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

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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by

Zhengming Li

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APPROVAL

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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 X10^{-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, ie., 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 $-70X10^{-3}$ 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)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($-10X10^{-3}$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-HCO3<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 $[H^+]$ 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(Cl^-), nitrate(NO_3^-), bromide (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 Cl^- is used as a tracer for 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 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 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 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 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

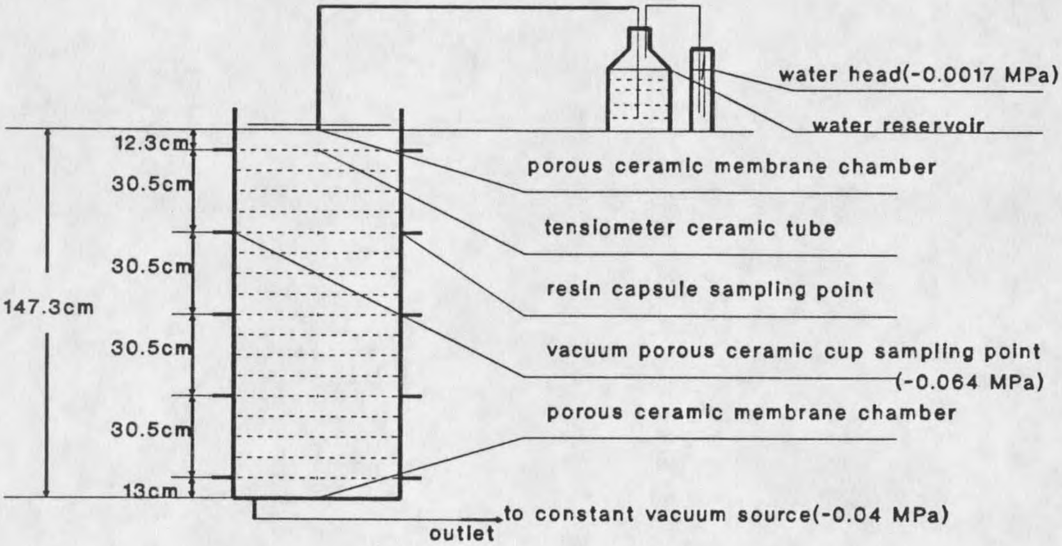

Fig. 1. Schematic diagram of soil column

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 X10^{-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 -40X10^{-3}MPa at the top and about -30X10^{-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°C for 3 days

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

Text-ure	pH	O.M. mg/kg	K_{exc} cmol/kg	K_{sat} mg/kg	Olsen-P mg/kg	$CaCO_3$ 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_{exc} by 1M NH_4OAC(PH 7.0) extraction; K_{sat} by saturated paste extraction; Olsen-P by 0.5N $NaHCO_3$(PH 8.5) extraction; $CaCO_3$(eq) by gravimetric; and S by 0.5M NH_4OAC + 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.

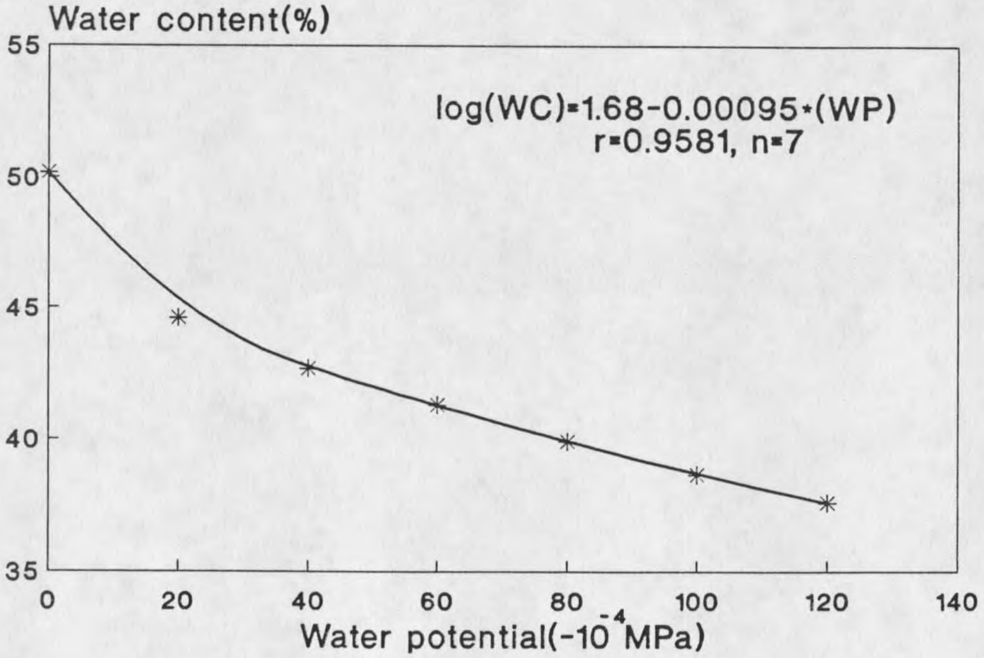

Fig. 2. Water desorption curve for column soil

The Resin Capsule Methodology

Resin. Amberlite IRN-150(Rohm and Haas Co., Independence Mall West, Philadelphia, PA) was used. Table 2 shows the physical and chemical characteristics of resin IRN-150. The resin is a 1:1 equivalent mixture of strongly acidic cation(H^+) and strongly basic anion(OH^-) exchange resin. The water desorption curve of the resin is shown in Figure 3.

Table 2. Physical and chemical characteristics of the resin.

Ionic forms	Parent Resin	Particle size,mesh	Effective size,mm	Moisture content,%	TEC*,wet meq/ml
H^+,OH^-	IRN-77, 78	16-50	0.50	60	0.55

*TEC--total exchange capacity.

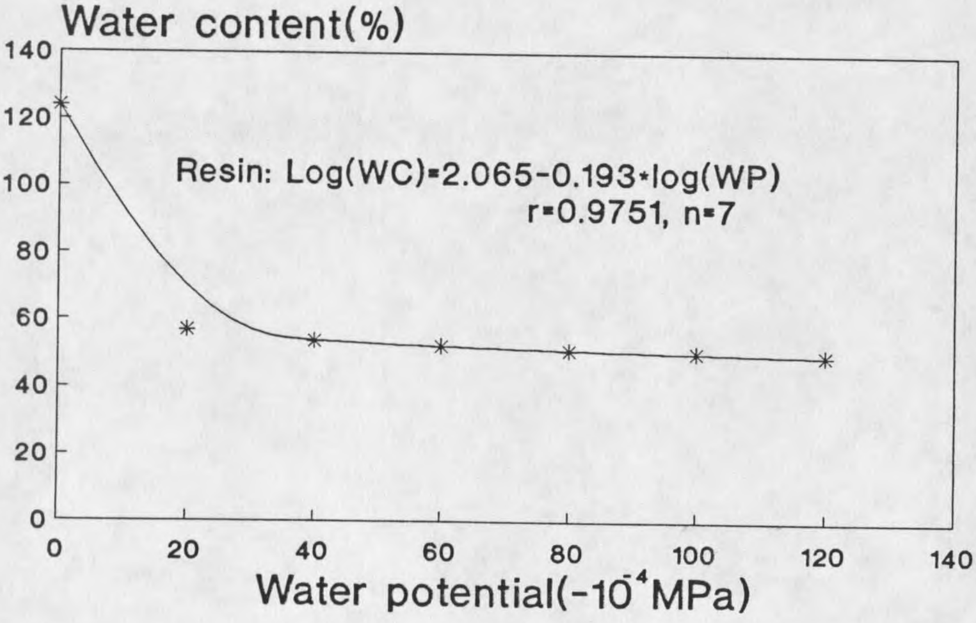

Fig. 3. Water desorption curve of the resin

Resin Capsules. Five ml of wet resin were packed into 100% polyester(150 mesh, 30 μm thread, 140 μm openings) cloth and tightly tied with braided polyester thread to form a tight sphere. The polyester cloth and thread were cleaned with acid and DDW prior to use. The resin capsules were trimmed of excess cloth and thread, and degassed under DDW by applying a vacuum(this assures that exchange sites are not blocked by air). Then, resin capsules were stored under DDW in sealed glass containers until use.

Sampling Procedure. A resin capsule was inserted into the soil column sampling point, making sure that one-half of the sphere was in complete contact with soil particles. The resin capsule was removed from the soil column after a predetermined period, and a new one reinserted. The used resin capsule was thoroughly washed with DDW, taking care to remove all adhering soil particles. The capsule was then placed in a small plastic bag and frozen until all were ready to be stripped.

Stripping Solution for Removing Br from Resin. To select the best stripping solution, a pilot study was conducted using acetic acid and sulfuric acid. The recovery of bromide from resin by sulfuric acid was nearly complete(up to 98%, Fig. 4), while acetic acid was very ineffective. Based on these results, 50 ml of 2N H_2SO_4 solution was chosen as the stripping solution for bromide in this research. This change in standard

PST methodology was necessary due to Cl interference in Br analysis by ion-selective electrode.

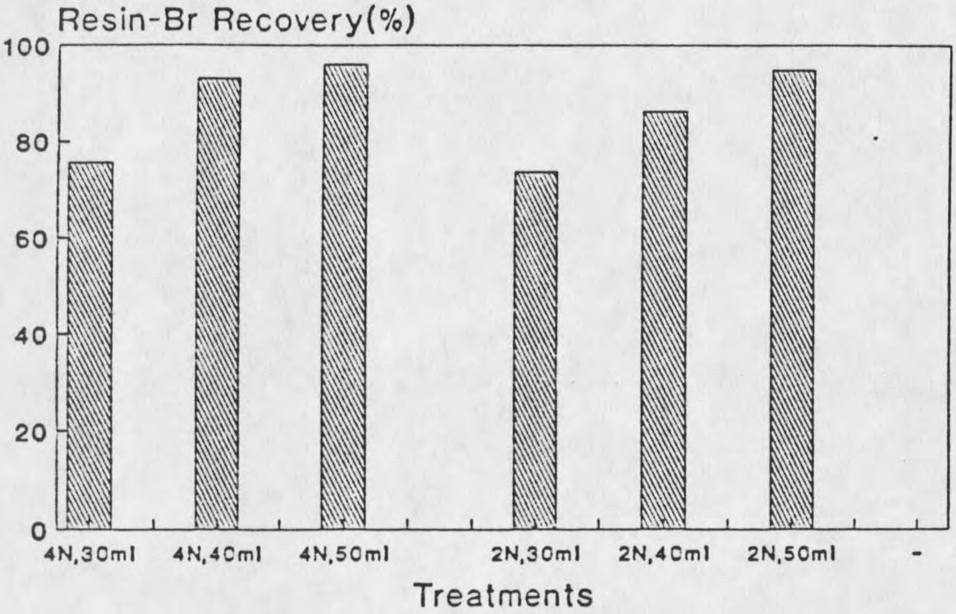

Fig. 4. Bromide recovery from resin capsules by sulfric acid.

Stripping Procedure. The procedure used for desorbing accumulated Br(and all other ions) from the resin capsules was essentially the same as described in Yang et al.(1991) with the exception that H_2SO_4 was selected as the stripping reagent, rather than HCl. After thawing at room temperature, by placing them in the middle syringe of a vacuum extractor(Centurion International Inc., Model 24, Lincoln, NB) and resting on Whatman #41 filter paper. The filter paper trapped any resin or other solids and prevented them from fouling the stripping solution. Ten ml of 2 N H_2SO_4 were added to the syringe to completely immerse the resin capsule. Following 10 minutes of equilibration time, the H_2SO_4 was vacuum extracted into the lower syringe at a rate of 2 ml per minute. Any air bubbles in the solution were removed by gently tapping the syringe. As soon as the 10 ml of stripping solution were recovered in the lower syringe, 40 ml of 2N H_2SO_4 were added to the upper syringe and a drop-wise extraction continued at a rate of 1 ml per minute until all solution was recovered in the lower syringe. This procedure removes nearly 100% of all adsorbed ions from resin, while minimizing the quantity of stripping solution and maintaining relatively high concentrations of ions in the solution.

Vacuum Extractor Method

Porous ceramic cup assemblies were reconstructed as a vacuum extractor(Fig. 5). The porous ceramic cups(Soil

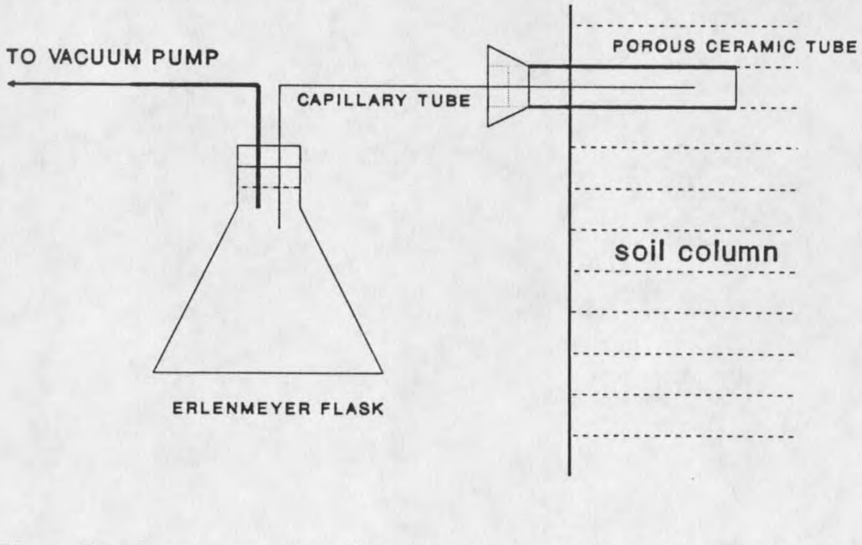

Fig. 5. Apparatus for vacuum porous tube extractor

Moisture Equipment Corporation, Santa Barbara, CA) have an inner diameter of 9 mm, an outer diameter of 12 mm, and overall length of 105 mm. The open end of the cup was fitted with a one-hole neoprene plug. One piece of small diameter tube was inserted into the plug and extended into the cup to remove water collected in the reservoir and transfer it to an Erlenmeyer Flask(sample collector). A small tube was used so that the volume of the tube would be minimized compared with the volume of the sample obtained. Thus, it was possible to remove samples as small as a few milliliters in volume from the soil.

The Erlenmeyer Flask was fitted with a two-hole rubber stopper. One hole was used for connecting the porous ceramic cup to the acrylic capillary tube. Suction was obtained by connecting the flask to a vacuum pump with thick-walled rubber tubing which had been inserted into another hole in the stopper(Fig. 5). A constant vacuum of $-60X10^{-3}$MPa(Jacober and Sandoval, 1971) was maintained with a laboratory vacuum pump. A trap in the line prevented the movement of solution into the vacuum pump. The cup assemblies were then simply inserted into the column soil a distance of 8-10 cm. Care was taken to ensure that the soil around the unit was in sufficiently close contact with the cup so that water could be drawn from the soil into the cup. Usually, soil solution samples of 5-8 ml were obtained by applying and maintaining a vacuum of $-60X10^{-3}$ MPa for 4-5 hours. Sample solutions were stored in 10 ml plastic bottles and frozen until analysis.

Bromide Ion-selective Electrode Method for Determination of Bromide Concentrations in Solutions

Several methods are available for measurement of Br concentration in food stuffs, plants, and soils. However, most methods require extensive analytical facilities. The bromide sensitive ion electrode offers the possibility of simple and rapid determination of Br in solution with a recovery of over 94%(Abdalla and Lear, 1975)

Orion model 94-35 bromide electrode with Orion model 90-02 double junction reference electrode(Orion Research Inc., Boston, MA) was used in determining Br concentrations. Potential reaction of sample solution Br with the Br/Silver sulfide membrane of the electrode was determined with a pH meter. Bromide concentrations were determined by relating the potential developed in unknown solutions with potentials developed in solutions of known Br concentrations. Figure 6 shows the standard curve between the Br concentrations and potentials.

The main steps of this method are:

1. pipet 2 ml ionic strength adjustor(ISA) per 100 ml of standard and sample;
2. stir all samples at uniform rate during measurement;
3. verify calibration every two hours by placing electrodes in a fresh standard solution;
4. always use fresh standard solutions for calibration;

5. always rinse electrodes with DDW and blot dry with clean and dry tissue between measurements;
6. allow all standards and samples to come to the same temperature for precise measurement;
7. prepare standard solutions with composition similar to those of the samples.

