

Resin Adsorption for Describing Bromide Transport in Soil under Continuous or Intermittent Unsaturated Water Flow

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ABSTRACT

Accurate information on movement of soil-applied chemicals toward water tables is necessary for improving agricultural and environmental management. Current methods for studying related processes have major limitations. Objectives of this research were to investigate resin capsule adsorption for measuring Br^- transport, to compare results with those from vacuum extraction, and to determine the utility of resin capsule technology for field studies. Laboratory experiments were conducted with a uniformly packed soil column under continuous or intermittent, unsaturated water flow using Br^- as a tracer. Field experiments were also conducted with intermittent water flow applied by a line-source irrigation system. Bromide accumulated by mixed-bed ion-exchange resin capsules inserted into the soil at several depths in the soil column was compared with Br^- in solutions collected at the same depths by vacuum extraction through porous ceramic candles. Delayed timing of peak Br^- leaching patterns (BLPs) at the uppermost sampling point, and earlier peak BLPs at the lowest sampling depth, when resin capsule data were used, suggest that the accuracy of measuring Br^- transport is method-dependent. Under intermittent water flow, distinct spikes of BLPs measured by resin capsules corresponded to soil water potential changes. Only broad plateaus for BLPs were measured with vacuum extraction, implying greater sensitivity of the resin capsule methodology to soil moisture changes. Field results demonstrated the utility of resin capsules for detecting Br^- transport as influenced by irrigation intensity, plant water use, and plant Br^- uptake. The resin capsule methodology may provide a simple, accurate alternative to vacuum extraction or repetitive soil sampling for studying solute transport. It provides "in situ solid-phase extraction" of the target solute simultaneously with other ions in soil solution.

CHEMICAL MOVEMENT IN SOILS, the vadose zone, and groundwater is becoming an increasingly important topic in soil and environmental management. The most common techniques for determining the time, rate, and quantity of solute movement in soil-water systems are (i) direct soil sampling followed by chemical extraction, and (ii) vacuum extraction of soil solution through porous cups placed in the soil. Both methods have major limitations. Results obtained from soil samples represent only the instant at which the sample was collected, requiring frequent sampling to represent dynamics of solute movement. This becomes time-consuming and expensive. Also, soil sampling cannot be repeated at the same spot.

Solutions collected through porous cups may poorly represent the actual soil solution (Grossmann and Udluft, 1991). Lowered pressure due to suction can cause degassing with resultant pH and solubility changes, altered seepage rates (van der Plog and Beese, 1977), and incorrect solution electrical conductivities (Jacobson and Sandoval, 1971). Any soil must be quite moist for this sampling method to work at all, and it is often difficult

to collect enough solution for analysis, even at low soil hydraulic potential, in clay soils. Porous cups can exhibit a "filter effect" and they may become plugged by particles in certain soils, preventing their extended use. These inherent problems limit the accuracy and usefulness of this sampling method (Runland, 1989; Barbee and Brown, 1986; Nagpal, 1982; Hansen and Harris, 1975). Furthermore, continuous system dynamics cannot be well known unless extraction is continuous. Clearly, a simple, accurate sampling technique for studying solute movement in soils is highly desirable.

The phytoavailability soil test (PST) is a new and simplified soil "extraction" based on accumulation of solutes by mixed-bed ion-exchange resin capsules placed into saturated-paste soil samples (Georgitis, 1989; Skogley et al., 1990; Yang et al., 1991a). The resin capsule acts as a continuous ion sink, accumulating solutes that reach the soil-capsule interface by diffusion or mass transport. This process simulates ion dynamics in the soil-root system. Yang and Skogley (1992) reported that the movement of nutrients to a resin capsule was characteristic of diffusion-controlled processes, sensitive to solution concentration, selective for nutrients, and soil dependent. The capsules will function whenever soil conditions allow water transport or ion diffusion to occur, even though the soil may be too dry to allow vacuum extraction. Solute accumulation is also continuous, rather than intermittent. The system functions as an "in situ solid-phase-extraction" method. These characteristics of the resin capsule system provide the basis for development of an alternative, simple methodology for studying solute movement through soils.

The objectives of this research were to evaluate the resin capsule methodology (compared to vacuum extraction) for describing solute movement in soil columns under either continuous or intermittent unsaturated water flow, and to determine applicability for field studies.

MATERIALS AND METHODS

Soil and Soil Column. The soil, a coarse-loamy, mixed Typic Calciboroll, was collected from the 15- to 30-cm depth of a farm near Manhattan, MT. Physical and chemical properties of the soil are listed in Table 1. The soil was oven-dried at 40 to 50 °C for 3 d, pulverized, and passed through a 2-mm sieve.

The column was made from a polyvinyl chloride (PVC) cylinder with inner diameter of 0.20 m, outer diameter of 0.215 m, and height of 1.50 m. Soil was uniformly packed to a bulk density of 1.38 Mg m^{-3} by alternately spreading a thin layer of dry soil into the column and then gently tamping it with a flat instrument. Three sampling holes were made in the column wall at depths of 0.13, 0.43, 0.73, 1.04, and 1.34 m (Fig. 1). One hole at each depth was fitted with a 30-mm diameter by 50-mm length PVC tube protruding into the soil column as a port through which resin capsules could be inserted and retrieved. Another hole at each depth was fitted with a porous ceramic candle for vacuum extraction of soil solution. A ceramic tube for water potential measurement was placed in the

Abbreviations: PST, phytoavailability soil test; PVC, polyvinyl chloride; BLPs, bromide leaching patterns.

