this research was to compare lysimeter, ion-exchange resin, and soil core methodologies for monitoring solute transport in the field under increased amounts of applied water.

LITERATURE REVIEW

Lysimeter

Lysimeter vacuum extraction of soil-water through porous cups embedded in the soil has been used for much of this century with little modification of the basic technique. In 1904, Briggs and McCall described a lysimeter consisting of a close-grained unglazed porcelain tube that could be placed in the soil and connected to the surface with lead tubing. A vacuum source attached to the tubing facilitated the determination of the amount of soil water supplied to the "artificial root" and provided a method for removing a portion of the soil-water solution for analysis. This type of extraction methodology continues to be the primary means of obtaining unsaturated soil solution samples (Rhoades and Oster, 1986).

The most commonly used porous cups are ceramic (Grossmann and Udluft, 1991), although cups comprised of alundum and teflon (Creasey and Dreiss, 1988) have been utilized. In one form of the vacuum extraction methodology, porous ceramic cups are placed in undisturbed soil or columns driven into the soil and connected to the surface with tubing to facilitate vacuum sampling. Installation of the porous cup equipment necessitates removal of soil to the depths

where the cups are to be inserted. Holes are drilled through the columns and a soil plug is removed to allow insertion of ceramic cups with attached tubing. A soil paste (Barbee and Brown, 1986) or silica flour (Lord and Shepherd, 1993) placed in the cavity ensures good soil particle contact with the sampling apparatus. Once in place, the system allows for repetitive undisturbed sampling of the site.

When adequate moisture is available in the soil, samples collected with lysimeters have been shown to be comparable to the soil core method (Webster et al. 1993). The movement of $\text{NO}_3\text{-N}$ during two successive winters using both techniques resulted in peak concentrations occurring at the same time. In a similar experiment, Alberts et al. (1977) reported that $\text{NO}_3\text{-N}$ detected throughout the soil profile depth was similar except at some specific depths. Li et al. (1993) demonstrated that simultaneous porous cup and resin capsule measurements of Br transport in disturbed soil columns provided similar results.

Several potential problems are associated with collecting representative samples using lysimeter vacuum extraction.

1. Fine soil types, such as clays, tend to plug the pores in the cups (Nagpal, 1982).
2. Adequate soil moisture is necessary for the system to function properly (Nagpal, 1982).

3. Use of vacuum pressure to siphon fluid into the cups may alter the natural flow of water within the profile (Barbee and Brown, 1986). For example, when water is removed through vacuum extraction from an area within the soil profile, water from the surrounding area may move into this zone and confound flow and drainage patterns. This effect is expected to vary with soil type. Lord and Shepherd (1993) detected little difference in $\text{NO}_3\text{-N}$ concentrations when varying suction was applied in sandy soils. They also noted that sample size did not affect the results when total sample volume was less than 20 ml for each sampling period.
4. Adsorption of materials to ceramic sampler cups may contaminate the samples. McGuire et al. (1992) reported that trace metals such as Co, Cr, Zn and Cd are differentially adsorbed to various sampler types and to a lesser extent to silica flour. Wagner (1962) reported that K, P, NH_3 and NH_4 adsorption to ceramic samplers is common, but not $\text{NO}_3\text{-N}$.
5. Intake rates of samplers may vary, resulting in differences in sample volumes.
6. The installation method described for this experiment does not continuously sample the soil profile which may result in chemicals passing

undetected through a sampling region between collection periods. However, in some experimental designs frequent sampling of the soil profile resulting in resident concentrations at the time of sampling is desirable.

Ion-Exchange Resin

The discovery of ion-exchange is generally attributed to an English landowner, H.S. Thompson, in 1845 (Kitchener, 1961). His curiosity over loss of ammonia from manure heaps led to the discovery that when ammonium sulfate solution percolated through a column of soil the leachate contained no ammonium, but large amounts of calcium sulfate. The phenomenon was reported to the Royal Agricultural Society and was confirmed in 1850 by J. T. Way. In 1876, Lemberg discovered a reversed ion-exchange process (Kunin, 1958). He was able to transform the mineral leucite to analcite by leaching the mineral with sodium chloride and then back to leucite with a treatment of potassium chloride. Furthermore, it was reported that Gans used the fledgling exchange technology in 1906 to soften water using complex aluminum silicates. Pauling (1927) carried out extensive work on the crystalline structure of clays. Bacon (1936) further clarified this concept and suggested the relationship between crystalline structure and ion-exchange capacity.

Experimental work by Adams and Holmes in 1935, led to the invention of synthetic ion-exchange resins, thus developing the potential for industrial uses (Kitchener, 1961). Furthermore, it was reported that the synthesis of resins from styrene and acrylics by D'Alelio demonstrated the possibility of designing an ion-exchange resin for a specific application. His pioneering work with ion-exchange polymers led to the development of Dowex 50^{®1}, introduced by Dow Chemical Co. in 1945 as the first commercial spherical ion-exchange resin. A specific industrial application of this technology is found in the sugar industry where resins are used to remove refining impurities (Anon, 1947).

Direct chemical extraction from the soil has been traditionally used to evaluate soil nutrient levels. Ion-exchange batch extraction, in which resins are shaken in a soil solution to place ions in contact with the active sites, compared favorably with chemical extraction in evaluating soil P (Curtin et al., 1987), Mo (Sherrell, 1989) and K (Lee and Gibson, 1974).

Plant roots act as a sink for diffusion of soil nutrients. The possibility that ion-exchange resins might remove ions from the soil solution in a similar manner was suggested by Amer et al. (1955). The rate of nutrient

¹ Mention of a specific brand, trade, or chemical name does not imply endorsement of that product over others of a similar nature or function.

diffusion in the soil is affected, in part, by temperature and water parameters. Similarly, resin uptake of ions is also dependent on these factors (Schaff and Skogley, 1982). The Phytoavailability Soil Test (PST) reported by Yang et al. (1991) is based on the presumption that resin will closely mimic root ion uptake characteristics. When placed in the soil, resin adsorbs ions via diffusion. Quantitative analysis of these ions should result in a reliable index of soil nutrient availability.

In another application, Schnabel (1983) used layered resins in soil columns to assess nitrogen leaching. More recent experiments using bromide as a tracer were successful in assessing solute transport (Schnabel et al., 1993). Crabtree and Kirkby (1985) worked with small resin-filled columns inserted in the soil to measure cation movement. This work demonstrated the potentiality of resin capsules as an alternative to solute sampling with soil cores and lysimeters.