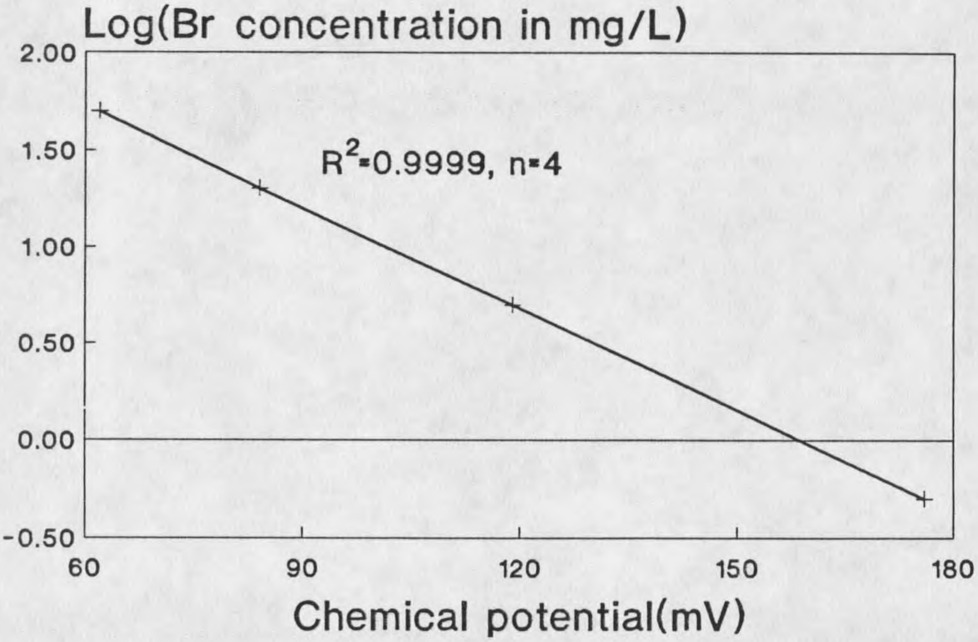

Fig. 6. Bromide standard curve determined by Br ion-selective electrode method

A Comparison of Vacuum Extraction and Resin Adsorption Methods for Monitoring Bromide Transport in A Soil Column under Continuous unsaturated Water Flow

The resin capsule method is based on the hypothesis that a quantity of mixed-bed ion exchange resin placed in direct contact with soil particles will extract ions from the soil solution by ion exchange as they are delivered to the resin capsule through the diffusion and mass flow processes. The soil-water system is dynamic, with water or ion concentration gradients constantly changing. In the resin-adsorption system, ions continuously diffuse to the resin sink in response to gradients established by dynamic equilibria, in a manner similar to nutrients being delivered to active plant roots. To study solute transport in the soil profile, successive determination of time and water dependent concentrations of selected ions is necessary. A uniform soil column under continuous water flow with Br as the tracer was used for this propose.

The objective of this study was to compare the resin capsule method with the vacuum porous cup method for evaluating Br transport through uniform soil column under continuous unsaturated water flow.

Material and Methods

A uniformly packed soil column as described above was used. A solution of KBr(1.88 g KBr dissolved in 50 ml DDW, equivalent to 100 Kg Br/ha) was sprayed onto the soil surface using a household sprayer. After several minutes when no solution remained on the surface,water was added. A continuous unsaturated water flow was controlled by a water reservoir with a water potential of -0.0017 MPa. Water flow rate was determined daily and was within a range of 1 to 2 cm per day.

Resin samples and vacuum extraction solutions were collected from the 13 cm sampling depth about once every 2-6 hours after water application, due to high water flow rate at the beginning of the experiment. After two days samples were taken daily. About 5-7 ml of vacuum extraction solution were collected, requiring 4-5 hours by applying a $-60\text{X}10^{-3}$ MPa suction. Resin capsules were replaced every 24 hours. Tensiometer readings were made at the time of sampling. Solution samples were stored in 20 ml plastic bottles and resin capsules were stored in small plastic bags. All samples were frozen until analysis.

Results and Discussion

Bromide Breakthrough Curves(BTCs). Bromide breakthrough curves(BTCs) at each sampling depth in the soil column under continuous water flow are plotted in Figure 7. Results illustrate the similarity of Br transport pattern as

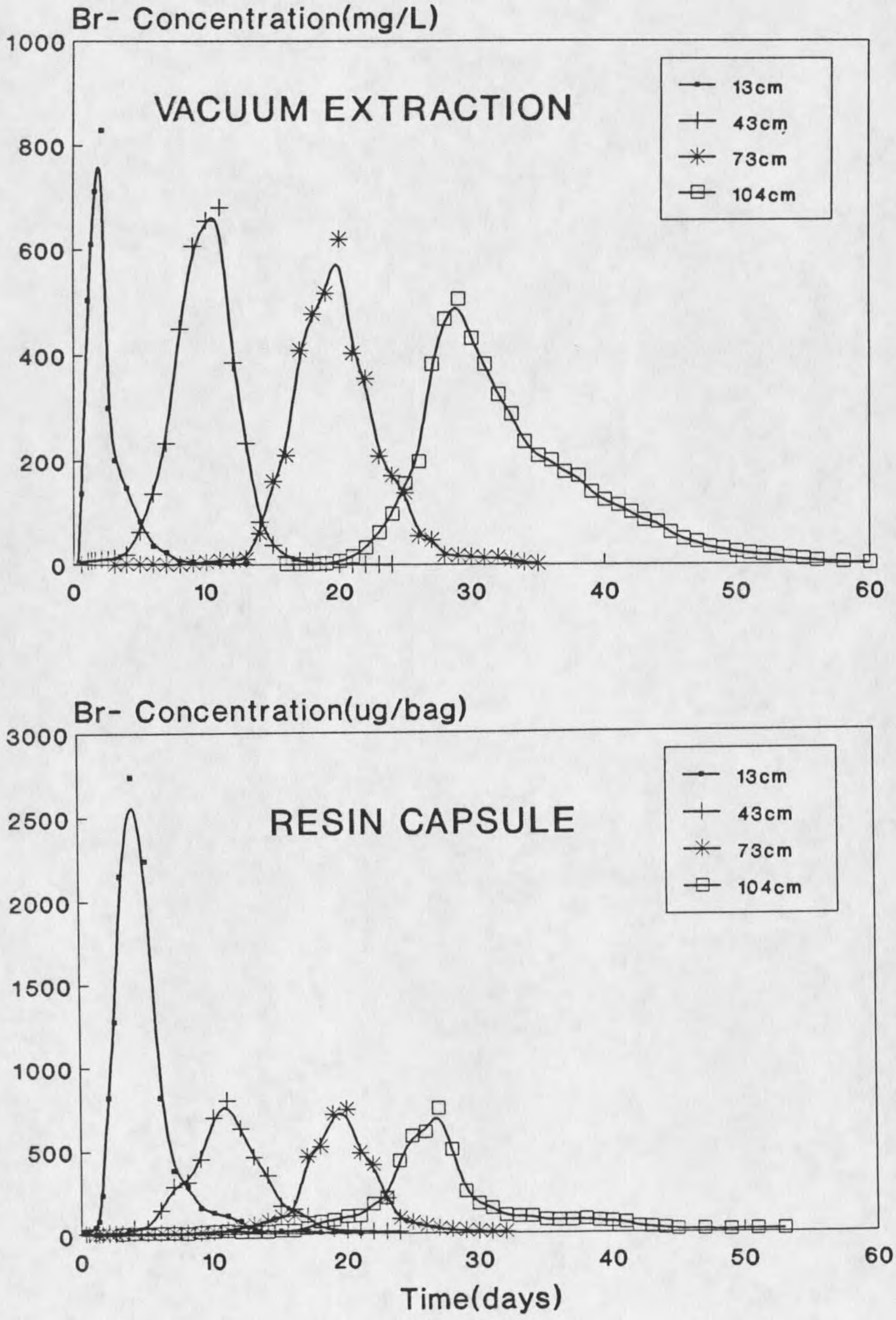

Fig. 7. Br BTCs under continuous unsaturated water flow.

described by both the resin capsule and vacuum extraction methods. Shapes of Br BTC patterns suggest that Br is not retarded in the soil.

The time required to reach peak concentrations for Br BTCs at each sampling depth as determined by both methods is listed in Table 3. Results show that peak concentrations occurred at different times for the two methods at the upper and lower sampling depths, but were essentially the same at the two intermediate depths. These results are shown graphically in Figure 8. At the 13 cm depth, Br peak concentrations determined by vacuum extraction occurred 3 days earlier than for the resin capsule method. At the lowest sampling depth(104 cm), the time of Br BTC peak concentrations determined by vacuum extraction occurred 2 days later than that measured by the resin capsule method. These results imply that the extraction of ions from soil by these two methods is fundamentally different. Under vacuum extraction, ions are extracted by an applied suction force which can mechanically separate soil solution from the soil solid phase. In contrast, the resin capsule method extracts ions by an exchange reaction

Table 3. Time(days) of reaching Br BTCs peak concentrations.

Depth(cm)	13	43	73	104
Resin capsule method	5	11	20	27
Vacuum extraction method	2	10	20	29

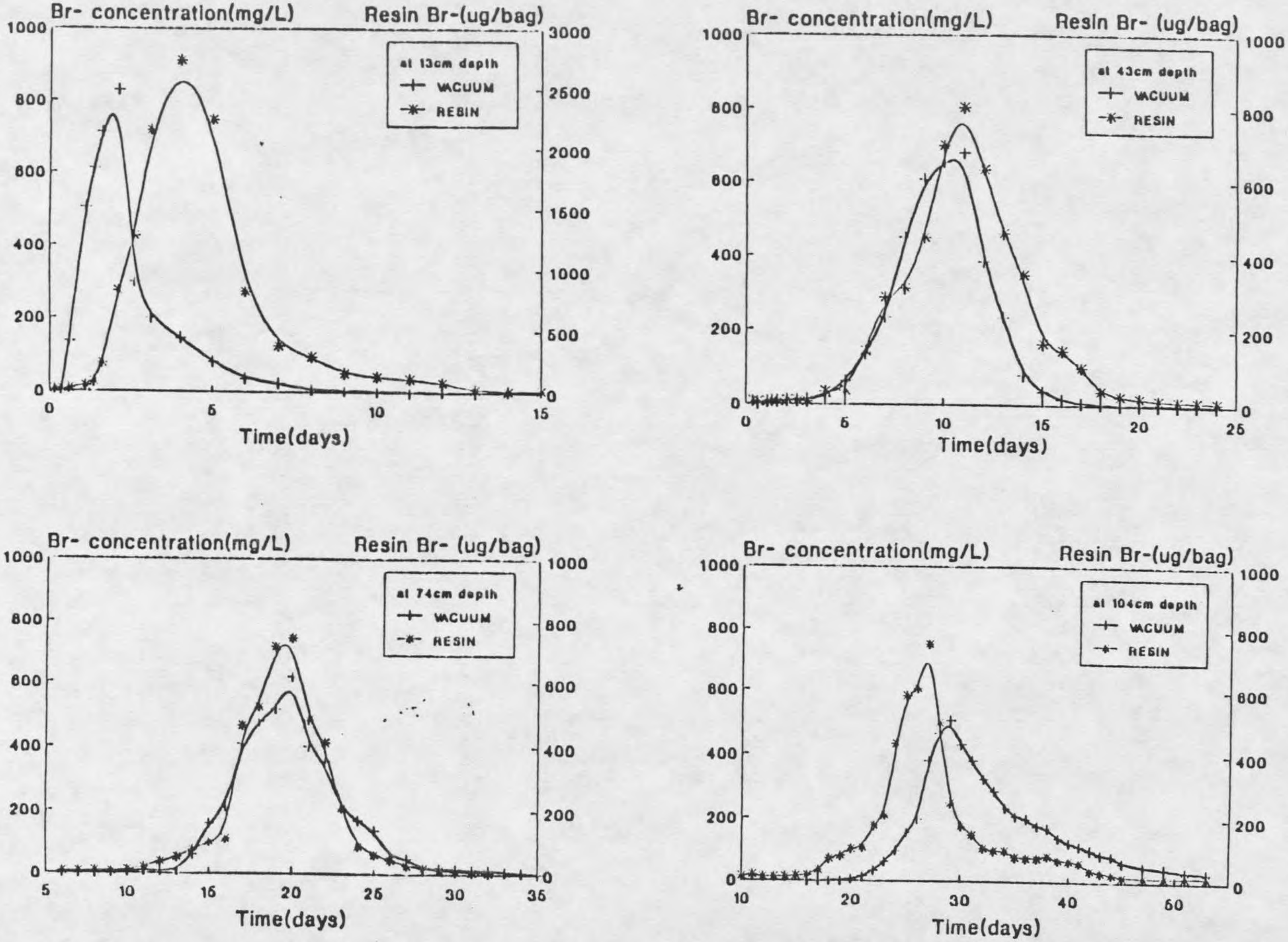

Fig. 8. Comparison of Br transport under continuous unsaturated water flow.

with counter ions(H^+ or OH^-) initially on resin particles. Specific ionic concentration gradients are developed and the rate of the resin adsorption of each ion is regulated by the diffusion characteristics of the soil-water system(Yang et al., 1991). This method does not involve the application of mechanical force. Van der Plog and Beese(1977) indicated that applying even small amounts of suction to extract soil solution may cause significantly higher seepage rates. The suction force applied to extract soil solution from this column probably caused higher rate of water flow than under natural drainage conditions at the upper sampling depth. Conversely, water drawn off at higher depths probably resulted in decreased rate of water movement to the lowest sampling depth, increasing the time required for peak Br concentrations to occur.

Cumulative Water Infiltration and Br Transport in the Soil. Br has been used by many researchers as a tracer of water movement in soils and groundwater, and its movement in soils is dependent upon water flow. The cumulative curves of Br transport and water infiltration are plotted in Figure 9 and 10. These results show that Br transport cumulative BTC patterns described by both methods are similar at all depths, except at 13 cm.

At 13 cm, Br cumulative amounts determined by resin

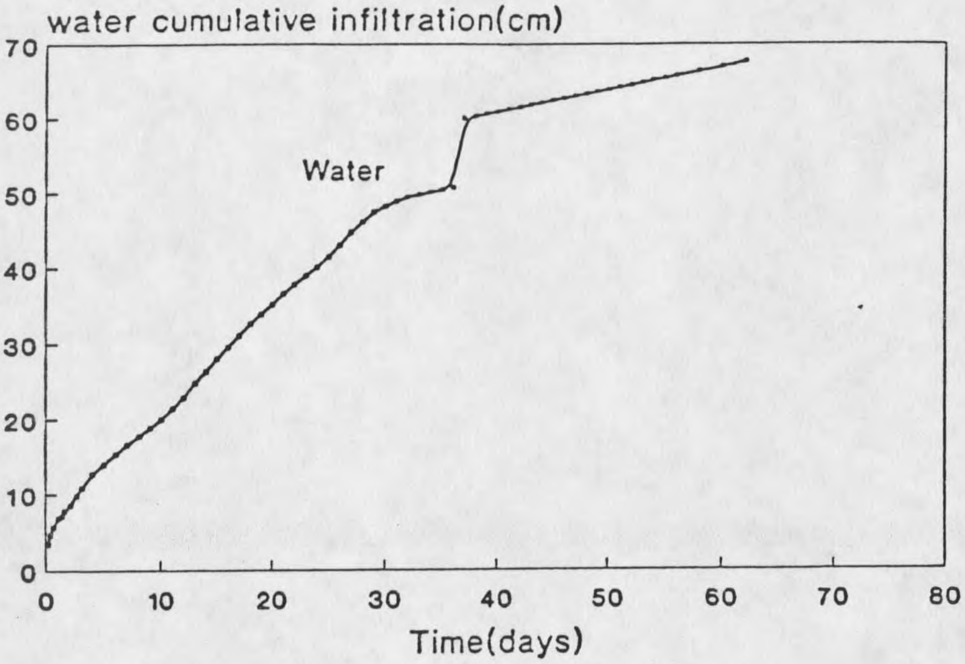

Fig. 9. Water infiltration in the column as continuous unsaturated water application.

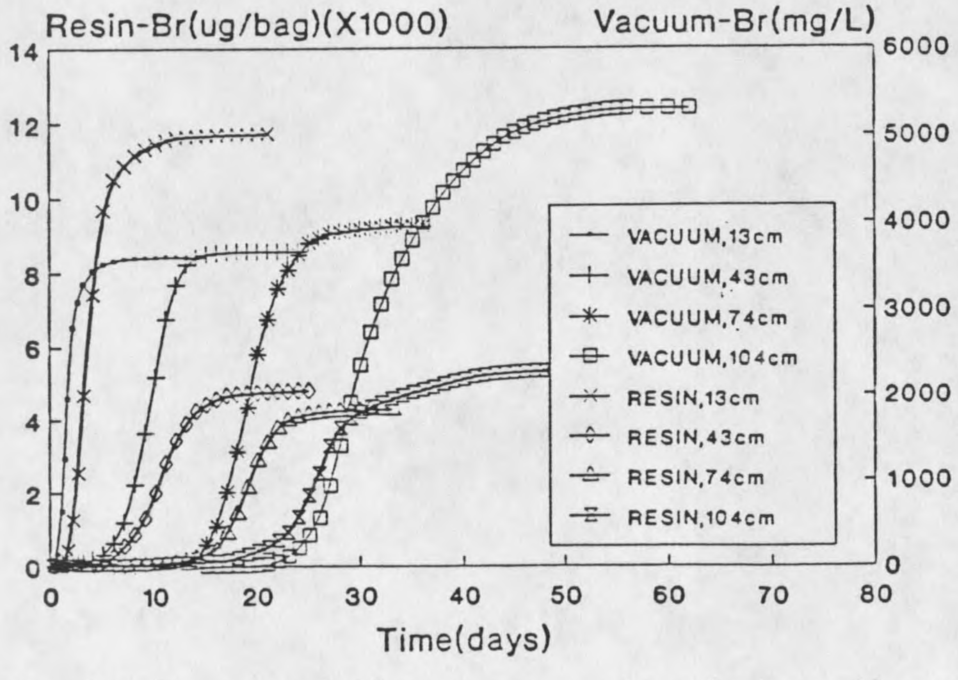

Fig. 10. Br cumulative transport under continuous unsaturated water flow.

capsules was higher than others. This may be due partially to vertical leaching of Br and interception of a large proportion by the resin capsules located in the top sampling point. All resin capsule sampling points in the column were in a direct vertical line position, and the amount of lateral Br movement between sampling ports may not have been adequate to compensate for this effect. The recovery of bromide at 13 cm depth sampling point by resin capsule was 88.8% of that which was surface applied to an area equivalent to the diameter of the resin capsule.

