



Verification of resin capsule method for monitoring bromide transport in soils  
by Zhengming Li

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:

Solute transport experiments were conducted in an unsaturated soil column and in the field under a line-source irrigation system with Br tracer. Accumulation of Br by mixed-bed ion-exchange resin capsules inserted into the soil column at depth intervals was compared with Br recovered by vacuum extraction through porous ceramic cups at the same depths. Results of Br BTCs indicated that the resin capsule method can predict Br transport effectively and accurately in the unsaturated conditions. Both the time to reach the Br BTCs peak concentrations and model parameters (pore water velocity ( $V$ ) and dispersion coefficient ( $D$ )) estimated by CDM using CXTfit program suggested that applied suction ( $-0.06$  MPa) can significantly affect the Br transport time-rate and pathway, especially at the upper layer. The recovery of Br by resin capsules was up to 99% of applied Br, which implies the good capability of the resin capsule method to monitor Br transport in a natural system. Field results demonstrated the ability of the resin capsule method to detect differences in Br transport as influenced by irrigation intensity and plant uptake. The uptake of Br by barley accounted for up to 38% of applied Br which may have a great effect on Br transport under cropping. Many problems inherent in vacuum extraction and repetitive, destructive soil sampling can be circumvented by use of this resin capsule methodology, while providing flexibility for sampling intensity and duration of study.

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MONTANA STATE UNIVERSITY  
Bozeman, Montana

February, 1992

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2-11-92  
Date

Earl D. Spigley  
Chairperson, Graduate Committee

Approved for the Major Department

2/11/92  
Date

[Signature]  
Head, Major Department

Approved for the College of Graduate Studies

2/21/92  
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Henry L. Parsons  
Graduate Dean

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ACKNOWLEDGMENTS

I wish to express my sincere gratitude to the following:

Dr. Earl Skogley for serving as my major professor and providing unselfish advice and great support.

Dr. Hayden Ferguson for serving as my supervisor and committee member, and his kind guidance and excellent assistance.

Dr. William Inskeep and Dr. Jeffrey Jacobsen for their suggestions and assistance while serving on my graduate committee.

Mr. Bernard Schaff, Dr. Steve Comfort, Dr. Hesham Gaber, and Mr. Dennis Hengel for their friendship and assistance on completion of this thesis.

The author appreciates the financial support of the research by Dr. Earl Skogley and Dr. Hayden Ferguson.

Special thanks to my wife, Yi Wang, for her love and great support toward finishing this thesis.

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## ABSTRACT

Solute transport experiments were conducted in an unsaturated soil column and in the field under a line-source irrigation system with Br tracer. Accumulation of Br by mixed-bed ion-exchange resin capsules inserted into the soil column at depth intervals was compared with Br recovered by vacuum extraction through porous ceramic cups at the same depths. Results of Br BTCs indicated that the resin capsule method can predict Br transport effectively and accurately in the unsaturated conditions. Both the time to reach the Br BTCs peak concentrations and model parameters (pore water velocity (V) and dispersion coefficient (D)) estimated by CDM using CXTfit program suggested that applied suction (-0.06 MPa) can significantly affect the Br transport time-rate and pathway, especially at the upper layer. The recovery of Br by resin capsules was up to 99% of applied Br, which implies the good capability of the resin capsule method to monitor Br transport in a natural system. Field results demonstrated the ability of the resin capsule method to detect differences in Br transport as influenced by irrigation intensity and plant uptake. The uptake of Br by barley accounted for up to 38% of applied Br which may have a great effect on Br transport under cropping. Many problems inherent in vacuum extraction and repetitive, destructive soil sampling can be circumvented by use of this resin capsule methodology, while providing flexibility for sampling intensity and duration of study.

## INTRODUCTION

Chemical movement in soils, groundwater, and surface water is becoming increasingly important in soil and environmental studies. Techniques for effectively monitoring the leaching of pollutants through the unsaturated zone of soils are needed to provide an early warning of potential groundwater contamination. At present, the conventional measurement of quantity and mobility of chemical movement in the soil-water system is usually accomplished by (1) direct soil sampling and chemical extraction; and (2) vacuum extraction of soil solution into a porous ceramic cup sampler placed in the soil. Both methods, however, have major limitations.

Direct soil sampling is time consuming, expensive, and non-reproducible (involving gross destruction of the soil) at a specific point. In addition, chemical extraction of collected soil samples does not adequately represent solute movement *in-situ*. Thus, the vacuum extraction method is preferred for most cases.