The Universal Bioavailability Environment/Soil Test (UNIBEST) reported by Skogley (1992) expanded the application of resins in soil solute sampling through the use of access tubes and resin capsules to allow continuous monitoring of the soil system. Li et al. (1993) made use of this methodology to study Br leaching in laboratory soil columns and in the field. Resin capsules proved reliable in the detection of Br movement through laboratory soil columns when

compared to lysimeters under both continuous and intermittent unsaturated flow. The resin capsule system was also effective in detecting Br movement in the field.

Preferential flow allows solutes to move more rapidly through the soil profile than under natural conditions. Access tubes used in solute sampling, including the resin capsule methodology, may result in preferential flow of soil water along tube walls.

Flux averaging is used with resin capsule solute transport monitoring data because of the continuous sampling aspect of this system. Ion concentrations that result from resin capsules placed in the soil for a given time period are presented at the mid-point of the period.

Units of concentration for resin capsules are $\mu\text{g capsule}^{-1}$. The standard expression for units of concentration in soil solution, commonly used for vacuum extraction samples, is meq l^{-1} . Units used for soil samples in this experiment are cmol kg^{-1} . The difference in units results in difficulty comparing the soil solution and soil sample data with the resin capsule Br transport data. Unlike the units used for solution and soil sampling, the $\mu\text{g capsule}^{-1}$ units are not at present commonly accepted units of concentration for soil testing.

Soil Core

Soil core sampling is the oldest methodology that has been used for monitoring chemical leaching characteristics of soils in the field. This sampling technique generally uses a tube or auger that is pushed into the soil allowing samples from varying depths to be retrieved for analysis. Collecting soil cores is labor-intensive and removal of samples does not permit repetitive sampling from the same location.

Alberts et al. (1977) reported similar results for soil coring and solution extraction techniques while monitoring $\text{NO}_3\text{-N}$. Everts and Kanwar (1988) compared suction tube lysimeters, soil cores, piezometers and tile drainage methods for monitoring $\text{NO}_3\text{-N}$ and Br solute transport on a poorly drained silt loam soil. In this study, all four methodologies generally gave similar results. Poor correlation between soil cores and lysimeters occurred in the top 0.6 m of the profile where unsaturated soil conditions resulted in solute concentration variability.

Bromide Tracer

Biological and chemical tracers have been used to track the movements of soil water and solutes. Requirements for a conservative tracer include:

1. it must not be significantly adsorbed to soils;

2. it must move with water and not alter the natural direction of the flow;
3. it must occur in low concentration in soils and ground water; and
4. it must not be significantly degraded chemically or biologically over the length of the experiment.

Other considerations in choosing a tracer are ease of detection in samples, expense, and potential impact to the environment if the tracer is applied in an unconfined field situation.

Davis et al. (1980) reviewed a number of tracers used in soil and ground water studies. Paper and straw have been employed in tracing movement of water from sink holes when attempting to identify the source of springs. Bacteria and viruses have been proven useful in ground water studies. The laboratory test for fecal coliforms is well developed and these types of bacteria are most commonly used in bacterial tracer studies. Stable isotopes, radioactive materials, organic dyes, gases and fluorocarbons have been tested as tracers in some experiments although cost, safety, adsorption characteristics, handling and detection facilities have limited their use.

Chlorine and bromine anions have traditionally been used as ground water tracers and are still used in many experiments. In some areas, Cl concentrations in soils, rocks, fertilizers, precipitation and irrigation water may be

excessive and confound the tracking of the tracer pulse. Bromide is the most widely used anion tracer. It was first isolated from the solution remaining after crystallization of salt from water obtained from marshes at Montpellier, France in 1826 by A.J. Balard (Martin, 1966). Following this discovery, it was found to occur naturally in small concentrations in water, soils, plants and animals. Generally, it occurs in nature as a bromide and concentrations found in soils range from 0.001 to 0.004%. Although Br is present in small amounts in most plants, it is neither considered essential for growth nor regarded as particularly toxic to plants.

Fertilizer-derived $\text{NO}_3\text{-N}$ has been detected in wells and ground water in many agricultural regions of the United States. Source determination of this pollutant in the soil is difficult because of the many naturally-occurring sources. In a laboratory disturbed soil study using uncropped soil columns, Smith and Davis (1974) investigated the effectiveness of Br as a tracer in predicting the movement of $\text{NO}_3\text{-N}$. Their findings indicated that Br and $\text{NO}_3\text{-N}$ movements in the subsoil are the same. Varying results were found in surface soils, the area of maximum biological activity. Microbial interactions involving the denitrification and immobilization of $\text{NO}_3\text{-N}$ affected concentrations and often delayed movement of $\text{NO}_3\text{-N}$ through the surface soil area. Onken et al. (1977) found that Br and $\text{NO}_3\text{-N}$ had similar leaching characteristics

in field plots of corn using furrow, sprinkler or subirrigation methods.

Kung (1990) demonstrated that potato plants absorbed at least 53% of applied Br. This absorbed tracer was reapplied to the soil surface as leaves withered and abscised from maturing plants, which resulted in a secondary pulse of Br through the soil. Sorghum has also been shown to take up large amounts of Br from the soil (Chao, 1966).

Abdalla and Lear (1975) demonstrated that over 94% of Br added to samples may be detected using a Br selective-ion electrode. This technique provides an inexpensive, rapid, reliable and simple means for Br detection in plant, soil, and water samples even though it does not provide the precision associated with ion chromatography (IC). Conversely, IC is complex, expensive and not easily adapted for use with large sample numbers on a quick turn-around basis.

MATERIALS AND METHODS

Field experiments were conducted in 1992 and 1993 near Manhattan, MT on a Brocko silt loam (coarse-silty, mixed, Borollic Calciorthid). Soil characteristics previously determined by Comfort et al. (1993) are given in Table 1. The experiments were designed to comparatively evaluate four different methodologies for monitoring Br transport through a specific soil profile. A 14.6 X 18.3 m experimental area was used with a line-source irrigation system placed parallel to the long axis of the plots. The experimental area was divided into 16 uniform subplots measuring approximately 3.7 X 4.6 m. The design provided 3 main-plot, fixed irrigation

Table 1. Characteristics of Brocko silt loam soil.†

Depth	pH	Organic Matter	Sand	Silt	Clay
m		g kg ⁻¹	-----	% -----	
0-0.15	8.1	15.0	12.0	61.0	27.0
0.15-0.30	ND‡	11.7	10.0	65.3	24.7
0.30-0.60	ND	4.0	12.7	74.0	13.3
0.60-1.12	ND	1.3	18.7	71.0	10.3

† Values represent means of two replicates.