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Table 1. Physical and chemical properties of the soil† used in column.

Texture	pH	K_{sat}	O.M.	mg kg ⁻¹			K_{exc}
				CaCO ₃	Olsen-P	S	
sil	8.2	22.5	24.0	40.4	11.8	3.8	1.98

† Soil was analyzed by Montana State University Soil Analytical Laboratory. pH by 1:1 soil/water; organic matter by acid-dichromate oxidation; K_{exc} by 1 M NH₄OAC (pH 7.0) extraction; K_{sat} by saturated paste extraction; Olsen-P by 0.5 M NaHCO₃ (pH 8.5) extraction; CaCO₃(eq) by gravimetric; and S by 0.5 M NH₄OAC + 0.25 M acetic acid extraction.

third hole. The bottom of the column was fitted with a porous ceramic plate connected to a constant vacuum source of -0.04 MPa to maintain water flow through the column. Prior to experimentation, the soil was wetted and equilibrated to a water potential of -0.03 MPa at the surface and -0.04 MPa at the bottom. Water was applied through a porous ceramic plate placed on the soil surface and controlled by a reservoir with a water potential of -0.0017 MPa to maintain uniform application and water flow rates. A schematic of the column is presented in Fig. 1.

In the first experiment, water was applied continuously, with flow rates determined daily. They ranged from 10 to 20 mm d⁻¹. In the second experiment, water was applied intermittently (Fig. 2).

Bromide Tracer and Its Application. The Br⁻ source was KBr, providing a conservative tracer (Bowman, 1984; Smith and Davis, 1974). A solution of KBr (1.88g KBr dissolved in 50 mL water, equivalent to 100 kg Br⁻ ha⁻¹) was sprayed uniformly onto the soil surface using a household sprayer. After several minutes when no solution remained on the surface, water was applied as described above.

Ion-Exchange Resin Capsules. Resin capsules were made with mixed-bed ion-exchange resin (IRN-150, nuclear grade, Rohm and Haas, Philadelphia, PA). This mixture consists of equal proportions of a strongly acidic cation exchange resin saturated with H⁺ and strongly basic anion exchange resin saturated with OH⁻, and provides a total exchange capacity of 550 cmol kg⁻¹. A 5-mL measured portion of resin was placed in a square of polyester mesh cloth (150-mesh, 30- μ m thread, 140- μ m openings) and tied into a tight sphere with polyester thread. The resin capsules thus formed were approximately 25 mm in diameter.

Sampling Procedure. A resin capsule was inserted at each soil sampling depth, making sure that one-half of the sphere was in complete contact with soil particles. At a predetermined time, the resin capsule was removed and a new one inserted in its place. The used resin capsule was thoroughly washed with deionized-distilled water, taking care to remove all adhering soil particles. Each capsule was placed in a small plastic bag and frozen until all were ready for stripping of accumulated ions.

Stripping Agent and Procedure. The normal stripping reagent in the PST procedure is HCl. However, because Cl⁻ would interfere with Br⁻ analysis by ion-selective electrode, 50 mL of 1 M H₂SO₄ solution was used. Except for this change, the procedure was the same as described by Yang et al. (1991a).

Vacuum Extraction Method. Porous ceramic assemblies (Soil Moisture Equipment Corp., Santa Barbara, CA) were employed as vacuum extractors. The candle assemblies extended 80 to 100 mm horizontally into the column. Soil solution was collected from the 0.13-m sampling point depth once every 2 to 6 h at the beginning of water application, depending on the rate of water flow. After 2 d, all samples were taken daily, and tensiometer readings were taken at the same time, using a portable pressure transducer (Tensiometer, Soil Measurement Systems, Tucson, AZ). Solution samples of 5 to 8 mL were obtained by applying and maintaining a suction of -0.06 MPa for 4 to 5 h, starting the same time each day.

Sampling Protocol. Resin capsules were replaced every 24 h, at the time that vacuum extraction was initiated. This provided a system in which results were obtained on a daily basis for both methods. However, data for vacuum extraction are intermittent and integrate a 4- to 5-h sampling period, while data from resin capsules provide continuous, 24-h integration. Data were plotted based on the time of resin capsule removal and initiation of vacuum extraction.

Bromide Analysis. Bromide concentrations in soil solutions and in resin stripping solution were measured using a Br⁻ ion-selective electrode method (Orion Research, Boston, MA) as described by Onken et al. (1975).

Field Studies. A field experiment was conducted near Manhattan, MT, on the same soil used for laboratory studies. The field was equipped with a line-source sprinkler irrigation system (Hanks et al., 1976). An area adjacent to the sprinkler was divided equally, each 5.6 m in length (parallel to the sprinklers) and 10 m in width, and used as main plots to study effects of cropping vs. fallow. The cropped area was seeded

