An Evaluation of Several Fluorinated Benzoic Acids for Use as Soil and Groundwater Tracers

by

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Abstract

In groundwater investigations involving multiple sources of water, or in cases where measurements are repeated over time, several unique tracers which can be used simultaneously are required. A group of fluorinated benzoic acid derivatives has previously been shown to be effective as soil and groundwater tracers. In this study, four related fluorobenzoates were examined in an attempt to enlarge the suite of proven tracers. The organic anions being evaluated were 2,3-difluorobenzoic acid (2,3-DFBA), 2,5-difluorobenzoic acid (2,5-DFBA), 3,4-difluorobenzoic acid (3,4-DFBA) and 3,5-difluorobenzoic acid (3-5 DFBA).

A high pressure liquid chromatography (HPLC) separation was developed for simultaneous detection of the four anions being evaluated, as well as bromide anion which was used as a standard against which the others were measured. The acid dissociation constants for these compounds were also determined. The laboratory phase of this evaluation consisted of batch studies to measure these compounds' resistance to degradation and affinity for sorption on soil surfaces. Column studies were conducted to measure the mobility and stability of the compounds during flow through porous media under ponded and trickle flow conditions. The field evaluations consisted of aquifer and vadose zone tracer tests designed to measure the behavior of the fluoro-organic compounds versus bromide under field conditions.

The batch studies using a low organic content eolian sand and a high organic content silty clay loam showed no loss of concentration of any of the fluoro-organics over an 85-day period. Both ponded and trickle irrigation columns indicated statistically identical mobility and stability characteristics of the fluoro-organics' compared to bromide. A field aquifer tracer test indicated similar mass recoveries of the four fluoro-organics' over a 3-month time span. A vadose zone tracer test using trickle irrigation indicated no loss of mass and similar mobility characteristics for the four fluoro-organics' compared to that of bromide over the three week duration of the test. It was the conclusion of this evaluation that these four fluoro-organics are suitable for use as soil and groundwater tracers in environments similar to those examined.

TABLE OF CONTENTS

I. INTRODUCTION.

II. MATERIALS AND METHODS

III. RESULTS AND DISCUSSION

IV. SUMMARY AND CONCLUSIONS

VI. APPENDICES

LIST OF TABLES

LIST OF FIGURES

ACKNOWLEDGEMENTS

To Laurie, whose love and support have made this project possible.

INTRODUCTION

1.1 Introduction

In every investigation of any hydrologic system, the collection of accurate data about the system is of upmost importance. This is often very difficult to do, however, due to the inaccessability of the subsurface environment and the large size of the system. Methods which can provide reliable information about a hydrologic system's characteristics will be useful to individuals responsible for making decisions affecting the system under study, and its surrounding environment.

Properly conducted tracer tests can be powerful tools in investigations of hydrologic systems, whether these systems are very small laboratory column studies or aquifers of regional size. These tests can determine an aquifer's flow direction, solute and water velocity, and even the age of the water present in the system. These tests can also aid in determining the porosity, hydraulic conductivity and dispersive characteristics of media present in the system.

Tracer tests can also be used to gain information about the behavior of fluids in the vadose zone, which is vital information in many contamination problems, since in many cases the pollutants must move through the vadose zone before they reach the groundwater. This information is also useful in agricultural settings, where it can be used to determine irrigation schedules or to predict the fate of pesticides in the soil.

Tracer tests can also be conducted in surface waters to aid in determining source areas for contaminants or to determine if a hydrologic connection exists between surface and subsurface systems.

As well as providing data about the physical characteristics of a site under study, water tracers can be utilized as monitoring tools. When placed in waters meant to be contained, such as holding ponds or pipelines, tracers present in samples collected from monitoring devices can alert investigators to leaks which may have potential for contaminating the surrounding environment.

The tracer method has been defined by Sheppard (l962) as: " a technique for observing a population of specific things such as molecules, living creatures, or other entities by labeling. Observation of the labeled and nonlabeled elements as they mingle yields information about the population as a whole".

For the purposes of this study the "specific thing" mentioned above is water moving through the subsurface and the label is some compound added to the water. This label may be tritiated water, other radioactive isotopes, dyes, anions or anything else that might give accurate data about the movement of the groundwater and the properties of the media through which it moves.

There is no ideal tracer, because for the tracer to act exactly as the water does it would have to be exactly identical to the water, and therefore would be indistinguishable from it. However, the concept of an ideal tracer is useful in that it supplies us with criteria to apply when selecting and evaluating compounds to be used as soil or groundwater tracers.

For a compound to act as a near-ideal tracer it must have certain properties:

- the natural, or background concentrations of the compound must not be so high as to make separation between material added and material already present difficult;
- it should be detectable in small amounts with equipment of reasonable cost and sophistication;

-it should be of reasonable cost and availability;

-it should not alter the physical characteristics of the media through which it moves, nor the fluid in which it is placed;

-it must not sorb to the media through which it moves;

-it must not be susceptible to chemical or biological transformations;

-it must (on average) obey the same laws of motion that the fluid particles do;

- it should be nontoxic; (Gaspar, 1987; Davis, et al 1985).

Much work has been done over the years identifying materials which will be effective soil or groundwater tracers. There are many compounds used as groundwater tracers, with different compounds filling different requirements in specific hydrologic investigations. These materials can be roughly divided into two groups, natural and artificial tracers.

Natural tracers are compounds which are already present in the system under study. These include stable isotopes such as ^{13}C or ^{18}O (Table 1) or radioactive isotopes such as ^{3}H or ^{14}C (Table 2). .Isotopes in the environment make tracing water movement over regional or continental scales possible, as well as determining the age of some waters.

Artificial tracers are compounds added to the ground or soil water system for the specific purpose of monitoring its behavior. They are generally used for site specific investigations over relatively small areas and time scales. The most common of these tracers are anions such as chloride (Cl^-) or bromide (Br^-). A list of ions used as tracers is given in Table 3. Anions are generally more acceptable than cations because there is generally less interference of

Table 1. Stable isotopes used as groundwater tracers.

Isotope	method of use	comments
^{2}H ^{1}H	ratio	Difference in mass causes fractionation when evaporation or condensation occur. Can be used to measure recharge.
^{16}O, ^{18}O	ratio	Used to trace large scale movements of water and to locate areas of recharge
^{14}N, ^{15}N	ratio	Used to determine origin of high nitrate levels in water
^{32}S, ^{24}S, ^{36}S	ratio	Can be used to indicate origin of sulfate between naturally dissolved gypsum and industrial sulfuric acid.

From Davis et al.(1985); Gaspar (1987).

Table 2. Radioactive isotopes used as groundwater tracers.

Radionuclide	Radiation Emitted	Half-life y=year,d=day,h=hour	Chemical Form
^{3}H	*B^-*	12.3y	H_2O
^{14}C	*B^-*	5730y	CO, CO_2
^{36}Cl	*B^-*	$3.1x10^5$y	Cl^-
^{39}Ar	*B^-*	269y	Ar (Gas)
^{32}P	*B^-*	14.3d	$Na_{-2}HPO_4$
^{51}Cr	*G*	27.8d	EDTA-Cr
^{60}Co	*B^-,G*	5.25y	EDTA-Co and $K_3Co(CN_6)$
^{82}Br	*B^-,G*	35.4h	Various Br compounds
^{85}Kr	*B^-,G*	10.7y	Kr (gas)
^{131}I	*B^-,G*	8.1d	Various I compounds

From Davis et al. (I985); Gaspar (I987). *B^-* = Beta radiation, *G* = Gamma radiation
h = hour, d = day, y = year

Table 3. Ionic Compounds used as soil and groundwater tracers.

Ion	Natural background levels (ppm)	Detection methods*	Detection limits (ppm)
Li^+	0.05 to 0.3	AA	0.5
K^+	0.2 to 10	AA	0.1
Mn^{2+}		AA	0.2
Mg^{2+}	2 to 40	AA	0.1
Cl^-	1-10,000	EC, ISP, CT, HPLC	0.05
NH_4^+	<5	Sp	0.1
Br^-	< 1	EC, ISP, HPLC	2.4×10^{-9}
I^-	<0.01	HPLC	3.1×10^{-9}

* AA = atomic absorption spectrometry; Sp= spectrophotometry; HPLC = high performance liquid chromatography; EC= electrical conductivity; ISP=ion specific probe; CT= chemical titration.

From Gaspar (I987); Davis et al. (I985).

compound movement from such phenomena as ion exchange. Dyes, which are often used in surface water studies, are generally unacceptable as groundwater tracers because of their high levels of sorption to soil particles. They may be useful, however, if the purpose of the tracer test is to mark flow paths through the shallow subsurface, which can then be examined by excavations.

Excellent summaries of water tracer history and methodology are given by Davis, et al (l985) and Gaspar (l987).

1.2 Past Work

An evaluation by Bowman (l984a) of pentafluorobenzoic acid (PFBA), meta-trifluoromethylbenzoic acid (*m*-TFMBA), ortho-trifluoromethylbenzoic acid (*o*-TFMBA), and 2,6-difluorobenzoic acid (2,6-DFBA) indicated that these four compounds can function effectively as soil or groundwater tracers. Some information on these fluoro-organic compounds is given in Table 4.

These four organic anions evaluated by Bowman are stable, nonsorbing to soils and are not present naturally in the environment. Their presence can be detected in samples down to part-per-billion levels, using trace enrichment techniques (Stetzenbach, et al l982). These compounds are particularly useful because analytical techniques exist which are capable of detecting and quantifying them simultaneously, in addition to the common tracer anions chloride and bromide (Bowman, l984b).

The fluorobenzoates listed in Table 4 have been used in hydrologic investigations around the United States and Europe. If they continue to function effectively, their use should increase and they will become an important suite of tracer compounds.

The Department of Energy's Waste Isolation Pilot Plant (WIPP) near Carlsbad, New Mexico, is designed to store and isolate low level radiaoctive waste in evaporite formations until such time as the waste is harmless. Detailed understanding of the region's hydrologic properties is essential if the waste storage system is to be properly sited and designed. In an effort to describe the solute transport properties of the host rock, *o*-TFMBA, *m*-TFMBA and PFBA were utilized in convergent flow and two-well recirculating tracer tests. The difficulty of conducting tracer tests in an extreme geochemical environment such as an evaporite sequence, which is naturally very high in ion

Table 4. Data on fluoro-organic compounds used as soil and groundwater tracers.

Compound	Separation Method	Detection Limits (ng)	pKa	Aqueous Diffusion Coefficient ($m^2s^{-1}x10^{10}$)
m-TFMBA	HPLC	1.2	3.79	7.4
o-TFMBA	HPLC	1.7	3.8	7.3
PFBA	HPLC	2.5	1.49	7.2
2,6-DFBA	HPLC	2.1	3.5	7.6

From Bowman (l984a,b); Walter (l982).

concentrations, is overcome somewhat by using the exotic fluoro-organic compounds, (WIPP Hydrology Program, l985).

The Swiss National Program for Radioactive Waste is using *m*-TFMBA as a groundwater tracer in a project designed to evaluate the suitability of certain crystalline rocks for use as a radioactive waste repository. (Chapman, l987).

A study by Los Alamos National Laboratory in Los Alamos, New Mexico, utilized *m*-TFMBA and PFBA to evaluate the importance of molecular diffusion as a mechanism for transporting dissolved substances from pores and fractures where convective transport dominates into a rock or soil matrix of much lower permeability (Walter, l982). This study indicated that matrix diffusion may be the dominant transport phenomena in tuffaceous rocks, and the fluoro-organic compounds aided in that determination.

A large-scale field study was conducted using the fluoro-organic PFBA to measure the importance of preferential flow patterns on the leaching of the herbicide bromacil through the vadose zone (Bowman & Rice, l986a). This study, conducted near Phoenix, Arizona, indicated that preferential flow produced leaching rates greater than that expected for the herbicide, which may influence decisions made concerning the potential for groundwater contamination from agricultural chemicals.

Bowman and Rice (l986b) also used *m*-TFMBA, *o*-TFMBA, 2,6-DFBA and PFBA to evaluate subsurface water movement under intermittent flood irrigation conditions. This study, also conducted near Phoenix, Arizona, was an attempt to help determine the effects that surface water management decisions have on the amount and quality of groundwater recharge in an agricultural environment. These researchers noted that both *m*-TFMBA and *o*-TFMBA showed evidence of degradation over the 10 month time span of this experiment.

The Illinois Geological Survey is utilizing PFBA, *o*-TFMBA and *m*-TFMBA to study flow through a compacted clay liner used to seal the bottom of storage ponds. Samples of water moving through the system are collected and analysed for the fluorinated benzoic acids to monitor the movement of the wetting front through the pond seal. (I.V. Krapac, personal communication, 1988).

Both *m*-TFMBA and PFBA were used to aid in modeling unsaturated flow through copper leach heaps. (Terrauds, 1985). Terrauds found that channeling was the major mechanism of leachate flow through the copper mill tailings, and her work at the New Mexico Institute of Mining and Technology (NMIMT), in Socorro, NM indicated that these two fluoro-organics were effective in monitoring that flow.

Researchers at NMIMT are currently using *m*-TFMBA, *o*-TFMBA, 2,6-DFBA and PFBA as soil water tracers. The compounds were placed in the soil near the surface and used to determine how the presence of vegetation affected the movement of water through the upper vadose zone in an arid environment. This experiment is being conducted at NMIMT's Desert Research Station, approximately 32 kilometers north of Socorro, New Mexico. (Stein, 1989).

In a separate study at NMIMT, researchers are using these four compounds, in addition to others, to monitor vertical and horizontal flow of applied water through the vadose zone. This field station is located on the west edge of the NMIMIT campus. (D.P. Grabka, personnal communication, 1989).

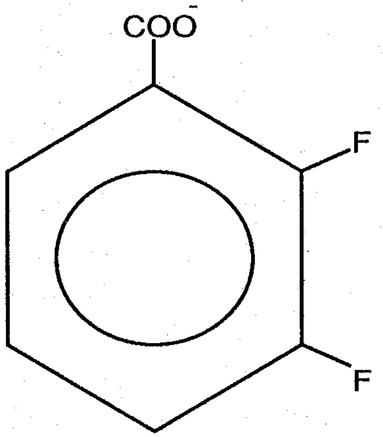
1.3 Research Objectives

The purpose of this study was to evaluate several more fluorinated benzoic acids for possible use as soil and groundwater tracers in both laboratory and field settings. It is felt that having more compounds available for use by investigators will allow them to conduct more sophisticated tracer tests utilizing many compounds simultaneously. A review of product catalogs from the Aldrich Chemical Company (Milwaukee, WI) and PCR Chemicals (Gainesville, Fl) was conducted to identify the fluoro-organic compounds which were available. The compounds selected for evaluation were 2,3-difluorobenzoic acid (2,3-DFBA), 2,5-difluorobenzoic acid, (2,5-DFBA), 3,4-difluorobenzoic acid (3,4-DFBA) and 3,5-difluorobenzic acid (3,5-DFBA). These compounds were purchased from the Aldrich Chemical Company. Their purity levels were all 98%, except for 3,5-DFBA which had a purity level of 97%. The structures of these compounds are shown in their ionized form in Figure 1. These four were selected for study because of their similarity to the fluoro-organics already used as soil or groundwater tracers, their reasonable cost and availability, and their lack of known toxological hazards.

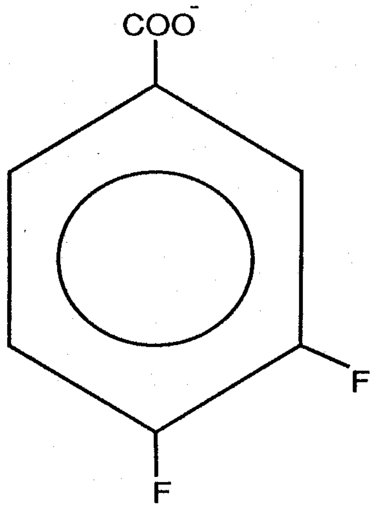
The objectives of this study were:

- to develop a liquid chromatographic separation technique which would allow for the simultaneous quantitation of the four fluoro-organics and bromide while limiting interference from anions common in natural waters.
- to evaluate the four fluoro-organics' affinity for sorption to soil surfaces.

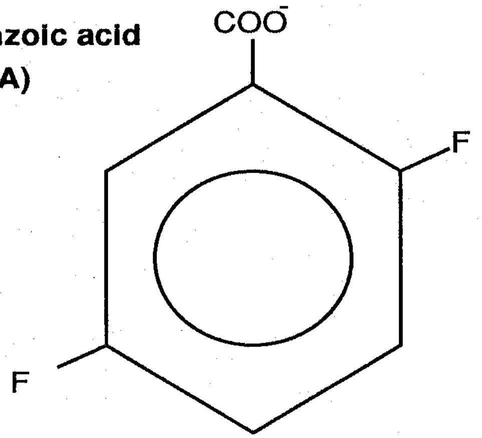
2,3-Difluorobenzoic acid
(2,3-DFBA)



3,4-Difluorobenzoic acid
(3,4-DFBA)



2,5-Difluorobenzoic acid
(2,5-DFBA)



3,5-Difluorobenzoic acid
(3,5-DFBA)

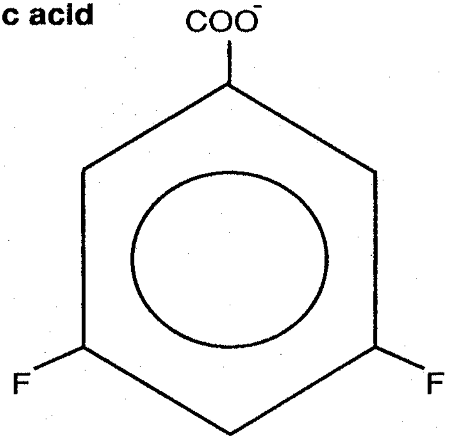


Figure 1. Structures of the four fluoro-organics evaluated in this study.