‡ Not Determined.

treatments with 4 replications of sub-plot solute transport sampling treatments. The line-source system was a size modification of the one originally reported by Hanks et al. (1980) and the experiment utilized a modified experimental block design described by Westesen et al. (1987). A neutron probe access tube, soil core sampling area, PVC column and trench lysimeters, and three resin capsule access tubes were placed parallel to each other at 1.8, 5.5, and 9.1 m from the irrigation source within each subplot. Sampling equipment placement was randomized within both replications and water regimes. Sampling depths in the vacuum extraction and resin capsule treatments were 0.3, 0.6 and 0.9 m. A hand-held coring tool (20 mm diam.) was used to take soil samples at 0 to 0.3, 0.3 to 0.6 and 0.6 to 0.9 m depths. A truck-mounted hydraulic core sampler (Giddings Machine Co., Fort Collins, CO) was used to install the neutron and resin access tubes.

Neutron probe (CPN Corp., Martineau, CA) readings at 0.2 m increments down to 1.2 m were recorded at approximately weekly intervals throughout the 1992 and 1993 field seasons. A field calibration equation was used to convert neutron count ratios to volumetric water content. Sites of the neutron access tubes were randomized within each replication in line with the sampling devices and/or areas used to monitor Br transport. Access tubes were not installed within the PVC columns.

The PVC columns (0.2 m diam., 1.2 m length) were driven into the soil with a tractor-mounted hydraulic post-pounder to a depth of 1.1 m. Each column had a stainless steel cutting bit attached to the bottom to aid driving and reduce compaction. Columns that visually exhibited soil compaction after placement were removed and driven again in a new area. Soil excavation exterior to the column was accomplished by hand for placement of round-bottom, straight walled, porous ceramic cups (10 mm diam., 100 mm length, Soil Moisture Equipment Co., Goleta, CA) in the column and in adjacent trench side-wall areas. Holes were drilled into the column and a machined tool similar to a cork borer was used to remove the soil core for placement of the ceramic cup into the cavity in the PVC column and trench wall at each specific depth. Vacant space was filled with a mixture of silica flour and water before insertion to obtain better soil-to-ceramic cup contact. Porous cups were attached with epoxy to 1.6 mm teflon tubing and connected to quick-release sample bottle adapters at the soil surface. Vacuum was supplied by a Welch Duoseal vacuum pump (Welch Vacuum Technology, Inc., Skokie, IL). Vacuum application varied from 30 min in the high water regime to several hours in the low water regime to obtain approximately 5 ml of sample.

Three resin capsule access tubes were installed at 60 degree angles with the aid of a Giddings Soil Sampler to each previously specified depth. A length of PVC tube

(31.75 mm diam.) was inserted into the soil sampler drill hole. Resin capsules (UNIBEST, Bozeman, MT), made from mixed-bed, ion-exchange resin (IRN-150, Rohm and Haas Co., Philadelphia, PA) enclosed in porous polyester, were positioned at the tip of a smaller diameter (19.05 mm) PVC insertion tube and extending slightly beyond the end of the access tube to ensure good soil-resin contact. A bushing (CPVC 19.1 x 12.7 mm) was glued to the tip of the insertion tube to provide a seat for the resin capsule. The resin capsule was retained with a fish hook and attached line secured to the top of the tube. A rubber stopper held the line to the access tube. A polyethylene bag was secured to the outside of the access tube to seal the chamber. The insertion tube was removed to exchange the resin capsule on each sampling date.

After installation of sampling equipment, 56 kg Br ha⁻¹ was applied at the beginning of the field season in 1992 and 112 kg Br ha⁻¹ was applied at the beginning of the field season in 1993 in the form of KBr. The tracer was applied with a pressurized backpack sprayer in 2 m wide continuous strips centered over the various sampling devices throughout the experimental area. The soil surface was left bare to simulate fallow conditions and weed control was maintained by hand throughout the duration of the experiment. Canal irrigation water was extremely limited during 1992 due to severe drought conditions. Samples were taken twice weekly

during the 1992 season when soil water levels allowed vacuum extraction. During the 1993 season, samples were taken on a weekly basis.

Irrigation water was applied on 10 dates to the experimental site in 1992 (Table 2). A total of 451, 351 and 221 mm of combined irrigation and precipitation were applied to the high, medium, and low irrigation treatments during the 1992 field season. Irrigation water was applied 15 times in 1993 for a total of 770, 648 and 532 mm of combined irrigation plus precipitation to the high, medium and low irrigation treatments, respectively (Table 3). Precipitation was monitored with a tipping-bucket rain gauge (LiCOR, Lincoln, NE). Applied irrigation was measured with collection cups installed in each treatment replication.

Soil core samples were prepared for analysis by oven-drying and grinding and a 10 g subsample was mixed with 50 ml of 0.01 M K_2SO_4 , shaken for 30 min. and filtered (Whatman 42) with the resulting fluid retained. Vacuum extraction samples were prepared by adding 5 ml of extracted soil water solution to 15 ml of 2 N H_2SO_4 . Exchange resin samples were prepared by stripping capsules with 50 ml of 2 N H_2SO_4 . All samples were assayed using a Br ion-selective electrode (Orion Research, Boston, MA, model 9435BN).

Statistical comparisons of the data was accomplished using the Smirnov's Maximum Deviation (SMD) test for similar populations (Bradley, 1968). Each individual measurement of

Table 2. Precipitation and irrigation during 1992 field season.

Date	Days after Br application	High	Medium	Low
-----mm-----				
7 June	2	35	25	8
10 June	5	27	16	6
11 June	6	32	25	10
12 June	7	10	10	10
15 June	10	22	22	22
16 June	11	28	28	28
17 June	12	4	4	4
22 June	17	24	20	10
24 June	19	37	23	15
25 June	20	3	3	3
2 July	27	29	21	13
4 July	29	3	3	3
5 July	30	51	47	36
8 July	33	44	26	9
13 July	38	59	40	16
22 July	47	43	38	28
Total		451	351	221

Table 3. Precipitation and irrigation during 1993 field season.

Date	Days after Br application	High	Medium	Low
-----mm-----				
21 May	2	50	45	32
26 May	7	55	38	34
29 May	10	21	21	21
1 June	13	43	36	27
7 June	19	32	32	32
14 June	26	48	38	35
19 June	31	35	27	15
21 June	33	37	32	21
25 June	37	33	20	15
28 June	40	43	33	17
1 July	43	36	26	22
3 July	45	45	45	45
9 July	51	45	42	35
15 July	57	17	17	17
16 July	58	54	45	33
17 July	59	19	19	19
19 July	61	29	25	20
23 July	65	36	26	22
26 July	68	38	38	38
30 July	72	23	17	13
5 Aug	78	31	26	19
Total		770	648	532

Br concentration was divided by the sum of the concentration over the field season for a specific water regime, depth and sampling methodology. Values were expressed as proportions of the total to allow comparisons between methodologies having different concentration units. Consequently, lysimeter, resin capsule and soil core raw data expressing Br as meq L^{-1} , $\mu\text{g capsule}^{-1}$ and cmol kg^{-1} , respectively, are presented as proportions. Cumulative proportions throughout the field season were utilized to employ the SMD test for comparisons ($P \leq .05$) between differential sampling methodologies over time. Graphs of the cumulative proportions of Br detected for all methodologies and soil depths were utilized in SMD determinations. An example is given for the high water regime during the 1993 field season shown in Figure 1.