The vacuum porous cup method is based on placement of a cup-shaped porous membrane in the soil. The soil solution is then separated from the soil by applying a suction ( $-60$  to  $-70 \times 10^{-3}$  MPa) to the inner side of the membrane. The membrane is

often made of fired clay or other ceramic materials, but it also can be made of porous glass or a synthetic polymer.

The samples collected in the porous cup samplers may inadequately represent the actual soil solution for the following reasons:

(1) due to considerable heterogeneity in a field soil, highly variable chemical concentrations are manifested (Haines et al., 1982);

(2) in structured soils, porous cup samplers may be completely circumvented by the channeling of water and chemicals through interpolated pores at high water potentials (Shaffer et al., 1979);

(3) applying even small amounts of suction to extract a soil solution sample may cause significantly higher seepage rates, compared with the rate under free drainage conditions. The radius of influence may be variable, is unknown, and may distort the seepage process that occurs in an unsaturated soil (Van der Plog and Beese, 1977);

(4) applying a vacuum for an extended period to obtain a sample creates the potential for loss of volatile compounds from the sample;

(5) porous suction cups do not continuously collect water or chemical constituents moving in the soil unless a continuous suction is applied. Therefore, they may fail to collect leachate at the critical time, i.e., after rainfall and additions of fertilizer or water;



(6) porous ceramic cups may release or adsorb some ions during the sampling period, which may cause overestimated or underestimated values;

(7) the lowered pressure (due to suction) can cause carbon dioxide degassing with resultant pH and solubility changes;

(8) placement of the cups is difficult without disturbing the overlying soil, and it is difficult to obtain a good "bond" with the overlying soil;

(9) since water potential applied is about  $-70 \times 10^{-3}$  MPa, the soil must be wetted to obtain samples, and in soils high in clay it is often difficult to collect enough solution samples at this potential. In addition, porous cups can become plugged by soil particles, preventing extended use in certain soils.

These inherent problems affect the accuracy of result from this method and limit its usefulness.

The resin capsule methodology, which is being developed at Montana State University, is a simplified soil "extraction" method based on ion exchange resin accumulation of elements from soils. The resin capsule extraction is accomplished with a mixed-bed ion exchange resin sink enclosed in a spherical porous mesh bag. The capsule can accumulate all inorganic ions simultaneously from a soil-water system as regulated by soil solution concentration of each element and diffusion processes (Yang, et al., 1991). The quantity of resin is such that it represents an effectively "infinite" sink which can accumulate

ions throughout the extraction period. The use of mixed-bed ion-exchange resin capsules provides a "universal" extractor for all inorganic ions, regardless of charge (Van Raij et al., 1986). Due to these characteristics, the methodology has promise for eliminating problems inherent in vacuum extraction *in situ* or chemical extraction of soil samples.

Only limited research has been done on using the resin capsule to predict solute transport in soils, groundwater, and surface water. The objectives of this research were (1) to verify that the resin capsule methodology has advantages over the vacuum porous cup method for monitoring solute transport in soils, while providing equally good or better data; (2) to evaluate the sensitivity of the resin capsule method for determining solute transport under unsaturated conditions; and (3) to evaluate the potential for using resin capsule *in situ* for studying solute dynamics in the field.

## LITERATURE REVIEW

Vacuum Porous Ceramic Cup Method

The quantity and mobility of soil solution moving downward through the soil toward groundwater is a topic of great interest to soil and environmental scientists. In such studies, it is generally necessary to separate water from soil solids by some means. Richards(1941) classified and described soil solution extraction methods under five headings: displacement; compaction; centrifugation; molecular adsorption; and suction or pressure membrane. Among these methods, use of suction membranes are superior to others, and have evolved as the conventional method for extracting soil solution from soils or soil samples(Reeve and Doering, 1965).