- to evaluate their chemical and biological stability in saturated and unsaturated subsurface environments.
- to evaluate their mobility through saturated and unsaturated subsurface environments relative to the mobility of bromide.

This evaluation consisted of batch studies, saturated and unsaturated laboratory column studies, and field tracer tests in aquifer and vadose zone environments. Bromide ion was used as a standard against which the four fluoro-organics were evaluated. Bromide is a widely used soil and groundwater tracer and has shown itself to be effective in a wide range of laboratory and field environments (Malcolm, et al, 1980). In all cases, behavior identical to bromide was considered acceptable behavior for a soil or groundwater tracer. All tests were conducted using the four fluoro-organics and bromide simultaneously.

In all experiments conducted throughout this study, the emphasis was on evaluating the four fluoro-organics' behavior compared to that of bromide under the same physical conditions. Less attention was paid to using the tracers to determine specific physical parameters of each system used in this evaluation.

MATERIALS AND METHODS

2.1 Chromatography

The first requirement in evaluating the four fluoro-organics for use as soil and groundwater tracers was to have an analytical technique which could accurately quantify them, along with bromide, at a reasonable cost.

High performance liquid chromatography (HPLC) was the analytical method chosen for this evaluation. The HPLC instrumentation used consisted of a Waters' Model 501 pump, a Model U6K injector, a Model 481 variable wavelength ultra-violet spectrophotometer, and a Model 745 Data Module. The analytical column was a Spherisorb Strong Anion Exchange (SAX) 5 micron cartridge type, 250 X 4.6 mm (Alltech Associates, Deerfield, IL). The Spherisorb column packing utilized quaternary ammonium functional groups as its exchanger, and the 5 micron term refers to the size of the packing used in the column. Prepacked stainless steel Spherisorb and Rex-Chrom separation columns were also used (Regis Chemical Company, Morton Grove, IL). The injection syringes used were Hamilton 800 series glass syringes, with injection volumes of 10, 25 and 100 micro-liters (*ul*). A schematic diagram of an HPLC system is shown in Figure 2.

A modification of the mobile phase described by Bowman (l984b) was used in this evaluation. A separation of the four fluoro-organics and bromide was achieved using a mobile phase chemistry of 0.03M potassium di-hydrogen phosphate (KH_2PO_4) buffer, pH adjusted to 2.85 with orthophosphoric acid, with 20% acetonitrile as an organic modifier. The flow rate of the mobile phase through the system was 1.0 ml/minute. Detector wavelength was 205 nanometers. This wavelength was selected to maximize the response of the

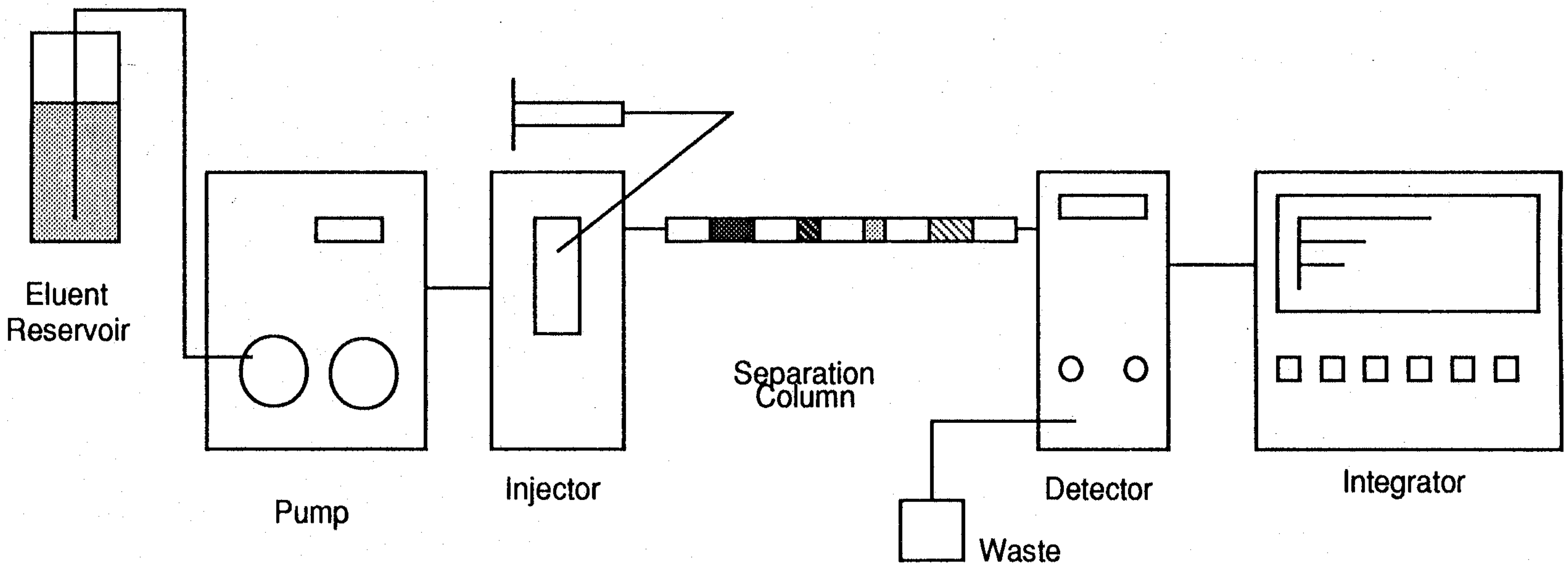


Figure 2. High Pressure Liquid Chromatography system.

four fluoro-organics and bromide while minimizing the response of anions common in water such as chloride and nitrate. This is discussed at greater length in the Results and Discussion section.

2.2 Acid Dissociation Constants

The acid dissociation constants for 2,3-DFBA, 2,5-DFBA, 3,4-DFBA and 3,5-DFBA were determined using a base titration method described in Nelson & Kemp (l981). Acid dissociation constants for *m*-TFMBA, *o*-TFMBA, 2,6-DFBA and PFBA were also measured, in order to compare the results from this procedure with previously reported values.

For this procedure 25 ml of a 0.01M fluoro-organic solution was placed in a 250 ml beaker and the pH of this solution was measured. A solution of 0.01M sodium hydroxide (NaOH) was titrated into the fluoro-organic solution 0.5ml at a time. The pH of the fluoro-organic solution was measured after each addition of base, and this information was recorded. This titration was continued until the pH of the fluoro-organic solution did not change with the additon of base. This experiment was conducted at room temperature, approximately 24 degrees Celcius, and it was repeated twice for each compound. The pH changes for each addition of base were then plotted versus the amount of NaOH added as a titration curve for each acid.

For a weak acid, such as all the fluoro-organic compounds evaluated here, the expression for the dissociation constant for the acid is pH = pKa - log[HA/A$^-$], where A$^-$ is the deprotonated acid. When the weak acid is titrated with a base, there is a point in the titration when the number of equivalents of base is half the number of equivalents of acid present. This is the point in the titration when 50% of the acid is protonated and 50% is anionic. At this point the ratio of of HA/A$^-$ is 1 and the pH of the solution equals the pKa of the acid. This point is identified as the1/2 equivalence point. The equivalence point occurs on the midpoint of the titration curve, where the pH changes most rapidly with the addition of base.

The equivalence point, and the volume of base added which corresponded to it were measured on each titration curve. The 1/2 equivalence point was taken as the point of the curve which corresponded to half the volume of base added for the equivalence point, and the pKa was determined as the pH at the 1/2 equivalence point.

2.3 Batch Study

Batch studies were conducted using the four fluoro-organics and bromide in two different soils to determine if any of the compounds selected for study would lose mass from solution over time, due to sorption to soil surfaces or chemical or biological degradation. The soils had widely different properties and were selected to evaluate the compounds over a wide range of soil types. Some data on the soils used in this evaluation is given in Table 5.

The batch study was first conducted using a fine grained sand (USDA Classification) collected from the NMIMT's Desert Reseach Station. The sand consisted mostly of quartz, and the clay was primarily smectites with some kaolinites. (G.S. Austin, personal communication, l989). It was then repeated using a silty clay loam collected south of Grand Forks, ND. The clay in this soil was primarily smectites. (J.R. Richardson, personal communication, l988).

For these batch tests, 20 ml of a known concentration of fluoro-organics and bromide were added to 20 grams of soil in polypropylene tubes. Blanks were prepared with fluoro-organic and bromide solution only, as well as soil and water only. Each mixture was prepared in triplicate, and two sets of samples were made, one of concentration 5 ppm fluoro-organic and 10 ppm bromide, and another of 50 ppm fluoro-organic and 100 ppm bromide.

The tubes were stored in the dark at room temperature (approximately 24^0 C) and shaken daily. At prescribed time intervals the tubes were centrifuged if necessary and a sample of solution was taken for analysis for the fluoro-organics and bromide. The same mixture was used for sampling for the duration of the batch study. These concentrations were then compared to initial concentrations to determine if any loss of mass had taken place.

Table 5. Physical characteristics of soil materials used in study.

Soil	Texture USDA Classification	%sand	%silt	%clay	CEC (meq/100g)	Organic Carbon %	pH (1:1extract)
Seviletta dune sand	sand	97	2	<1	0.18*	0.02***	7.5
Beardon aeric kalciaquoll	silty clay loam	10	60	30	32.0 **	3.5 **	7.2
Seviletta aquifer sand	sand	96	2	2	2.03*	<1(estimated)	7.3

* Determined using method described by Polemio & Rhoades (l977).
** J.R. Richardson, personal communication
*** E. Hagan, personal communication

Samples were collected by pipeting 1 to 2 ml of solution from each tube on sampling occasions. The samples were stored in 4 ml borosilicate vials with black plastic lids. Samples were then analysed for fluoro-organic and bromide concentrations, and this data was used to determine if any loss of mass of any of the compounds was occuring over time. Samples were taken at 1,3,5,7, 14, 21 and 28 days, and once a week thereafter, with the final sample taken at 85 days.

2.4 Ponded Column Study

To measure the fluoro-organics' stability and mobility during flow through porous media under saturated conditions two flow columns were prepared, referred to hereafter as column 1 and column 2. Columns 1 and 2 were both constructed of blue 0.64 cm wall poly-vinyl chloride (PVC) pipe, 75 cm long X10.2 cm inner diameter in size. They were held side by side and upright in a wooden stand, and secured with two metal straps. Both columns were fitted with an outflow valve at the bottom, which consisted of a plastic stopcock connected to the column with approximately 7.5 cm of 1.27 cm inner diameter plastic tubing. A very fine nylon mesh was placed at the bottom of each column, along with another screen with 0.25 cm openings. These were put in place to keep solid material from moving out of the column. Both columns were covered with tin foil on the sides and top, in order to limit the growth of algae and to prevent evaporation of the ponded water.

Columns 1 and 2 were packed with Seviletta sand to a bulk density of 1.58 g/cm^3 and 1.60 g/cm^3, respectively. Packing was accomplished using a glass funnel with several inches of 1.27 cm inner diameter tubing attached to it. Sand was placed in the funnel, and the bottom of the tubing was kept very close to the surface of the sand already in the column. This was done to try to prevent sorting of the sand during packing. Column 1 received 8911 grams of sand, and column 2 received 8636 grams. Based on a particle density of 2.65 g/cm^3, the porosities were calculated at 0.41 and 0.42, respectively.

The valves at the bottom of each column were used to introduce tap water into the columns. Both columns were then wetted from the bottom to remove trapped air. After water reached the soil surface it was ponded to a depth of 5 cm.

Flow from the top to the bottom of each column was then initiated, with the outflow controlled by the valve at the bottom. A constant ponded depth was maintained using a mariotte siphon apparatus, one for each column. (Figure 3). The mariotte siphons were 4-liter glass bottles, fitted with #6 rubber stoppers and utilizing 0.32 cm inner diameter glass tubing and 0.64 cm inner diameter plastic tubing.

The columns were allowed to run for several days until the flow rate stabilized at 1.0 ml/min. The column pore volume, which is the measure of the amount of water present in the column at equilibrium, was determined for each column by comparing the weights of the columns full of sand and dry with the weights of the columns under saturated conditions. Column pore volumes were 2.41 liters for column 1 and 2.26 liters for column 2. After weighing, each column was allowed to flow for several days until the flow rates had again stabilized at 1 ml/min. Data on both flow columns is given in Table 6.

At this time, the flow of tap water to each column was interrupted and replaced with flow from a 3.0-pore volume pulse of 50 ppm fluoro-organics and 100 ppm bromide. For column 1 this was equivalent to 7.23 liters of solution, and for column 2 it was equivalent to 6.78 liters. To limit mixing, the ponded tap water on the soil surface was also removed and replaced immediately with tracer solution ponded to 5 cm. It is believed that this had a minimum effect on column flow and equilibria. After the entire fluoro-organic and bromide solution had been applied to each column, flow with tap water was resumed. The experiment was continued until 8 column pore volumes had passed through each column.

Concurrent with tracer pulse application to the top of the columns, sampling of column outflow commenced, and was continued at time intervals

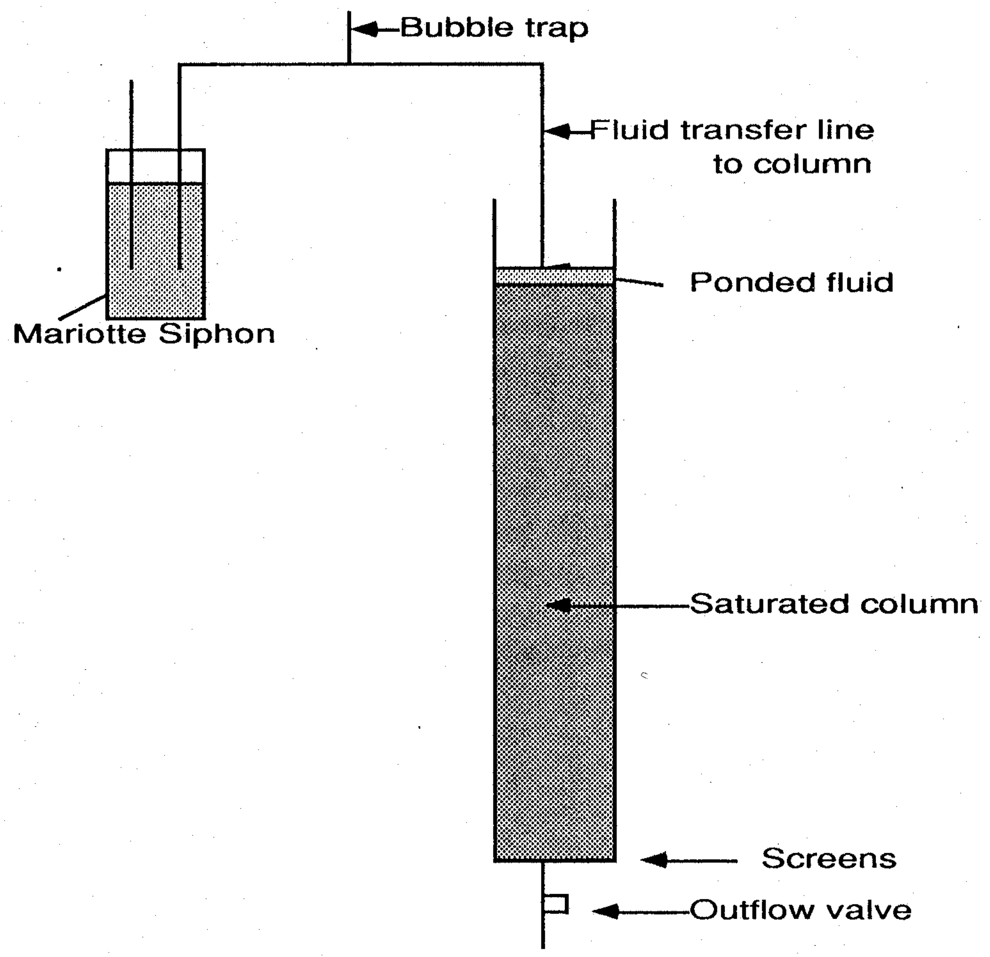


Figure 3. Equipment arrangement for ponded water column study.

Table 6. Data on columns used in mobility study.