Significant differences between the sampling methodologies were compared over 48 days in 1992 and 78 days in 1993. Eighteen comparative tests between the sampling methodologies at each soil depth under high and medium irrigation regimes were utilized in 1992. Results from the 1993 data were obtained from 54 comparison tests under high, medium and low irrigation regimes.

Data in 1992 were extremely limited due to the unavailability of water. Additionally, sufficient soil core samples were not taken during the early part of the 1992 season to make reliable comparisons with the other methodologies.

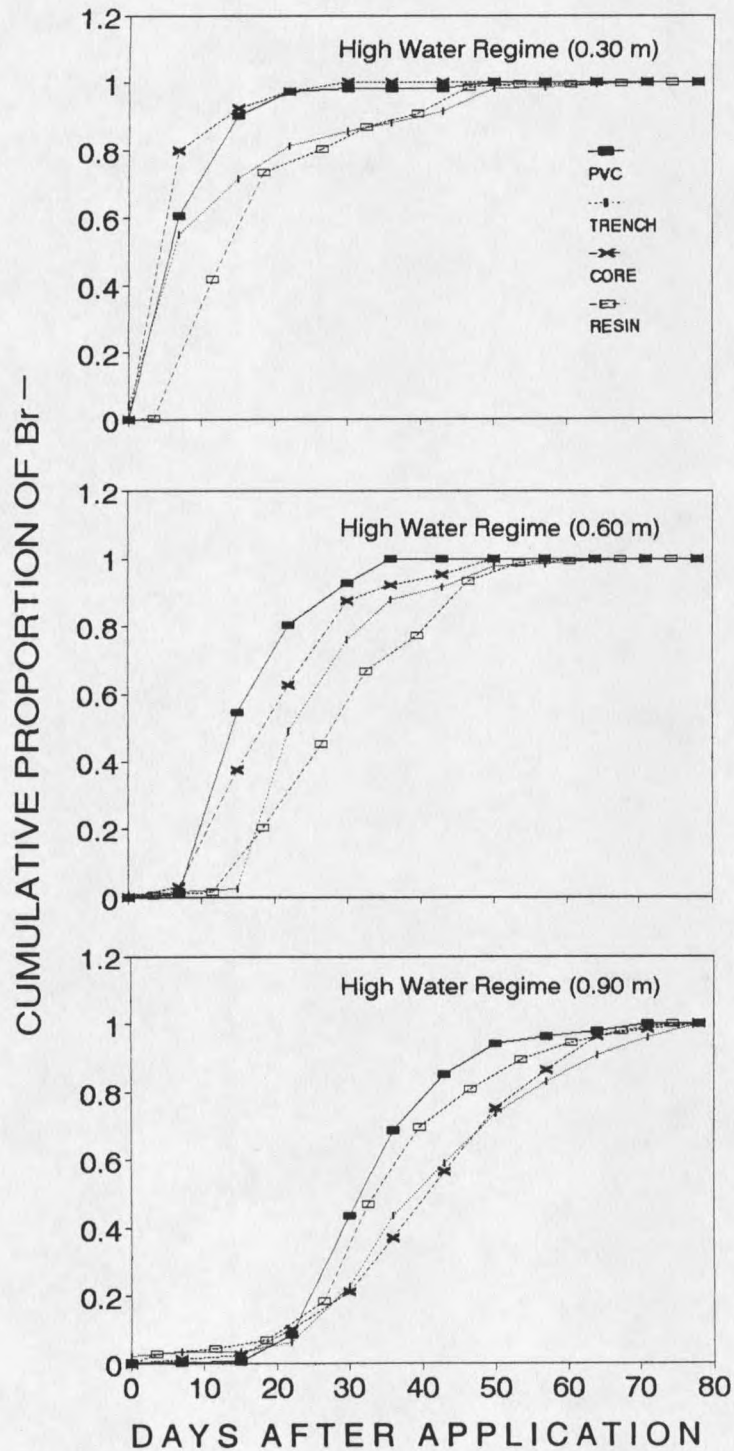


Figure 1. Cumulative Br proportions for PVC and trench lysimeters, resin capsules and soil cores under high water regime at 0.3, 0.6, and 0.9 m soil depths in 1993. Mean values ($n=4$) are expressed as cumulative proportions to allow comparisons using Smirnov's Maximum Deviation test for similar populations.

RESULTS AND DISCUSSION

In 1992, initial soil volumetric water contents (θ_v) were low, but subsequently increased as a combined result of early season precipitation and irrigation (Figure 2). In comparison, the initial θ_v determinations in 1993 were 25% greater (Figure 3) than those observed in 1992 due to the higher levels of precipitation and irrigation. Consequently, comparison tests were extended over a longer time period in 1993 and included the low water regime.

Comparisons of detected Br concentrations over time for each methodology based on SMD tests were significantly different ($P \leq .05$) between PVC and trench lysimeters and between PVC and resin capsules only in the high irrigation regime at the 0.3 m soil depth in 1992 (Table 4). Comparison of all other treatment combinations were statistically non-significant.