The cumulative amounts of water required to leach Br beyond specific depths are presented in Table 4. The amount of water for Br to leach beyond 13 cm as determined by vacuum extraction was less than that measured by resin capsules. The same reasoning can be used to explain this as for the time required to reach peak Br concentrations. In contrast, the amount of water needed for Br to leach beyond 104 cm as determined by vacuum extraction was more than that measured by resin capsules. These results suggest that higher soil water content was required to obtain a solution sample by vacuum

Table 4. Cumulative amounts of water(cm) needed for Br leaching beyond a certain depth from the surface.

Depth(cm)	13	43	73	104
Resin capsule method	15.3	24.7	40.1	50.4
Vacuum extraction method	12.7	24.7	41.5	61.2

extraction at the lower column depth. The resin capsule method provides a means whereby samples can be collected to determine ionic leaching even under conditions of low water content.

Discussion on Conversion of Units for the Two Methods. One problem with understanding the principle of the resin capsule method is that its concentration unit can not be directly expressed as mg per liter of solution, which is the standard for vacuum extraction data. There are two approaches to convert the unit of μg per resin capsule into mg per liter solution. One method is to convert resin data based on water flux(F), section area(A) of the resin capsule through which the solution passes during the sampling duration(t). If the quantity of soil solution passing the resin capsule during the sampling interval was known, these values could be converted into the standard values for comparison. The conversion to mg per liter of soil solution can be accomplished using the following equation:

$$C_{(mg/L)} = C_{(\mu g/bag \cdot d)}/(F \times A \times t) \qquad [1]$$

If F is constant and the sampling intervals uniform, an average value of F can be used to obtain a reasonable estimation. For this study, F was 1.1 cm/d, A was 1.57 cm^2, and t was 1 d, so the equation [1] becomes

$$C_{(mg/L)} = 0.60 \times C_{(\mu g/bag \cdot d)} \qquad [2]$$

However, several uncertainties involved this conversion. For example, the cross section area of the resin capsule is not the actual A which contributes to the accumulation of solute by the capsule. Diffusion of solute occurs throughout the sampling period, and the amount of solute diffusing is a function of soil water content, solute concentration, soil properties, and other factors. Therefore, this conversion can serve only for the particular conditions under which these data were obtained.

Another alternative approach for comparison of resin capsule and vacuum extraction values is a statistical conversion based on the correlationship between vacuum and resin extracted Br concentrations. Within a given study, where the data are obtained under the same conditions, this approach will probably provide the most useful and reliable conversion. From Figure 7, it is clear that the time required to reach the Br BTC peak concentration as determined by the resin capsule and vacuum extraction methods is the same only at 73 cm. So, it is reasonable to calculate the correlation between vacuum and resin extracted Br concentrations using data from this depth. The calculated correlation is expressed by the following equation:

$$C_{\text{vacuum-Br(mg/L)}} = 0.85 \times C_{\text{resin-Br}(\mu\text{g/bag}\cdot\text{d})} \quad (r=0.98^{**}, n=31)$$

Under these laboratory conditions, the conversion factor from resin-Br concentration(μg bag^{-1}) into vacuum-Br concentration (mg L^{-1}) was 0.85. The larger coefficient of conversion in this statistical comparison, as compared to that calculated above, provides evidence for the uncertainties surrounding attempts to convert from resin capsule units to those used in vacuum extraction methodology.

It may be more appropriate to develop an understanding of how the resin capsule functions, and become familiar with the data units, which represent the actual flux of solutes through the system, rather than attempting to convert to units which are "standard", but relate to different processes.

Conclusions

These results indicate that the resin capsule method is effective for describing Br leaching in a uniformly packed soil column under continuous water flow. The amount of applied water and required time for peak concentrations of Br BTCs at various column depths apparently are affected by the applied suction force in the vacuum extraction method. This may cause incorrect prediction of solute leaching. Results from the resin capsule method are probably more accurate for predicting solute transport under continuous unsaturated water flow.

A Comparison of Vacuum Extraction and Resin Capsule Methods for Monitoring Br Transport in Soil Column under Unsaturated Simulation of Rainfall

Solute transport during steady soil water flow is a much-studied phenomenon. However, solute movement during intermittent flow has received inadequate attention, despite being the norm in the field. The objectives of this portion of the research project were to(1)examine the applicability of the resin capsule method; and (2)evaluate the sensitivity and accuracy of both methods for predicting bromide transport under conditions of simulated rainfall.

Material and Methods

The same soil column was used as in the first experiment. The water potential in the soil column at the beginning of operation was near $-40X10^{-3}$MPa at the 13 cm depth and $-30X10^{-3}$ MPa at the bottom of the column(134 cm). A solution of KBr (3.76 g KBr dissolved in 50 ml DDW, equivalent to 200 kg Br/ha) was sprayed onto the soil surface using a household sprayer. After several minutes when no solution remained, water was applied using a water reservoir with a water head of -0.0017 MPa. Application of water was intermittent to provide conditions of simulated rainfall(Fig. 11). After a

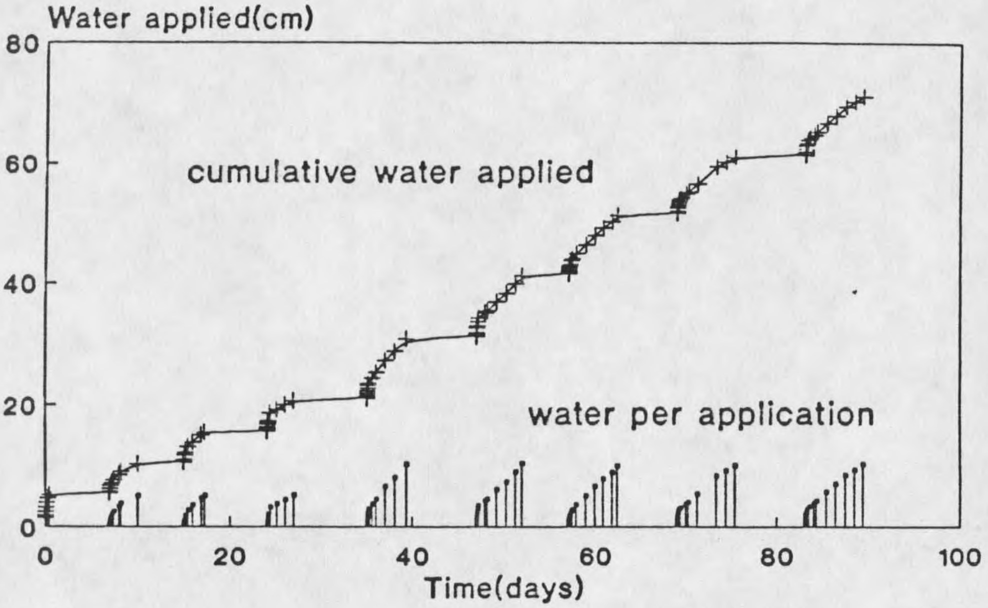

Fig. 11. Water applied as simulation of rainfall

desired quantity of water was applied, the water reservoir was removed for a certain time interval. This was continued until all Br was leached down through the whole column. In the first four water applications up through day 25, water was added at amounts of 5 cm per rain. After this time, the amount of water applied was adjusted to 10 cm per rain. The time interval between two rains was about 7 days. Samples and tensiometer readings were taken as described earlier.

Results and Discussion

Bromide BTCs under Simulated Rainfall. The Br breakthrough curves determined by both the resin capsule method and vacuum extraction method in a soil column

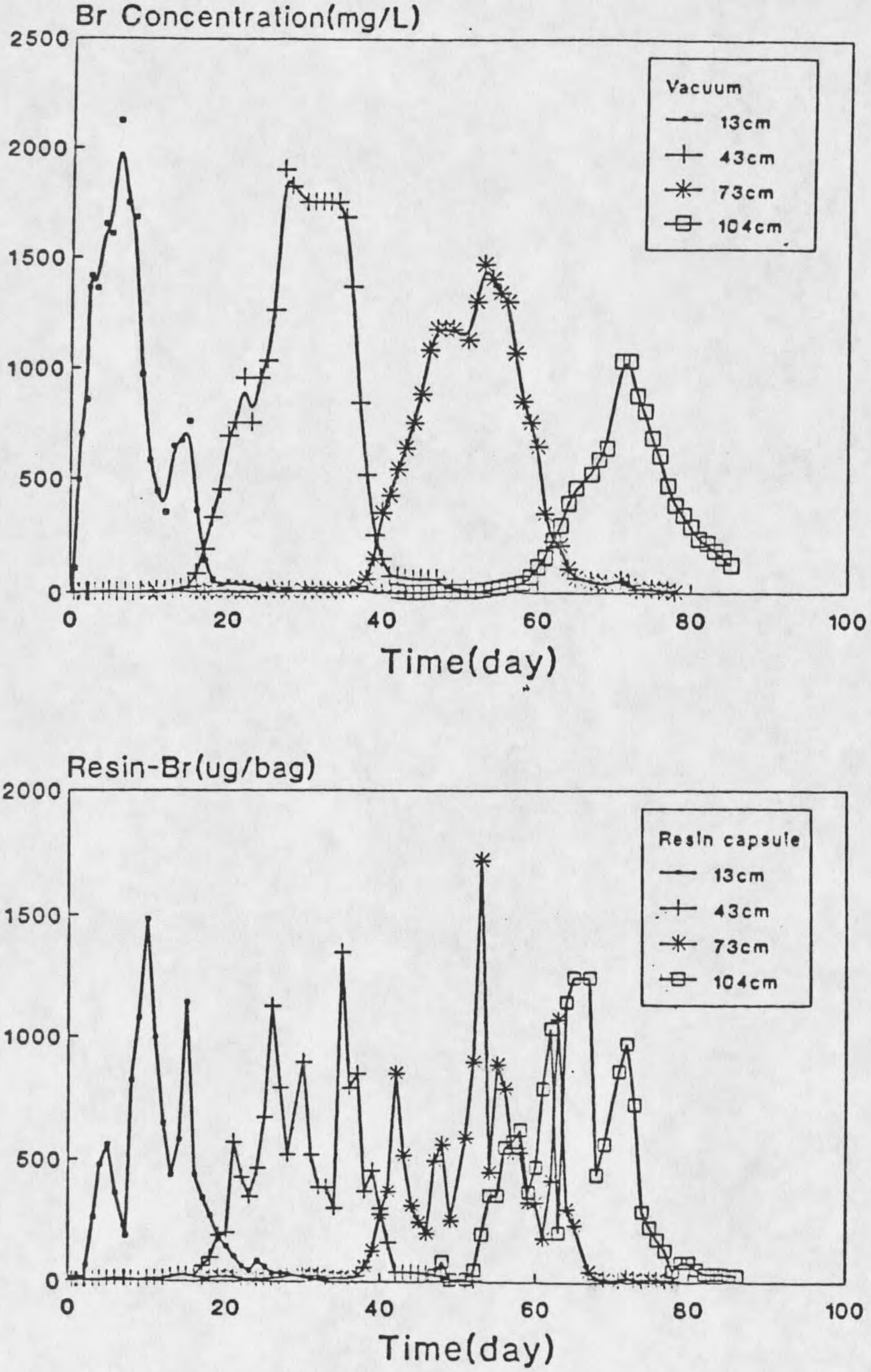

Fig. 12. Br transport under simulated rainfall

under simulated rainfall are plotted in Figure 12. The time to reach Br BTC peak concentrations has a similar tendency to that observed under continuous water flow. The time to reach mean peak concentrations determined by vacuum extraction method was less for the 13 cm depth and greater for 104 cm depth, as compared to results obtained by the resin capsule method. Again, this indicates that the mechanisms of ion extraction from the soil by these two methods is not the same.

Results presented in Figure 12 also suggest differences in sensitivity for determining BTCs as influenced by changing water status in the column. Distinct spikes of Br BTCs described by the resin capsule method demonstrate the good response to water changes represented by water potential changes. On the other hand, the Br BTCs determined by vacuum extraction reached a plateau, rather than a peak, at all depths under simulated rainfall. This suggests poor sensitivity to soil moisture changes. Normally, the vacuum extraction method is only used under soil moisture contents near field capacity(Nagpal, 1982). At the low moisture contents in this study, applied suction may cause extraction of soil solution from nearby higher moisture zones, rather than from immediately around the porous cup. This may cause error in Br concentrations from some sampling points. In the resin capsule method, even at low moisture contents, ions can be extracted by ion exchange reactions through the ion diffusion process. The recovery of Br by resin capsule was up to 99% of applied Br and more Br was adsorbed by resin capsule due to strongly intensive leaching under simulated rainfall.

Bromide Transport and Soil Water Changes

Figures 13 and 14 show the relationship between soil moisture changes(represented by water potential changes) and Br concentration-time BTCs determined by the resin capsule method. As a generality, higher Br adsorption by the resin capsule correspond to water potential changes, indicating that Br is being delivered to the resin capsule by downward water flow. Also, Br siddusion to the capsule would probably be more rapid at the higher water contents.

Table 5 lists the correlation coefficients between Br concentrations and water potentials at 13, 43, 73,

Table 5. Correlation coefficients[@] between water potentials and Br concentrations.

Depth(cm)	13	43	73	104
Resin capsule method	0.75^{**} n=26	0.83^{**} n=29	0.83^{**} n=28	0.90^{**}n=16
Vacuum extraction method	0.34 n=23	0.50* n=29	0.42^{*} n=28	0.57^{*} n=16

*, ** Significant at level of 0.05 and 0.01, respectively.

@ in order to calculate the coefficients, all analyzed data were shifted to same Br BTC peak concentrations (same as followings)

and 104 cm depths. The correlation coefficients between water potentials and Br concentrations determined by the resin capsule method under simulated rainfall are significant at the

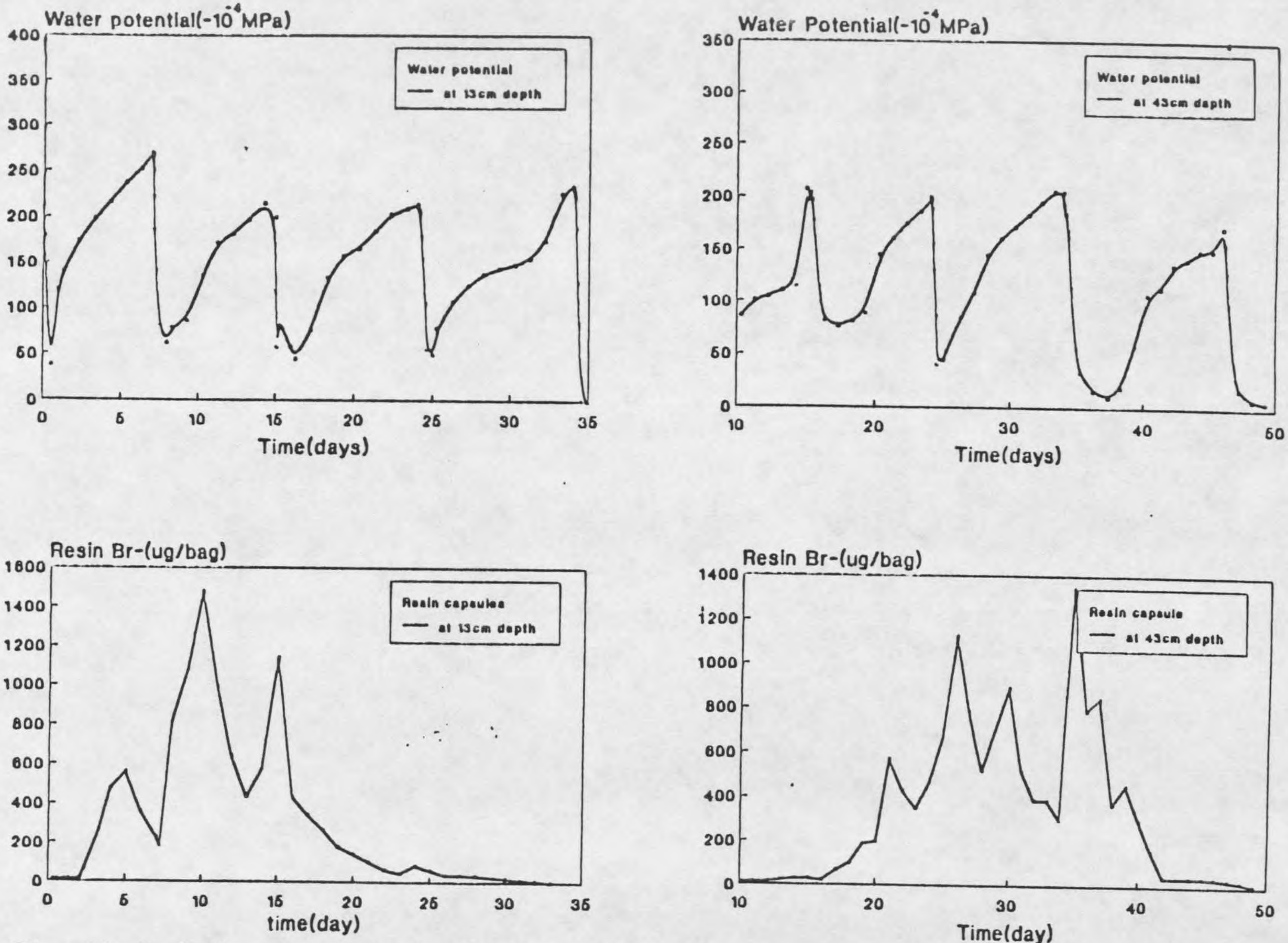

Fig. 13. Relationships between Br BTCs determined by resin capsules and soil water potential changes(I)