Ponded flow conditions

	Bulk Density (g/cm^3)	Volumetric Water Content (cm^3/cm^3)	Pore Volume (liters)	Specific Discharge (cm/min)	Pore Water Velocity (cm/min)
column 1	1.58	0.41	2.41	0.011	0.026
column 2	1.60	0.40	2.26	0.010	0.025

Trickle flow conditions

	Volumetric Water Content (cm^3/cm^3)	Pore Volume (liters)	Specific Discharge (cm/min)	Pore Water Velocity (cm/min)
column 1	0.27	1.41	0.0061	0.0023
column 2	0.25	1.29	0.0061	0.0024

equivalent to 0.2 of a column pore volume eluting from the column, approximately 8 hours for each column. Samples were typically 4 ml volume, and they were stored in glass vials with plastic snap-tops. Sampling was conducted for the duration of the experiment (14 days). The total volume of column effluent was recorded for each column and material not used for sample analysis was discarded. These samples were then analysed for fluoro-organic and bromide concentrations to determine the mobility and stability characteristics of the fluoro-organics versus bromide.

2.5 Trickle Flow Column Study

The column flow study was repeated under aerobic conditions where the possibilty for degradation of the four fluoro-organics was potentially greater. For this unsaturated column flow experiment, the same columns used previously were allowed to drain. With the outflow valve left open, trickle flow of tap water onto the top of the soil surface was commenced at 0.5 ml/min. A small constant head reservoir for each column was used to aid in keeping the flow rate onto the columns constant, and a small tinfoil screen was used to disperse the flow across the top of the soil surface. The constant head reservoirs consisted of 10 cm slices of 3.04 cm inner diameter clear acrylic tubing, fitted on the bottom with #10 rubber stoppers. Glass tubing with 0.32 cm inner diameter was placed through the rubber stopper, and a small piece of rubber tubing was fitted with a metal screw compression clamp to control the flow rate. The constant head in the reservoir was maintained using the same mariotte siphons used in the previous column study. (Figure 4). This flow was allowed to continue until the inflow rate equaled the outflow rate. Data on the columns under trickle flow conditions is given in Table 6.

The columns were then weighed to determine the water content and the column pore volumes for each column. For column 1 the mean water content was 0.27 (averaged throughout the entire column) and the column pore volume was 1.41 liters. For column 2 the mean water content was 0.25 and the column pore volumn was 1.29 liters. These values were considered sufficiently different from the conditions under the saturated flow to assume that aerobic conditions were present in each column. Saturated conditions were also present at the bottom of each column, which allowed outflow from the column to occur.

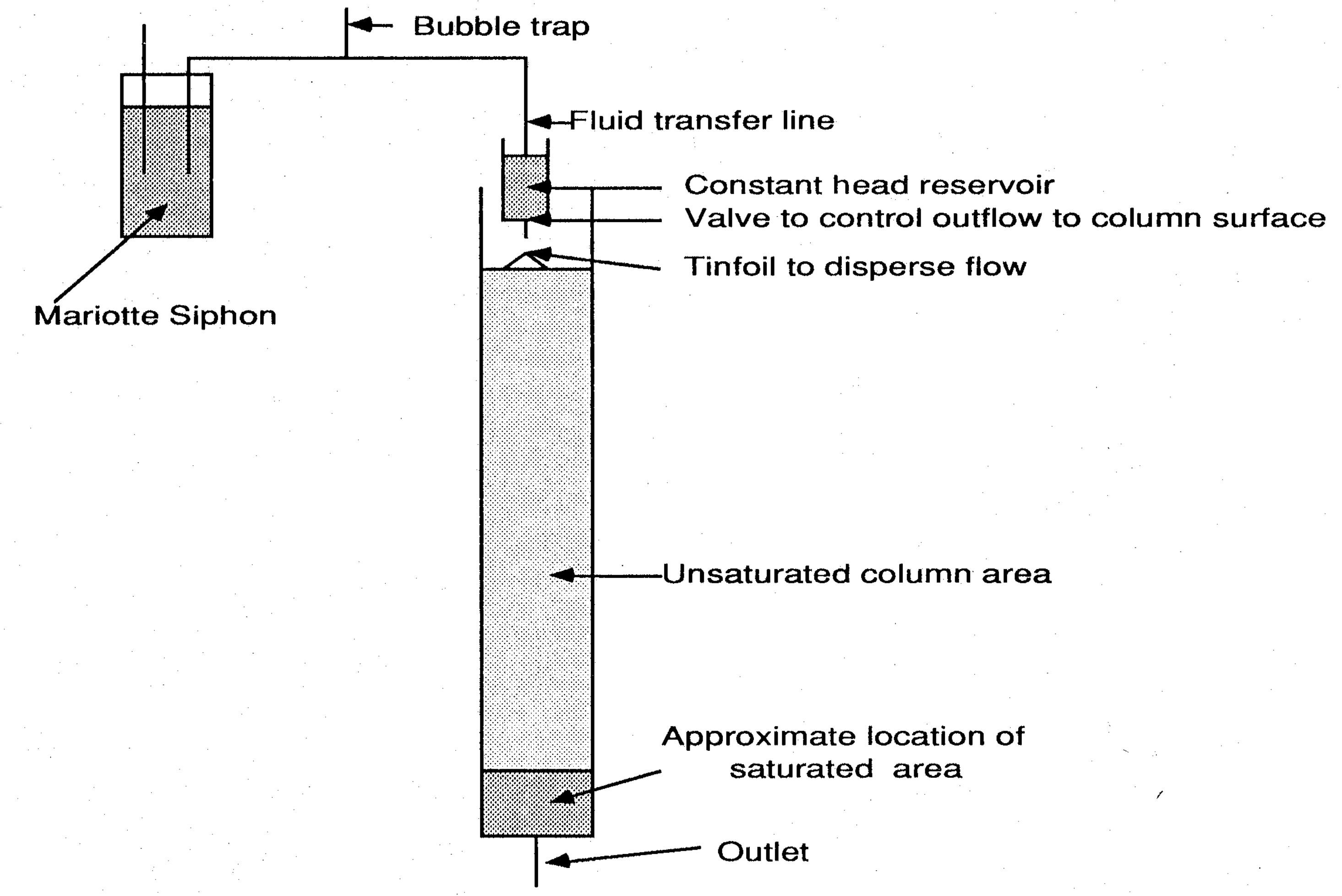


Figure 4. Equipment arrangement for trickle flow column study.

Flow was continued for another week to allow the columns to reach equilibrium. At this point, tap water flow was interupted, and a 2.0- pore volume pulse of 50 ppm fluoro-organics and 100 ppm bromide was applied to each column. This was equivalent to 2.82 liters for column 1 and 2.60 liters for column 2. Sampling of the column effluent was initiated at the beginning of the pulse application, and continued at time intervals equivalent to 0.2 of a column pore volume eluting, which for both columns was approximately 8 hours. Samples were collected using the same type of glass vial used in the saturated column study. Column effluent not used for sampling was measured to determine the volume of outflow and then discarded. These samples collected were then analysed for fluoro-organic and bromide concentration, and this data was used to compare the mobility and stability behavior of the fluoro-organics' with that of bromide.

2.6 Aquifer Tracer Test

The field site selected for evaluating the four fluoro-organics under saturated conditions was located near the Rio Salado, on the Seviletta Wildlife Refuge, approximately 32 kilometers north of Socorro, New Mexico. (Figure 5). The site is located in the floodplain of the Rio Salado, an ephemeral stream which drains the Ladrone and Magdalena Mountains located to the west, and flows into the Rio Grande near San Acacia, New Mexico.

The aquifer into which the fluoro-organics and bromide were placed had a matrix of medium to coarse sand with cobbles, overlain by 8 to 10 cm of fine-grained eolian sand. (Stephens & Knowlton, l986). Data on the aquifer matrix is given in Table 5. The water table was located at 3.2 m when the site was instrumented. Due to the ephemeral nature of the Rio Salado the direction and velocity of ground water flow and the water table elevation were all seasonably variable.

The site had been previously instrumented with three monitoring wells placed in the pattern shown in Figure 6. All three wells were 5.0 cm I.D. PVC pipe, 8.3 m deep, with a 1.6 m slotted screen interval at the bottom. Because of the wide variability of flow directions and velocities, this amount of instrumentation was insufficient to conduct a natural gradient tracer test. However, the site was suitable to evaluate the stability of the four fluoro-organics over an extended period of time, and to measure their mobility under pumped conditions.

The test was designed to place a pulse of the four fluoro-organics and bromide into the aquifer for 3 months, and then recover the pulse by pumping. The relative concentrations of the four fluoro-organics would be compared to that of bromide to determine if any of the compounds had lost mass during the

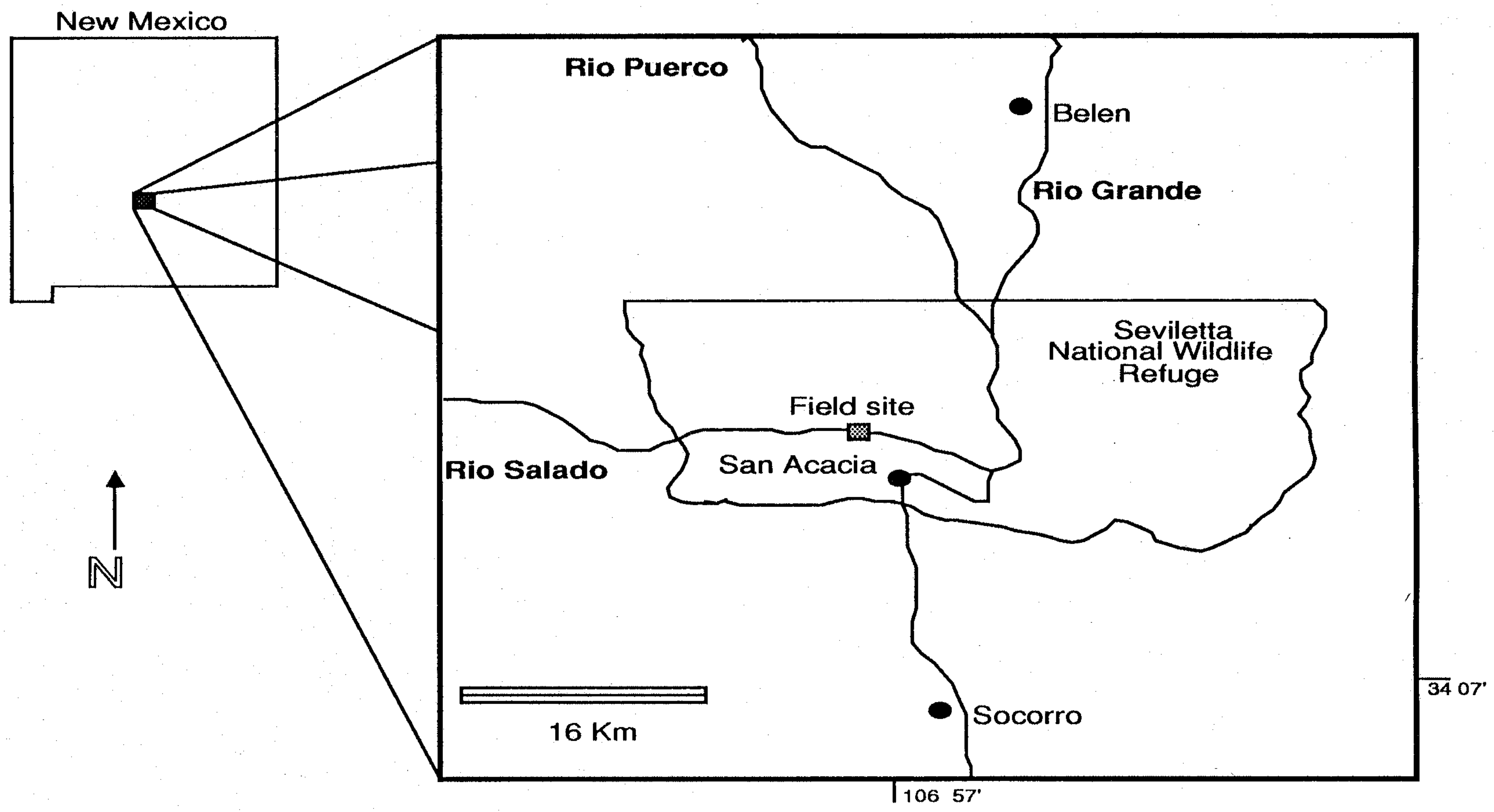


Figure 5. Location of field site for aquifer tracer test.

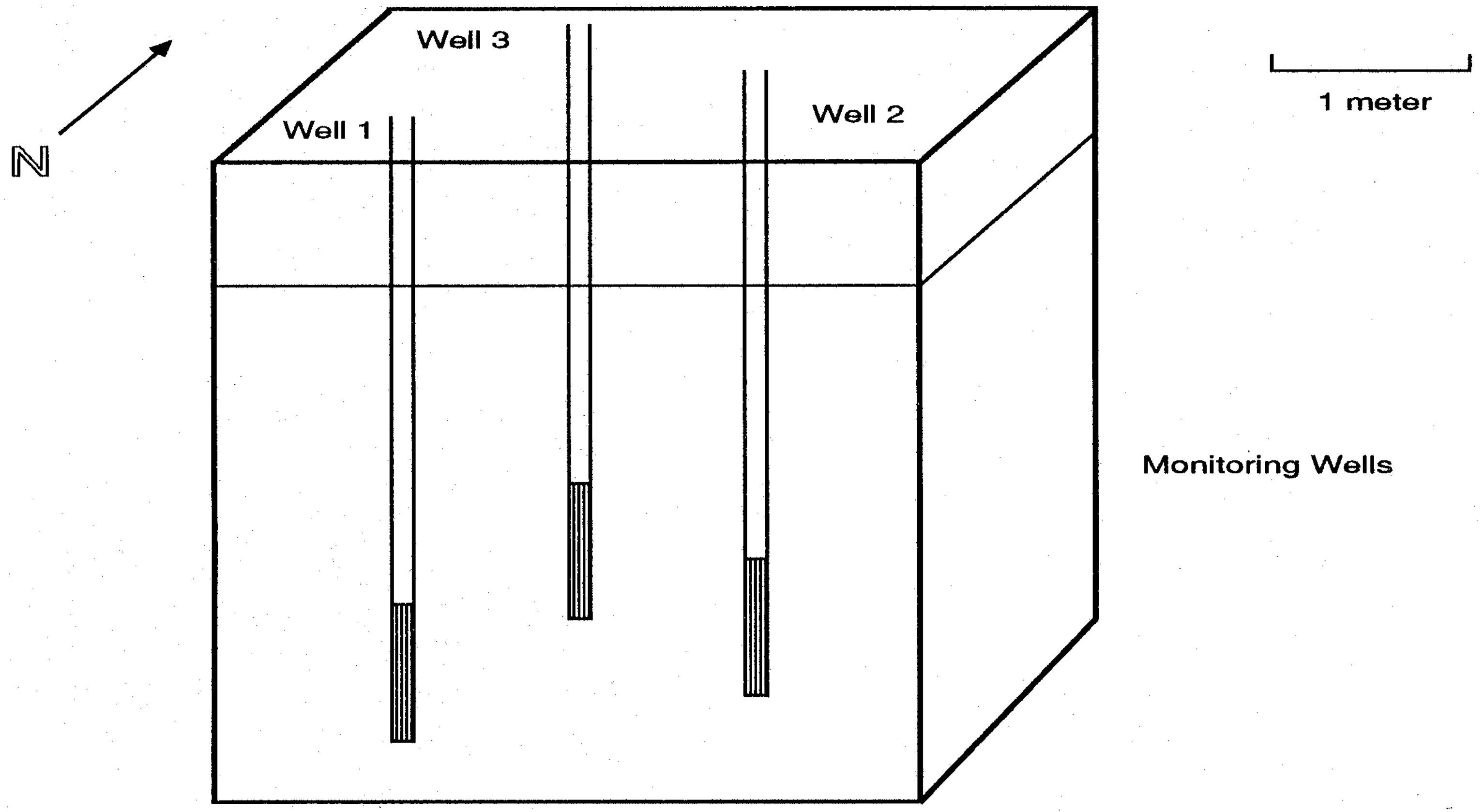


Figure 6. Design of monitoring wells used in aquifer tracer test.

duration of the field test, due to biological or chemical transformations. The breakthrough curve resulting from the pumping was also utilized to give an indication of the fluoro-organics mobility versus bromide under the same conditions.

A 20-liter pulse of 150 ppm fluoro-organics and 1000 ppm bromide was placed in well 1, and pumping was started immediately from well 3, in order to move the pulse out of the well bore and into the aquifer. Pumping was stopped after 7 hours and the aquifer allowed to return to equilibrium. The pulse was left in the aquifer for 3 months, at which time pumping at a rate of 56 liters/min was conducted from well 2 in order to capture the pulse. Samples of pump outflow were taken every 5 minutes for 12 hours, and analysed for tracer concentrations. The mass recovery of each fluoro-organic and bromide was then calculated to determine if any mass was lost due to chemical or biological degradation during the 3 months the compounds were in the aquifer.