The porous ceramic cup(heat fused clay) has been used as a semipermeable membrane to separate water from soil solid to study water composition or energy relations(Grover and Lamborn,1970). Briggs and McCall(1904) suggested that ceramic cups can be used as artificial roots to study soil nutrient availability to plants as well as soil solution composition. Little change has been made in the original design of Briggs and McCall(1904). The major problem is that conditions involving their use are not entirely natural. Krone et

al.(1952) tested the device and improved the equipment using a porous tube or "probe" to which negative pressures or tensions were applied. The probe is a convenient sampling device for extracting water from soils by forming a hydrodynamic sink. Experimental data indicated that the disturbance caused by the sampling tension( $-10 \times 10^{-3}$ MPa) scarcely affected the general pattern of flow through the soil. Cole(1958) constructed a new type of lysimeter from a porous alundum disc, a tension column, and a receiving container for periodic removal of the leachate. A commercial version of the porous ceramic cup, manufactured by Soil Moisture Equipment Corporation, Santa Barbara, CA, was tested by Wagner(1962). Harris and Hansen(1975) described a newly designed soil-water sampler utilizing a miniature porous ceramic cup which is suitable for either collecting large samples or for microtechniques.

Although such samplers have been extensively used in laboratory and field experiments, their use is not without problem(Runlund,1989; Barbee and Brown,1986; Nagpal, 1982; Hansen and Harris,1975). Nagpal(1982) suggested that in studies related to migration of environmental contaminants through the soil-water system, the accuracy of results obtained from water samples extracted with porous ceramic cups is questionable. His results showed that a significant quantity of ortho-P and K may be retained by ceramic porous cups during soil water sampling, and the use of ceramic porous

cups is limited to wetter conditions (soil moisture at or near field capacity). He also advised that the sample collected in the last extraction should be used to determine true soil solution quantity. Grover and Lamborn (1970) found that ceramic cups contribute excessive amounts of Ca, Na, and K to water samples drawn through the cups; at the same time the cups adsorbed significant amounts of P from solutions. Sorption and screening of P and nitrate ions by ceramic cups was also studied by Hansen and Harris (1975). Under acidic conditions, Karske et al. (1989) found adsorption of Al and sulphate, forming a precipitate on the cups.

Jacober and Sandoval (1971) reported that applied vacuum suction significantly affected ECs of all experimental soils and their behavior responded differently in soils due to the different contents of organic matter and clay. Soil with high carbon content responded more to changes in vacuum than did the soil low in O.M.. Huntington et al. (1990) compared mechanical vacuum extraction into porous cups (MVE) with a typical batch extraction involving shaking followed by filtration in a Buchner funnel (SF) for estimation of exchangeable cations in acidic forest soils. Significant differences between those two methods were observed for Ca, Al, and Na, but not for Mg and K. They found that the MVE method estimated 7% higher Ca, 26% higher Al, and 41% lower Na than the SF method. They explained that the reaction conditions are remarkably different for the two methods. In

the batch reaction of the SF procedure an equilibrium is established quickly, whereas in the MVE method the constant-flow reaction is more dynamic, with fresh extractant constantly added and exchanged ions constantly removed.

### Resin Adsorption Methodologies

#### Discovery of "Base Exchange" in Soils

The principle underlying use of resin capsules relates to their ion exchange characteristics and resultant interactions with solutes in the soil-water system. About 1845 an English landowner, H.S. Thompson(1850), engaged a York analyst, Spence, to investigate the loss of ammonia from manure heaps. Spence discovered that when a solution of ammonium sulphate was allowed to percolate through a column packed with soil, the effluent from the column contained no ammonium sulphate but considerable amounts of calcium sulphate instead. Spence's discovery was reported in the Royal Agricultural Society in British early in 1850 and was promptly confirmed by J.T. Way(1850), an agricultural chemist, who then carried out a masterly investigation which established this newly found phenomenon of base exchange.

#### Synthetic Ion-exchange Resins

Synthetic resins were invented by two English chemists,

B.A. Adams and E.L. Holmes(1935), working at the chemical research laboratory, Teddington(London). The first resins made by Adams and Holmes were obtained by heating various dihydric phenols with formaldehyde. Later, polymerization resins were developed, which can be synthesized to suit requirements rather than produced by hit-and-miss methods. The first successful ion-exchange polymer, patented by d'Alelio(1944), was a carboxylic acid resin prepared by co-polymerizing a cross-linking agent such as ethylene dimethacrylate with a vinylic acid such as acrylic acid.

d'Alelio also succeeded in preparing an anion-exchange resin from cross-linking polystyrene by first nitrating it and then reducing the nitro- to amino-groups. By the end of 1945, d'Alelio's sulphonated polystyrene resin was put on the market by the Dow Chemical Co.(U.S.A.) under the name "Dowex 50". It was the first commercial ion-exchange resin to be produced in the form of spherical particles, all earlier resins consisting of irregular granules produced by crushing lumps of resin (Kitchener, 1959).