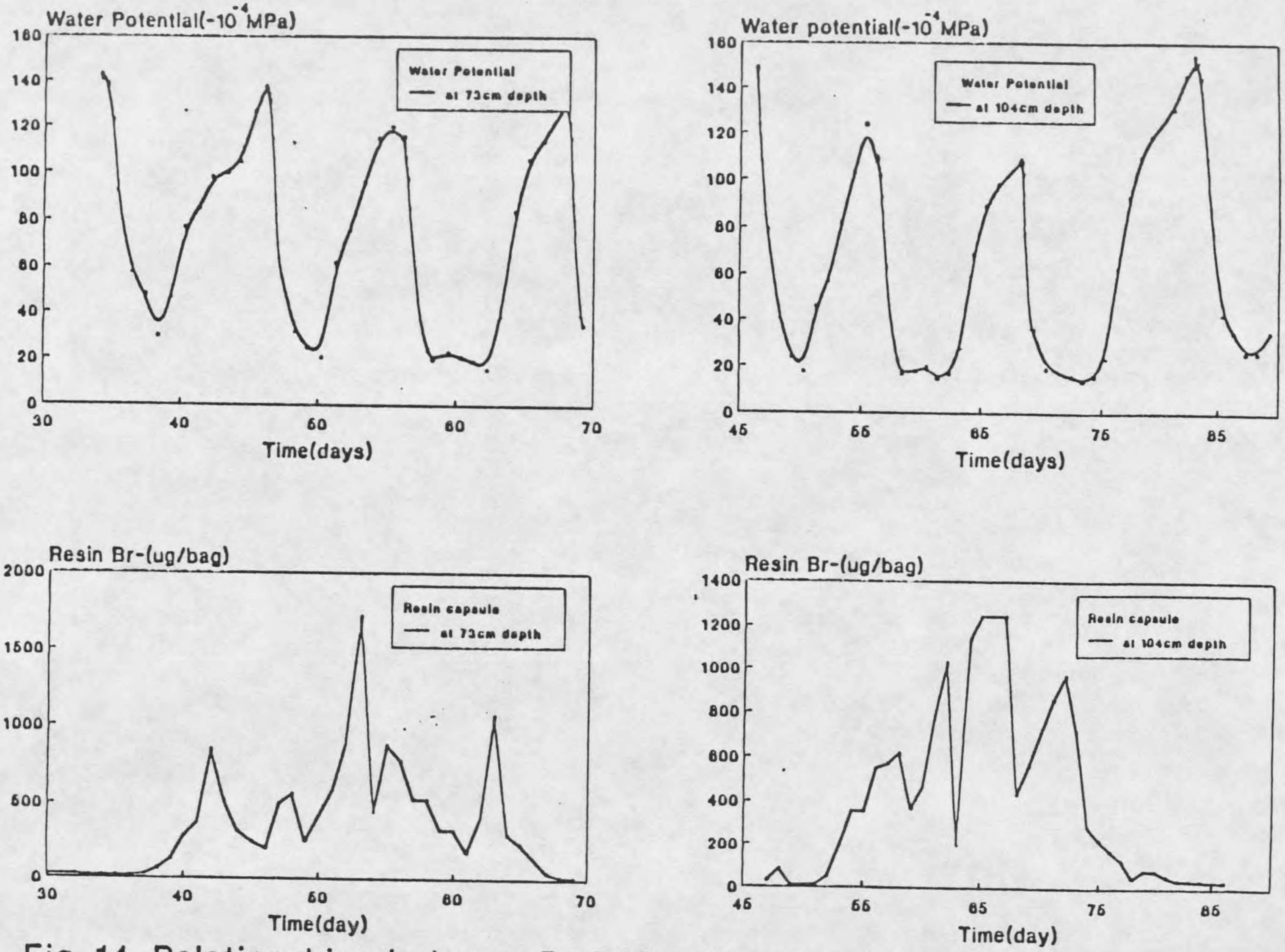

Fig. 14. Relationships between Br BTCs determined by resin capsules and soil water potential changes(II)

99% confidence level at all depths; while the coefficients between water potentials and Br concentrations determined by vacuum extraction method are significant only at the 95% confidence level for the lower three depth. At the 13 cm depth, Br concentrations measured by vacuum extraction were not significantly correlated to water potential changes. Such results suggest that the vacuum extraction approach may not be suitable for representing actual solute transport in surface soil layers under natural conditions. Applied suction may have more influence on upper soil layers than on lower layers. These data from the resin capsule method indicate that it is more sensitive to soil water changes and provides a better approach to prediction of Br transport under simulated rainfall than does the vacuum extraction method.

The total correlation coefficient between Br concentrations determined by vacuum extraction and water potentials is significant at the 95% confidence level ($r=0.24^{*}$, n=99). However the total correlation coefficient between water potentials and Br concentrations determined by resin capsules is much higher and significant at the 99% confidence level($r=0.75^{**}$, n=102) (Fig. 15).

The coefficients of variation in total samples(n=99) are 52%, 77%, and 81% for water potential data, Br concentration data determined by resin capsule method, and Br concentration data determined by vacuum extraction method , respectively. This means when soil moisture contents have a variation of

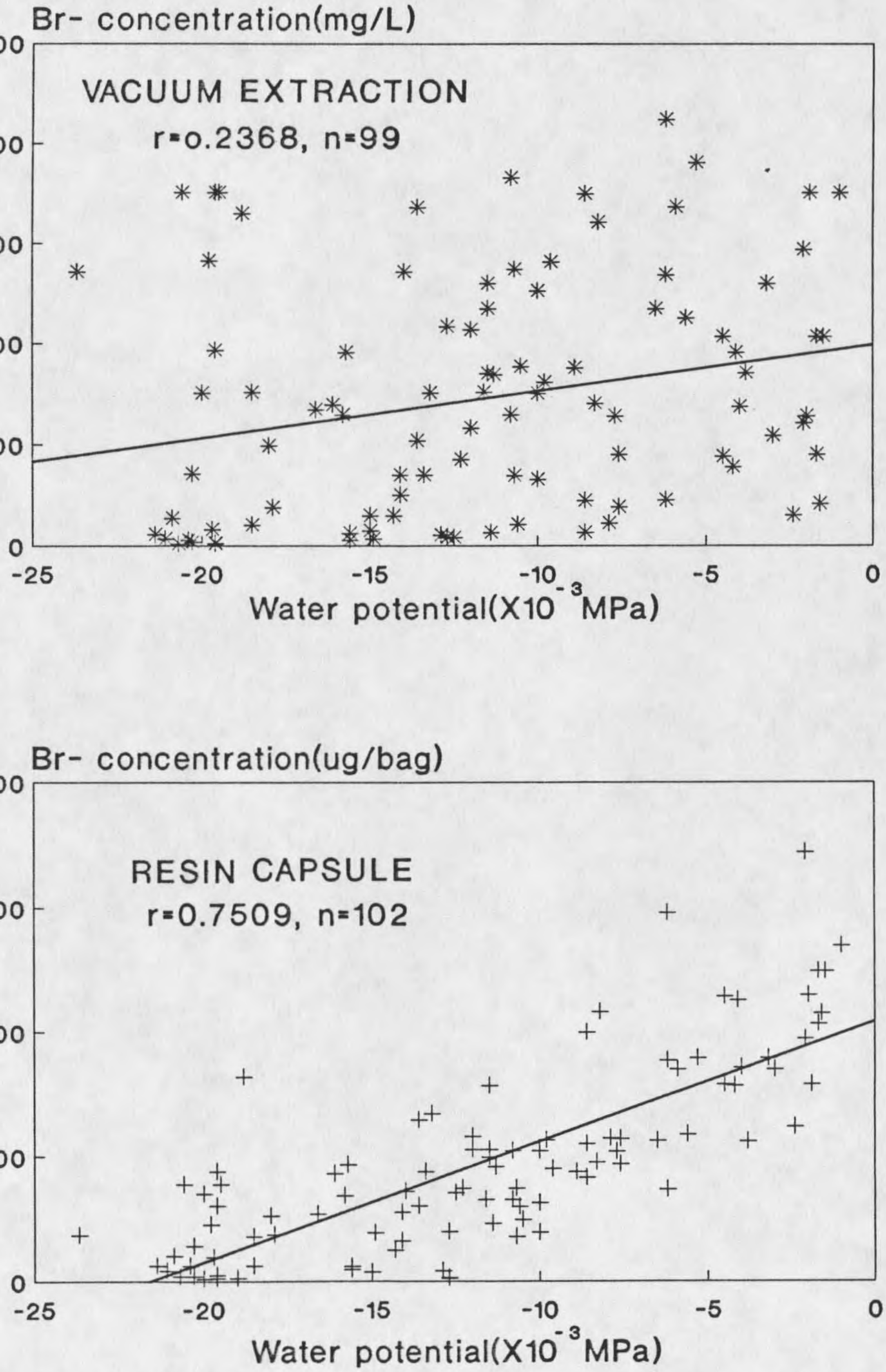

Fig. 15. Relationships between Br concentrations and water potential changes

52%, the Br concentrations determined by resin capsule method and vacuum extraction method have a variation of 77% and 81%, respectively. Thus, data for changes in Br concentrations determined by the resin capsule method are more closely related to changes in water potential than are data determined by vacuum extraction.

Relationship between Resin and Vacuum Extracted Br Concentrations. The resin extracted and vacuum extracted Br concentrations are plotted in Figure 16. The correlation coefficient between data collected by these two methods is significant at the 99% confidence level($r=0.56^{**}$, n=99) when comparing all samples. A reasonably good relationship is expected to exist between these methods of Br determination because Br transport is basically dependent on water movement. Even though both methods can be used to predict Br transport, the sensitivity to changes in rate of Br transport due to changes in soil water potential resulting from simulated rainfall was greater when resin capsules were used.

Conclusions

The patterns for Br concentration vs. time under simulated rainfall conditions as determined by the two methods were generally similar. However, distinct peaks were indirectly related to soil water potential changes measured

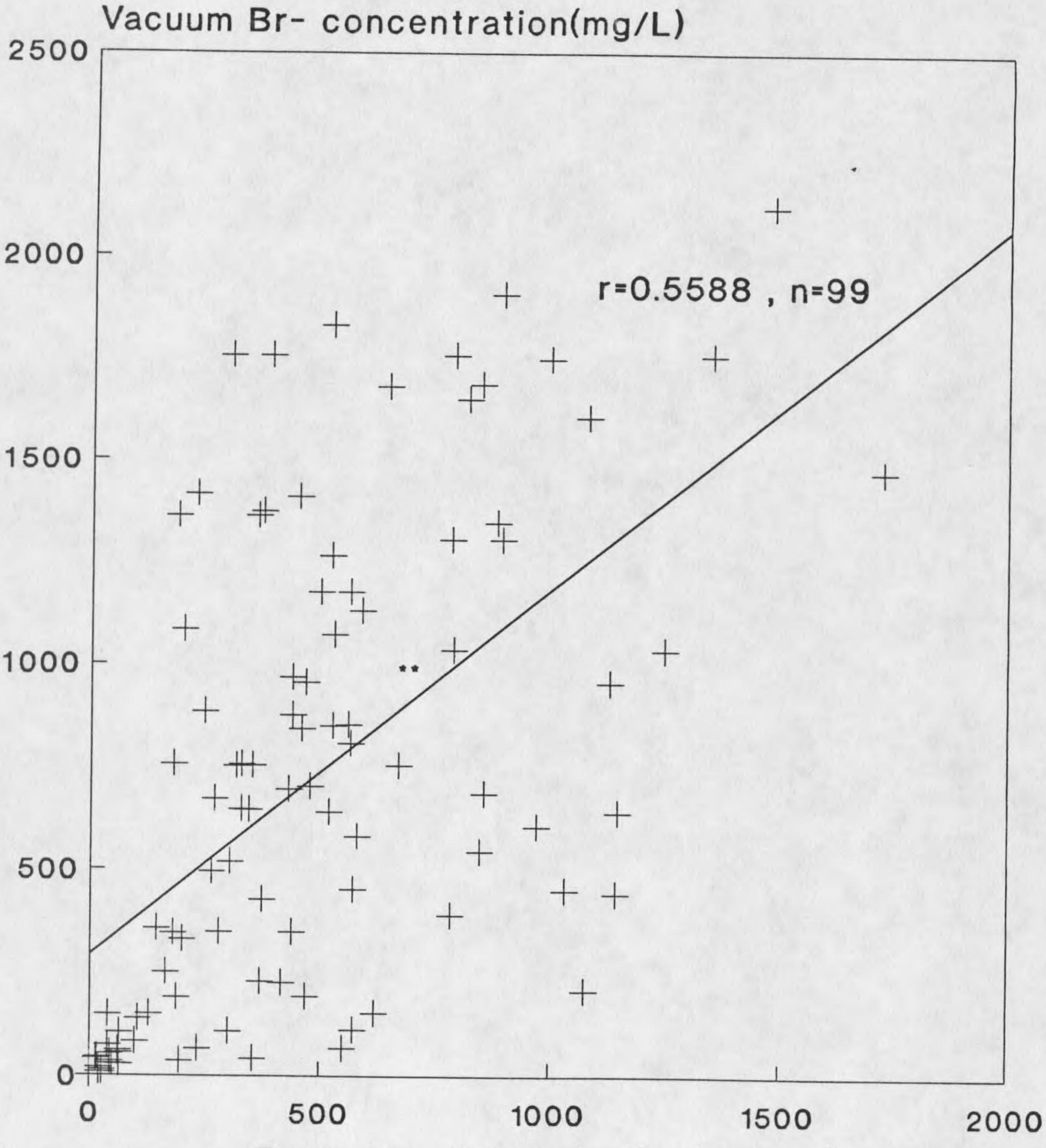

Fig. 16. Relationship between resin and vacuum extracted Br concentrations

with resin capsules, whereas the vacuum extraction method did not provide significant sensitivity to allow detection of these differences. These results suggest that the mechanisms of ion extraction from the soil by resin capsules is better than the physical mechanism employed with vacuum extraction of soil solution. Bromide concentrations as determined by resin capsules were more highly related to soil water movement than those measured by vacuum extraction. However, the relationship between resin extracted and vacuum extracted bromide concentrations was highly significant. This is expected because bromide transport is basically a function of water movement.

Modelling Bromide Transport in a Soil Column under Continuous Unsaturated Water Flow

Concern about the behavior of various chemicals in the subsurface environment has resulted in the development of a number of theoretical models describing the basic processes of solute transport in soils and groundwater. An important problem remaining is that of quantifying various model parameters, e.g., dispersion coefficients, retardation factors, and degradation constants. One popular method for determining these parameters is to fit them to observed laboratory or field displacement data. In particular, least-square inversion methods have proved to be accurate and reliable tools for this identification process(Parker and van Genuchten, 1984a).

Laboratory soil column experiments are performed routinely to obtain mechanistic information regarding solute transport in soil profiles. In modelling the data obtained, one generally uses some version of the one-dimensional convection-dispersion model(CDM), with appropriate boundary and initial conditions to fit experimental breakthrough curves and to quantify the model parameters(Parker and van Genuchten, 1984a).

When analyzing concentration data from a dispersive system, one must distinguish between resident and flux concentrations(Brigham, 1974; Parker and van Genuchten, 1984b). Kreft and Zuber(1978) defined the resident concentration, C_R ,as "the mass of solute per unit volume of fluid contained in an elementary volume of fluid at a given instant". They defined the flux concentration, C_F, as "the mass of solute per unit volume of fluid passing through a given cross section at an elementary time interval". It can be verified that if C_R satisfied CDM, then so does C_F(Parker and van Genuchten, 1984b).

The objective of this portion of the research program was to compare data from bromide breakthrough curves as determined by the resin capsule and vacuum extraction methods to fit an existing transport model(CDM). A computer program of the least square fitting technique(CXTfit) of Parker and van Genuchten (1984a) was used for this comparison.