2.7 Vadose Zone Tracer Test

The site for the evaluation of the four fluoro-organics was selected because it had sufficient instrumentation and equipment to allow for the application of a pulse containing the four fluoro-organics and bromide near the surface, and sampling of the pulse could occur at various depths. The site had originally been designed to monitor the movement of a wetting front through the vadose zone. Additional instrumentation allowed for sampling of the water moving from near the surface to depth. The site design and instrumentation had been conducted by graduate students working under Dr. Daniel Stephens, NMIMT.

The tracer test was designed to utilize this site to evaluate the stability and mobility of the four fluoro-organics compared to that of bromide during flow through the vadose zone. A pulse of fluoro-organics and bromide was added to the water applied to the site, and sampling was conducted at depths of 1, 2 and 3 m. It was expected that the pulse would take approximately 14 days to move past the lower samplers.

The field site was located west of the NMIMT golf course, in the northeast corner of the physical plant storage yard. (Figure 7). The field site was divided into two regions, a heavily instrumented inner section of 10 m x 10 m located within a larger 30 m x 30 m area. This site was fairly level and had never been previously irrigated. Depth to water in this area is approximately 20 m. (Parsons, l989). The stratigraphic profile beneath the site is stratified and heterogeneous, consisting of two major facies types, with several cobble layers present. A red brown silty sand and pebbles of the Piedmont slope facies derived from Socorro Peak overlies well sorted tan fine to coarse sands of ancestral Rio Grande origin. (Figures 8 and 9). The mean porosity of the

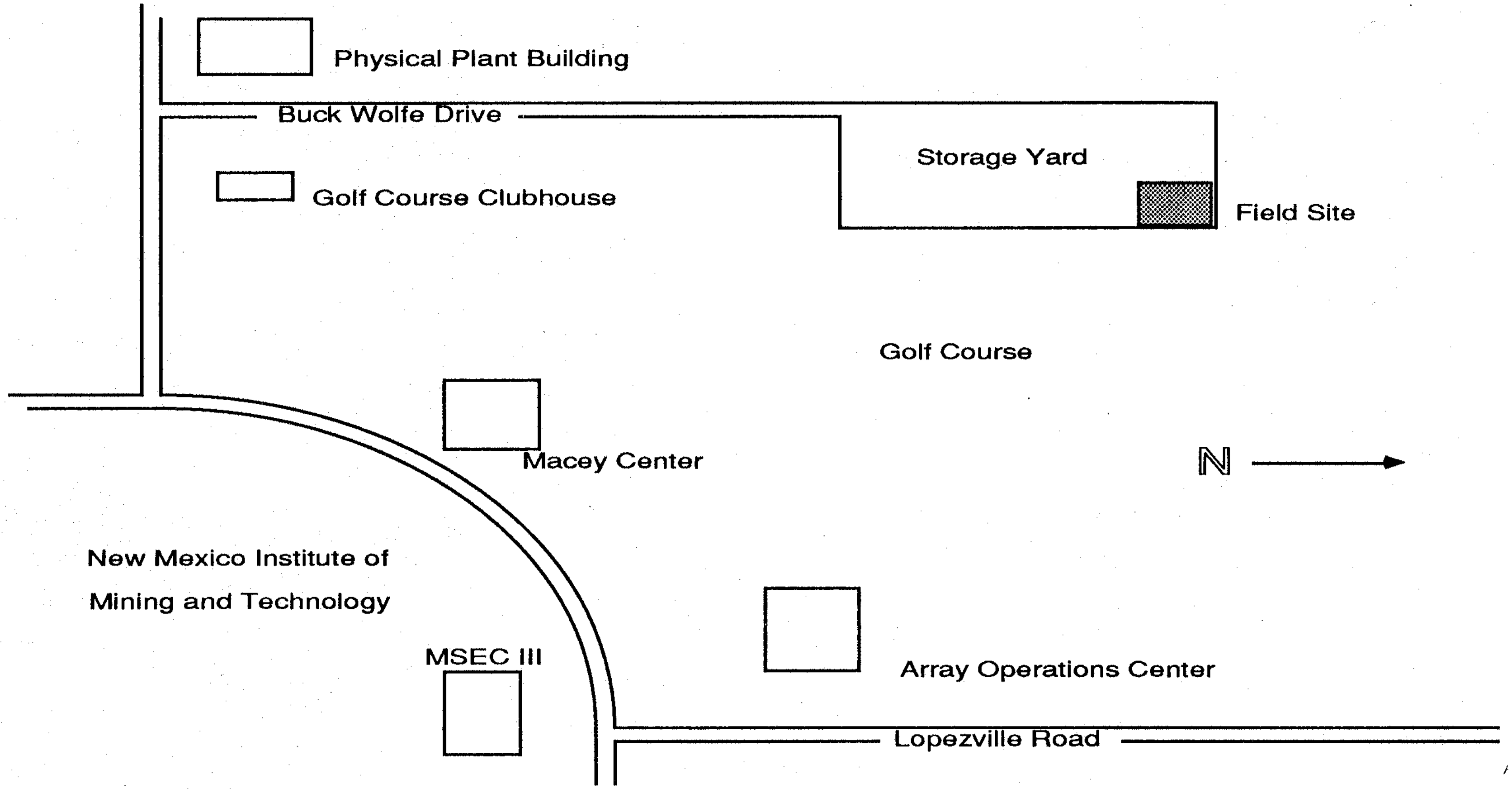


Figure 7. Location of field site for vadose zone tracer test. (Not to scale).

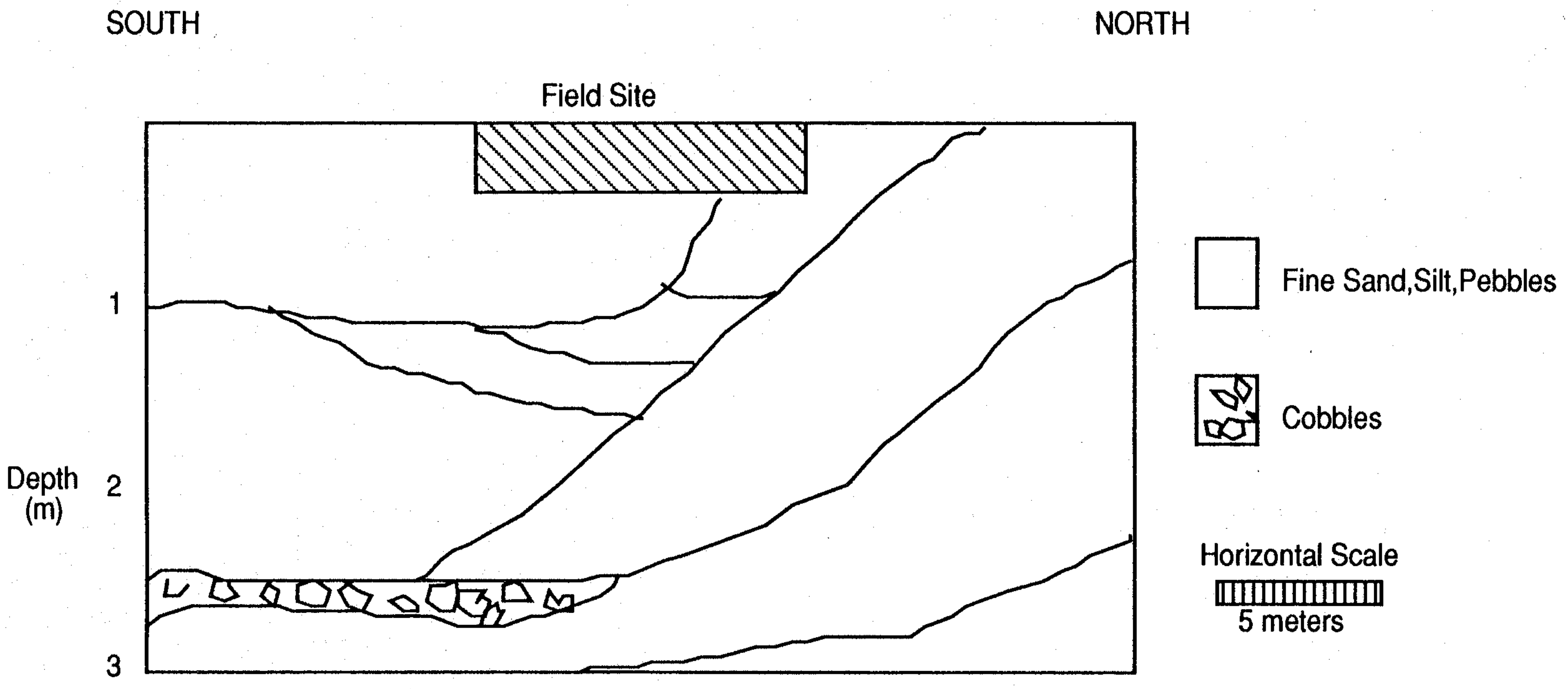


Figure 8. Geologic cross-section of North-South transect. Parsons (l989).

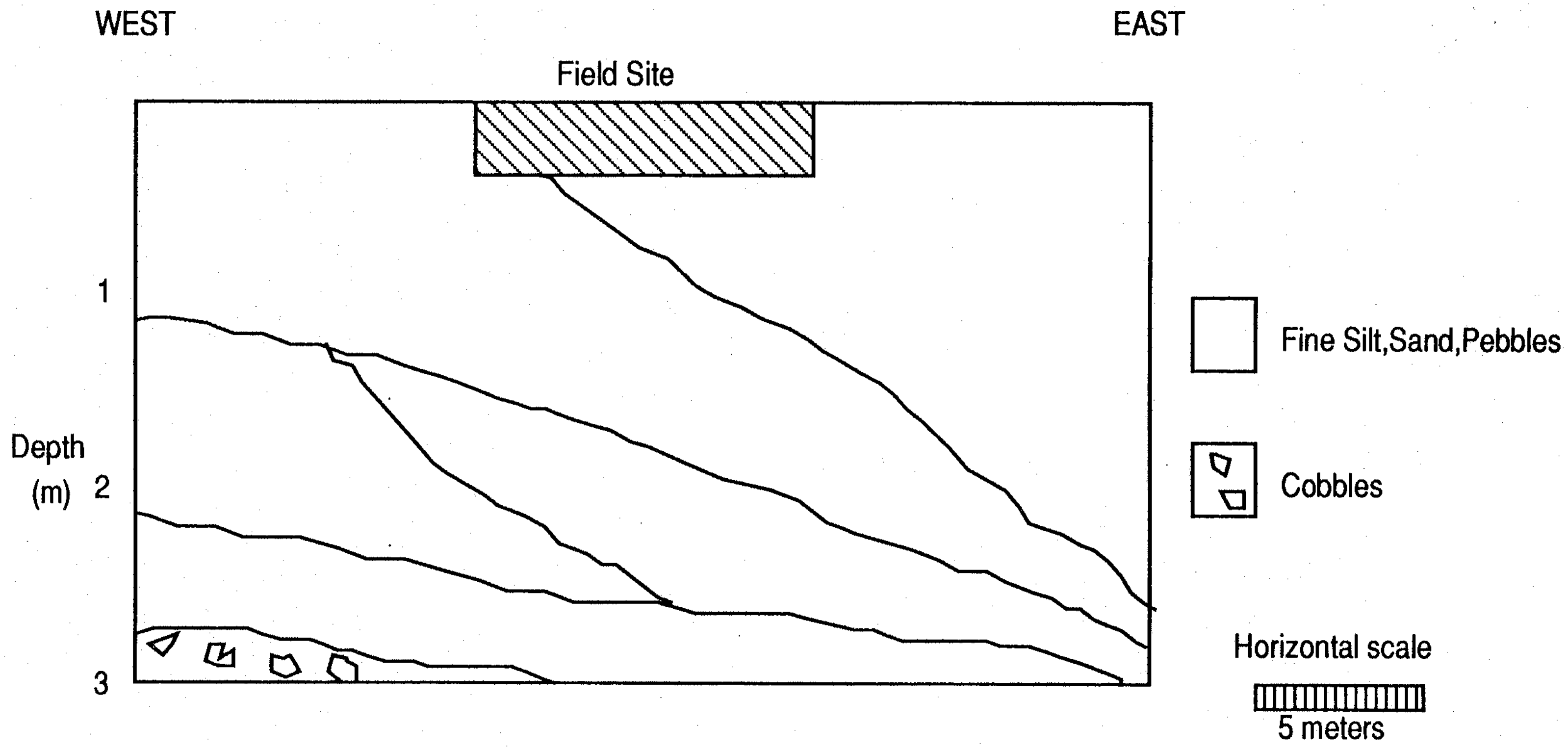


Figure 9. Geologic cross-section of East-West transect. Parsons (1989).

Piedmont slope material is 0.43, while the mean porosity of the fluvial sands is 0.36. An excellent description of the site's geological and hydrological characteristics is provided by Parsons. (l989).

The site was instrumented with neutron probe access tubes, tensiometer nests and 1-bar porous cup samplers (Figure 10). Depths of instrumentation ranged from 1 to 10 m, with the deepest instruments placed on the outer portion of the site. Sampling of water moving through the site was conducted using porous cup samplers which had been previously emplaced at various depths and locations. The porous cup samplers had been equiped with two lines of 0.32 cm inner diameter black plastic tubing, with clamps on the outside end. The top of the tube was sealed with epoxy so that it would hold a seal, and the samplers were constructed so that 0.3 to 0.5 m of tubing was free at the surface. (Figure 11). During porous cup installation, silica flour was placed around the ceramic cup to help keep the cup from clogging. Several layers of bentonite clay were put in place during backfill, to prevent water from moving preferentially down the side of the tube.

Samples were retrieved by sealing one tube and applying approximately a 20 lb suction to the cup with the other tube, using a small vacuum pump. This tube was then sealed and the porous cup sampler left for a specified period of time, during which the suction caused water to move into the cup. To retrieve the sample from the cup, one tube was placed into a sealed jar, and a small amount of compressed air was injected into the cup through the other tube. This forced the water in the cup into the sealed jar.

Water was supplied to the site via a drip irrigation system, with 21 lines forming a grid of water emitters spaced a 50 cm intervals. (Figure 12). These were buried several centimeters below the surface and were covered with plastic sheeting to prevent evaporation of the applied water, as well as to

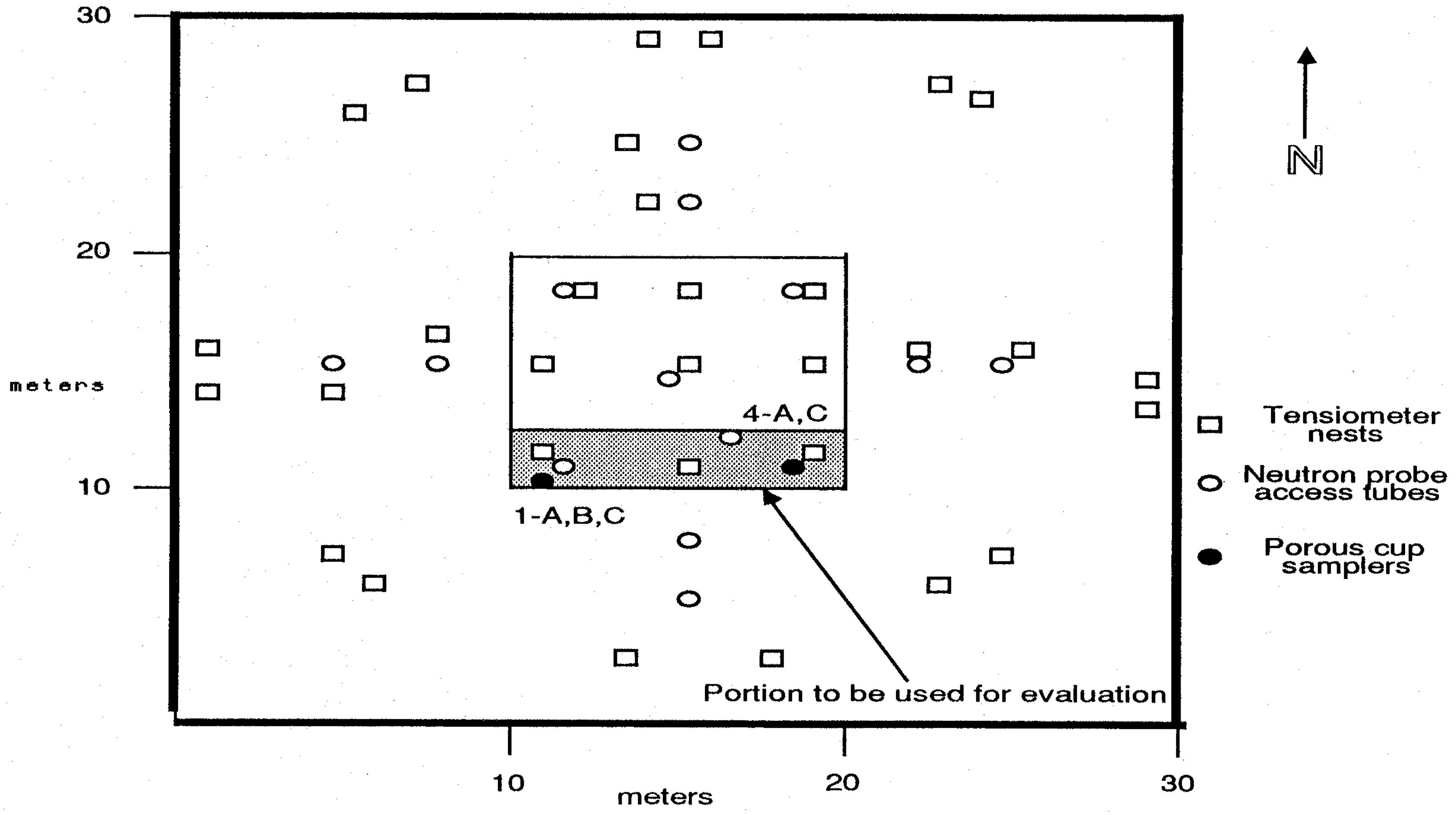


Figure 10. Plan view of field site for vadose zone tracer test.