#### Ion-exchange Resin Batch Methods

There is an ever-increasing demand for soil analysis and more efficient methods are continually being sought. From the time of introducing the use of citric acid as an extraction solution to extract P from soils, soil scientists have endeavored to extract the fraction of soil elements that can

be considered to be available to plants. The common problem with extracting agents is that, since the reagent reacts with soil components other than the target ion, the nature of soil is changed. Williams(1951) showed that plants were able to take up more P from soils after the removal of the "available" P by means of diluted acetic or sulfuric acid than from the same soils before treatment. He found that the amounts of P removed in pretreatment, although large compared with P content in normal crops, are very small compared with total P in soils. He suggested that the acid treatments probably produced several changes in the soil, such as removal and deactivation of fixing agents, partial hydrolysis of relatively insoluble P, and conversion of one form of phosphate to another.

The extraction of soil P by means of the anion-exchange resin batch method was introduced by Amer et al.(1955), who showed that resin adsorption behavior was more nearly analogous to P withdrawal by plant roots than the process of isotopic exchange technique and it adsorbed a small quantity of P from solution quantitatively. Moser et al.(1959) showed that the quantity of P released from soils to resin was well correlated with the uptake of P by a crop grown in soils. Comparing resin extraction method with 0.025 M sulfuric acid extraction in the estimation of plant-available P, Van Raij et al.(1986) found that there was no consistent relationships. The critical point is that the results of resin extractable P



presented closer correlation with cotton response to P application in 28 field experiments ( $r=0.85^{**}$ ) as compared with 0.025 M sulfuric acid extractable P ( $r=0.68^*$ ). In another pot experiment with flooded rice, they found the relationship between resin extractable P and P uptake by rice plant was highly significant ( $r=0.98^{**}$ ). Whereas when using 0.0125 M sulfuric acid in 0.05 M HCl to extract P from the soil produced no significant relationship. The resin batch method gave better correlation with P uptake by plants than did other methods using single chemical extractants (Cook and Hislop, 1962; Gunary and Sutton, 1967; Kadeba and Boyle, 1978; Van Raij et al., 1986) presumably because resins simulate the desorbing effect of plant roots better than the usual chemical extractants (Bache and Ireland, 1980). Vaidyanathan and Talibudeen (1970) suggested that the rate of P transfer to the resin was controlled by diffusion within resin particles rather than by chemical reactions between soil and solution, whereas Sibbesen (1978) concluded that P desorption from soil to water was the rate-determining step. Yang et al. (1991) showed that the mass of nutrients adsorbed by the resin as a function of time was consistent with a "film diffusion" process, meaning that ion diffusion through the soil was rate-limiting.

Dalal (1985) carried out an experiment to compare cation-anion mixed resins with anion resin alone in prediction of yield response and P uptake from soil. He found that P uptake

and grain yield were better correlated with cation-anion exchange resin P(CAER-P) than with anion-exchange resin P(AER-P). The quantity of AER-P was less than the CAER-P at all desorption periods for 18 south Australian soils. Curtin et al.(1987) examined the potential of different combinations of mixed anion-cation resins as sinks for labile soil P. They found that the amount of P extracted followed the order: AER-HCO<sub>3</sub><AER-OH/CER-Na<AER-OH/CER-H for all soils studied. They suggested that the success of the AER-OH/CER-H system in extracting P is attributed to its ability to remove exchangeable Ca and Mg, and to reduce the ionic strength of the equilibrating solution. An alternative suggestion is that the AER-OH/CER-H system results in acidification of the soil due to greater exchange of cations(which predominant in soils) than anions, the increased [H<sup>+</sup>] results in greater solubilization of Ca-phosphates and increased amounts of P adsorbed by the resin.

The use of ion exchange resins to extract nutrients from soils has been applied mostly to phosphate and in general, anion exchange resins have been used. Since there is evidence that a cation exchange resin, saturated with a monovalent cation, increases the adsorption of P on the resin (Vaidyanathan and Talibudeen, 1970), it may be possible to use a mixture of anion and cation exchange resins to enhance the efficiency of P extraction. Van Raij et al.(1986) proposed a new procedure in which a mixture of anion and cation resins

was used to simultaneously extract P, K, Ca, and Mn from soils. The mode of extraction is similar to plant roots in both uptake mechanism and capacity (Sibbesen, 1978; Smith, 1979).