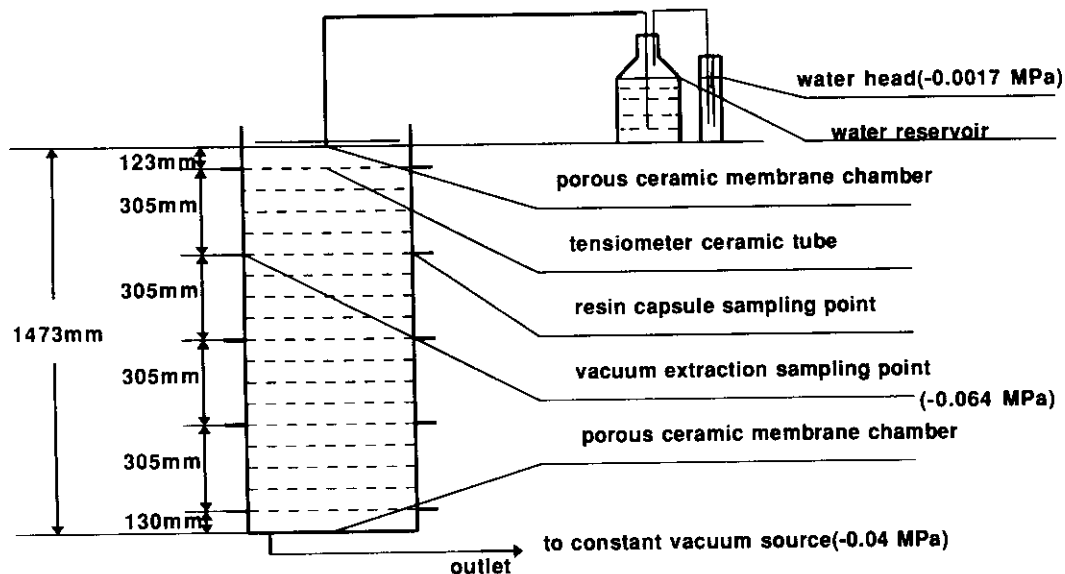


Fig. 1. Schematic diagram of soil column.

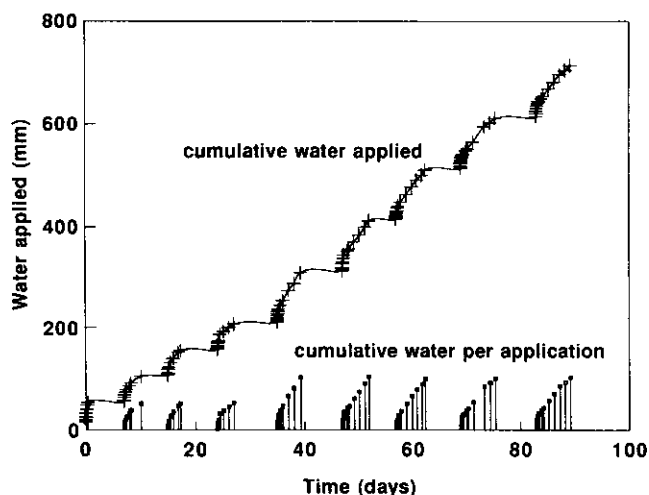


Fig. 2. Water applied as simulation of rainfall in soil column studies.

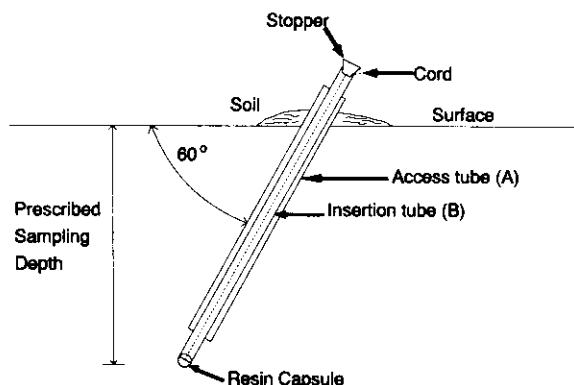


Fig. 3. Schematic of resin capsule sampling system for field study.

to barley (*Hordeum vulgare* L. cv. Klages) on 24 May, and harvested on 19 Sept. 1991. The continuous variation in water application rate extending outward from the line-source sprinkler system was arbitrarily divided into five water regimes, with samplers installed in each of these areas. Water applications varied from 305 mm adjacent to the sprinkler (Water Regime 1) to 9 mm in Water Regime 4. Growing season precipitation was 106 mm (Water Regime 5) and pan evaporation totaled 698.5 mm. No Br^- leaching was detected in Water Regime 4 or 5.

Figure 3 illustrates schematically the sampling system for resin capsules. A length of PVC tubing (A) with 25.4 mm inside diameter was inserted to the desired depth through a drill hole made with a soil sampler. This tube was placed in the soil at approximately 60° , so that it would not interfere with vertical flow of water and solutes at the point of sampling. Soil was tightly packed around the upper end of this tube and mounded up slightly to prevent the free flow of water down along the tube. A second PVC (B) with 20 mm inside diameter was cut to extend 50 to 80 mm beyond the end of the A tube. Prior to initial capsule insertion, a hemispherical cavity was formed in the bottom of the soil hole using a wooden rod having the same diameter (20 mm) as the resin capsule. A resin capsule was held tightly, by means of an attached cord, to the end of the B tube, inserted through the A tube, and pushed snugly into the pre-formed cavity. The B tube assembly, with attached resin extractor, could be removed at any

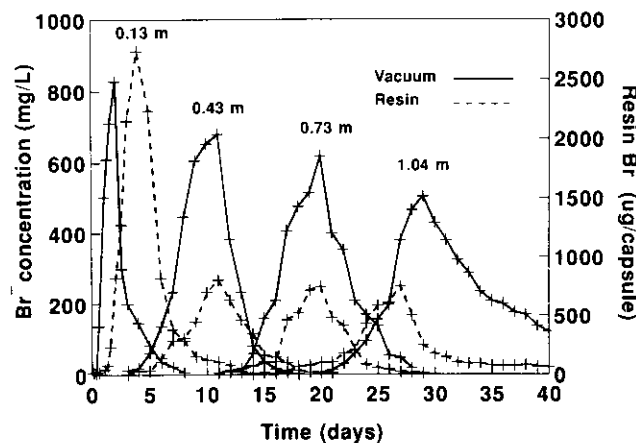


Fig. 4. Bromide leaching patterns during continuous, unsaturated water flow in soil column.