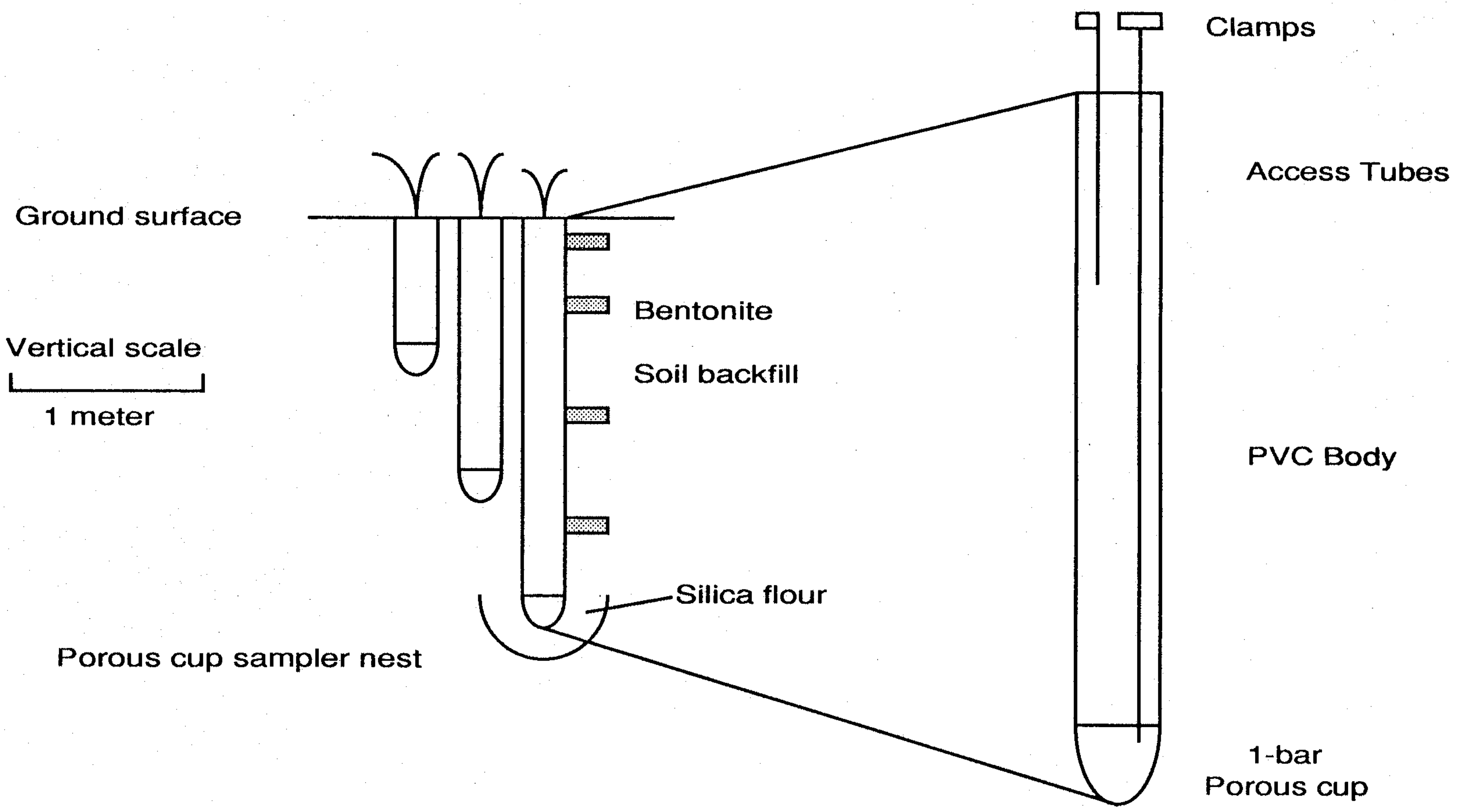


Figure 11. Porous cup sampler nest and view of porous cup sampler.

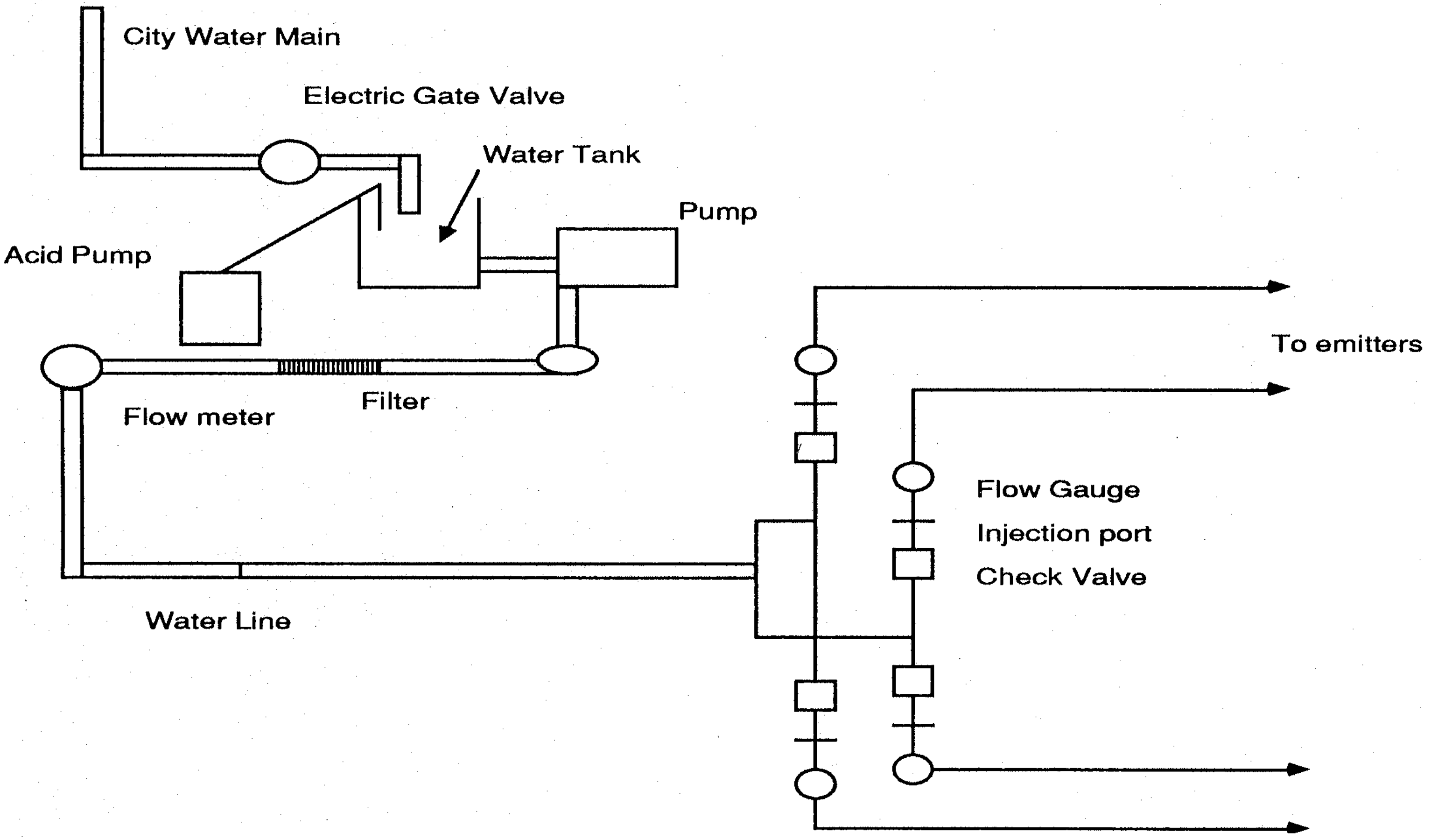


Figure 12. Schematic of water application system. (Not to scale).

prevent infiltration of natural precipitation. (Figure 13). Water from the city of Socorro's municipal system was stored in a 100 gallon tank located at the site. This water has a pH value of 7.8 and a hardness of 273 ppm calcium carbonate. (Parsons, l988). Water flow to the emitters was maintained by a positive displacement pump which delivered a prescribed volume of water to the drip lines at predetermined time intervals.

During each cycle the pump ran for 3 minutes, lowering the level in the storage tank. The timer then opened the city water line to the tank and it was refilled to its original level. A mechanical float acted as a shutoff switch when the water reached the proper level. This cycle was repeated four times per hour. Each 3-minute pumping cycle sent approximately 24 gallons of water to the site. At steady state the region below the emitters had a moisture content of approximately 20%, a flux of approximately 6 cm/day, and a mean pore water velocity of approximately 30 cm/day. (R. Schmidt-Peterson, personal communication, l989). A small pump was activated each day to send several hundred milliliters of hydrochloric acid to the storage tank, in order to lower the pH and prevent buildup of calcium carbonate in the flow lines.

Due to other experimental work going on at the site, the evaluation of the four fluoro-organics was conducted on only the southernmost portion of the site, 2.5 m X 10 m. The pulse of fluoro-organics and bromide was applied by adding a concentrated solution of fluoro-organics and bromide to the water being supplied to the site. This was accomplished using a syringe pump connected to the pipeline supplying water to the portion of the site being used. (Figure 14).

The timer activating the pump supplying water to the site was also connected to the syringe pump, so that when the main pump turned on for each pumping cycle, the syringe pump also operated. The pump pulled back on a 20 ml syringe, opening check valve #1 to draw tracer solution from the container

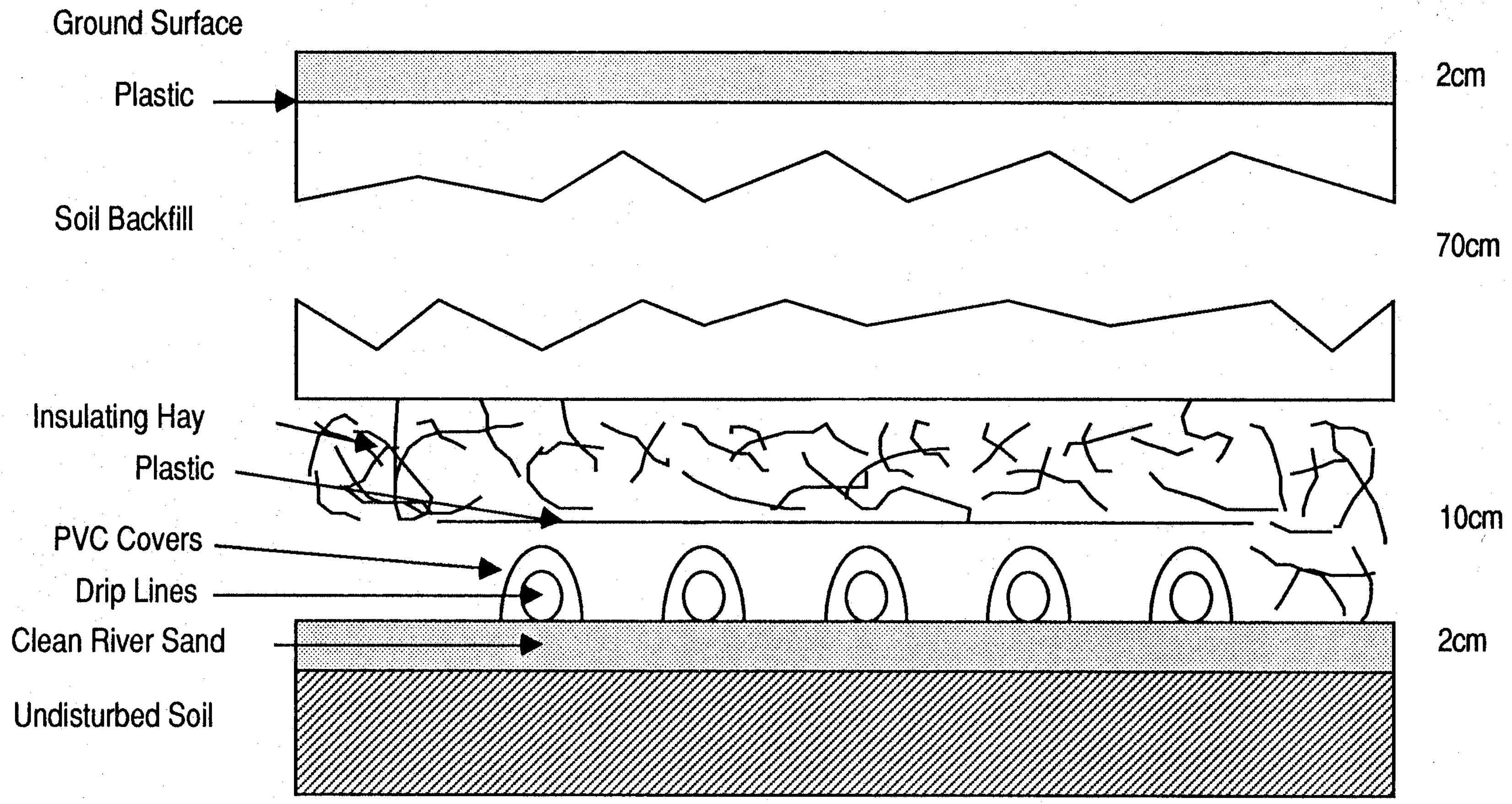


Figure 13. Cross-section through irrigation plot. Parsons (1989).

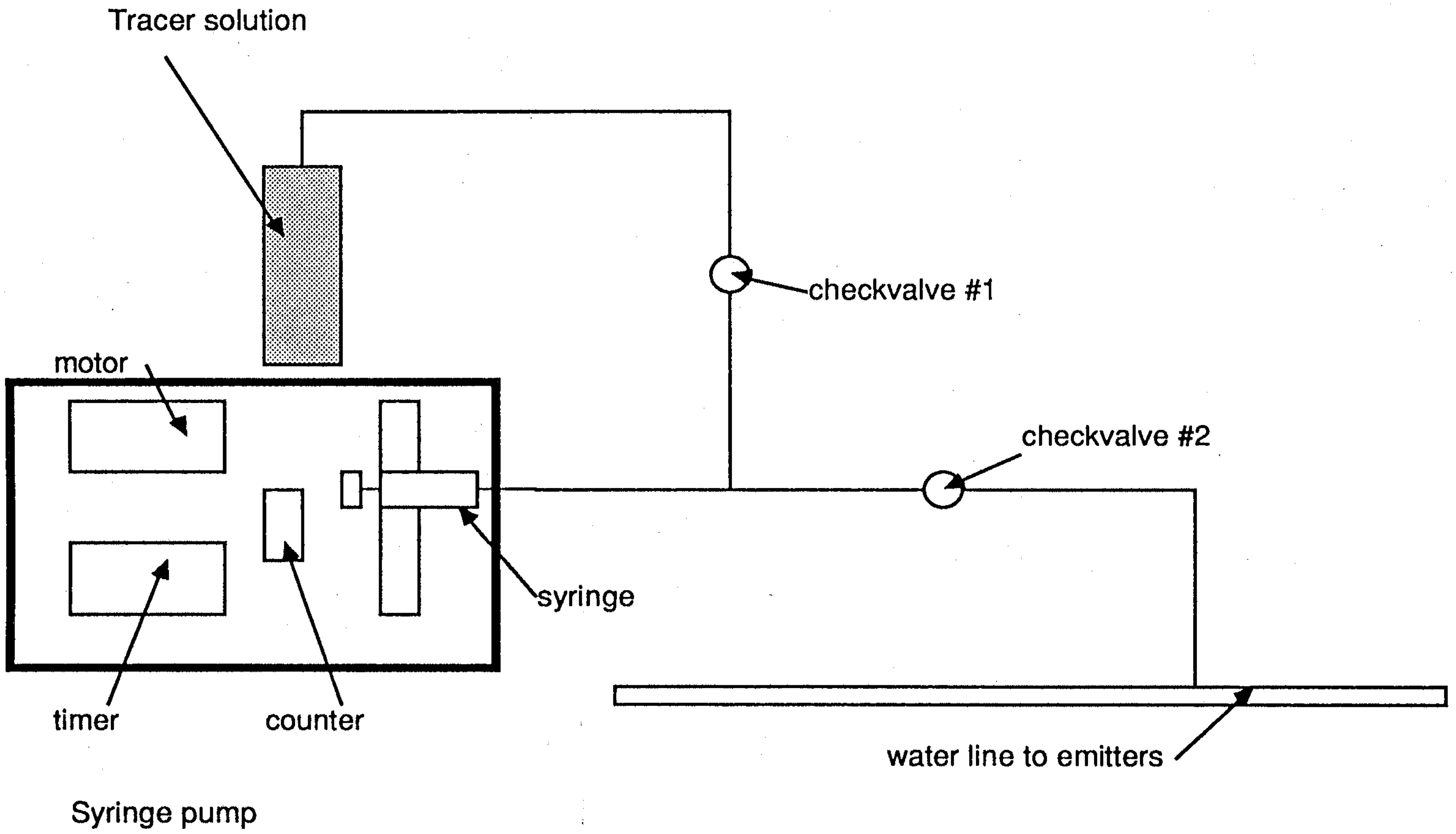


Figure 14. Injection system for applying tracer to site for vadose zone tracer test.

into the syringe, and closing checkvalve #2, to ensure that no fluid moved from the water line to the syringe. As the syringe pump pushed the syringe forward checkvalve #1 was closed, preventing tracer from going back into the container. Checkvalve #2 was then opened, allowing the concentrated tracer solution to be placed into the water line.