Transport Equations

For steady-state fluid flow conditions, the following partial differential equation has been proposed for describing the transport of a solute through soils(Lapidus and Amundson, 1952):

$$\frac{\partial c}{\partial t}+\frac{\rho}{\theta}\frac{\partial s}{\partial t}=D\frac{\partial^2 c}{\partial x^2}-V\frac{\partial c}{\partial x} \qquad [1]$$

where C is solution-phase solute concentration(ug cm^{-3}), t is time(d), ρ is soil bulk density(g cm^{-3}), θ is volumetric water content(cm^3 cm^{-3}), s is sorbed-phase solute concentration (ug g^{-1}), D is hydrodynamic dispersion coefficient(cm^2 d^{-1}), x is distance from where solute is introduced(cm), and V is average pore water velocity(cm d^{-1}). One of the most important steps in model formation is the description of the $\partial c/\partial t$ term. When conditions of local equilibrium, adsorption-desorption singularity, and isotherm linearity are assumed,

$$S=K_d \times C \qquad [2]$$

where K_d is the distribution coefficient(cm^3 g^{-1}), the expression for $\partial s/\partial t$ becomes(Brasseau et al., 1989):

$$K_d\partial c/\partial t \qquad [3]$$

substitution of [3] into [1] yields:

$$\frac{\partial c}{\partial t}R=D\frac{\partial^2 c}{\partial x^2}-V\frac{\partial C}{\partial x} \qquad [4]$$

Where the dimensionless retardation factor R is defined as

$$R=1+\frac{\rho}{\theta}K_d \qquad [5]$$

Equation [4] is commonly used to describe one-dimensional steady-state fluid flow in a homogeneous soil profile and has been commonly termed the convective-dispersion model(CDM).

The least square fitting program CXTfit of Parker and van Genuchten(1984a) has been used to estimate for each observed local concentration profile the three unknown V, D, and t_o, where t_o is an equivalent pulse duration. The CXTfit code assumes steady-state flow and the absence of any sources or sinks of water and solutes.

Materials and Methods

Br BTC Relative Concentration(C/Cmax) Data: obtained from experiment I under continuous water flow. C_i is measured Br concentration at each time interval. Cmax is the maximum Br concentration among measured Br concentrations at depths of 43, 73, and 104 cm.

CXTfit: a computer program developed by Parker and van Genuchten(1984a).

Procedure:

(1) input the observed Br BTC relative concentration data into the CXTfit program;

(2) the CXTfit program estimates the three model parameters(V,D,t_0);

(3) the CXTfit program uses these model parameters by fixing one of them to predict Br BTC data based on pairs of observed Br BTC data;

(4) finally plot these predicted Br BTC data with time to get predicted Br BTCs.

Results and Discussion

Estimating Transport Parameters from Br BTCs. The transport parameters: pore water velocity(V), dispersion coefficient(D), and pulse(t_0) were estimated from the Br BTCs. This was accomplished by fitting the BTCs to a one-dimension convective-dispersion equation(CDE) with the computer program CXTfit. The bottom boundary condition assumed a resident-average concentration detection model I. In the CXTfit analysis, the retardation factor R is assumed equal to 1.0, and the pulse t_0 was fixed for CXTfit estimation.

Table 6 lists the modeling parameters estimated by CXTfit program. The pore water velocity(V) decreased as water

Table 6. Estimated transport parameters from Br BTCs by the CXTfit program.

Depth (cm)	Resin capsule method				Vacuum extraction method			
	t_0* (d)	V (cm d^{-1})	D (cm^2d^{-1})	R^2	t_0* (d)	V (cm d^{-1})	D (cm^2d^{-1})	R^2
43	5.50	5.26 (0.068)†	6.55 (0.835)	0.97 n=30	5.50	6.01 (0.067)	4.62 (0.737)	0.98 n=23
73		4.38 (0.030)	1.81 (0.273)	0.95 n=29		4.34 (0.030)	2.03 (0.285)	0.96 n=27
104		4.42 (0.031)	2.04 (0.316)	0.90 n=43		3.78 (0.045)	3.19 (0.547)	0.83 n=38

* Pulse(t_0) value was fixed at 5.5 days in the CXTfit analysis.

† Values in parentheses indicate standard deviation of estimation.

moved down. However, the decrease in V estimated by the CXTfit program using data from the resin capsule method was much less than when data from vacuum extraction were used. With vacuum extraction, the pore water velocity decreased dramatically from 6.01 cm d^{-1} at depth 43 cm to 3.78 cm d^{-1} at 104 cm depth. The coefficient of variation(CV) was 24.6%. In contrast, using resin capsule data, only a slight decrease in V was observed, and the CV was reduced to 10.5%. These results indicate that applied suction may significantly change the pore water velocity or at least its estimated value. Near the soil surface, applied suction can increase pore water velocity by forcing water to move down faster, while at lower depths, applied suction at upper depths may reduce the pore water velocity by decreasing the amount of water moving to at lower depths.

The dispersion coefficients(D) estimated from the CXTfit program using data from either method were least at the intermediate column depth. The correlation coefficient between D's and V's was highly significant($r=0.99^{**}$, n=3) in the case of data from resin capsules, but not significant when vacuum extraction data were used($r=0.76$, n=3). However, with only three data values for comparison, little importance can be attached to this comparison.

Br BTC Patterns

The observed and CXTfitted Br BTCs for three column depths are given in Figure 17. At all depths, Br BTCs

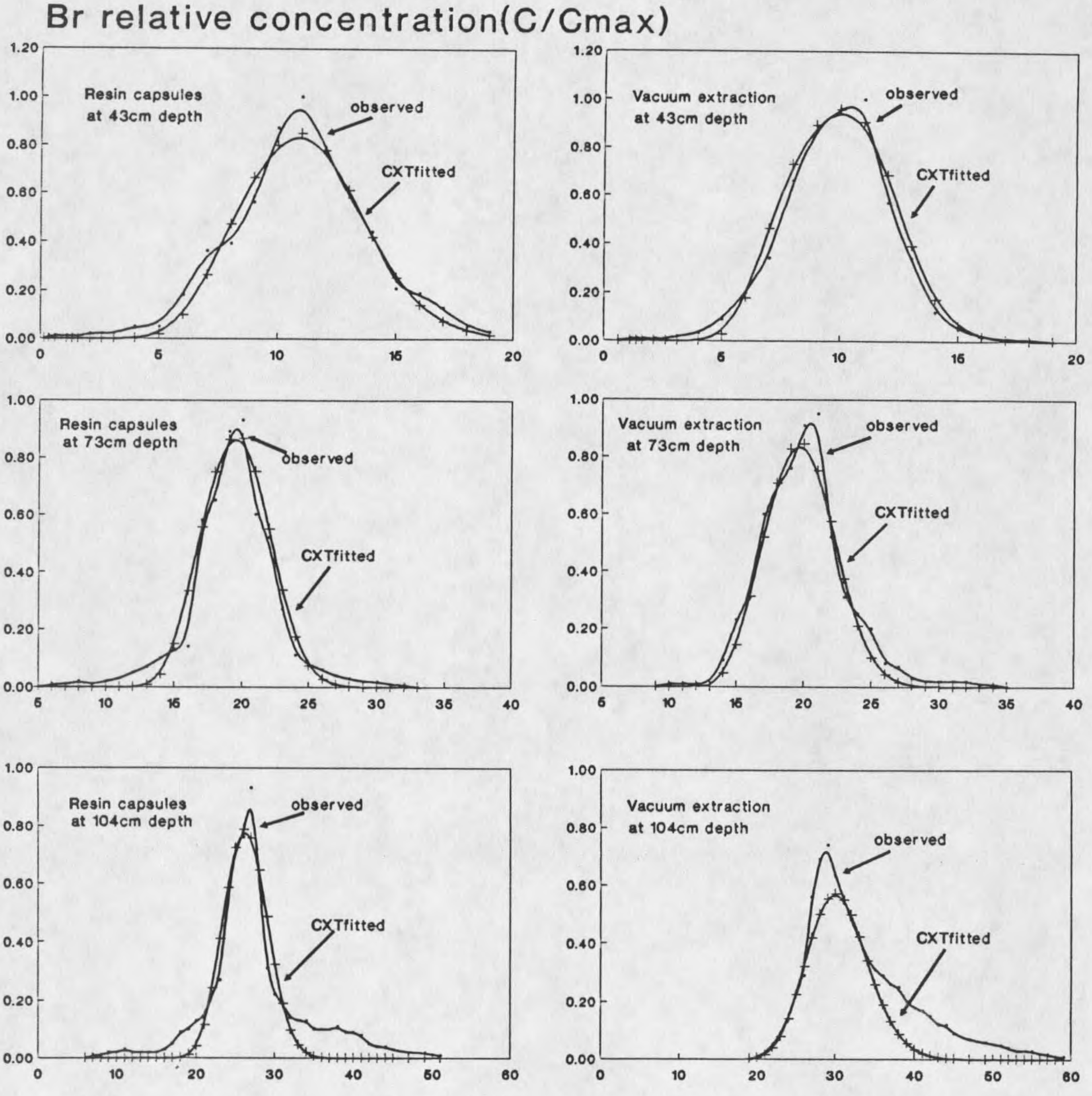

Fig. 17. Br observed and predicted BTCs by the CXTfit program at different depths under continuous, unsaturated water flow

determined by either method compare well to curves predicted by the CXTfit program. The only divergence from a normal distribution occurred at 104 cm depth when vacuum extraction data were used. In this instance observed data peaked considerably higher than predicted by the CXTfit and the curve was skewed to the right, rather than having a normal distribution. Again, it is likely that these results occur in response to changes in the normal pattern of water and solute movement induced by applied vacuum at several depths in the soil column.

Conclusions

Data obtained for Br BTCs by the resin capsule method under continuous water flow were exceptionally well fitted to an existing transport model(CDM) by the CXTfit program. A good fit was also shown for data obtained by vacuum extraction, but with some divergence at the lowest column depth. Better data uniformity for calculation of model parameters and improved relationships between these parameters when resin capsule data were used provides evidence that this method may be more accurate for determining solute leaching under conditions of continuous, unsaturated water flow. The resin capsule method eliminates the potential for altering water flow rates and patterns that can occur when a vacuum is applied at several locations in the soil column.

FIELD STUDIES

Monitoring Br Transport by the Resin Capsule Method under Field Conditions

Transport of salts and other water-soluble chemicals through the root zone under field conditions is of immense concern to soil managers, agronomic researchers and to environmental scientists. Whether for agricultural, municipal, or industrial purposes, numerous field trials have been conducted, especially within the last decade, to test or observe the movement of salts or potential pollutants in the soil profile. Unlike uniformly packed laboratory soil columns, field soils are heterogeneous. Highly variable observations of solute concentrations and soil-water properties can occur. The determination of water and solute transport as well as development of technology for sampling field soils must account for this natural spatial variability. Technology for assessing the leaching of solutes in a field soil remains inadequate(Amoozegar-Fard et al., 1982). The suction porous ceramic cup extraction method is the main technique for sampling soil-water solution under field conditions. However, this method has many inherent disadvantages, as discussed above. Additional problems related to the field use include (1)difficulty in installing suction cups without disturbance of surrounding soil and (2)poor reproducibility of results. The resin capsule methodology has proved to be very effective and useful for sampling soil solutions in laboratory soil column studies. It is of great interest to examine this resin capsule sampling technology under field conditions to verify its potential value for *in-situ* applications.

The objectives of this field experiment were to (1)examine and evaluate the applicability of the resin capsule method for monitoring bromide transport under field conditions, and (2) determine its sensitivity to the influence of growing plants on bromide transport through the soil under varying levels of applied irrigation water.

Materials and Methods

Field Plot Design. A field experiment was conducted in a coarse-loamy, mixed typic Calciboroll(the same soil used for the column experiments) in southcentral Montana from June to September of 1991. The physical and chemical properties of the soil were shown in Table 2. Two 56 m^2 areas were chosen to conduct studies of time, soil depth, and water application on Br transport in a field soil. One area was seeded to barley and the other was maintained as fallow. Figure 18 shows the experimental plot arrangement and treatments of soil depth and water application. Three sampling depths (15, 30, and 90 cm) and five moistures(from

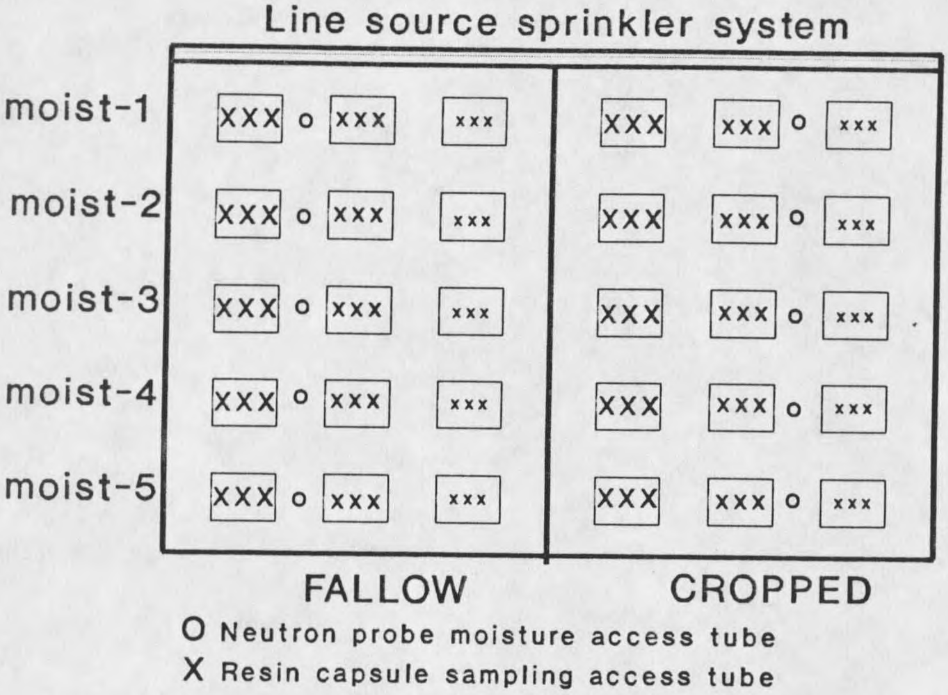

Fig. 18. Field plot design

excess irrigation to dryland) applied with a linear source sprinkler were used for conducting the Br transport experiment. A 500 ml KBr solution dissolved with 18.6 g Br(equivalent to 100 Kg Br ha^{-1}) was uniformly sprayed onto the soil surface of each plot of 1.86 m^2(1.22X1.53 m). Water was periodically applied with a modified "line source" sprinkler system, providing for five different water application rates. Access tubes were installed through which neutron probe water content measurements were made. During the last phase of the field work, soil and plant samples were taken, and biomass of barley for each treatment was determined.

The Resin Capsule Adsorption Technique. Figure 19 illustrates schematically the resin capsule set-up in the

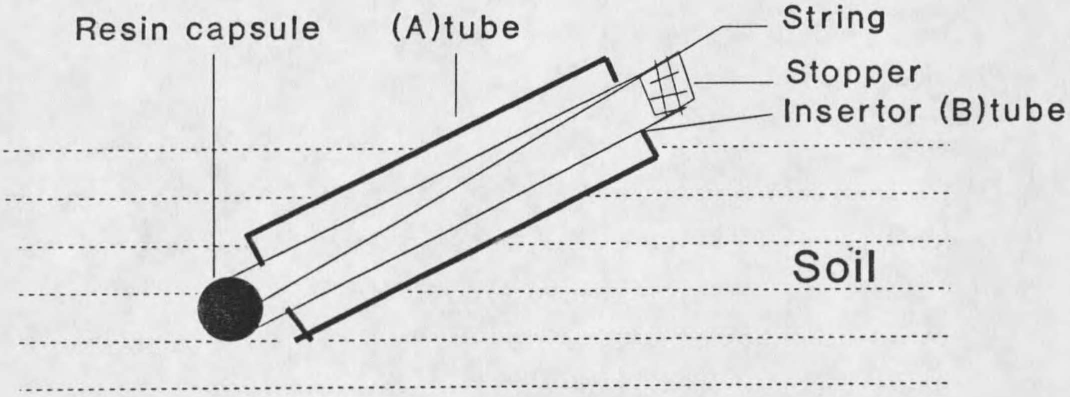

Fig. 19. Schematic of resin capsule set-up in the field

field. A length of PVC tubing(A) was placed in the soil to predetermined depth in a main drill hole made with a soil sampler. A second tube(B) of the same inside diameter as that of the resin capsule(2 cm) was cut to extend 5-8 cm beyond the end of A-tube. A resin capsule was tightly held, by means of an attached cord, to the end of the B-tube and inserted through A-tube and pushed into the soil at least 5 cm beyond the end of the A-tube. The B-tube assembly, with attached resin extractor, can be removed at any time and a new resin capsule inserted to allow sampling at specific time intervals. Prior to capsule insertion the first time, a half-sphere cavity was formed in the soil with a wooden rod of exact diameter to that of the resin capsule. In this system, exactly one-half of the resin capsule surface is held in intimate contact with the soil during the sampling interval. The A-tube was placed in the soil at an approximately 60 degree angle, similar to the placement of mini-lysimeters used in root studies. Three replicate insertion tubes were placed in each sampling depth.

After retrieval from the field, the resin capsules were washed using DDW and stored in a small plastic bag and frozen until analysis.