time and a new resin capsule inserted to allow sampling at specific intervals. Resin capsules used in this study were molded (UNIBEST, Bozeman, MT) and had a small flange around the middle. This provided a means whereby one-half of the resin capsule surface was held in intimate contact with the soil during the sampling interval. As in the column studies, the effective cross-sectional area of the resin capsule is only half as much as when the entire capsule is in contact with the soil. Changing capsules was facilitated by use of a small barbless fish hook at the end of the cord. Three replicate insertion tubes were placed at each sampling depth (0.15, 0.30, and 0.90 m) within each of the five water regimes, for both fallow and cropped treatments.

Prior to seeding and the first irrigation, a solution of KBr (18.6 g dissolved in 500 mL of water, equivalent to $100 \text{ kg Br}^- \text{ ha}^{-1}$) was uniformly sprayed onto the soil surface of subplots measuring 1.22 by 1.53 m surrounding the sampling tubes. All samples were collected from below this area. This experiment was designed to investigate only the utility of the resin capsule methodology for detecting solute movement under these field conditions, so no vacuum extraction system was established for comparison.

Resin capsules were retrieved at approximately 1-wk intervals early in the growing season, and at 2-wk intervals toward the latter stages. New capsules were reinserted immediately. After retrieval, each resin capsule was handled in the same manner as in the column studies. Plant samples were collected just prior to harvest and biomass measured for each treatment. Water-extractable plant Br^- was also determined by the ion-selective electrode method.

RESULTS AND DISCUSSION

Continuous Unsaturated Water Flow

Comparative Br^- Leaching Patterns. Bromide leaching patterns (BLPs) under continuous, unsaturated water flow are plotted in Fig. 4 for each sampling depth in the soil column. Results illustrate the similarity of BLPs using both the resin capsule and vacuum extraction methods. The notable difference was in the time for peak concentrations to occur for the two methods at the upper and lower sampling depths (Table 2). At the 0.13-m depth, peak Br^- concentration determined by vacuum extraction occurred 2 d earlier than for the resin capsule method. Peak concentrations occurred at essentially the same time for both methods at the two intermediate sampling depths. At the deepest sampling depth (1.04 m),

the time of Br⁻ peak concentrations determined by vacuum extraction occurred 2 d later than that measured by the resin capsule method.

These discrepancies are probably due to fundamental differences in the manner in which ions are removed from soil. Vacuum extraction involves application of a suction force to mechanically separate soil solution from the soil solid phase. The suction force applied to extract soil solution may have caused a higher rate of water flow, or "channeling" effect, at the uppermost sampling point. Van der Plog and Beese (1977) indicated that applying even slight suction to extract soil solution may cause significantly higher seepage rates. This effect could cause earlier appearance of peak Br⁻ concentration than if the water in the system remained undisturbed. In contrast, the resin capsule functions as a "solid-phase-extractor" (Newman, 1992). Water moves through the resin capsule at the same rate as in the soil, due to the presence of large pores between resin beads and the "channel structure" within beads (Dorfner, 1991). Adsorption of solutes involves only ion exchange, with no alteration in water content of the soil (Schaff and Skogley, 1982).

There are at least two plausible explanations for the delay in detecting peak Br⁻ concentration at the lowest sampling depth, when using vacuum extraction. First, at the lower depth the suction cups may have been less able (than at the top sampling depth) to distort the flow-field and provide short-circuit routes to themselves. Second, the amount of water remaining in the column at this lowest depth (as a result of daily extraction of solution from the three upper sampling points) was about 5% less than that moving past the uppermost sampling point. Thus, less water was available to transport Br⁻ to the lower depth (at any given time) in the vacuum extraction system than with resin capsules.

Cumulative Water Infiltration and Br⁻ Transport in the Soil. Bromide is considered to be a conservative tracer for solute movement in soils and groundwater, and its movement dependent upon water flow. Cumulative amounts of water added to the soil surface to leach Br⁻ beyond specific points are included in Table 2. The amount of water for Br⁻ to leach beyond 0.13 m, as determined by vacuum extraction, was less than that measured by resin capsules. In contrast, the amount of applied water to leach Br⁻ beyond 1.04 m, as determined by vacuum extraction, was more than that as measured by resin capsules. The same reasoning can be used to explain these differences as for the time required to reach peak Br⁻ concentrations.

Intermittent, Unsaturated Water Flow

Bromide Leaching Patterns. Bromide leaching patterns determined by the two methods in a soil column under simulated rainfall are plotted in Fig. 5. As was the case with unsaturated continuous water flow, peak concentrations determined by vacuum extraction occurred earlier for the 0.13-m depth and later for the 1.04-m depth, compared with resin capsule data. We discussed probable reasons for these differences earlier.

Under these conditions, the most notable difference was in the shapes of the BLPs. Distinct spikes of Br⁻ concentration occurred with resin capsule data for all depths under simulated rainfall (Fig. 5). On the other hand, BLPs determined by vacuum extraction tended to

Table 2. Time and quantity of water to reach BLP peak concentrations as determined by the resin capsule and vacuum extraction methods under continuous, unsaturated water flow.