Forty grams of each fluoro-organic and 520 grams of bromide were added to 52 liters of water for a solution concentration of 770 ppm for each fluoro-organics and 10000 ppm for bromide. Because of these high concentrations the pH of the tracer solution was raised to 12 with potassium hydroxide (KOH) to increase the solubility of the fluoro-organics. After all the compounds had dissolved the pH of the tracer solution was lowered to 7 using hydrochloric acid (HCl). Tracer application was conducted for 24 hours, and 30 liters of solution were applied to the portion of the site used in this evaluation. After the tracers had been applied, flow with water only was continued. This system was calculated to produce a pulse with fluoro-organic concentrations of 15 ppm and a bromide concentration of 135 ppm. The point of tracer pulse injection into the water line was placed a sufficient distance from the application points that the tracers would be mixed throughout the water moving to the emitters. Samples were taken at 8 hour intervals directly from the emitters to determine the concentration of the pulse as it was applied to the soil, and to determine if this concentration had remained reasonably constant over the 24 hours of tracer application.

Samples were taken from all the porous cups at 8 hour time intervals for 14 days. Sampling was then conducted once daily for seven days, and once every three days thereafter. For the purposes of this evaluation, only data from porous cup locations 1-A, 1-B, 1-C, 4-A and 4-C was used. (Figure 10). The depths of these porous cups were 1 m for 1-A and 4-A, 2 m for 1-B and 4-C and 3 m for 1-C.

RESULTS AND DISCUSSION

3.1 Chromatography Results

One potential obstacle to accurate quantitation of the fluoro-organics and bromide was interference from anions which may be present naturally in soil and groundwater samples. The operating wavelength selected on the variable wavelength detector was chosen to maximize the response of the tracers while minimizing the response of common anions such as chloride (Cl^-), nitrite (NO_2^-) and nitrate (NO_3^-). Figure 15 presents the detector resonses for the four fluoro-organics, bromide, Cl^-, NO_3^- and NO_2^- versus wavelengths of 190 to 225 nanometers (nm). The response for each compound was normalized to that of 3,5-DFBA. All samples were 100 *ul* injections of 5 ppm solutions.

Based on Figure 15 the wavelength of 205 nm was chosen as the level for tracer detection and quantitation. Lower wavelengths increased the response for the fluoro-organics and bromide, but the response for Cl^- is enhanced at lower wavelengths. Detector wavelengths above 215 nm increased responses for the fluoro-organics while decreasing responses for Cl^-, NO_3^- and NO_2^-. However, the response for bromide was also reduced at the higher wavelengths.

The relationship between the detector response and the mass injected for the four flouro-organics and bromide is shown in Figure 16. The concentrations of the standards ranged from 1 ppm to 50 ppm for the fluoro-organics and 2 ppm to 100 ppm for bromide, with sample volumes of 25*ul*. This relationship should be linear to insure accurate quantitation when using a

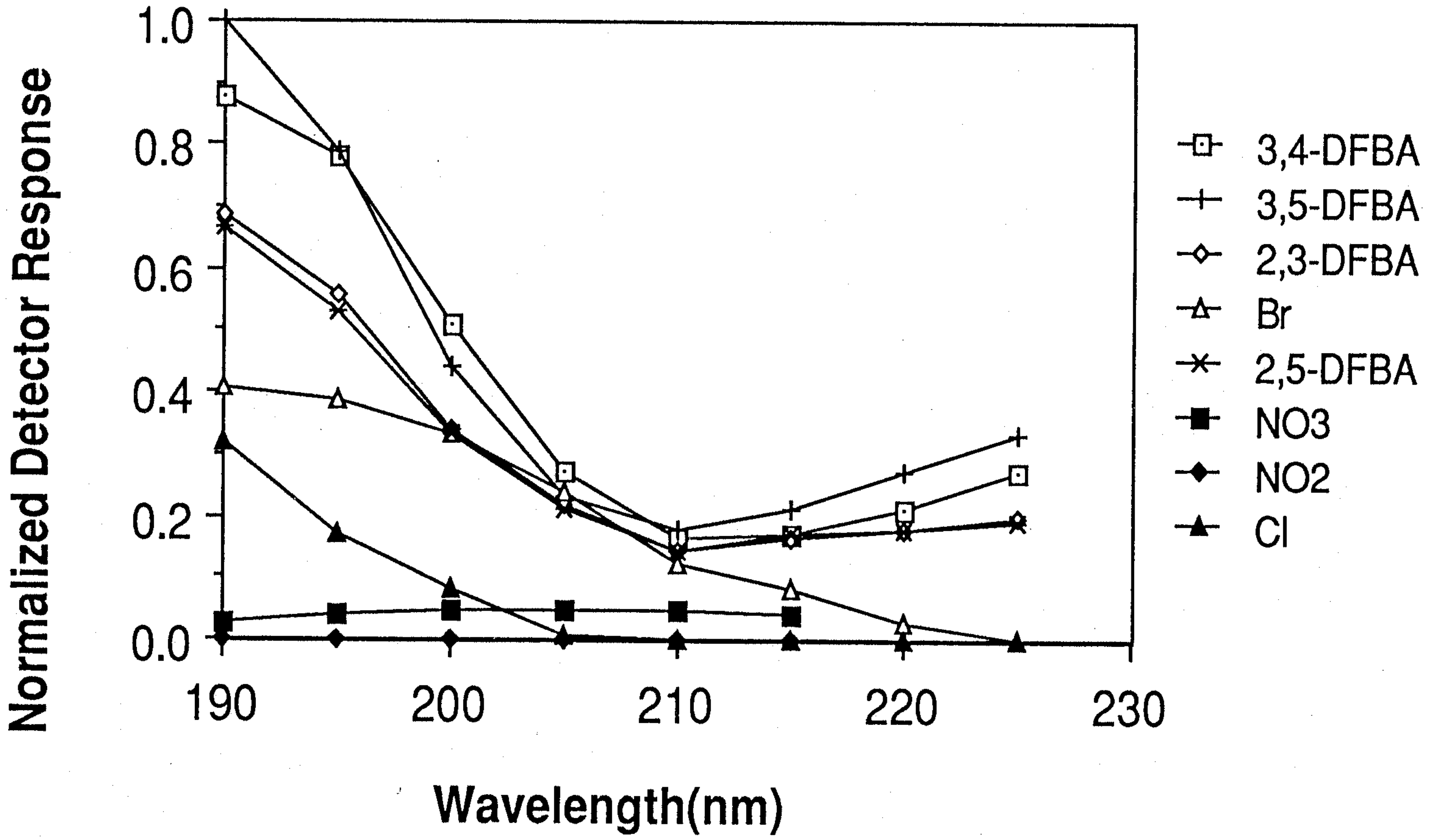


Figure 15. Detector response vs. wavelength for the four fluoro-organics, bromide, nitrate, nitrite and chloride. Response is normalized to that of 3,5-DFBA for 100 *ul* injections of 5 ppm solutions.

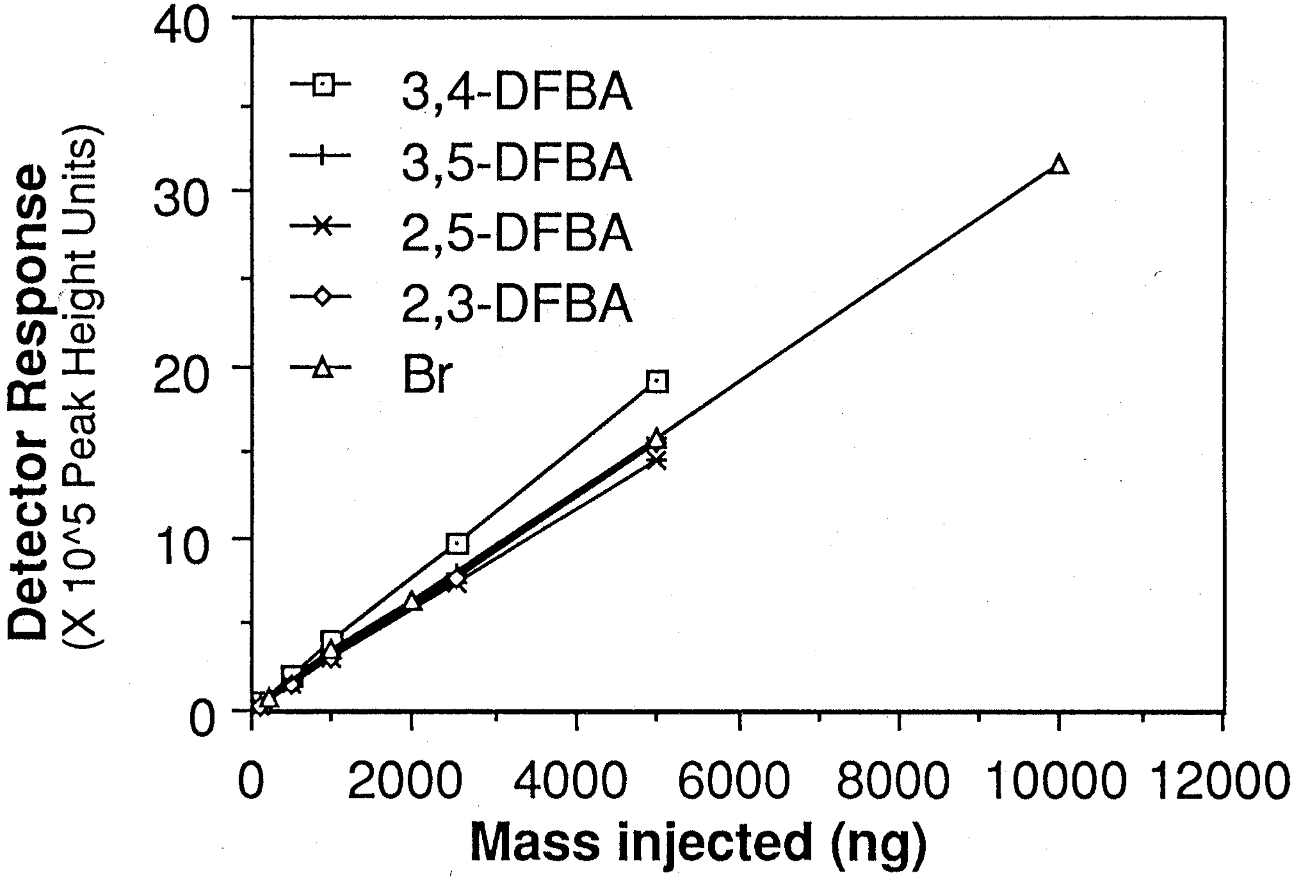


Figure 16. Detector response vs. mass injected for the four fluoro-organics and bromide.

single external standard. If the relationship is non-linear, standards of different concentrations must be used.

The four fluoro-organics exhibit linear behavior up to 5000 nanograms (ng) of injected mass, and the bromide appears to be linear up to 10,000 ng of injected mass. These values correspond to 100 *ul* injections of 50 ppm fluoro-organic and 100 ppm bromide. Throughout this evaluation sample injection volumes were always 100 *ul* or less with sample concentrations of 50 ppm fluoro-organic and 100 ppm bromide or less. External standards were used and the system was calibrated after every 10 samples.

The time required for the complete elution of a sample under the conditions described above is 10 minutes. Figure 17 is a chromatogram for a 10 *ul* injection of 50 ppm fluoro-organics and 100 ppm bromide, along with the three anionic contaminants. The presence of these three compounds did not interfere with the detection and quantitation of any of the selected compounds in this study.

The detection limits for the four fluoro-organics and bromide were measured by determining the smallest mass which would produce a peak twice the normal baseline. This data is presented in Table 7 along with reported detection limits for bromide and the four fluoro-organics previously evaluated. The error associated with the measured detection limits is presented as a standard deviation. The higher error associated with 2,5-DFBA and 2,3-DFBA may be due to the close proximity of the peaks for these two compounds.

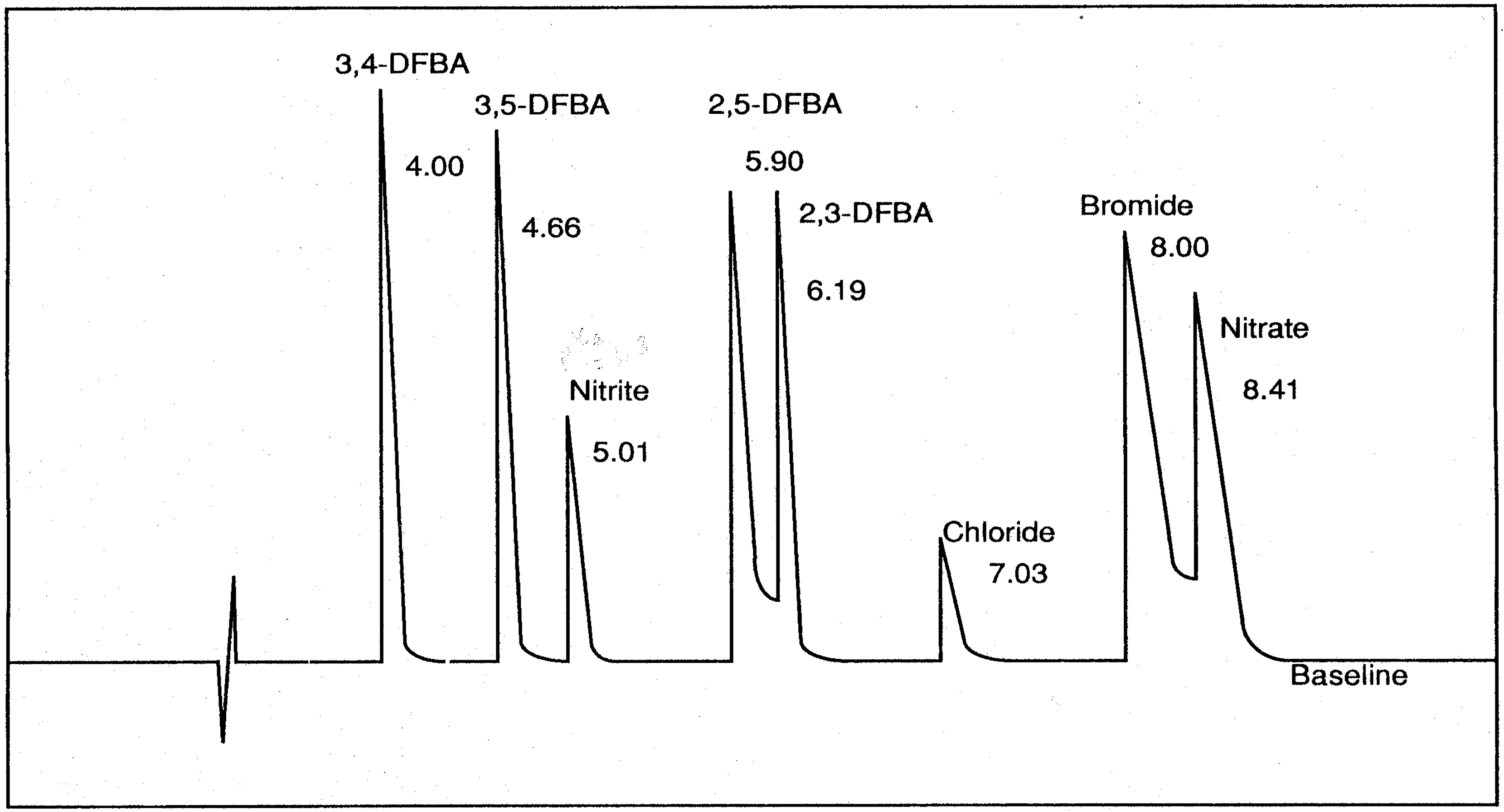


Figure 17. Chromatogram showing the separation of the four fluoro-organics, bromide and anions common in natural waters. Retention times are given in minutes from time of injection.