In situ ion-exchange resin samplers have been used to extract solutes from rainfall (Egner et al., 1949; Crabtree and Trudgill, 1981) in an effort to solve the problems of low solute concentrations, analytical accuracy, and sample storage effects on rainwater. Crabtree and Kirkby (1985) used an ion-exchange resin column to extract the solutes flowing with soil water through a column of soil; they demonstrated that the technique can be seen as a practical compromise which offers some improvement over conventional solute-flux measurement techniques. The method minimizes soil water flow disturbance in and around soil-emplaced columns.

The anion-exchange resin method also can improve the accuracy of estimation of plant-available molybdenum in soils (Jackson and Meglen, 1975; Bhella and Dawson, 1972). There have been several studies on the release of K from soils to cation exchange resins (Binkley, 1984; Goulding, 1984; Haagsma and Vimpany, 1963; Barber and Matthews, 1962; Arnold, 1958). Lee and Gibson (1974) found that the resin K method is easier, safer (in that it avoids the use of boiling nitric acid), and quicker than chemical extraction methods. Acquaye et al. (1972) employed a cation-exchange resin method in predicting the availability of copper, iron, manganese, and zinc in soils. Herron and Wellington (1990) applied exchange

resin to develop a new method for extracting the streptomycetes spore from soils. Gibson et al.(1974) used a resin-loaded paper technique in estimation of available sulphur in soils.

The method commonly used is the batch procedure where a 1:1 ratio of soil to resin is shaken in a water supersaturated state for a given period of time. This procedure, since first described by Amer et al.(1955), has become a routine procedure in some laboratories. However, the procedure involves direct mixing of resin with finely divided soil and, as a result, two troublesome steps occur; (1)the required grinding of soil samples and (2)the separation of resin from soil suspension. In addition, results from batch studies are influenced by soil: soil solution ratio, shaking intensity, time, and method of separation of resin from soil suspensions. These practical difficulties can be overcome by placing the resin in porous bags.

#### Single Type Ion-exchange Resin Bag Methods

The use of a netted bag for holding resin was introduced by Sibbesen(1977) as a technique which would simplify the retrieval of the resin in the batch method. Comparing with the resin batch method, the bag procedure has certain advantages (Sibbesen,1977):

- (1)the severe grinding during the preparation of the soil sample has been avoided;

(2) moist soil samples, if need be, can be taken directly from the field and subjected to analysis without drying and grinding;

(3) separation of soil and resin can be very quickly performed.

Sibbesen(1977) demonstrated that the resin bag procedure resulted in slightly higher amounts of P adsorbed than did the resin batch procedure. The use of resin bags was distinctly modified by Binkley and Mateson(1983), by their use as an *in-situ* ion exchange resin sink assessment of available nitrogen. They found that the resin bag method correlated well with more traditional N-availability indices, and the *in situ* resin bag method can reflect the effects of forest floor morphology, temperature, and moisture fluctuations through an annual cycle of N mineralization and ion transport. Smith(1979) showed that the resin bag method was the only method which yielded reproducible plant-available P estimates on Marion Island soils, South Africa. In these soils chemical extractants are hampered by high iron, aluminum, and organic mater contents. Ritchie(1988) and Sherrel(1989) indicated that the resin bag method is a more effective approach to determine plant-available Mo in soils.

Mixed-bed Ion-exchange Resin Capsule Method--The Phytoavailability Soil Test(PST)

In spite of the apparent advantages of the single type resin bag method for extracting soil ions, it is generally

considered inadequate for use in routine soil testing laboratories which process large numbers of soil samples. The Phytoavailability Soil Test (PST) is a new and simplified soil-testing approach based on mixed-bed ion-exchange resin capsule extraction of ions from saturated-paste soil samples (Georgitis, 1988; Skogley et al., 1990). The PST procedure, besides having all advantages of the single type resin bag method, provides universal extraction for all nutrients, and it is a methodology that could be standardized for use in all regions (Skogley et al., 1990). When used in a manner allowing measurement of ion diffusion to the resin sink, the mechanism of PST extraction is similar to that of the soil-root system. When ions move to the resin capsule (or root) surface, nutrients are sorbed from soil solution by releasing counter ions such as  $H^+$ ,  $OH^-$ , and  $HCO_3^-$ . The mixed-bed resin capsule can adsorb all inorganic ions simultaneously from the soil-solution system in a manner simulating nutrient movement to plant roots. Skogley et al. (1990) examined the effect of different shapes of resin extractors on accumulation of nutrients from soils and found that the spherical shape was superior to others, creating good reproducibility. Therefore, the PST approach provides a theoretically accurate basis for soil testing.