Method	Depth, m			
	0.13	0.43	0.73	1.04
	d			
Resin capsules	4	11	20	27
Vacuum extraction	2	10	20	29
	water, mm			
Resin capsules	153	247	401	504
Vacuum extraction	127	247	415	612

exhibit plateaus. Again, these results provide further evidence that the methods of collecting Br⁻ are mechanistically different, and that they differ in sensitivity to changing water status in the column. The resin capsules apparently collected the mass flux of Br⁻. As water potential decreased, water (and Br⁻) flux would likewise decrease, and this effect was registered by resin capsule data. However, at the low moisture contents in this study, applied suction probably resulted in extraction of soil solution from only the larger pores where the water potential was lowest. To obtain a similar amount of soil solution from drier soil, the same size pores may have been extracted, but perhaps at greater distances from the porous candle. Thus, the concentration of Br⁻ in solution

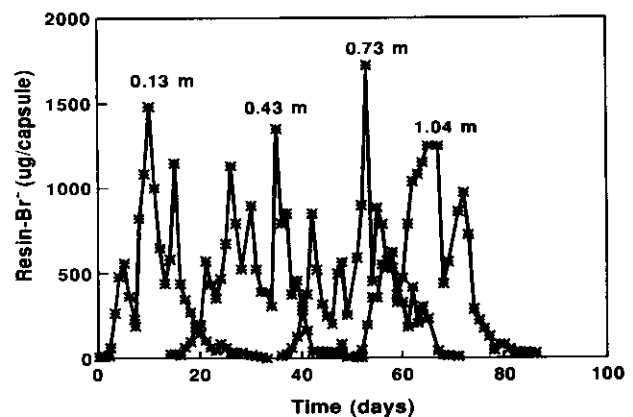
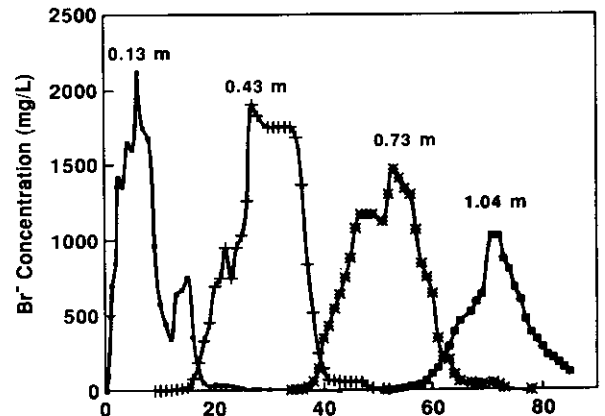


Fig. 5. Bromide leaching patterns during intermittent unsaturated water flow in soil column.

may not have changed much at all, as reflected in vacuum extraction data.

Using the resin capsule methodology will also extend the range of conditions under which solute transfer can be measured, compared to using vacuum extraction. The upper limit for obtaining sufficient sample volume with vacuum extraction is generally about -0.03 MPa water potential. Results from related studies showed that the rate of ion accumulation by resin capsules decreased with decreasing water potential (unpublished data), but the capsules continued to function at soil water potential less than -0.15 MPa.

Bromide Transport and Soil Water Changes. Bromide leaching patterns were well related to soil water changes at all sampling depths. Figure 6 clearly shows the relationship between changes in soil water potential and Br^- concentration for two depths as determined by the resin capsule method. At each depth, Br^- concentration spikes occurred within a day or two after minimum water potential, and decreased as the soil became drier.

Table 3 lists correlation coefficients for Br^- concentrations and water potentials under simulated rainfall at each column depth. These coefficients for resin capsule data are significant at the 99% confidence level at all

depths. Coefficients for data determined by vacuum extraction were significant only at the 95% confidence level, and only for the lower three depths.

The total correlation coefficient (all depths combined) between Br^- concentrations determined by vacuum extraction and water potentials was significant at the 95% confidence level ($r = 0.2368^*$, $n = 96$). This relationship determined by resin capsules was much higher, and significant at the 99% confidence level ($r = 0.7509^{**}$, $n = 99$).

Resin vs. Vacuum-Extracted Br^- Concentrations. Bromide transport is basically dependent on water movement, so a strong relationship is expected to exist between results from methods of measuring this process. The correlation coefficient between data (all samples combined) collected by these two methods is significant at the 99% confidence level ($r = 0.5588^{**}$, $n = 99$).

Comparison of Units for the Two Methods. A potential problem with utilizing the resin capsule method is that the data cannot be directly expressed as milligrams per liter of solution, which is the standard unit for vacuum extraction data. At least two approaches could be used to convert resin capsule data (mass of solute per capsule per unit time) into milligrams per liter of solution. One method is to convert resin data based on the water flux (F), which occurred through the area (A) of the resin capsule during the sampling duration (t). This approach is based on assumptions that all Br^- transported into the cross-sectional area of the resin capsule would be adsorbed by the resin, and that no Br^- diffused into the capsule from the soil extending out beyond the capsule. The conversion to milligrams per liter of soil solution can be accomplished using the following equation:

$$C_{(\text{mg/L})} = C_{(\mu\text{g}/\text{bag.d})}/(FA t) \quad [1]$$

where C is concentration of Br^- . For this study, F (average) was 1.1 cm d^{-1} , A was 2.45 cm^2 (only one-half of the capsule surface was in contact with the soil), and t was 1 d, so Eq. [1] becomes

$$C_{(\text{mg/L})} = 0.37C_{(\mu\text{g}/\text{bag.d})} \quad [2]$$

However, several uncertainties are involved in this conversion. For example, we know the above assumptions to be incorrect. Diffusion of solute from surrounding soil toward the capsule occurs throughout the sampling period, increasing the effective cross-sectional area of the capsule. The amount of solute diffusing, and the distance from the resin surface through which diffusion occurs,