The SMD test gives a comparative analysis as a function of overall time effects throughout the duration of an experiment and does not identify differences at specific time periods. Standard errors of the mean at pre-peak, peak, and post-peak time periods were used with individual performance curves for each separate methodology to interpret BTC effects before all the data were transformed to proportions to

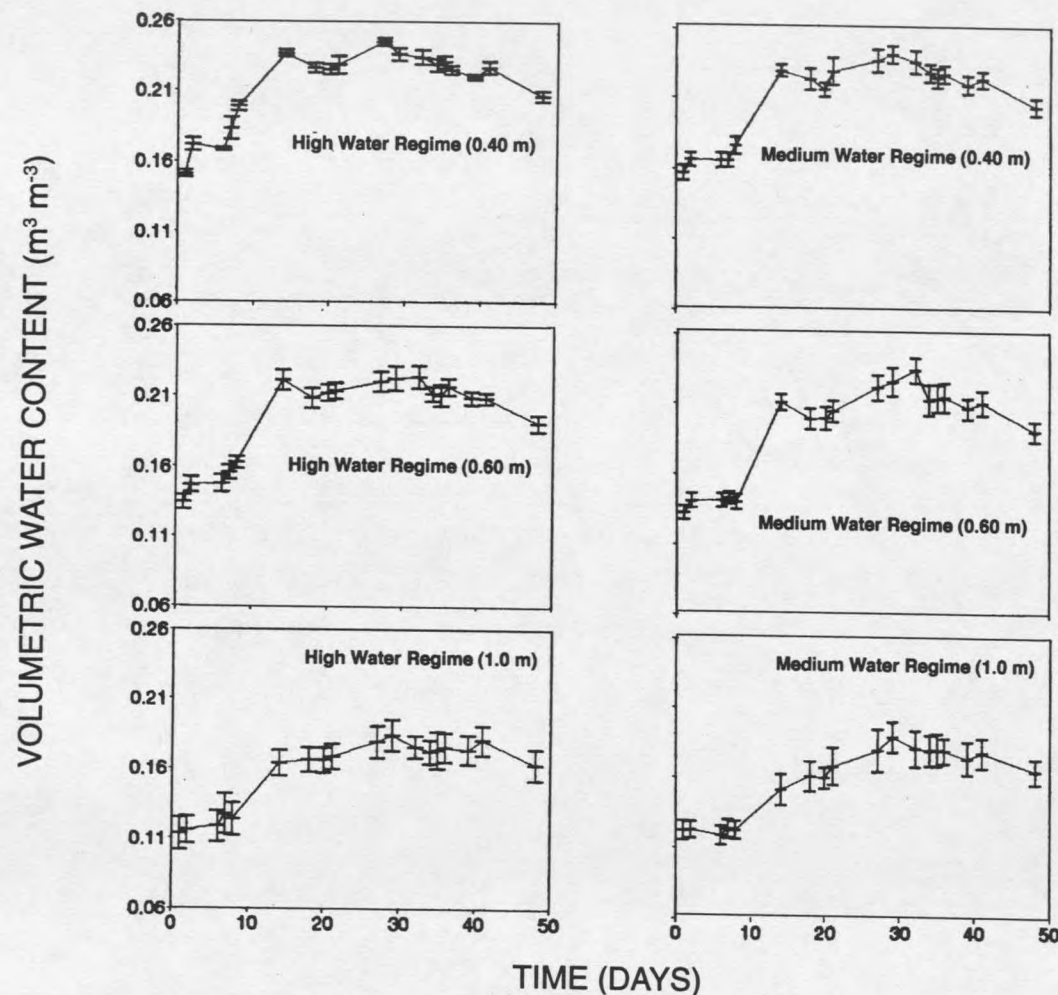


Figure 2. Volumetric water contents under high and medium water regimes at 0.4, 0.6, and 1.0 m soil depths in 1992. Vertical bars indicate $\pm$ standard error of mean ($n=4$); where absent, bars fall within symbols.

VOLUMETRIC WATER CONTENT ($\text{m}^3 \text{m}^{-3}$)

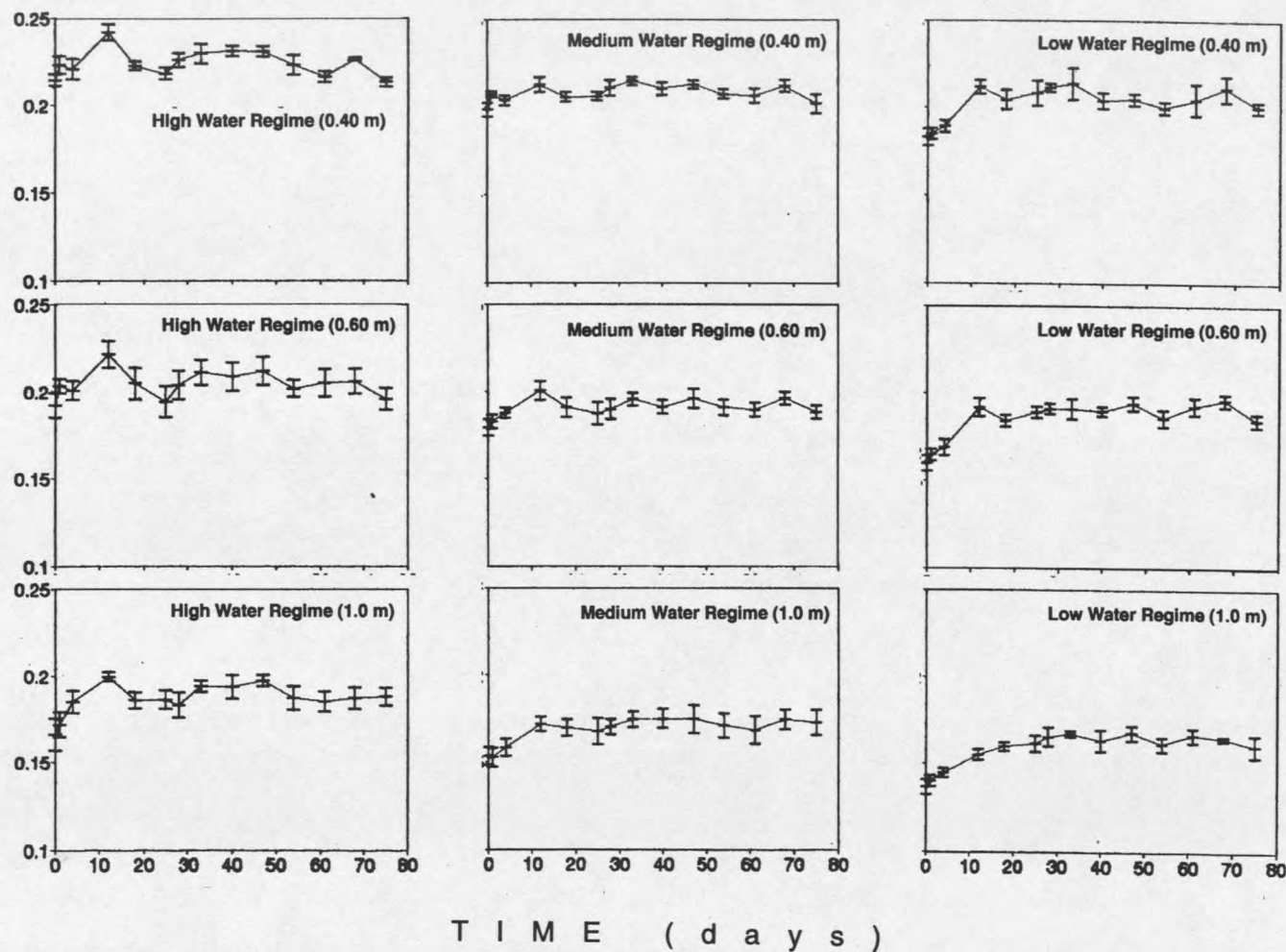


Figure 3. Volumetric water contents under high and medium water regimes at 0.4, 0.6, and 1.0 m soil depths in 1993. Vertical bars indicate $\pm$ standard error of mean (n=4); where absent, bars fall within symbols.