Resin Br Stripping Procedure and Br Determination. The procedures for Br stripping and determination are the same as described for column studies.

Procedure of Plant Br Determination.

a. 1 g plant samples + 25 ml DDW;
b. shake for 1 hour;
c. bring volume up to 50 ml with DDW;
d. filter using No. 41 filter paper;
e. determine Br concentration using Br sensitive electrode method, as described earlier.

Results and discussion

Br Detection and Transport in the Field. The quantity of Br accumulated by the resin capsule in the sampling time period for the three wetter water regimes at three depths under cropping and fallow are given in table 7. The data of

Table 7. Bromide concentrations(μg/bag) determined by resin capsules under field conditions.

Time (d)	Cropped			Fallow		
	depth(cm)					
	15	30	90	15	30	90
	Water regime 1(305 mm)					
8	466	12	9	13	8	7
15	560	20	9	344	23	8
20	385	116	10	582	191	11
29	252	162	20	773	341	13
36	9	7	5	190	219	14
50	39	16	13	709	1342	37
71	15	12	10	1687	1620	20
Total	1726	345	76	4298	3744	110
	Water regime 2(235 mm)					
8	30	17	12	8	7	6
15	65	8	28	222	11	8
20	140	17	23	415	12	9
29	112	21	24	526	22	15
36	5	4	9	172	10	6
50	10	9	14	837	40	20
71	54	9	12	1363	50	16
Total	417	85	122	3543	152	80
	Water regime 3(126 mm)					
8	9	10	15	7	6	6
15	10	9	10	21	8	6
20	16	13	13	59	10	9
29	18	26	22	174	21	13
36	5	9	6	122	9	8
50	24	13	11	264	25	18
71	13	9	10	454	10	10
Total	95	89	87	1101	89	70

irrigation and the quantity of water added under each regime are listed in table 8; a total of only 9 mm of water was added to regime four and no Br movement was detected under that irrigation. Because of lack of water, the last irrigation was on day 32.

Table 8. Amounts of irrigation water(mm) applied in the field study.

Time(d)	Regime 1	Regime 2	Regime 3
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

The quantity of Br detected by a resin capsule was, then, a function of the length of time of sampling, water movement to the capsule depth, water content near the capsule (because at least some of the Br collected was a function of Br diffusion to the capsule and not only water flow), and plant uptake.

Based on 55 capsules placed in soils not affected by Br, the background level of Br in the soil averaged 8 μg/bag with a range of 4 to 14 μg/bag. The data of table 2 are not corrected for background. Considerably more Br was collected in the capsule under cropping than fallow at the 15 cm depth by day 8 in the two higher water regimes. With cropping, the soil was drier and water flow downward in this non-swelling/non-cracking soil would be more as a uniform wetting front that would carry a large amount of Br. In the wetter fallow system, initial infiltration would be slower and early water movement would be likely to be more "fingered" with movement mainly through the large pores that had emptied of water. this could account for the lesser amount of Br which was initially carried downward in the fallow plots. Maximum Br collection occurred by day 15 in the cropped, water regime 1(305 mm irrigation water) plots; after this date less Br was collected by the capsule in the cropped plots than in the fallow plots. After day 29 only a small amount of Br was collected in the cropped plots at the 15 cm depth whereas a large amount of Br continued to be collected in the fallow plots. This should be expected; crop uptake(discussed later) was significant, water flow to deeper depths was restricted by the drier soil, and the zone around the capsule was drier which would reduce diffusive movement for Br. Bromide reached the 30 cm depth at about the same time in the cropped and fallow system under high water regimes. Except for this and the fact that the Br concentration peaked at day 29 in the cropped plots, the general pattern was much the same as at 15 cm. With the highest water regime about 11 times as much Br was collected under the fallow than in the cropped soil at the 30 cm depth, compared to about 2.5 times at 15 cm. Almost no

Br reached the 90 cm depth in the cropped plots and a small amount reached 90 cm in the fallow plots.

In water regime 2(235 mm irrigation water), the pattern of Br collected at the 15 cm depth was similar to regime 1; less Br movement occurred but about 8 times more was collected in the fallow plots. Little Br was collected at 30 cm in the cropped plots but in the fallow plots significant amounts of Br were collected at this depth at the last two sampling dates. Very little Br reached 15 cm in the cropped plots of regime 3(126 mm irrigation water) but after day 20 a significant amount of Br was collected from this depth in the fallow plots, indicating a considerable amount of movement to this depth. Several data outliers seem to have occurred in some of the results where generally low levels of Br accumulation were being measured. For example, in water regime 2, somewhat more Br was recovered at 90 cm during the first 29 days under cropped as compared to fallow. This could have resulted from "finger" type water movement and transfer of small amounts of Br to this depth. It is also possible that some water leaked down around the access tubes if the soil did not snugly contact the tube. To guard against this source of error, it may be desirable to place a collar around the access tube, just below the soil surface, to intercept and divert any free water moving in this manner.

Figure 20 shows the difference and variation of volumetric water contents at different depths under cropped

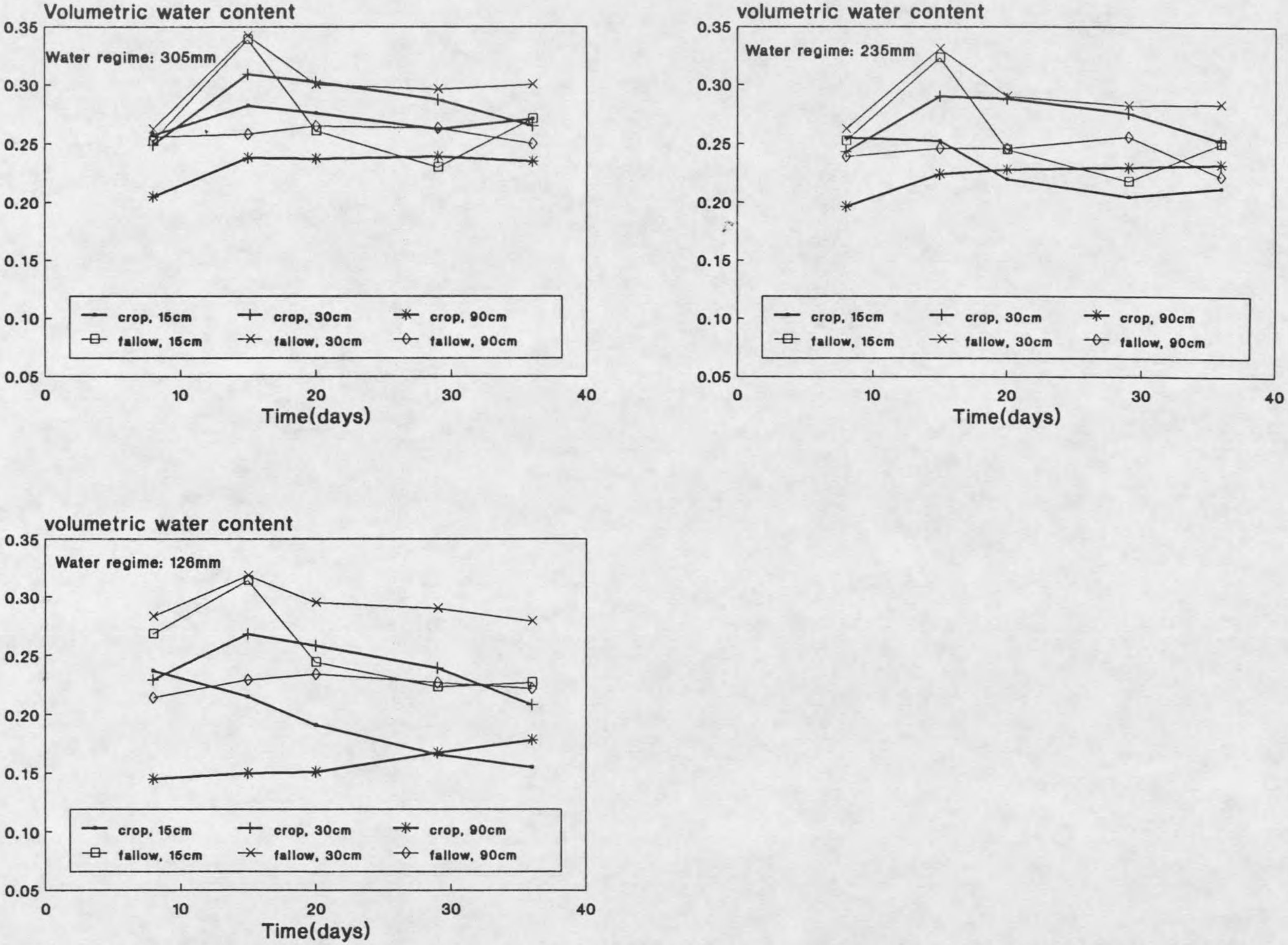

Fig. 20. Soil water content changes under varying water regimes in the field

and fallow systems. In general, the volumetric water contents in the cropped field were lower than those in fallow at all three sampling depths. This provides indirect evidence that evapotranspiration was greater with a growing crop than with fallow. The volumetric water contents at 30 cm depth were higher than those at 15 cm depth in all water regimes under both cropped and fallow systems. Apparently, more evaporation or evapotranspiration occurred from surface soil than from lower depths. The variation in volumetric water contents was not the same for all water regimes. The higher water regime had less variation than did the lower water regime in the cropped field. These variations in the cropped field might be caused by different time intervals between any two irrigations, different evapotranspiration rates, or root system density. No significant variation at the three depths was observed due to varying water regimes in the fallow field. These differences could result in different pore water velocities and, therefore, affect Br transport rates and distribution in the soil, as discussed earlier.

Effects of Plant Uptake on Br Transport. The differences in relative amounts of Br detected in cropped and fallow fields under varying water regimes can be explained partially as responses to the different amounts of plant Br uptake. Although Br is not a required plant nutrient, the amount taken up by plants can be similar to that of NO_3-N(Owens et al., 1985). Therefore with vigorous vegetative growth, considerable amount of Br can be taken up by the plant.

Figure 21 illustrates the biomass, Br content, Br uptake, and recovery by barley plant as influenced by water regimes. Barley biomass decreased linearly as the water regime decreased from 305 to 126 mm. Apparently the water supply was the limiting factor for barley production in this experimental area. However, the Br contents in barley did not decrease directly with water regime reduction. At the first three water regimes, the Br contents increased as the amounts of applied water decreased from 305 to 126 mm. At the lower water regimes, Br contents in the plant decreased considerably, probably due to limited water supply reducing the quantity of Br moved to the root zone and restricting Br absorption by the plant. In these studies, barley recovered up to 38.5% of surface-applied Br at water regime of 305 mm. These results are similar to those reported by other researchers. Owens et al.(1985) showed that, in a field study, as much as 32% of applied Br was taken up by grass. Kung(1990) reported that at least 53% of applied Br was absorbed by potato plants and about 44% of the absorbed Br ion could be redistributed to the soil surface when the dead leaves and vines decayed. In a laboratory column study, Gish and Jury(1982) indicated that 5% of applied Br was taken up by wheat. Bromide leaching can therefore be grossly overestimated by using Br breakthrough curves if crop uptake is not considered(Kung,1990).

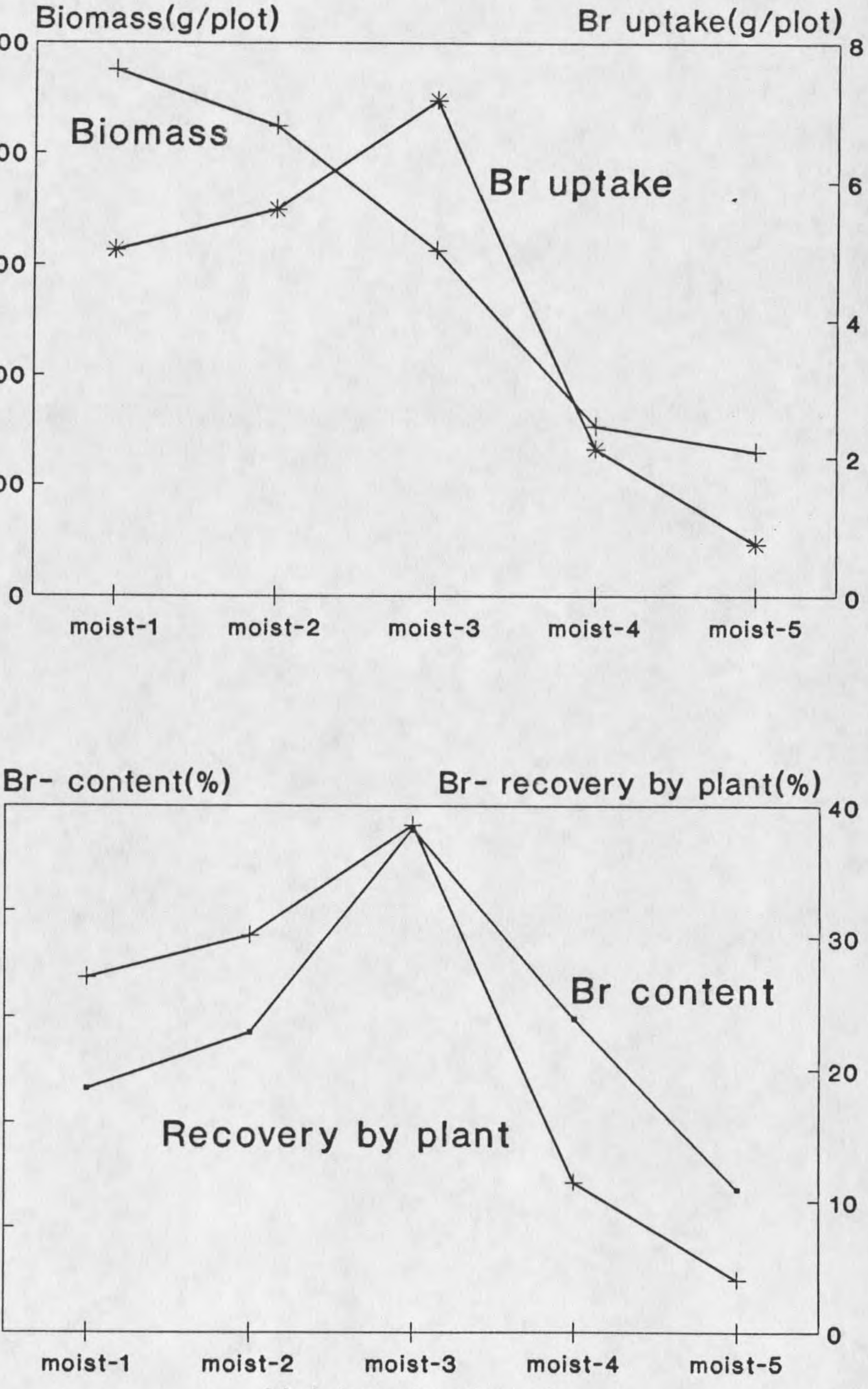

Fig. 21. Br content, uptake, and recovery by barley

The Resin Capsule Method and Plant Uptake. Br transport in soils mostly depends on water movement. Figure 22 shows the relationship between amounts of applied water and Br cumulative concentrations determined by resin capsules under cropping and fallow systems. Highly significant correlation was observed(r=0.9997, n=3) between amounts of applied water and Br cumulative concentrations with fallow. This correlation in the barley field was non-significant (r=0.8885, n=3), at 15 cm depth. However, with only three value to compare in these relationships, no definite conclusions can be made.

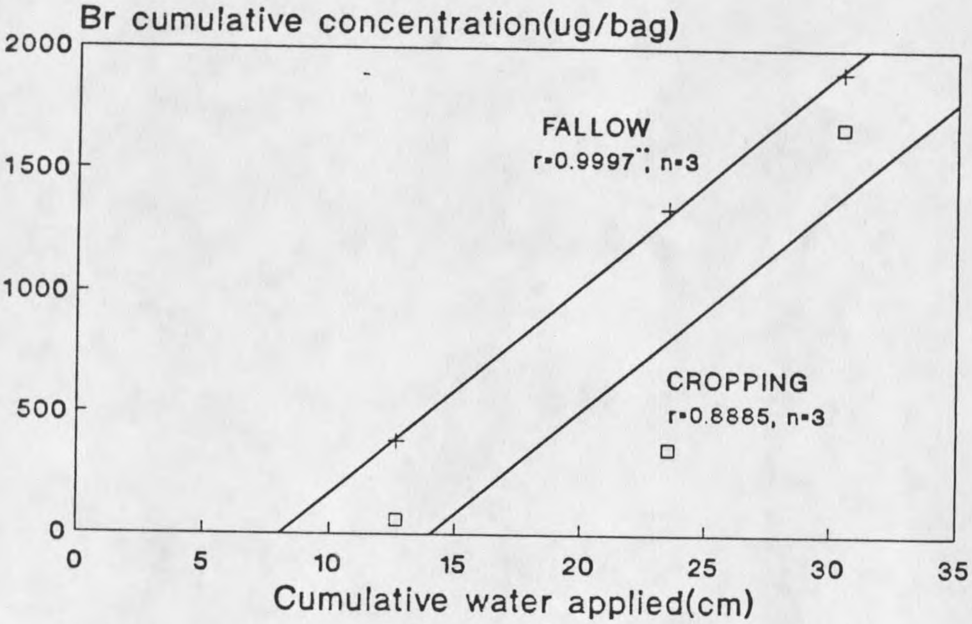

Fig. 22. Relationships between amounts of applied water and Br transport determined by the resin capsule method in the field

The relationship was even less clear at lower depths. Nevertheless, these results provide evidence that the resin capsule method is not only sensitive to the influence of amounts of applied water on Br movement, but it can also reflect the influence of plant Br uptake on Br transport in the soil.