Yang et al. (1990a,b; 1991) showed that PST is sensitive to microwave radiation and temperature induced changes in availability of  $NO_3^-$ ,  $NH_4^+$ , S, P, K, Ca, and Mg in soils. Yang

et al.(1991) reported that the PST can improve the predictability of elemental availability for those nutrients that are highly dependent on diffusion, such as K and P. Furthermore, nutrients accumulated by the resin capsule were strongly related to nutrient activities in soil solution. Therefore, the PST may also serve as a reliable approach for determining bioavailability of nutrients such as N and S. Yang and Skogley(1992) reported that the movement of nutrients to the resin capsule was characteristic of diffusion-controlled processes, selective for nutrients, and soil dependent.

An *in-situ* mixed-bed ion-exchange resin capsule sampling technique was developed to measure inorganic solute movement in Yellowstone National Park for comparing nutrient cycling on fire-burned vs. unburned sites(Skogley, 1990). The results showed that *in-situ* resin capsule extraction discriminated nutrient movement between sites, as caused by the 1988 forest fire. Nutrient movement was specific to elements and sites, and differed in soils developed from different parent materials. This strongly supports the potential of applying the mixed-bed resin capsule sampling technique to monitor solute movement in the field.

These principles support the theoretical basis for developing the mixed-bed resin capsule methodology and techniques for monitoring solute transport in soils.

### Bromide Tracer

Tracers have long been used to follow the direction and velocity of soil water in the laboratory and in the field. A tracer, as used in hydrology, is matter or energy carried by water which will give information concerning the direction and/or velocity of the water and potential soluble contaminants which could be transported by the water (Davis et al., 1980). Although the perfect chemical tracer probably does not exist, there are three main requirements for an effective soil water tracer:

- (1) the tracer should not be significantly sorbed or otherwise retarded by the soil of interest;
- (2) the tracer should be present naturally at low concentrations;
- (3) the tracer should be conservative in that it is not significantly degraded chemically or biologically during the course of an experiment.

Other considerations in choosing a tracer include easy of detection and measurement in a soil solution matrix and the lowest potential for adverse environmental impact.

Many compounds have been used as tracers in soils, ground water, and surface water (Davis et al., 1980). Many tracers used for monitoring surface and ground water flow are



unsuitable for use in soil water studies due to the greater surface activity and solid/water ratio of soils, which results in increased sorption. Tracers commonly used for soil water studies have included chloride( $\text{Cl}^-$ ), nitrate( $\text{NO}_3^-$ ), bromide ( $\text{Br}^-$ ), and deuterated and tritiated water(HDO and HTO) (Bowman, 1984).

Chloride has been used as an indicator of anion movement(Dyer, 1965), but must be applied in concentration sufficiently high to mask that present in soils, fertilizers, irrigation water, and other natural sources. This may not be practical in a field crop study. Furthermore, if  $\text{Cl}^-$  is used as a tracer for  $\text{NO}_3^-$ , its quantitative movement from another source, such as irrigation water, cannot be monitored simultaneously. Nitrate is subject to an array of chemical and biological transformations which can cause it to be a nonconservative tracer under both aerobic and anaerobic conditions. Water molecules labelled with heavy isotopes of hydrogen are likely the most ideal soil water tracers. Unfortunately, deuterated water is expensive to use at required enrichment rates, and the mass spectroscopic analysis needed for greatest sensitivity is both time-consuming and costly. Tritiated water is inexpensive, and analysis by liquid scintillation counting is rapid and accurate; since it is radioactive, however, the use of HTO is precluded on most field studies.

Of the common used soil water tracers, Br is the most

suitable and has been successfully used as tracer in groundwater studies. Bromide is usually present in natural waters at levels less than one percent of the Cl concentration (Davis et al., 1980). Bromide background levels in soils are quite low, with values ranging from 5 to 40 mg/kg (Maw and Kempton, 1982; Bowen, 1966; Martin, 1966), and Br is not regarded as toxic to plants (Martin, 1966). Bromide is not sorbed by most soils, and it is not subject to significant chemical or biological transformations.