Table 4. Smirnov Maximum Deviation comparisons of selected solute transport methodologies during 1992 field season.

Applied Water Regime	Soil Depth m	PVC and Trench Lysimeter	PVC Lysimeter and Resin Capsule	Trench Lysimeter and Resin Capsule
High	0.3	X	X	
	0.6			
	0.9			
Medium	0.3			
	0.6			
	0.9			
Low	0.3			
	0.6			
	0.9			

X=Significantly different comparison.

facilitate the comparisons of different units of expression. Consequently, it is suggested that BTC differences occurred, as a function of time, since SMD is a comparative analysis of a transformed curve and is not meant to identify effects at specific time intervals.

Some distinct differences among the methodologies were observed in 1992 for breakthrough curves (BTCs) in relation to time, duration and height (Figure 4). The PVC and trench lysimeter BTCs peaked eight days after tracer application as compared to the resin capsule curve which gradually increased up to 24.5 days after application in the high water regime at the 0.3 m depth. Additionally, peaks for the PVC lysimeter BTC were generally more distinct than for the trench lysimeter and the resin capsule. Resin capsule BTCs exhibited relatively dispersed peaks at each depth. In general, at specific time intervals, the PVC lysimeters showed the highest BTCs when compared to the other methodologies under both the high and medium water regime at 0.3 and 0.6 m depths. As expected, the peak concentrations generally coincided with a large increase in θ_v which occurred early in the season.

In 1993, comparisons over time for each methodology based on SMD tests showed no significant difference when comparing PVC with trench lysimeters, PVC lysimeters with soil cores, and trench lysimeters with resin capsules over all water regimes and soil depths (Table 5). However,

PROPORTION OF Br^-

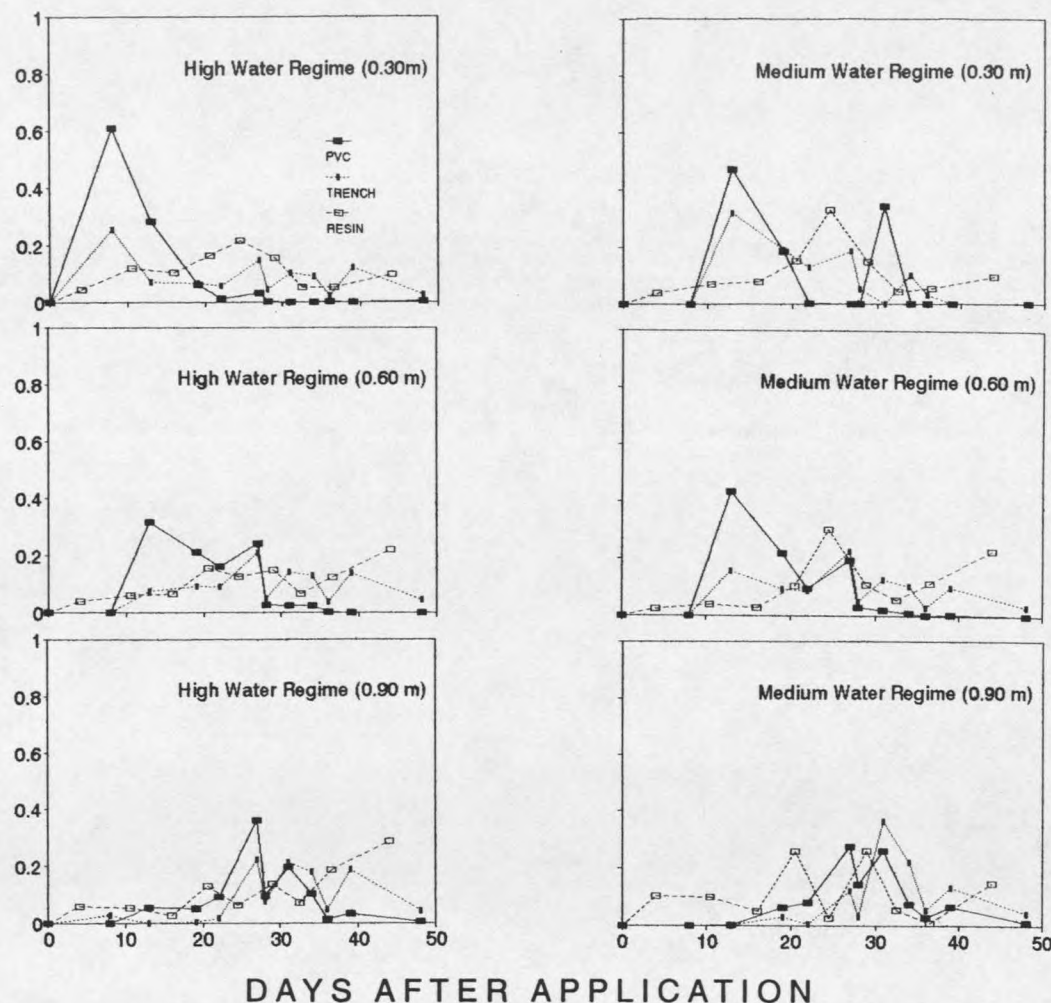


Figure 4. Bromide proportions for PVC and trench lysimeters and resin capsules under high and medium water regimes at 0.3, 0.6, and 1.0 m soil depths in 1992. Mean values ($n=4$) are expressed as proportions of the total to allow comparisons between methodologies having different concentration units.

Table 5. Smirnov Maximum Deviation comparisons of selected solute transport methodologies during 1993 field season.