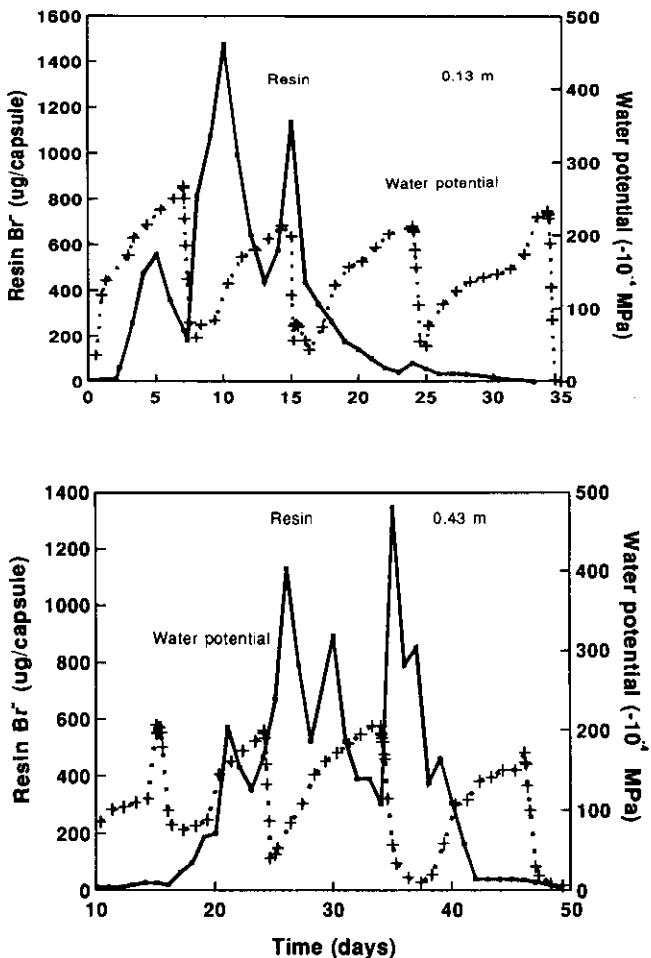


Fig. 6. Relationships between bromide leaching patterns measured by resin capsules and soil water potential at two selected depths within the soil column.

Table 3. Correlation coefficients† between soil water potentials and Br^- concentration.

Depth, m:	0.13	0.43	0.73	1.04	Total
Resin capsule method	0.7547**	0.8343**	0.8316**	0.8957**	0.7508**
	$n = 26$	$n = 29$	$n = 28$	$n = 16$	$n = 99$
Vacuum extraction method	0.3393	0.4973*	0.4182*	0.5717*	0.2368*
	$n = 23$	$n = 29$	$n = 28$	$n = 16$	$n = 96$

*,** Significant at 0.05 and 0.01.

† To calculate the coefficients, each analyzed water potential value was shifted to each corresponding BLP concentration based on the time of occurrence of peak concentration.

are functions of soil water content, solute concentration, soil properties, and other factors (Yang et al., 1991a,b). Also, whether or not the capsule adsorbs all Br^- that reaches its surface is a function of water flux. Usually, under unsaturated flow, water flux would be slow enough to allow complete adsorption of solutes.

An alternative approach for comparison of resin capsule and vacuum extraction values is statistical correlation of values. Within a given study, where the data are obtained under the same conditions, this approach would probably provide the most useful conversion. To illustrate this, data from Fig. 3 can be used. It is clear that the time required to reach Br^- peak concentrations, as measured by both methods, was the same only at 0.73 m. Using data from this sampling depth to calculate the correlation between vacuum and resin-extracted Br^- concentrations resulted in the following equation:

$$C_{\text{resin-Br}}(\mu\text{g}/\text{bag}) = 1.18C_{\text{vacuum-Br}}(\text{mg}/\text{L}) (r = 0.98^{**}, n = 31) \quad [3]$$

The reciprocal of this is 0.85, or the conversion factor from resin- Br^- concentration ($\mu\text{g bag}^{-1}$) into vacuum- Br^- concentration (mg L^{-1}). The larger coefficient of conversion in this statistical comparison, as compared with that calculated by Eq. [1], provides evidence for uncertainties surrounding attempts to convert resin capsule units into those used in vacuum extraction methodology. Studies would need to be done to develop these relationships if it was necessary to use commonly accepted units of measure.

However, major problems inherent in vacuum extraction have been previously noted. Because of these limitations, vacuum extraction results often lack diagnostic rigor. The volume of soil from which the solution sample was derived is unknown, necessitating concurrent measures of soil water content and flux. Even then, the sample represents only the conditions at time of sampling, with no way of knowing if a solute transfer event was missed during the interval between samplings. These inherent problems are eliminated in the resin capsule approach. Further studies to elucidate resin capsule function in transient flow systems could lead to a more accurate, simple system for continuous evaluation of solute flux through the medium, albeit with other units of measure. Comparative values for solute accumulation at different sites, but during a specific time, would provide a direct means of diagnosing relative magnitudes of solute transport. The need to develop quantitative relationships and to become familiar with different units of measurement should not seriously detract from the utility of the methodology.