Bromide has utility for following the potential path of  $\text{NO}_3^-$  movement through soils (Smith and Davis, 1974). On irrigated plots, Hargrove and Bausch (1973) used the leaching rate of Br as a standard of comparison for the leaching of three N fertilizer sources. Onken et al. (1977) used large irrigated field plots and reported that  $\text{NO}_3^-$  and Br move similarly in soil under field conditions. Owens et al. (1985) showed that Br movement and plant uptake was similar to  $\text{NO}_3^-$  in soils. Hubbard et al. (1989) carried out an experiment using bromide as a conservative tracer to compare herbicide transport under simulated rainfall.

Bromide is readily analyzed by several methods, including ion selective electrode (Abdalla and Lear, 1975; Onken et al., 1975), automated colorimetric detection (Moxon and Dixon, 1980), and high performance liquid chromatography (Stetzenbach and Thompson, 1983).

Because Br functions as a non-agricultural chemical

commonly used as a conservative tracer for studying movement of agricultural chemicals and water in soils and aquifers, it was selected for use in these studies.

## LABORATORY STUDIES

An ideal approach to studying solute movement in the soil profile requires discrete sampling of the soil water from a specific soil profile at a known time and depth. In a broad sense, there are two approaches to studying chemical leaching—field and laboratory. Field approaches test a chemical's mobility under natural environmental conditions, but they are also subject to temperature and moisture fluctuations, and the inherent spatial variability of pertinent soil properties. Field approaches provide data varying in accuracy, precision, and detail and are generally labor intensive and costly compared to laboratory studies.

Laboratory or greenhouse approaches to studying chemical leaching seek to control certain factors so that specific effects of other factors can be isolated. Soil columns are commonly used to study the mobility of chemicals under controlled conditions. Column methods or approaches vary with respect to column dimensions, soil status (intact vs. disturbed), method of analysis, method of chemical application, water status during leaching (saturated vs. unsaturated), amount and frequency of water additions, and durations (Helling and Dragun, 1981). Soil columns have a high degree of control and are more of a closed system compared to

the field, thus they are especially suited for determining comparative fates and mobilities of chemicals.

### Material and Methods

#### Soil Column

The column was made from a polyvinyl chloride cylinder (PVC) with an inner diameter of 20 cm, outer diameter of 21.5 cm and height of 150 cm. Soil was uniformly repacked at a bulk density of  $1.38 \text{ gcm}^{-3}$ . Three sampling holes were made at each desired depth of 13, 43, 73, 104, and 134 cm from the soil surface (Fig. 1). One hole at each depth was fitted with a 3 cm