Conclusions

The field experimental results demonstrated that the resin capsule method was effective for determining Br transport under varying water regimes and with or without a growing crop. Not only did the resin capsules show differences due to amount of applied water, but they also responded to the influence of plant Br and water uptake. In this study, barley took up between 27 and 38% of applied Br when enough water was applied to leach the Br into the root zone.

GENERAL SUMMARY

Results from this research provide evidence that the resin capsule methodology is simple, accurate, and economical for monitoring chemical transport in soils under laboratory and field conditions. Results indicate that it measures the time rate and quantity of chemical leaching. Resin capsules function through ion exchange mechanisms as mass flow and diffusion processes move ions to the surface of the resin capsule. Solute concentrations determined by the resin capsule method are cumulative quantities of a leaching chemical during a specific sampling time interval, providing the "resident concentration".

The mechanisms of ion extraction from soils by the resin capsule and vacuum extraction methods are totally different. Ion extraction by vacuum extraction is a mechanical separation of soil solution from soil solids by applying a suction force. Ion extraction by resin capsules is an ion exchange mechanism, with no mechanical force applied. Results of Br breakthrough curves in a laboratory column indicate the resin capsule method is equal to, or more accurate than the conventional vacuum extraction method for monitoring Br transport under continuous water flow.

At the upper layer of the soil profile, an applied suction force can greatly influence chemical transport velocity by pulling the solution down faster than that under natural drainage conditions. When water is removed by vacuum extraction at upper depths, this can reduce the amount and rate of water and solute movement recorded at lower depths. With the resin capsule method, no force is applied to the soil-water system, and therefore no extraneous effects are imposed on the system or its solute transport processes. Thus, results from the resin capsule method should better describe the natural processes of chemical transport in soils.

Bromide concentration-distance BTCs as determined by both methods were essentially the same under continuous water flow. These results suggest that the applied suction force affected only the time rate of chemical transport, and had no significant influence on Br distribution in the soil profile.

The Br recovery by resin capsule in this research ranged from 88% to 99% of applied Br under both continuous and simulated rainfall implying that the resin capsule method has good potential for monitoring quantatively Br transport in soils.

Under simulated rainfall conditions, Br BTCs as determined by the two methods were not the same. Distinct spikes of Br BTCs as determined by resin capsules indicated good response to soil moisture changes, whereas a plateau of Br BTCs as measured by vacuum extraction implied the lack of sensitivity to soil moisture changes. Applied suction apparently masked the actual Br concentrations by sucking soil solution from surrounding areas of lower water potential into the sampler during periods of soil moisture change. In contrast, the resin capsule method can more accurately trace Br transport by mass flow and diffusion processes. These results indicate that the resin capsule method is superior to vacuum extraction for prediction of Br transport under simulated rainfall.

The correlation between Br concentrations as determined by the resin capsule and vacuum extraction methods is highly significant(r=0.56, n=99). This suggests that either method can be used to predict Br transport in soils under these experimental conditions, even though the mechanisms of ion extraction are different. However, the relative accuracy and sensitivity of the two methods are different.

Bromide BTCs as determined by both the resin capsule and vacuum extraction methods were well described by an existing transport model. Results of calculating model parameters as estimated by CDM using the CXTfit program also suggested that applied suction may influence the water flow rate and pathway. This can result in shifting the peak of Br BTCs, especially at upper soil depths.

The resin capsule method was also shown to be effective for describing Br transport rates and patterns in the field under different water regimes. It was also sensitive to the effect of plant uptake on Br transport. Barley plant uptake accounted for up to 38% of applied Br in the field under these experimental conditions. Differences in the soil-water system created by growing plants and their root systems, and resultant influences on Br transport, were also measured by the resin capsule method.

From these results involving both laboratory column and field studies, it can be concluded that the resin capsule method is generally equal or superior to the vacuum extraction method for monitoring Br transport under conditions of unsaturated water flow. Furthermore, it appears to be more sensitive to changes in Br transport as induced by changing soil water conditions similar to those occurring with intermittent rainfall. These results, plus the ease, simplicity, speed, and cost aspects of the resin capsule method, provide the basis for an improved alternative approach to solute transport studies.

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APPENDIX

Table 9. Br data determined by vacuum extraction and resin capsule methods under continuous water flow

Time(days)	Vacuum extraction method(mg/L) depth(cm) 13	43	73	104	Resin capsule methed(ug/bag) depth(cm) 13	43	73	104
0.15					18.55			
0.35	4.07				22.63	6.02		
0.60	136.35	1.51			24.93	5.17		
1.10	504.10	7.18			45.33	4.02	2.69	
1.35	610.65	7.85			79.65	6.46	2.69	
1.60	711.84	8.57			234.39	5.58	3.33	
2.10	829.78	10.19			821.83	9.57	4.02	
2.60	300.23	10.19			1278.60	7.42	4.02	
3.10	200.49	12.60	0.00		2153.61	6.46	4.02	4.02
4.00	147.29	19.06	1.56		2738.88	33.05	5.58	4.77
5.00	82.42	62.76	1.03		2241.67	36.21	6.46	6.46
6.00	36.22	136.35	1.56		821.83	143.16	6.46	7.42
7.00	23.35	233.85	0.59		381.79	287.36	6.46	5.58
8.00	7.18	449.30	0.59		287.36	311.71	7.42	3.67
9.00	5.45	606.65	2.21		155.49	448.88	6.46	10.79
10.00	3.15	654.99	5.09		126.41	699.62	10.79	13.52
11.00	0.80	680.59	8.17		107.70	804.41	18.28	17.38
12.00	1.23	385.36	8.17		77.21	633.88	35.43	10.69
13.00	0.72	233.85	9.77		22.25	461.04	50.42	10.69
14.00		81.33	59.10	0.00	10.08	348.63	74.03	10.69
15.00		36.60	159.19	0.00	17.24	164.86	101.25	14.78
16.00		16.10	209.65	0.18	10.05	146.06	109.89	15.57
17.00		6.70	408.30	0.00	15.57	101.25	464.38	31.98
18.00		4.13	477.50	0.37	5.18	38.23	522.79	69.74
19.00		1.12	516.36	1.21	5.18	23.12	716.59	79.04
20.00		0.56	619.43	5.44	5.18	17.24	745.36	101.25
21.00		0.42	402.79	14.15	0.00	14.02	483.09	105.49
22.00		0.07	354.99	31.79		11.00	412.44	177.00
23.00		0.07	209.05	60.74		10.00	210.00	210.00
24.00		0.07	170.91	95.75		8.50	88.00	433.50
25.00			137.62	155.66			61.50	583.00
26.00			55.22	197.92			44.50	608.00
27.00			47.27	382.04			26.50	751.00
28.00			18.03	467.11			18.50	500.50
29.00			16.54	506.17			12.50	249.50
30.00			14.86	431.04			8.50	177.00
31.00			12.52	382.04			6.50	149.00
32.00			13.28	325.17			5.00	105.00
33.00			8.43	288.07				96.50
34.00			3.96	235.29				96.50
35.00			1.50	208.30				77.00
36.00				200.00				74.76
37.00				176.99				74.76
38.00				169.64				81.28
39.00				138.43				68.73
40.00				122.34				65.89
41.00				112.64				60.53
42.00				99.45				35.89
43.00				84.14				29.94
44.00				80.68				24.86
45.00				59.95				16.81

Table 9.(Continued)

Time(days)	Vacuum extraction method(mg/L)				Resin capsule methed(ug/bag)			
	depth(cm)				depth(cm)			
	13	43	73	104	13	43	73	104
46.00				48.31				
47.00				42.07				15.16
48.00				32.26				
49.00				29.48				13.63
50.00				23.40				
51.00				20.28				15.97
52.00				18.40				
53.00				16.66				15.16
54.00				10.92				
55.00				8.66				
56.00				5.88				
58.00				3.05				
60.00				1.44				
62.00				0.17				

Table 10. Cumulative water application as continuous water flow

Time(d)	cumulative water infiltration(cm)	Time(d)	cumulative water infiltration(cm)
0.00	0.00	27.00	44.80
0.15	3.40	28.00	46.10
0.35	4.60	29.00	47.40
0.60	5.60	30.00	48.20
1.10	6.80	31.00	48.90
1.35	7.10	32.00	49.50
1.60	7.70	33.00	49.80
2.10	8.50	34.00	50.10
2.60	9.80	35.00	50.40
3.10	10.80	36.00	50.70
4.00	12.70	37.00	60.00
5.00	14.00	38.00	60.30
6.00	15.30	39.00	60.60
7.00	16.60	40.00	60.90
8.00	17.70	41.00	61.20
9.00	18.80	42.00	61.50
10.00	19.90	43.00	61.80
11.00	21.40	44.00	62.10
12.00	22.70	45.00	62.40
13.00	24.70	46.00	62.70
14.00	26.20	47.00	63.00
15.00	27.90	48.00	63.30
16.00	29.50	49.00	63.60
17.00	31.00	50.00	63.90
18.00	32.60	51.00	64.20
19.00	33.90	52.00	64.50
20.00	35.20	53.00	64.80
21.00	36.60	54.00	65.10
22.00	37.80	55.00	65.40
23.00	39.00	56.00	65.70
24.00	40.10	58.00	66.30
25.00	41.50	60.00	66.90
26.00	43.00	62.00	67.60

Table 11. Br data determined by the vacuum extraction and resin capsule methods under simulated rainfall

	vacuum extraction(mg/L)			resin capsules(ug/bag)		
Time(days)	depth(cm)					
	13	43	73	13	43	73
0.25	2.67			8.94		
0.50	103.99	0.00		8.94	1.65	
1.00	494.05	1.81		10.07	1.91	
1.25	701.54	2.38		11.94	3.73	
2.00	852.42	2.38		14.04	5.21	
2.25	1360.48	2.03		63.86	5.21	
3.24	1414.53	2.03		264.27	6.93	
4.00	1360.48	2.03		478.05	6.93	
5.00	1649.22	2.88		559.51	10.07	
6.00	1604.86	9.29		362.75	10.67	
7.00	2120.83	3.20		228.77	11.10	
7.25	1747.09	2.26		187.02	8.75	
8.00	1679.68	2.26		818.45	8.75	
9.00	968.24	5.81		1079.58	7.71	
10.00	580.53	7.08		1480.84	11.10	
11.00	441.29	8.62		997.50	11.10	
12.00	348.07	8.62		645.29	11.10	
13.00	644.99	13.84		438.37	19.61	
14.00	671.04	19.77		580.02	26.22	
15.00	755.70	27.14		1142.02	26.22	
16.00	356.08	82.25	7.64	438.37	19.61	
17.00	137.64	188.95	6.72	344.60	63.92	12.93
18.00	55.35	328.97	6.72	270.66	97.42	12.93
19.00	34.42	451.60	8.53	180.51	188.01	19.61
20.00	41.22	694.95	8.96	143.94	199.76	18.89
21.00	38.06	752.51	6.52	103.34	571.14	18.89
22.00	38.06	955.41	6.02	62.21	431.08	11.04
23.00	35.15	752.51	6.52	43.88	352.41	12.37
24.00	23.61	955.41	6.52	83.79	467.20	12.37
25.00	15.86	1034.55	6.52	59.58	670.54	12.37
26.00	9.84	1262.27	10.93	35.07	1128.16	13.81
27.00	12.25	1905.07	8.43	36.38	789.09	15.60
28.00	11.51	1828.48	8.79	33.12	521.83	21.35
30.00	9.98	1754.98	8.43	20.29	893.11	24.80
31.00	9.98	1754.98	8.43	12.48	521.83	24.80
32.00	9.98	1754.98	8.43	8.67	390.30	24.80
33.00	9.98	1754.98	8.43	0.00	390.30	15.60
34.00	9.98	1754.98	8.43		304.04	15.60
35.00	8.47	1684.42	10.79		1348.72	15.60
36.00	8.47	1371.99	10.79		789.09	15.60
37.00	8.98	842.70	28.17		847.65	23.28
38.00	5.52	518.03	60.86		373.94	61.27
39.00	3.26	249.67	148.51		459.11	127.04
40.00	0.00	147.38	348.00		304.40	280.30
41.00		73.97	426.22		163.41	373.94
42.00		71.03	543.61		39.18	847.65

Table 11. (Continued)

Time(days)	vacuum extraction(mg/L)			resin capsules(ug/bag)		
	depth(cm)					
	43	73	104	43	73	104
43.00	62.90	639.34		39.18	519.14	
44.00	60.40	751.92		39.18	317.20	
45.00	60.40	884.32		37.43	247.62	
46.00	60.40	1083.08		35.74	201.26	
47.00	60.40	1174.57	5.30	28.26	498.32	28.26
48.00	31.57	1174.57	5.30	22.16	563.42	83.03
49.00	19.41	1174.57	5.30	9.26	254.12	8.68
51.00	12.94	1127.90	5.52	7.08	588.42	12.54
52.00	9.77	1302.08	6.87	6.12	893.03	48.67
53.00	0.00	1470.74	10.56		1721.67	195.37
54.00		1408.16	15.63		451.01	195.37
55.00		1343.97	20.56		882.34	355.52
56.00		1302.08	29.24		783.99	549.63
57.00		1070.54	35.57		528.33	571.79
58.00		850.29	41.60		528.33	618.78
59.00		755.82	66.56		328.36	369.92
60.00		646.23	110.73		328.36	469.22
61.00		345.36	151.47		180.27	783.99
62.00		224.12	227.17		416.66	1032.81
63.00		206.30	291.28		1074.26	203.37
64.00		106.32	389.28		300.83	1146.47
65.00		64.67	459.44		233.52	1245.94
67.00		52.57	520.25		44.41	1245.94
68.00		44.54	589.10		16.57	439.03
69.00		41.00	639.99		14.05	564.34
71.00		55.01	1033.98		9.86	856.59
72.00		37.97	1033.98		19.43	970.62
73.00		17.35	876.86		12.83	722.16
74.00		17.35	807.50		9.51	288.72
75.00		18.84	684.80		14.36	224.39
76.00		14.72	605.17		12.11	174.14
77.00		13.01	472.61		9.51	129.26
78.00		4.64	384.62		9.51	47.04
79.00		0.00	339.90			80.33
80.00		0.00	288.25			80.33
81.00		0.00	234.58			53.89
82.00		0.00	216.02			35.64
83.00		0.00	183.20			35.64
84.00		0.00	155.36			34.00
85.00		0.00	121.33			30.92
86.00			89.90			28.08
87.00			79.33			
88.00			48.11			
89.00			34.47			
90.00			29.18			

Table 12. Cumulative water application under simulated rainfall

Time(d)	cumulative water added(cm)	Time(d)	cumulative water added(cm)
0.008	1.50	47.083	33.10
0.010	1.90	47.167	33.80
0.021	2.50	47.250	34.40
0.042	3.20	47.938	35.20
0.125	4.00	48.229	35.50
0.292	4.80	49.229	37.00
0.396	5.30	50.229	38.30
7.010	5.60	51.229	39.90
7.017	5.80	51.983	41.20
7.083	6.30	57.003	41.50
7.125	6.80	57.010	41.80
7.271	7.30	57.024	42.10
7.438	7.80	57.063	42.50
8.000	8.60	57.104	42.80
8.271	9.10	57.167	43.10
10.104	10.40	57.333	43.70
15.010	10.70	57.417	44.00
15.017	10.90	57.875	44.80
15.045	11.10	58.917	46.30
15.125	11.80	59.917	47.80
15.208	12.20	60.833	49.10
15.500	13.10	61.792	50.10
16.000	13.90	62.392	51.10
16.917	15.10	69.003	51.50
17.292	15.50	69.010	51.80
24.003	15.70	69.031	52.40
24.008	15.90	69.042	52.60
24.015	16.10	69.083	53.00
24.035	16.40	69.125	53.40
24.083	16.90	69.167	53.60
24.125	17.20	69.250	53.90
24.208	17.50	69.458	54.20
24.417	18.70	70.000	54.80
25.083	19.20	70.292	55.20
26.042	20.00	71.292	56.50
26.958	20.70	73.375	59.50
35.003	21.10	74.458	60.30
35.010	21.50	75.417	61.10
35.024	21.90	83.003	61.50
35.052	22.30	83.010	62.00
35.083	22.70	83.024	62.50
35.125	23.20	83.062	63.10
35.208	23.60	83.146	63.50
35.583	24.40	83.271	64.00
36.000	25.30	83.479	64.40
37.042	27.30	83.938	64.90
38.083	28.80	84.271	65.40
39.300	30.90	85.271	66.80
47.003	31.30	86.271	68.10
47.007	31.70	87.313	69.60
47.014	31.90	88.313	70.40