Applied Water Regime	Soil Depth m	PVC and Trench Lysimeter	PVC Lysimeter and Soil Core	PVC Lysimeter and Resin Capsule	Trench Lysimeter and Soil Core	Trench Lysimeter and Resin Capsule	Resin Capsule and Soil Core
High	0.3				X		X
	0.6			X			
	0.9						
Medium	0.3			X	X		X
	0.6			X			
	0.9						
Low	0.3						X
	0.6						
	0.9						

X=Significantly different comparison.

comparisons between PVC lysimeters and resin capsules were significantly different in the high water regime at 0.6 m and in the medium water regime at 0.3 and 0.6 m. Additionally, significant differences occurred between the trench lysimeters and soil cores under the high and medium water regimes at 0.3 m and between resin capsules and soil cores for all water regimes at 0.3 m. Consequently, significant differences among the treatment combinations occurred in only eight of the 54 possible comparisons for methodologies, water regimes and soil depths. Of the eight significant differences, six of them occurred at the 0.3 m depth. These data indicate that under these specific soil and environmental conditions there are very few differences among the methodologies over time in the lower soil profile depths.

As in 1992, distinct differences occurred in relation to the timing of BTCs irrespective of SMD determinations. Breakthrough curves occurred seven days after tracer application for the PVC and trench lysimeters and soil core methodologies as compared to 11.5 days for the resin capsule under the high water regime at 0.3 m in 1993 (Figure 5). The BTCs for PVC lysimeter and soil core, trench lysimeter, and resin capsule occurred 15, 22 and 26.5 days, respectively, after application at the 0.6 m depth. At the 0.9 m depth, the PVC lysimeter BTC occurred 30 days after application. In comparison, the BTCs for the other methodologies were less distinct and ranged from 32.5 to 43 days. Resin capsule BTCs

PROPORTION OF Br⁻

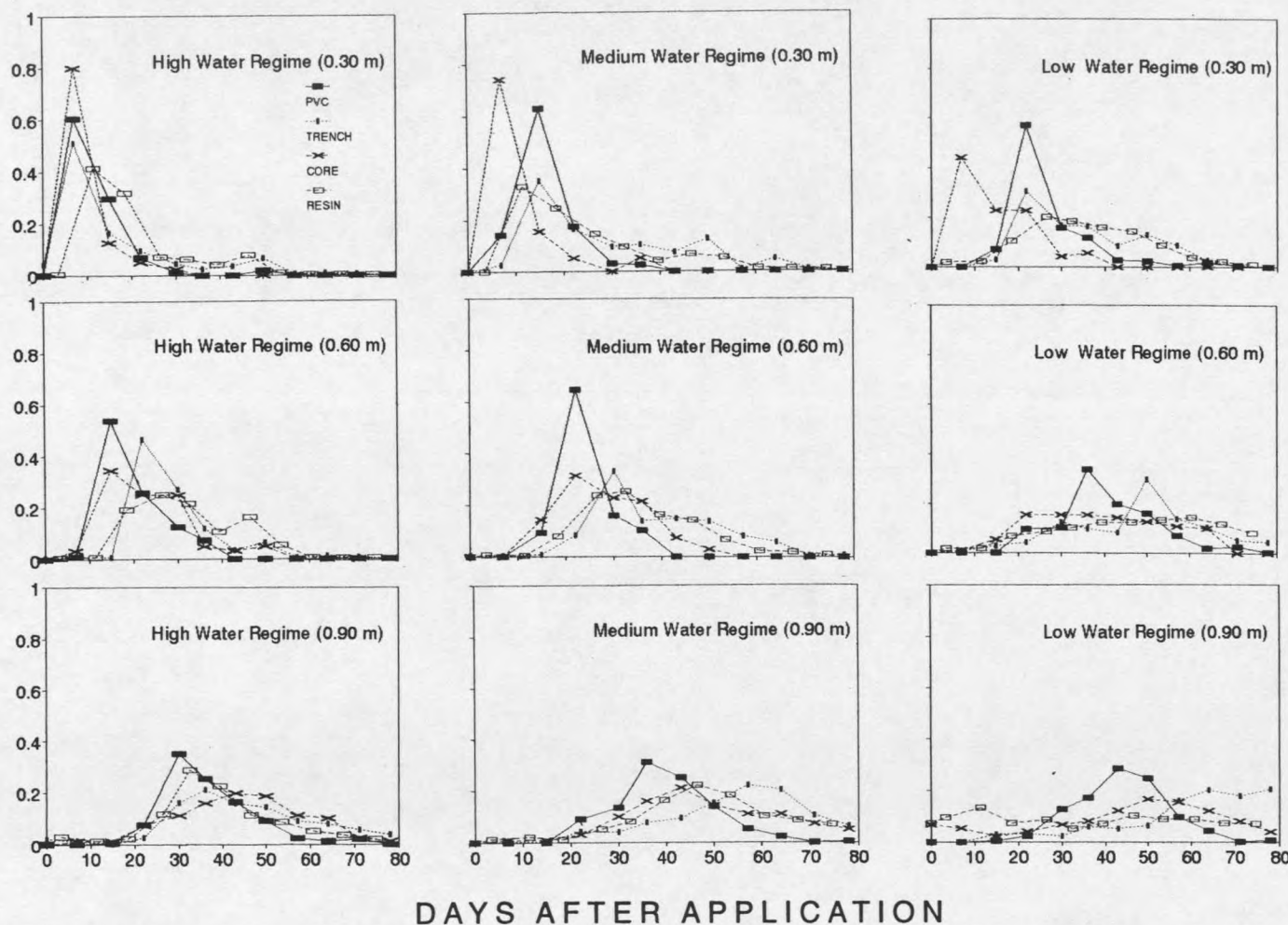


Figure 5. Bromide proportions for PVC and trench lysimeters, resin capsules and soil cores under high, medium and low water regimes at 0.3, 0.6, and 0.9 m soil depths in 1993. Mean values (n=4) are expressed as proportions of the total to allow comparisons between methodologies having different concentration units.

occurred later than the other methodologies except at the 0.9 m depth.

Soil core BTCs occurred earlier, in the upper soil profile, than those of the other methodologies when applied water was decreased (medium and low water regime). Under the medium water regime at 0.3 m, the BTC for the soil core occurred seven days after tracer application as compared to 11.5 to 15 days for the other methodologies. However, this pattern was not observed at the lower soil profile depths (0.6 and 0.9 m). At the 0.6 m depth, BTCs for PVC lysimeter and soil core, trench, and resin capsule occurred 22, 30 and 32.5 days after application, respectively. The PVC lysimeter BTC occurred the earliest and was much more distinct than those for other methodologies at 0.9 m.

The BTC for the soil core occurred first and at the same time in the low water regime at 0.3 m as was observed in the medium water regime. Additionally, BTCs for the PVC and trench lysimeter occurred at the same time 22 days after tracer application and the resin capsule BTC was less distinct with a peak at 26.5 days.