Detection of Br^- Transport in the Field. The quantity of Br^- accumulated by a resin capsule under field conditions should be a function of (i) the duration of sampling, (ii) water (and Br^-) movement to the capsule depth, (iii) water content near the capsule (which would influence the amount of Br^- diffusing to the capsule), and (iv) plant Br^- uptake (on the cropped plots). Sensitivity of the resin capsule data to these influences would indicate promise for development of this methodology. The effect of duration of sampling was not directly tested, as all capsules were removed from all plots at the same time.

Table 4. Amounts of irrigation water (mm) applied during the field study, rainfall, and total growing season water for three water regimes.

Time d	Regime 1	Regime 2	Regime 3
	water, mm		
0	55	42	19
7	64	45	18
14	47	38	22
27	55	45	26
31	27	17	14
32	57	48	27
Total	305	235	126
Rainfall (total)	106	106	106
Total growing season	411	341	232

Dates of irrigation and quantities of water added for the three wettest regimes are listed in Table 4. Only 9 mm of water were added to Regime 4 and no Br^- movement was detected in these plots, nor in the plots receiving no irrigation (Regime 5), so data from these water regimes are not presented. Quantities of Br^- accumulated by resin capsules at three depths for the three wettest regimes under cropping and fallow are given in Table 5. The data are corrected for an average Br^- background of $8 \mu\text{g capsule}^{-1}$ ($n = 55$) where no Br^- was applied to the soil.

Contrary to expectations, considerably more Br^- was collected during the first 8 d in capsules under cropping than fallow at the shallowest sampling depth (0.15 m) in the two wettest regimes. This may have been due to increased water channeling as a result of rapid root growth

Table 5. Bromide concentrations measured in resin capsules under field conditions.

Time d	Depth, m					
	Cropped			Fallow		
	0.15	0.30	0.90	0.15	0.30	0.90
$\mu\text{g capsule}^{-1}$						
Water regime 1; 411 mm						
8	458	4	1	5	0	0
15	552	12	1	336	15	0
20	377	108	2	574	183	3
29	244	154	12	765	333	5
36	1	0	0	182	211	6
50	31	18	5	701	1334	29
71	7	4	2	1679	1612	12
Total	1670	301	23	3541	3688	55
Water regime 2; 341 mm						
8	22	9	4	0	0	0
15	57	0	20	214	3	0
20	132	9	15	407	4	1
29	104	13	16	518	14	7
36	0	0	1	164	2	0
50	2	1	6	829	32	12
71	46	1	4	1355	42	8
Total	363	33	66	3487	97	28
Water regime 3; 232 mm						
8	1	2	7	0	0	0
15	2	1	2	13	0	0
20	8	5	5	51	2	1
29	10	18	14	166	13	5
36	0	1	0	114	1	0
50	16	5	3	256	17	10
71	5	1	2	446	2	2
Total	42	33	33	1046	35	18

during the early stages of plant growth. However, by the second or third week, more Br^- was detected under fallow in all water regimes at all depths. After Day 29, only a small amount of Br^- was detected in the cropped plots at the 0.15-m depth, whereas a large amount of Br^- continued to be detected in the fallow plots.

Under Water Regime 1 (411 mm), Br^- reached the 0.30-m depth in significant quantities at about the same time (20 d) in the cropped and fallow systems, but much more was detected under fallow. At this depth, peak Br^- concentration occurred by Day 29 in the cropped plots, but continued to increase to the end of the growing season in the fallow plots. About 11 times more Br^- was collected under fallow than under cropping at the 0.30-m depth. This difference was only about 2.5 times at the 0.15-m depth. Relatively little Br^- was detected at the 0.90-m depth in the cropped plots, but more reached this depth in the fallow plots.

In Water Regime 2 (341 mm), the pattern of Br^- detected at the 0.15-m depth was similar to that for Regime 1, but with lesser quantities of Br^- leached. About eight times more Br^- was collected at the 0.15-m depth in the fallow plots than with cropping. Little Br^- was detected at 0.30 m in the cropped plots at any time, but in the fallow plots significant amounts of Br^- were detected at 50 and 71 d. Little Br^- was detected at 0.90 m in this water regime under cropping or fallow throughout the sampling period.

In Water Regime 3 (232 mm), little Br^- reached 0.15 m in the cropped plots, but by 20 d a continually increasing amount of Br^- was detected at this depth in the fallow plots. Little or no Br^- was detected at the lower depths in these plots.

Barley plant Br^- measurements (at harvest) indicated that 27 to 38% of applied Br^- was taken up (data not shown) when enough water was applied to leach the Br^- into the root zone (Water Regimes 1, 2, and 3). This was similar to results reported by others (Owens et al., 1985; Kung, 1990), involving similar rates of applied Br^- . Our results indicate that the resin capsule data reflected this reduced amount of Br^- that was available to be leached in cropped fields as compared with fallow.

Results from this field study suggest that this methodology is sensitive to conditions that would be expected to influence solute flux. Results can be interpreted to indicate macropore water flow and associated Br^- transport in the cropped soil down to at least 30 cm. This was shallower, due to crop uptake of water and Br^- , than in the fallow soil where Br^- moved to greater depths.

Several data outliers occurred in some of the results where generally low levels of Br^- accumulation were being detected. The unusually high values could have resulted from water channeling and associated transfer of Br^- . It is also possible that some water leaked down around the access tubes if the soil did not contact the tube tightly. To guard against this source of error, a collar could be placed around the access tube (at a depth greater than where saturated soil conditions would occur during irrigation) to intercept and divert any free water moving in this manner.