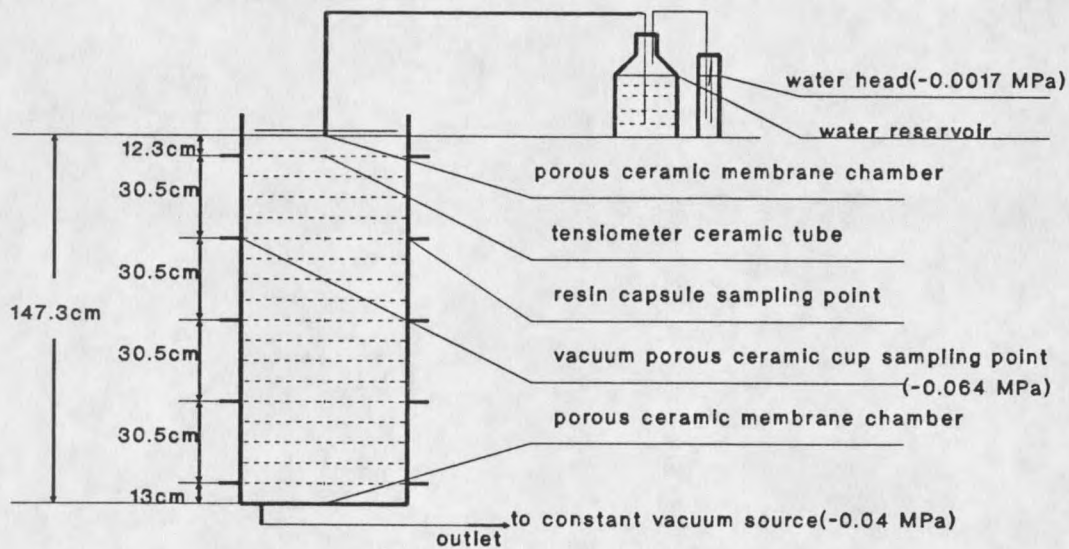


Fig. 1. Schematic diagram of soil column

diameter by 5 cm length PVC tube as the resin capsule sampling point so that resin capsules could be easily inserted and retrieved at any desired time interval. Another hole at each depth was fitted with a porous ceramic cup as the vacuum extractor sampling point. A tensiometer ceramic tube for water potential measurement was placed in the third hole. At the bottom of the column, a porous ceramic semipermeable chamber was fitted and connected to a constant vacuum source of  $-40 \times 10^{-3}$  MPa in order to maintain the water flow throughout the column. Water was applied through another porous ceramic semipermeable chamber placed on the top of soil surface and controlled by a water reservoir with a water head of  $-0.0017$  MPa to maintain uniform application and water flow rate. The soil column was first wetted by adding DDW to wet the column to approximately field capacity and unsaturated conditions. After that, the soil column was drained until the water potential readings were about  $-40 \times 10^{-3}$  MPa at the top and about  $-30 \times 10^{-3}$  MPa at the bottom before beginning the bromide leaching experiment.

### Soil

The soil column was packed using soil taken from the subsurface (15 to 30 cm) near Manhattan, MT. The soil is classified as a coarse-loamy, mixed typic Calciboroll. The physical and chemical properties of the soil are listed in Table 1. The soil was first oven-dried at  $40-50^{\circ}\text{C}$  for 3 days

Table 1. Physical and chemical properties of the soil\*.

Text- ure	pH	O.M. mg/kg	K <sub>exc</sub> cmol/kg	K <sub>sat</sub> mg/kg	Olsen-P mg/kg	CaCO <sub>3</sub> mg/kg	S mg/kg
sil	8.2	24.0	1.89	22.5	11.8	40.4	3.8

\*Soil was analyzed by Montana State University Soil analytical Laboratory. PH by 1:1 soil/water; organic mater by acid-dichromate oxidation; K<sub>exc</sub> by 1M NH<sub>4</sub>OAC (PH 7.0) extraction; K<sub>sat</sub> by saturated paste extraction; Olsen-P by 0.5N NaHCO<sub>3</sub> (PH 8.5) extraction; CaCO<sub>3</sub>(eq) by gravimetric; and S by 0.5M NH<sub>4</sub>OAC + 0.25M acetic acid extraction.

and then passed through a 2-mm sieve. The water desorption curve of the soil is potted in Figure 2.

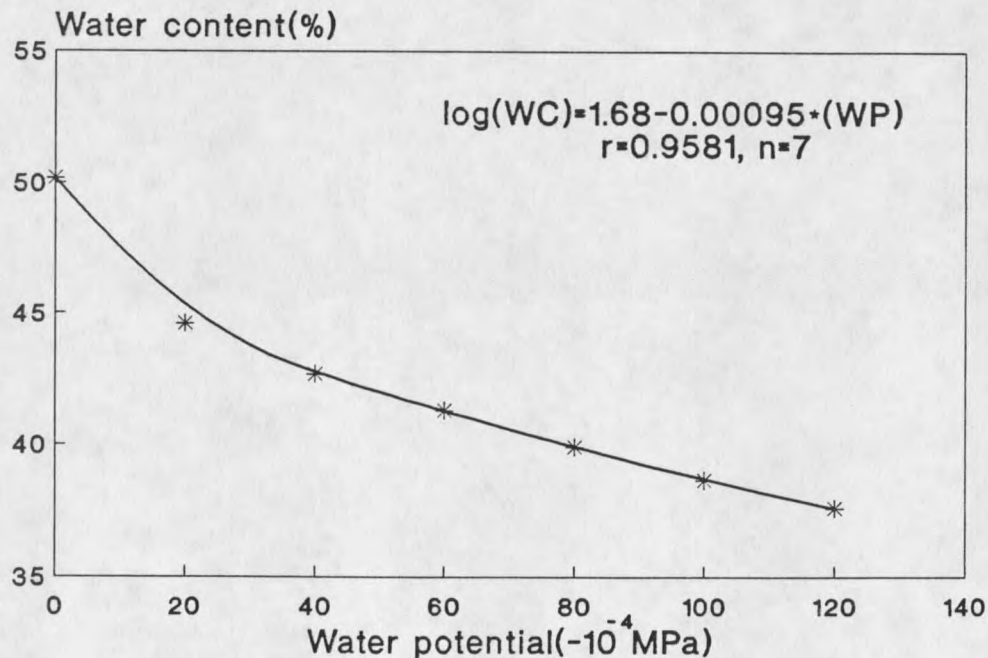


Fig. 2. Water desorption curve for column soil



















































































































































