Table 13. Water potential data determined by tensiometer under simulated rainfall

Time(d)	water potential(-mbar) depth(cm)			
	13	43	73	104
0.00	395.00	328.00	303.00	288.00
0.01	300.00	326.00	303.00	288.00
0.02	215.00	316.00	303.00	288.00
0.04	185.00	311.00	303.00	288.00
0.13	180.00	310.00	303.00	288.00
0.29	83.00	308.00	303.00	288.00
0.54	38.00	278.00	303.00	288.00
0.96	120.00	184.00	288.00	288.00
1.29	140.00	170.00	233.00	288.00
2.29	174.00	184.00	227.00	288.00
3.29	198.00	198.00	224.00	288.00
4.29	216.00	220.00	230.00	280.00
5.29	237.00	236.00	240.00	276.00
6.29	252.00	247.00	250.00	270.00
7.00	269.00	256.00	259.00	270.00
7.03	267.00	254.00	259.00	270.00
7.05	252.00	253.00	260.00	270.00
7.09	224.00	251.00	258.00	270.00
7.14	188.00	216.00	256.00	270.00
7.29	142.00	198.00	244.00	270.00
7.46	82.00	176.00	246.00	270.00
7.96	62.00	157.00	246.00	270.00
8.29	79.00	133.00	239.00	270.00
9.29	86.00	92.00	194.00	249.00
10.29	136.00	86.00	171.00	220.00
11.29	172.00	101.00	129.00	208.00
12.29	182.00	104.00	137.00	202.00
13.29	197.00	110.00	137.00	211.00
14.29	215.00	115.00	155.00	216.00
15.01	200.00	207.00	149.00	217.00
15.02	120.00	196.00	148.00	220.00
15.13	58.00	197.00	146.00	231.00
15.21	78.00	203.00	145.00	225.00
15.29	81.00	204.00	147.00	220.00
15.39	80.00	197.00	147.00	218.00
15.49	77.00	179.00	132.00	216.00
16.00	58.00	100.00	118.00	205.00
16.29	45.00	82.00	100.00	176.00
17.29	76.00	76.00	100.00	156.00
18.29	134.00	81.00	116.00	162.00
19.29	158.00	89.00	116.00	166.00
20.29	166.00	145.00	142.00	174.00
21.29	185.00	161.00	146.00	180.00
22.29	203.00	175.00	146.00	182.00
23.29	209.00	186.00	156.00	184.00
24.01	214.00	196.00	156.00	190.00
24.02	211.00	200.00	150.00	197.00
24.09	209.00	198.00	147.00	205.00

Table 13.(continued-2)

Time(d)	water potential(-mbar)			
	depth(cm)			
	13	43	73	104
24.13	206.00	190.00	145.00	186.00
24.23	181.00	157.00	140.00	183.00
24.29	157.00	132.00	140.00	180.00
24.50	106.00	87.00	135.00	175.00
24.58	56.00	41.00	129.00	168.00
25.04	50.00	45.00	117.00	156.00
25.23	78.00	53.00	95.00	130.00
26.29	107.00	85.00	90.00	119.00
27.29	125.00	108.00	106.00	125.00
28.29	138.00	145.00	108.00	133.00
29.29	144.00	161.00	114.00	149.00
30.29	148.00	172.00	121.00	154.00
31.29	155.00	183.00	131.00	159.00
32.29	175.00	195.00	133.00	162.00
33.29	226.00	206.00	136.00	169.00
33.99	235.00	205.00	146.00	178.00
34.01	233.00	196.00	156.00	182.00
34.04	232.00	194.00	144.00	190.00
34.08	229.00	190.00	142.00	198.00
34.12	224.00	185.00	143.00	208.00
34.20	190.00	185.00	141.00	197.00
34.29	130.00	170.00	141.00	190.00
34.36	86.00	164.00	141.00	185.00
34.57	2.00	115.00	139.00	184.00
34.99	0.00	57.00	123.00	166.00
35.29	0.00	34.00	93.00	134.00
36.33	0.00	16.00	58.00	84.00
37.40	0.00	10.00	48.00	61.00
38.33	6.00	19.00	30.00	40.00
39.33	86.00	59.00	47.00	46.00
40.29	108.00	107.00	77.00	72.00
41.29	143.00	113.00	85.00	73.00
42.29	159.00	136.00	98.00	87.00
43.29	167.00	141.00	100.00	90.00
44.29	172.00	150.00	105.00	107.00
45.29	182.00	150.00	127.00	126.00
46.08	195.00	172.00	138.00	136.00
46.15	193.00	159.00	137.00	145.00
46.23	182.00	157.00	135.00	156.00
46.33	138.00	130.00	132.00	149.00
46.50	92.00	100.00	115.00	125.00
47.02	2.00	30.00	65.00	86.00
47.29	0.00	18.00	56.00	79.00
48.29	0.00	8.00	32.00	41.00
49.29	0.00	6.00	25.00	24.00
50.29	4.00	17.00	21.00	18.00
51.29	67.00	66.00	62.00	46.00
52.29	105.00	92.00	76.00	57.00
53.29	110.00	99.00	96.00	82.00

Table 13.(continued-3)

Time(d)	water potential(-mbar) depth(cm) 13	43	73	104
54.29	121.00	138.00	115.00	103.00
55.29	182.00	155.00	120.00	124.00
56.00	192.00	157.00	115.00	110.00
56.13	68.00	155.00	116.00	108.00
56.17	21.00	149.00	108.00	110.00
56.20	19.00	131.00	107.00	109.00
56.40	9.00	84.00	98.00	102.00
56.50	2.00	60.00	86.00	93.00
56.95	2.00	34.00	60.00	64.00
57.30	0.00	26.00	38.00	42.00
57.93	0.00	8.00	24.00	23.00
58.29	0.00	15.00	20.00	17.00
59.45	0.00	19.00	23.00	18.00
60.37	0.00	16.00	21.00	20.00
61.29	0.00	17.00	19.00	15.00
62.29	3.00	17.00	16.00	17.00
63.29	36.00	50.00	39.00	28.00
64.29	58.00	70.00	84.00	69.00
65.29	76.00	123.00	106.00	89.00
66.29	80.00	136.00	114.00	98.00
68.00	107.00	157.00	132.00	107.00
68.03	64.00	149.00	129.00	108.00
68.10	55.00	151.00	127.00	108.00
68.12	52.00	122.00	127.00	109.00
68.20	46.00	112.00	123.00	108.00
68.29	36.00	94.00	116.00	103.00
68.45	9.00	58.00	88.00	78.00
69.00	3.00	27.00	40.00	37.00
69.29	3.00	25.00	35.00	36.00
70.29	3.00	15.00	23.00	19.00
72.37	7.00	17.00	21.00	16.00
73.29	11.00	23.00	22.00	14.00
74.29	12.00	22.00	24.00	16.00
75.29	59.00	47.00	38.00	24.00
76.29	117.00	93.00	75.00	63.00
77.29	153.00	130.00	110.00	93.00
78.29	171.00	147.00	125.00	110.00
79.29	180.00	159.00	137.00	119.00
81.29	195.00	170.00	146.00	131.00
82.29	207.00	183.00	160.00	146.00
83.00	216.00	190.00	170.00	150.00
83.04	214.00	186.00	175.00	155.00
83.08	211.00	183.00	165.00	155.00
83.15	200.00	184.00	158.00	151.00
83.29	160.00	161.00	155.00	152.00
83.59	86.00	91.00	140.00	145.00
84.00	5.00	58.00	90.00	110.00
84.29	3.00	47.00	69.00	89.00
85.29	3.00	29.00	37.00	43.00

Table 13.(continued-4)

Time(d)	water potential(-mbar) depth(cm) 13	43	73	104
86.29	10.00	26.00	32.00	35.00
87.29	17.00	27.00	24.00	26.00
88.29	24.00	33.00	32.00	26.00
89.29	36.00	43.00	38.00	35.00
90.29	119.00	95.00	76.00	60.00
91.29	150.00	128.00	103.00	95.00
92.29	164.00	142.00	108.00	100.00
93.29	177.00	149.00	125.00	106.00
95.29	192.00	158.00	129.00	107.00

Table 14. Data used for calculating correlation coefficients between br concentrations and water potientials under simulated rainfall

Water potential (X0.1 MPa)	Resin-Br ug/bag	Vacuum-Br mg/L	Water potential (X0.1 MPa)	Resin-Br ug/bag	Vacuum-Br mg/L
-39.50	10.07		-11.30	459.11	842.70
-30.00	11.94		-13.60	304.40	518.03
-18.50	14.04		-14.10	163.41	249.67
-18.50	63.86	103.99	-15.00	39.18	147.38
-18.00	264.27	494.05	-15.00	39.18	73.97
-8.30	478.05	701.54	-15.60	61.27	60.86
-3.80	559.51	852.42	-14.30	127.04	148.51
-14.00	362.75	1360.48	-14.10	280.30	348.00
-19.80	228.77	1414.53	-12.30	373.94	426.22
-23.70	187.02	1360.48	-3.00	847.65	543.61
-18.80	818.45	1649.22	-7.70	519.14	639.34
-8.20	1079.58	1604.86	-10.00	317.20	751.92
-6.20	1480.84	2120.83	-10.50	247.62	884.32
-8.60	997.50	1747.09	-12.70	201.26	1083.08
-13.60	645.29	1679.68	-11.50	498.32	1174.57
-19.60	438.37	968.24	-6.50	563.42	1174.57
-12.00	580.02	580.53	-5.60	588.42	1127.90
-4.50	1142.02	441.29	-3.20	893.03	1302.08
-13.40	438.37	348.07	-2.10	1721.67	1470.74
-15.80	344.60	644.99	-9.60	451.01	1408.16
-16.60	270.66	671.04	-6.20	882.34	1343.97
-18.50	180.51	755.70	-11.50	783.99	1302.08
-20.30	143.94	356.08	-12.00	528.33	1070.54
-20.90	103.34	137.64	-11.50	526.33	850.29
-21.10	43.88	34.42	-10.80	328.36	646.23
-20.70	19.61	8.62	-10.70	180.27	345.36
-19.60	26.22	8.62	-8.60	416.66	224.12
-19.60	26.22	13.84	-1.60	1074.26	206.30
-20.30	19.61	19.77	-10.60	300.83	106.32
-20.40	63.92	27.14	-11.40	233.52	64.67
-19.70	97.42	82.25	-12.90	44.41	52.57
-17.90	188.01	188.95	-12.70	16.57	44.54
-10.00	199.76	328.97	-12.70	14.05	41.00
-7.60	571.14	451.60	-15.60	48.67	29.24
-16.10	431.08	694.95	-14.90	195.37	35.57
-20.00	352.41	752.51	-12.50	355.52	41.60
-15.70	467.20	955.41	-8.60	549.63	66.56
-13.20	670.54	752.51	-7.90	571.79	110.73
-4.10	1128.16	955.41	-2.40	618.78	151.47
-4.50	789.09	1034.55	-6.20	369.92	227.17
-10.00	521.83	1262.27	-7.60	469.22	191.28
-5.30	893.11	1905.07	-4.20	783.99	389.28
-10.80	521.83	1828.48	-1.70	1032.81	450.25
-19.50	390.30	1754.98	-2.00	1146.47	639.99
-20.60	390.30	1754.98	-1.50	1245.94	1033.98
-19.60	304.04	1754.98	-1.70	1245.94	1033.98
-1.00	1348.72	1754.98	-8.90	439.03	876.86
-1.90	789.09	1754.98	-9.80	564.34	807.50
-5.90	847.65	1684.42	-4.00	856.59	684.80
-10.70	373.94	1371.99	-2.10	970.62	605.17

Table 15. Br- relative concentrations(C/Cmax) as determined by the resin capsule method and as predicted by the CXTfit program under continuous water flow

Time(day)	resin capsule method Observed 13cm	 43cm	 104cm	 Predicted 13cm	 43cm	 104cm
0.00						
0.15	0.0000			0.0000		
0.35	0.0100			0.0000		
0.60	0.0100			0.0000		
1.10	0.0100			0.0000		
1.35	0.0100			0.0000		
1.60	0.0100			0.0000		
2.10	0.0200			0.0000		
2.60	0.0200			0.0000		
3.10	0.0200			0.0000		
4	0.0500			0.0011		
5	0.0500	0.0000		0.0192	0.0000	
6	0.1800	0.0100	0.0000	0.0987	0.0000	0.0000
7	0.3600	0.0100	0.0100	0.2623	0.0000	0.0000
8	0.3900	0.0200	0.0100	0.4704	0.0000	0.0000
9	0.5600	0.0100	0.0200	0.6631	0.0000	0.0000
10	0.8700	0.0200	0.0200	0.8010	0.0000	0.0000
11	1.0000	0.0300	0.0300	0.8494	0.0000	0.0000
12	0.7900	0.0500	0.0200	0.7784	0.0008	0.0000
13	0.5800	0.0700	0.0200	0.6116	0.0083	0.0000
14	0.4400	0.1000	0.0200	0.4177	0.0452	0.0000
15	0.2100	0.1300	0.0200	0.2536	0.1490	0.0000
16	0.1900	0.1400	0.0300	0.1399	0.3332	0.0000
17	0.1300	0.5800	0.0500	0.0715	0.5560	0.0003
18	0.0500	0.6500	0.0900	0.0344	0.7493	0.0023
19	0.0300	0.8900	0.1000	0.0157	0.8627	0.0119
20	0.0300	0.9300	0.1300	0.0069	0.8666	0.0434
21	0.0200	0.6000	0.1400	0.0029	0.7514	0.1166
22	0.0200	0.5200	0.2200	0.0012	0.5510	0.2429
23	0.0200	0.2700	0.2700	0.0005	0.3377	0.4107
24	0.0100	0.1100	0.5400	0.0005	0.1733	0.5853
25	0.0000	0.0800	0.7300	0.0005	0.0752	0.7229
26		0.0600	0.7600		0.0279	0.7866
27		0.0400	0.9300		0.0090	0.7579
28		0.0300	0.6200		0.0026	0.6458
29		0.0200	0.3100		0.0007	0.4856
30		0.0200	0.2200		0.0002	0.3223
31		0.0100	0.1900		0.0000	0.1893
32		0.0100	0.1400		0.0000	0.0990
33		0.0000	0.1300		0.0000	0.0464
34			0.1300			0.0196
35			0.1000			0.0064
36			0.1000			0.0027
37			0.1000			0.0009
38			0.1100			0.0003
39			0.0900			0.0001
40			0.0900			0.0000
41			0.0800			0.0000

Table 16.Br- relative concentrations(C/Cmax) as determined by vacuum extraction method and as predicted by the CXTfit program under continuous water flow

	vacuum extraction method					
Time(day)	Observed			Predicted		
	13cm	43cm	104cm	13cm	43cm	104cm
1.10	0.0100			0.0000		
1.35	0.0100			0.0000		
1.60	0.0100			0.0000		
2.10	0.0100			0.0000		
2.60	0.0100			0.0000		
3.10	0.0200			0.0000		
4.0000	0.0300			0.0009		
5.0000	0.0900			0.0291		
6.0000	0.2000			0.1798		
7.0000	0.3400			0.4622		
8.0000	0.6600			0.7310		
9.0000	0.8900	0.0000		0.8934	0.0000	
10.0000	0.9600	0.0100		0.9581	0.0000	
11.0000	1.0000	0.0100		0.9065	0.0001	
12.0000	0.5700	0.0100		0.6852	0.0011	
13.0000	0.3400	0.0100		0.3922	0.0000	
14.0000	0.1200	0.0900		0.1737	0.0472	
15.0000	0.0500	0.2300		0.0624	0.1448	
16.0000	0.0200	0.3100		0.0190	0.3136	
17.0000	0.0100	0.6000		0.0051	0.5206	
18.0000	0.0100	0.7000		0.0012	0.7085	
19.0000	0.0000	0.7600	0.0000	0.0003	0.8279	0.0017
20.0000		0.9100	0.0100		0.8458	0.0060
21.0000		0.9500	0.0200		0.7519	0.0168
22.0000		0.5200	0.0500		0.5747	0.0396
23.0000		0.3100	0.0900		0.3754	0.0800
24.0000		0.2500	0.1400		0.2102	0.1420
25.0000		0.2000	0.2300		0.1017	0.2246
26.0000		0.0800	0.2900		0.0430	0.3208
27.0000		0.0700	0.5600		0.0161	0.4181
28.0000		0.0300	0.6900		0.0054	0.5009
29.0000		0.0200	0.7400		0.0016	0.5551
30.0000		0.0200	0.6300		0.0005	0.5721
31.0000		0.0200	0.5600		0.0001	0.5508
32.0000		0.0200	0.4800		0.0000	0.4976
33.0000		0.0100	0.4200		0.0000	0.4235
34.0000		0.0100	0.3500		0.0000	0.3408
35.0000		0.0000	0.3100		0.0000	0.2604
36.0000			0.2900			0.1896
37.0000			0.2600			0.1319
38.0000			0.2500			0.0880
39.0000			0.2000			0.0565
40.0000			0.1800			0.0350
41.0000			0.1700			0.0209
42.0000			0.1500			0.0121
43.0000			0.1200			0.0068
44.0000			0.1200			0.0038
45.0000			0.0900			0.0020