CONCLUSIONS

Results from this study clearly indicate that resin capsule methodology is effective for describing Br^- leach-

ing in a uniformly packed soil column under either continuous or intermittent, unsaturated water flow. In the vacuum extraction method, the amount of surface-applied water and time required for Br^- peak concentrations to occur at various column depths appeared to be affected by the applied suction force and removal of solution.

Patterns for Br^- concentration vs. time under simulated rainfall conditions were similar for the two methodologies, but distinct peaks (which were inversely related to measured soil water potential) were measured with resin capsules. The resin capsule results probably relate more directly to Br^- flux, as influenced by changing water flux, while the vacuum extraction results probably relate more closely to solute concentration in soil macropores. We speculate that these effects are related to the fundamental difference in the mechanisms for collecting the solute sample.

Results from field studies demonstrated that the resin capsule method was effective for detecting Br^- transport under varying water regimes, and that differences caused by transpiration and plant absorption of Br^- were readily detected.

These results, involving both laboratory column and field studies, provide evidence that the resin capsule methodology may provide an alternative (in situ solid-phase-extraction) to the vacuum extraction method for measuring Br^- transport under conditions of unsaturated water flow. Increased sensitivity to water flow changes, plus the ease, simplicity, and rapidity of sample removal, provide the basis for an improved approach for studying solute dynamics. Problems inherent in vacuum extraction could thus be eliminated. It should be realized that solutes other than the target solute are also being adsorbed, allowing simultaneous data collection on a broad range of solutes. Additional studies need to be conducted to determine quantitative relationships pertaining to the units of measure for the resin capsule method under various soil and solute transfer conditions.

REFERENCES

- Barbee, G.C., and K.W. Brown. 1986. Comparison between suction and free-drainage soil solution sampling. *Soil Sci.* 141:149-154.
- Bowman, R.S. 1984. Evaluation of some new tracers for soil water studies. *Soil Sci. Soc. Am. J.* 48:987-993.
- Dorfer, K. 1991. Synthetic ion exchange resins. p. 321. *In* K. Dorfer (ed.) *Ion exchangers*. Walter de Gruyter Berlin, New York.
- Georgitis, S.J. 1989. The development and characteristics of the phytoavailability soil test for K, S, and P. Ph.D. diss. Montana State University, Bozeman (Diss. Abstr. AAD90-19881).
- Grossmann, J., and P. Udluft. 1991. The extraction of soil water by the suction-cup method: A review. *J. Soil Sci.* 42:83-93.
- Hanks, R.J., J. Keller, V.P. Rasmussen, and G.D. Wilson. 1976. Line source sprinkler for continuous variable irrigation-crop production studies. *Soil Sci. Soc. Am. J.* 40:426-429.
- Hansen, E.A., and A.R. Harris. 1975. Validity of soil water samples collected with porous ceramic cups. *Soil Sci. Soc. Am. Proc.* 39:528-536.
- Jacober, F., and F. Sandoval. 1971. Effect of soil grinding, suction, and extraction time on salt concentration of saturation extracts. *Soil Sci.* 112:263-266.
- Kung, K.J.S. 1990. Influence of plant uptake on the performance of Br^- tracer. *Soil Sci. Soc. Am. J.* 54:975-979.
- Nagpal, N.K. 1982. Comparison among and evaluation of ceramic porous cup soil water samplers for nutrient transport studies. *Can. J. Soil Sci.* 62:685-694.
- Newman, A. 1992. A solid approach to extractions. *Environ. Sci. Technol.* 26:1294-1295.
- Onken, A.B., R.S. Hargrove, C.W. Wendt, and O.C. Wilke.

1975. The use of a specific ion electrode for determination of Br^- in soils. *Soil Sci. Soc. Am. Proc.* 39:1223-1225.
- Owens, L.B., R.W. van Keuren, and W.M. Edwards. 1985. Groundwater quality changes resulting from a surface Br^- application to pasture. *J. Environ. Qual.* 14:543-548.
- Runland, R.K. 1989. Al contamination and other changes of acid soil solution isolated by means of porcelain suction-cups. *J. Soil Sci.* 40:95-101.
- Schaff, B.E., and E.O. Skogley. 1982. Diffusion of potassium, calcium, and magnesium in Bozeman silt loam as influenced by temperature and moisture. *Soil Sci. Soc. Am. J.* 46:521-524.
- Skogley, E.O., S.J. Georgitis, J.E. Yang, and B.E. Schaff. 1990. The phytoavailability soil test-PST. *Commun. Soil Sci. Plant Anal.* 21:1229-1243.
- Smith, S.J., and R.J. Davis. 1974. Relative movement of bromide and nitrate through soils. *J. Environ. Qual.* 3:152-155.
- Van der Plog, R.R., and F. Beese. 1977. Model calculations for the extraction of soil water by ceramic cups and plates. *Soil Sci. Soc. Am. J.* 41:466-470.
- Yang, J.E., and E.O. Skogley. 1992. Diffusion kinetics of multnutrient accumulation by mixed-bed ion-exchange resin. *Soil Sci. Soc. Am. J.* 56:408-414.
- Yang, J.E., E.O. Skogley, B.S. Schaff, and A.H. Ferguson. 1991a. Phytoavailability soil test: Development and verification of theory. *Soil Sci. Soc. Am. J.* 55:1358-1365.
- Yang, J.E., E.O. Skogley, and B.S. Schaff. 1991b. Nutrient flux to mixed-bed ion-exchange resin: Temperature effects. *Soil Sci. Soc. Am. J.* 55:762-767.