Table 7. Acid dissociation constants and detection limits for fluoro-organic compounds.

	2,3-DFBA	2,5-DFBA	3,4-DFBA	3,5-DFBA	Br	*m*-TFMBA	*o*-TFMBA	PFBA	2,6-DFBA
measured pKa	3.2	3.2	3.7	3.4	--	3.8	3.0	2.7	3.0
reported pKa						3.79**	3.8*	1.49**	3.5*
measured# detection limits (ng)	2.9 (0.06)***	2.8 (0.073)	2.1 (0.026)	2.6 (0.028)	2.4 (0.041)				
reported detection limits (ng)					2.1* (0.023)	1.2* (0.025)	1.7* (0.036)	2.5* (0.039)	2.1* (0.029)

*Bowman, R.S. (1984a)
**Walter, G.R. (l972)
***Values expressed as (+/-) a standard deviation
#Based on 3 replicate injections

27 June 1990
Aldrich Chemical
Co. (Technical Info)
has a pKa for
PFBA of 2.24 - did

3.2 Acid Dissociation Constant Determination

The acid dissociation constants for the four fluoro-organics selected for evaluation and the four fluoro-ogranics already used as tracers were determined using the base titration curve determined for each compound. The equivalence point was located on each graph, and the volume of base added corresponding to this point measured. The half equivalence point was then determined as the point of the curve corresponding to half the volume of base at the equivalence point. The pH of the solution at the half equivalence point equals the pKa of the acid. The titration curves for 2,3-DFBA and 2,5-DFBA are given in Figure 18. The titration curves for 3,4-DFBA and 3,5-DFBA are given in Figure 19. The curves for *o*-TFMBA and *m*-TFMBA are presented in Figure 20, and those for 2,6-DFBA and PFBA are given in Figure 21. The acid dissociation constants determined for each fluoro-organic compound are presented in Table 7, along with the reported values for the fluoro-organics already used as tracers.

A comparison of the pKa values for 2,6-DFBA, *m*-TFMBA, *o*-TFMBA and PFBA measured with the technique described above indicates some variation from the values reported by Bowman (l984a) and Walter (l982). The values for *m*-TFMBA match closely while the values for the others differ by as much as 40%.

The values for *o*-TFMBA and 2,6-DFBA reported by Bowman are estimates, and Bowman states that the true values may be lower. If ion exchange is the primary process in the chromatographic separation, the fluoro-organic compounds should elute in order of descending pKa values. This is the pattern seen for the four selected fluoro-organics under the HPLC conditions used for this evaluation. If the values reported by Bowman are correct, *o*-

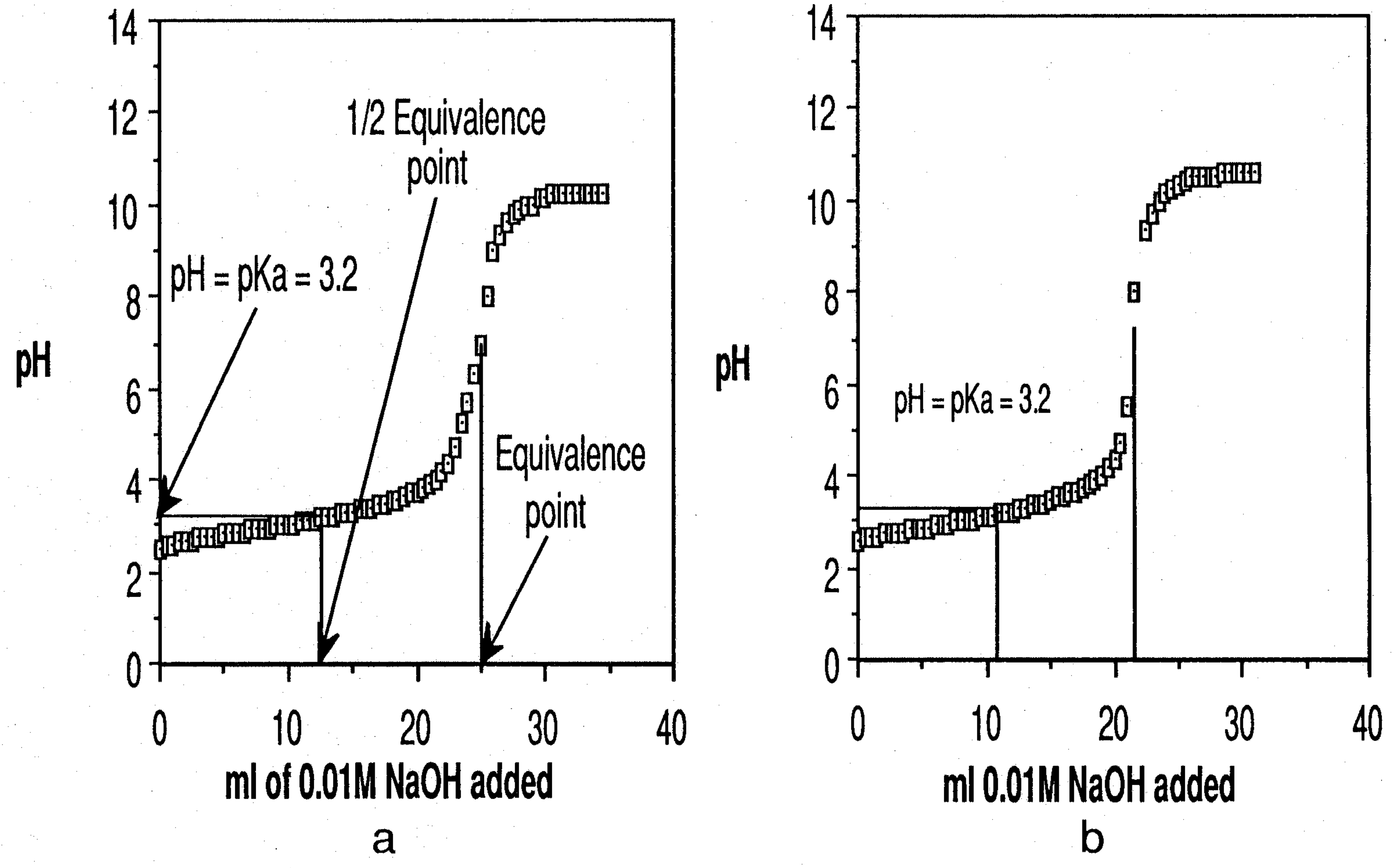
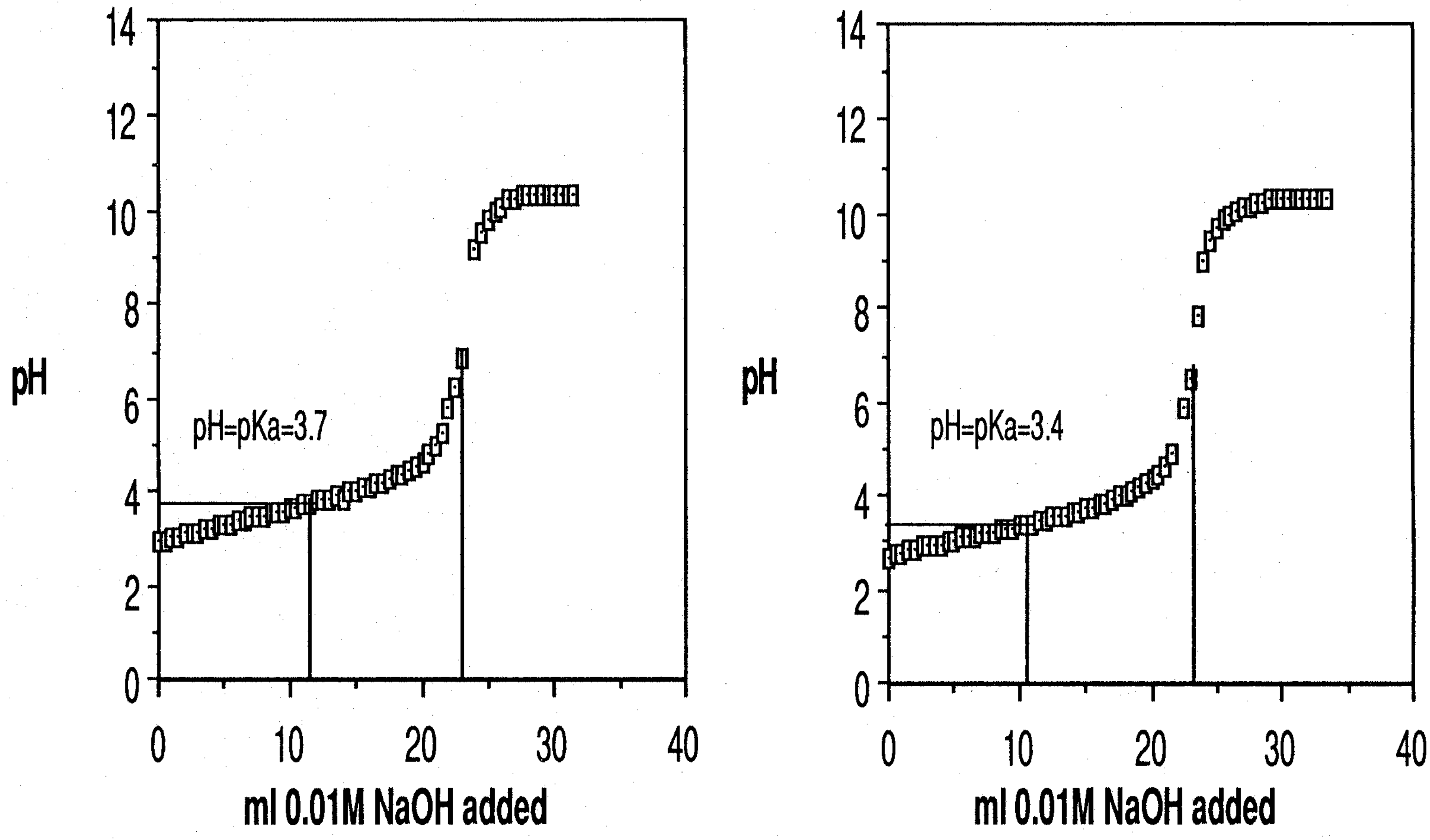


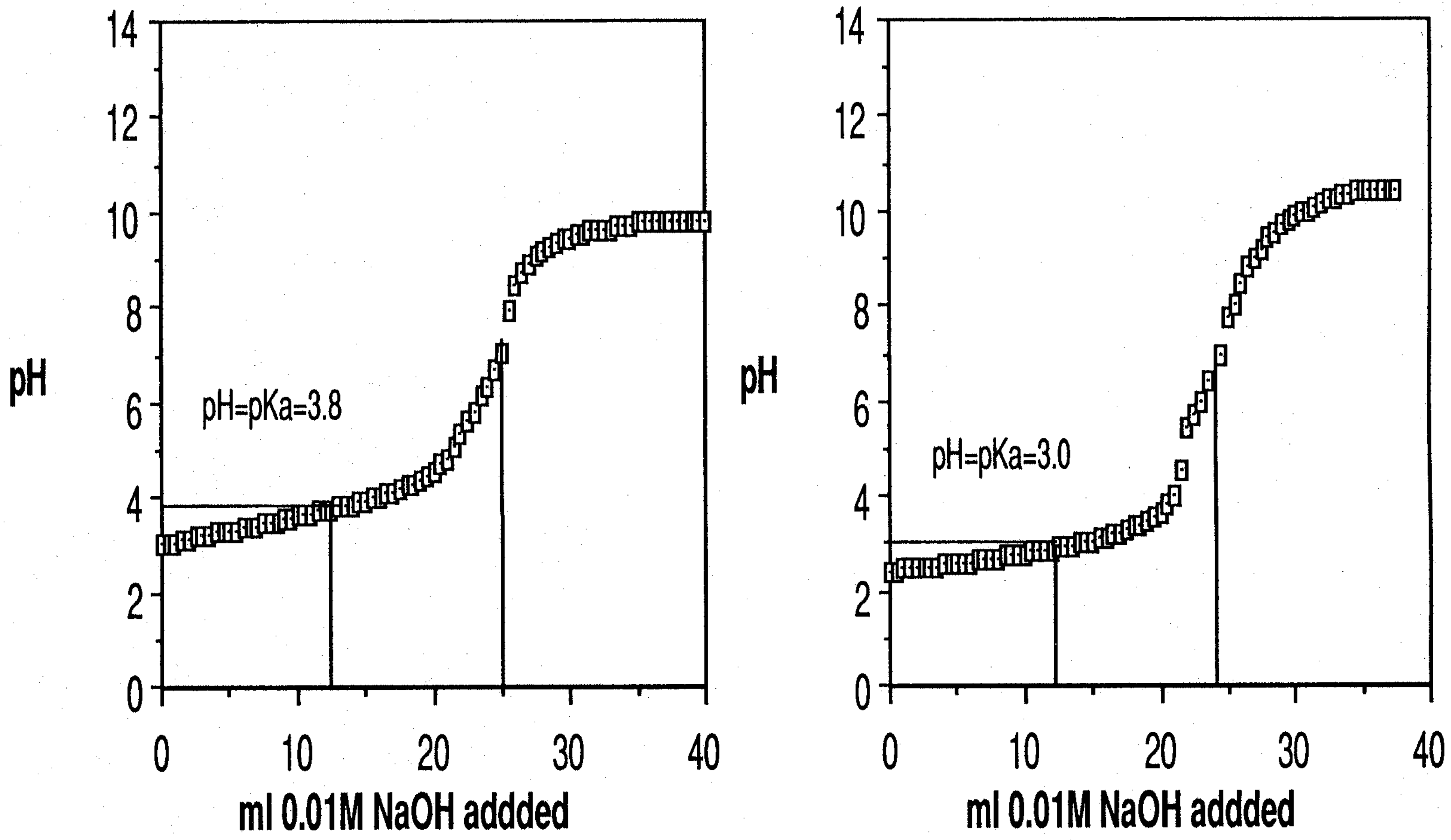
Figure 18. Titration curves for 0.01M 2,3-DFBA (a) and 0.01M 2,5-DFBA (b).



a

b

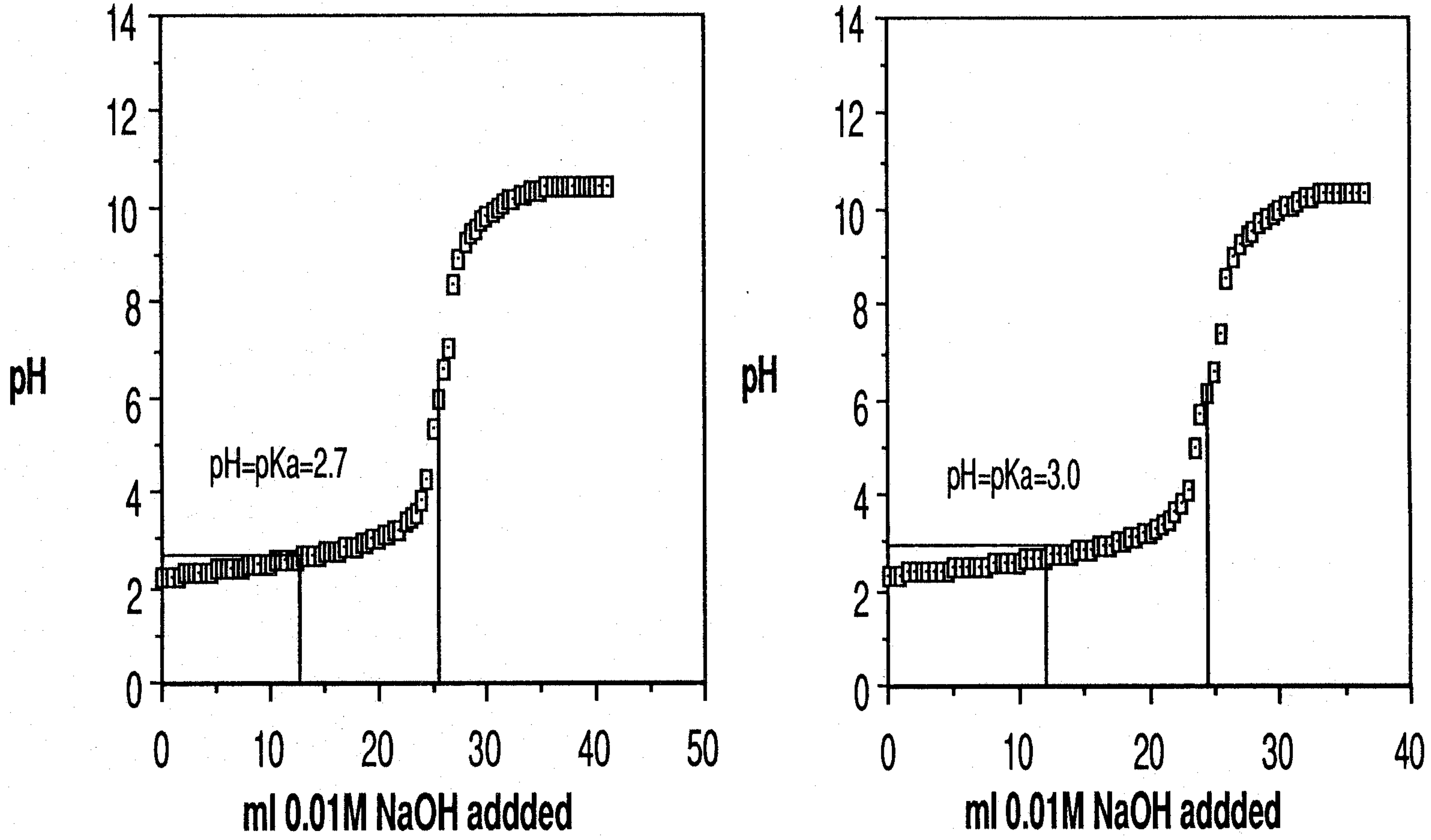
Figure 19. Titration curves for 0.01M 3,4-DFBA (a) and 0.01M 3,5-DFBA (b).



a

b

Figure 20. Titration curves for 0.01M *m*-TFMBA (a) and 0.01M *o*-TFMBA (b).



a

b

Figure 21. Titration curves for 0.01M PFBA (a) and 0.01M 2,6-DFBA (b).