Under the low water regime at 0.6 m, distinct BTCs were observed only for the PVC and trench lysimeter at 36 and 50 days, respectively. Peak heights and areas under the curves were markedly less for methodologies at 0.6 as compared to the 0.3 m depths. Curves at the 0.9 m depth were comparatively flattened. The BTC for the PVC lysimeter was

more distinct than the other methodologies and occurred before the BTC for the trench lysimeter. Breakthrough curves for the PVC lysimeters were 6 to 21 days earlier than trench lysimeters and 3.5 to 11.5 days earlier than resin capsules at the 0.6 and 0.9 m depths for all water regimes throughout the 1993 study period.

There are several possible explanations for the earlier PVC lysimeter BTCs. Vacuum extraction has been reported to distort soil drainage patterns (van der Ploeg and Beese, 1977). Soil water extraction rates may be significantly higher than percolation rates under vertical drainage conditions even when small amounts of suction are applied. Additionally, manipulation of drainage patterns may be even more severe within the confines of a column than in the less restricted setting of porous cups in a trench wall.

Suspected greater soil water content and resulting differences in hydraulic conductivity between the column lysimeters and other methodologies may have caused some variability in the timing of BTCs. Within the PVC columns, no runoff from high irrigation or precipitation occurred since the tops of the columns extended above the soil surface (5-7 cm). However, it is virtually impossible to completely eliminate run-off in the field around uncontained solute sampling systems when high levels of irrigation are utilized even though application rates and timing are closely monitored. Additional increased soil water content inside

the PVC columns may have resulted from the columns protruding above the soil surface which could have provided a boundary area of relatively calm air compared to the other sampling techniques. Consequently, an extended column rim may act as a barrier to both sun and wind effects on the evaporation potential of soil water. The practice of leaving 5 to 7 cm of a PVC lysimeter extended above the soil surface to control potential run-off of surface water adjacent to the column back into the containment area may greatly reduce the potential for evaporation when compared to the soil surface outside the columns. Furthermore, line-source irrigation may present problems with ponding and runoff because of the relatively high water application rate inherent with the system (Hanks et al., 1976). Attempts to minimize runoff by shutting down the irrigation system when runoff was observed alleviated part of the problem, although heavy and frequent precipitation during the 1993 field season resulted in some runoff.

Suspected increased water content within the PVC columns may have affected the earliness of BTCs and also contributed to a more rapid completion of BTCs as was observed within the columns at the 0.6 and 0.9 m depths in comparison to the other methodologies. Earlier BTCs and higher proportions of Br observed in the soil cores at 0.3 m and the tendency for resin capsule BTCs to occur later than the other sampling techniques in all water regimes at 0.3 and 0.6 m may be

explained by the differential characteristics of the sampling methodologies.

The soil core techniques utilized in this study, encompassed a broad soil profile sampling increment (0 to 0.3, 0.3 to 0.6 and 0.6 to 0.9 m), and may have resulted in earlier BTCs with larger proportions at the 0.3 m depth than was observed with the other methodologies that were dependent on soil water transport of Br to specific sites for detection. Soil core sampling precision for Br detection may have been improved by taking soil cores at 0.15 to 0.45, 0.45 to 0.75 and 0.75 to 1.05 m depths. This would have bracketed and centered the other point source sampling techniques within the soil core sampling range. More precise comparisons of the methodologies may also have been attained by sectioning intact cores taken from the total profile (0 to 0.9 m) and removing subsamples for analysis at 0.3, 0.6 and 0.9 m soil depths.

Lysimeters which employ vacuum extraction sample a sphere of soil the size of which is unknown and dependent on amount and duration of vacuum, volume of sample, soil moisture, and soil type. Collection of ions from the soil by resin capsules is dependent on diffusion, and mass flow is primarily responsible for transport of Br to the resin capsule depths. Diffusion from an area up to 5 mm surrounding the resin capsule is reported to encompass the sphere from which ions are collected from the soil solution

(Skogley and Schaff, 1985). Consequently, as a result of the smaller soil sampling range for resin capsules as compared to lysimeters and soil cores, the resin BTCs could be expected to occur later. The early levels of Br monitored by resin capsules in 1992 seen in the medium water regime at 0.9 m may be associated with possible errors in stripping and detection procedures. Additionally, factors such as preferential flow, macropore movement of solutes and variable soil-resin capsule contact may confound data in any soil type.

CONCLUSION

In general, comparisons of methodologies using SMD were not significantly different at the lower soil depths. Breakthrough curves for PVC lysimeters generally showed narrower and more distinct peaks than other methodologies. This may have resulted from suspected greater θ_v within the columns caused by the protruding rims preventing runoff and shading a portion of the soil surface within the columns lessening evaporation. Trench lysimeter BTCs generally occurred later than the PVC BTCs in the lower sampling depths and were less distinct. Of all the methodologies, soil core BTCs were the most variable occurring sporadically before, during and after those of other methodologies with no obvious pattern related to either the irrigation regime or soil depth. Therefore, this would suggest that soil core techniques that utilize a large depth increment and are not centered at a desired sampling depth should not be used for comparative studies involving point source sampling methodologies. Resin capsule BTCs generally occurred later and were more dispersed than other methodologies. The later BTCs may be a function of the smaller volume of soil sampled by the resin capsule compared to other methodologies.

Most differences between methodologies were observed at 0.3 m in the high and medium water regimes. Below 0.3 m little difference occurs when comparing methodologies used to monitor Br transport which is similar to the results of Li et al. (1993) when comparing resin and PVC lysimeters and Everts and Kanwar (1988) when comparing soil cores, suction tube lysimeters, piezometers and tile drainage methods.

Suction lysimeter solute sampling is still the primary method used to obtain samples of unsaturated soil solution (Rhoades and Oster, 1986). Unlike any of the other methodologies tested, lysimeters provide an actual sample of the soil solution for analysis. Additionally, the partially confined system of PVC columns allows researchers to monitor environmentally hazardous solutes in the laboratory and field even though preferential flow along column walls may be a problem. Soil core sampling is particularly versatile and does not require specialized equipment. Depths and locations of sampling sites are easily modified. However, when the soil core is removed from the area that specific location cannot be used again. Unlike the other methodologies resin capsules provide a sink for elements and facilitate continuous monitoring of the soil solution. Additionally, the slant-placement technique does not disturb the soil in the area above the sampling site, although there is a potential for preferential flow along access tubes used in this technique. Comparison of the resin capsule

concentration units with those of other widely accepted sampling methodologies has not been conclusively documented. Resin capsules detect the movement of solutes through the soil profile, but the amount of transported solutes is not certain.

When selecting the type of methodology best suited for monitoring solute transport, consideration should be given to equipment, installation, location variables and the sample units that are needed for a specific purpose. Each sampling technique has unique characteristics that may make one more suitable than others in specific situations.

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