TFMBA should elute near 3,4-DFBA and 2,6-DFBA should elute near 3,5-DFBA under the same HPLC conditions. However, *o*-TFMBA and 2,6-DFBA elute much later than 3,4-DFBA and 3,5-DFBA under the same conditions. (D.P. Grabka, personal communication). This would suggest that the actual pKa values for these compounds are lower than the reported values listed in Table 7, and the values of 3.0 measured in this study may be more accurate. If the reported value for PFBA of 1.49 is correct, it should be strongly retained in the separation column and elute very late relative to the other fluoro-organic compounds. However, PFBA elutes just after 2,6-DFBA under the HPLC conditions used in this evaluation, suggesting that a pKa value of 2.7 for PFBA is a more reasonable figure.

3.3 Batch Study Results

The samples which had been collected at the designated time periods from the batch studies using the fine-grained eolian sand and the silty clay loam were analysed for fluoro-organic and bromide concentrations using the HPLC technique. The samples which had been collected from the soil blanks and the tracer blanks were also analysed. The percent error of the HPLC analysis was determined using the response values for the standards which were run during the analysis of the batch study samples. For these samples the analytical error, expressed as the coefficient of variation was 2%.

The results of the analysis of the samples taken from the tracer plus soil mixtures for the fine-grained eolian sand with initial solution concentrations of 50 ppm fluoro-organic and 100 ppm bromide are shown in Figure 22. The results are presented as C/Co versus time. The C/Co term refers to the concentration of each compound in the sample divided by the initial concentration. Time is given in days, indicating the amount of time which had elapsed when each sample was taken. The graph indicates that there was no loss of concentration of any of the four fluoro-organics or bromide over the 85 days of sampling for this initial concentration. The results of the batch study using 5 pm fluoro-organic and 10 ppm bromide in this soil were the same. There appears to be no sorption of the four fluoro-organics or bromide to the soil surfaces, nor any biological or chemical transformations of the compounds taking place under batch conditions at ambient temperaures using this fine-grained eolian sand.

The results for the samples taken from the tracer-only mixtures are identical to the results for the tracer plus soil mixtures. This data also shows no loss of concentration over the 85 days of the test for any of the four fluoro-

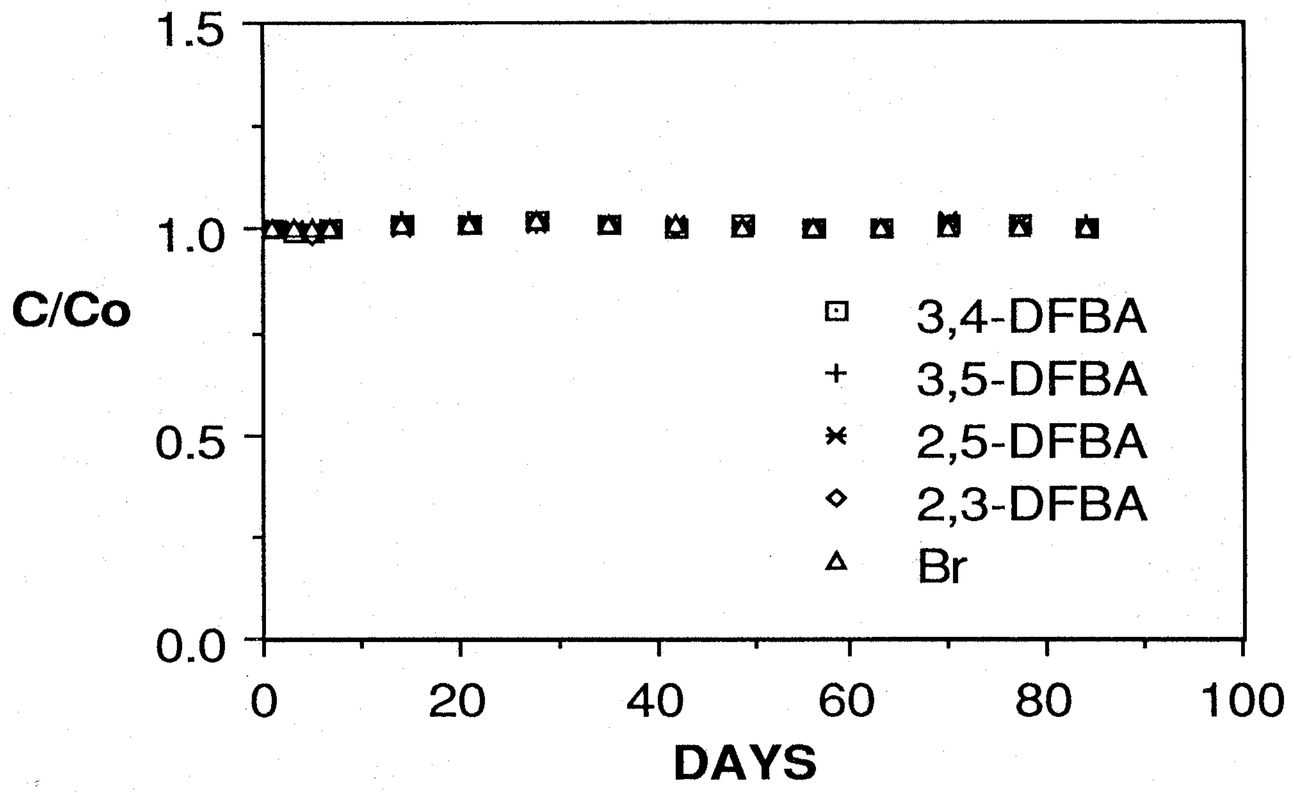


Figure 22. Batch study results using fluoro-organics and bromide in eolian sand. Test was conducted at room temperature - approximately 24^0 C.

organics as well as bromide for both initial concentrations used. This would appear to indicate that sorption to the polypropylene tubes of any of the fluoro-organics or bromide had not ocurred.

The results for the samples taken from the water plus soil mixtures indicated no fluoro-organic or bromide concentration present in any of the mixtures. This indicated there was no fluoro-organic or bromide present naturally in this fine-grained eolian sand.

The results of the batch study using a silty clay loam plus fluoro-organics and bromide with initial concentration of 50 ppm fluoro-organic and 100 ppm bromide are shown in Figure 23. This data indicates no loss of concentration of any of the fluoro-organics or bromide over the 85 days of the batch test with this initial concentration. The results of the batch study using 5 pm fluoro-organic and 10 ppm bromide in this soil were the same. This would appear to indicate there is no sorption to soil surfaces nor any biological or chemical transformations of any of the fluoro-organics or bromide under batch conditions at ambient tempertures using this silty clay loam. The samples which were taken from the soil plus water mixtures indicated there was no fluoro-organic nor bromide present naturally in this silty clay loam.

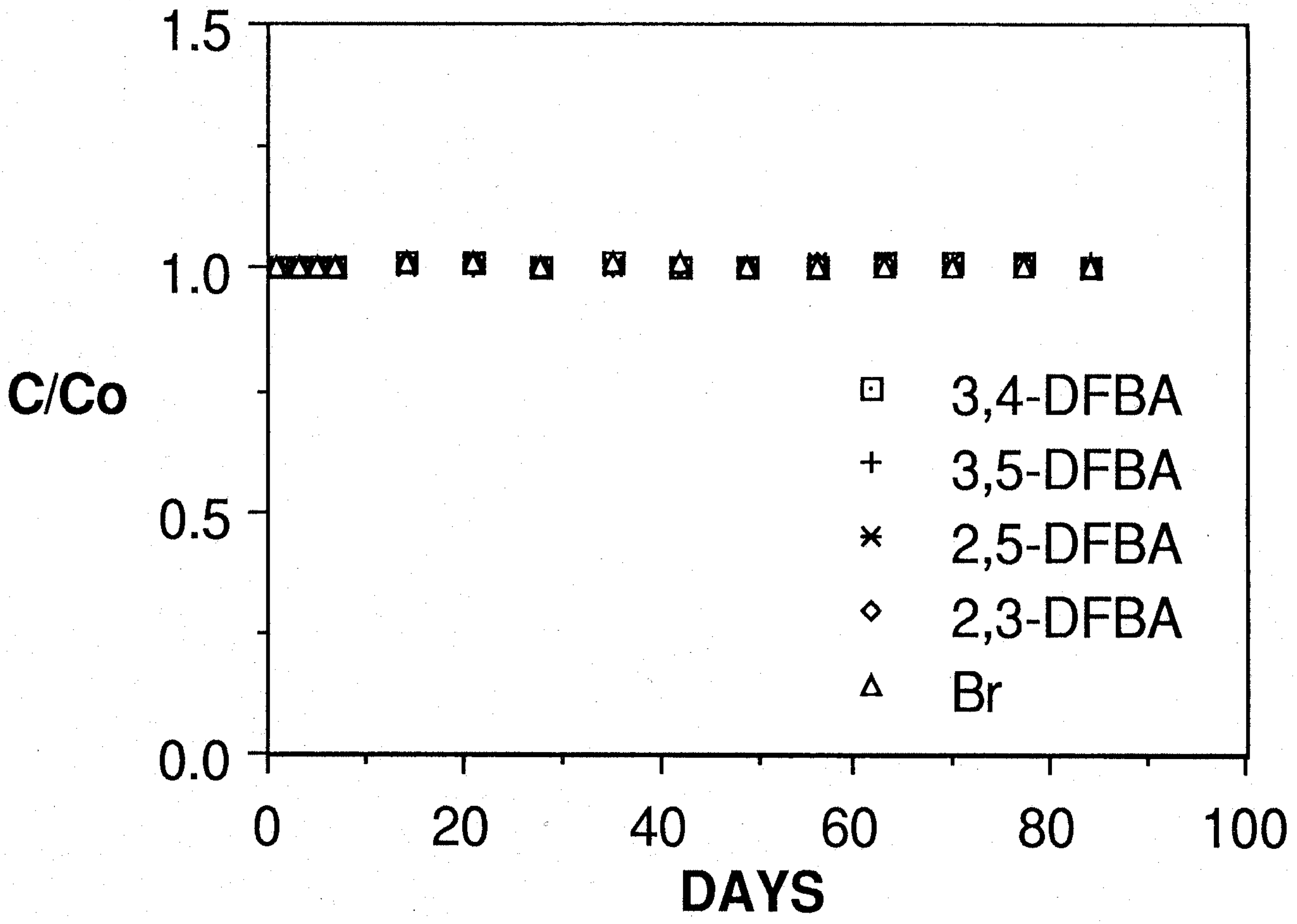


Figure 23. Batch study results using fluoro-organics and bromide in silty clay loam. Test was conducted at room temperature - approximately 24^0 C.

3.4 Ponded Water Column Study Results

All of the samples of column outflow for both columns under ponded, saturated conditions were analysed for fluoro-organic and bromide concentrations using the HPLC technique. The percent error of the HPLC analysis was determined using the response values for the standards which were run during the analysis of these saturated column study samples. For these samples the coefficient of variation was 3.5%. The data is presented as C/Co versus cumulative pore volumes for column 1 in Figure 24, and for column 2 in Figure 25.

The computer model called CXTFIT (Parker & van Genuchten, l984) was used to fit breakthrough curves to the observed outflow data for bromide for each column. Model 2 of the program was run using normalized flux concentrations, a pore water velocity of 0.026 cm/min, a 3.0 pore volume pulse injection, no first order decay, no zero-order production, no bromide present in the column prior to the pulse injection and an initial pulse concentration of 100 ppm. The program estimated the retardation and dispersion of bromide using 15 iterations from an estimated value of 1 for each.

The fitted data for column 1 is included in Figure 24, and the fitted data for column 2 is included in Figure 25. This computer analysis generated an estimate of retardation of 0.96 and dispersion coefficient of 0.67 cm^2/day for bromide for column 1 and estimated retardation of 0.94 and dispersion coefficient of 0.66 cm^2/day for bromide for column 2. For each fluoro-organic compound and bromide, the residuals between the observed relative concentrations and the fitted values were determined and the mean and standard deviations of these residuals were calculated. This was done for both columns and these values are presented in Table 8. The values for the four

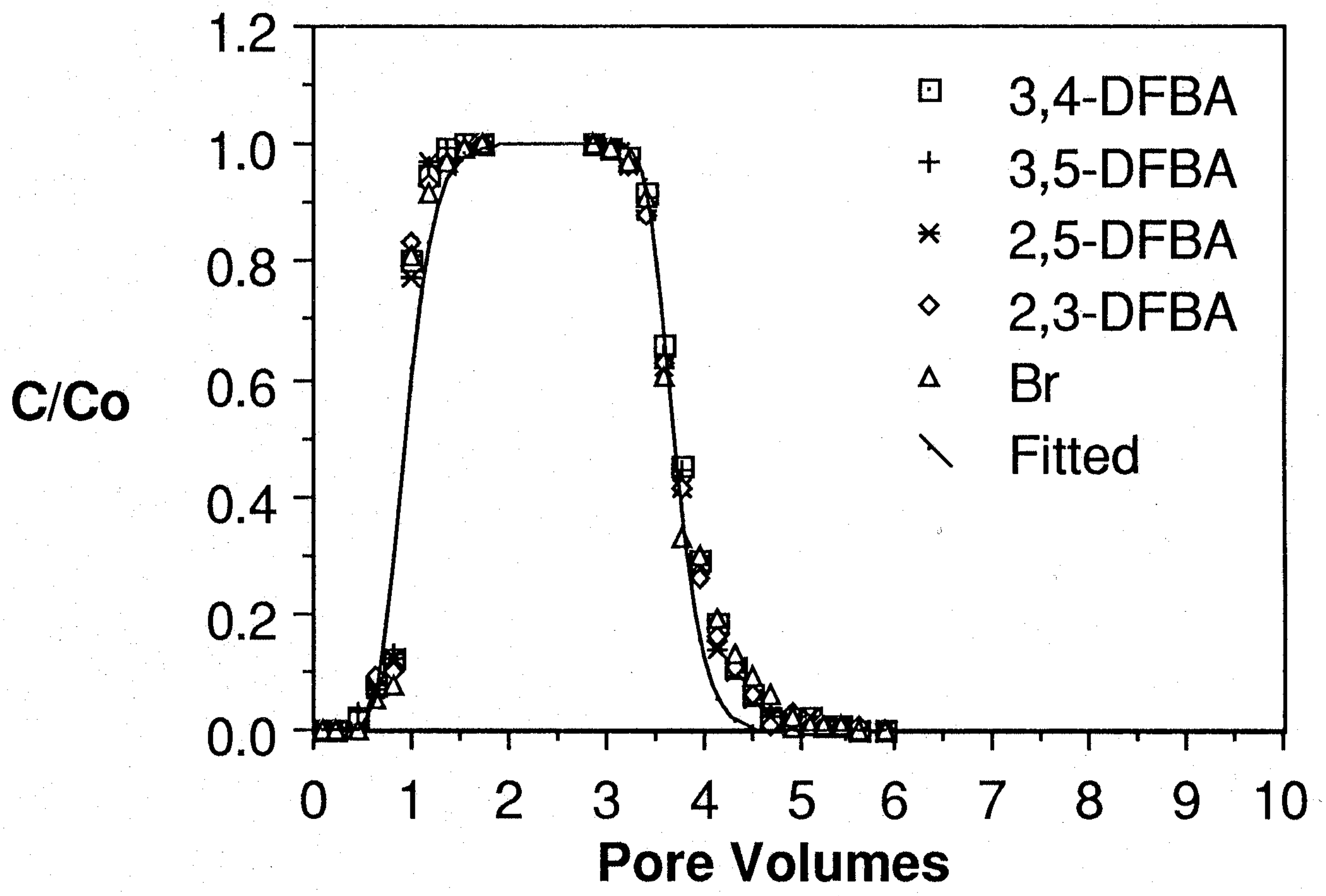


Figure 24. Observed and fitted breakthrough curves for the four fluoro-organics and bromide from column 1under ponded flow conditions.

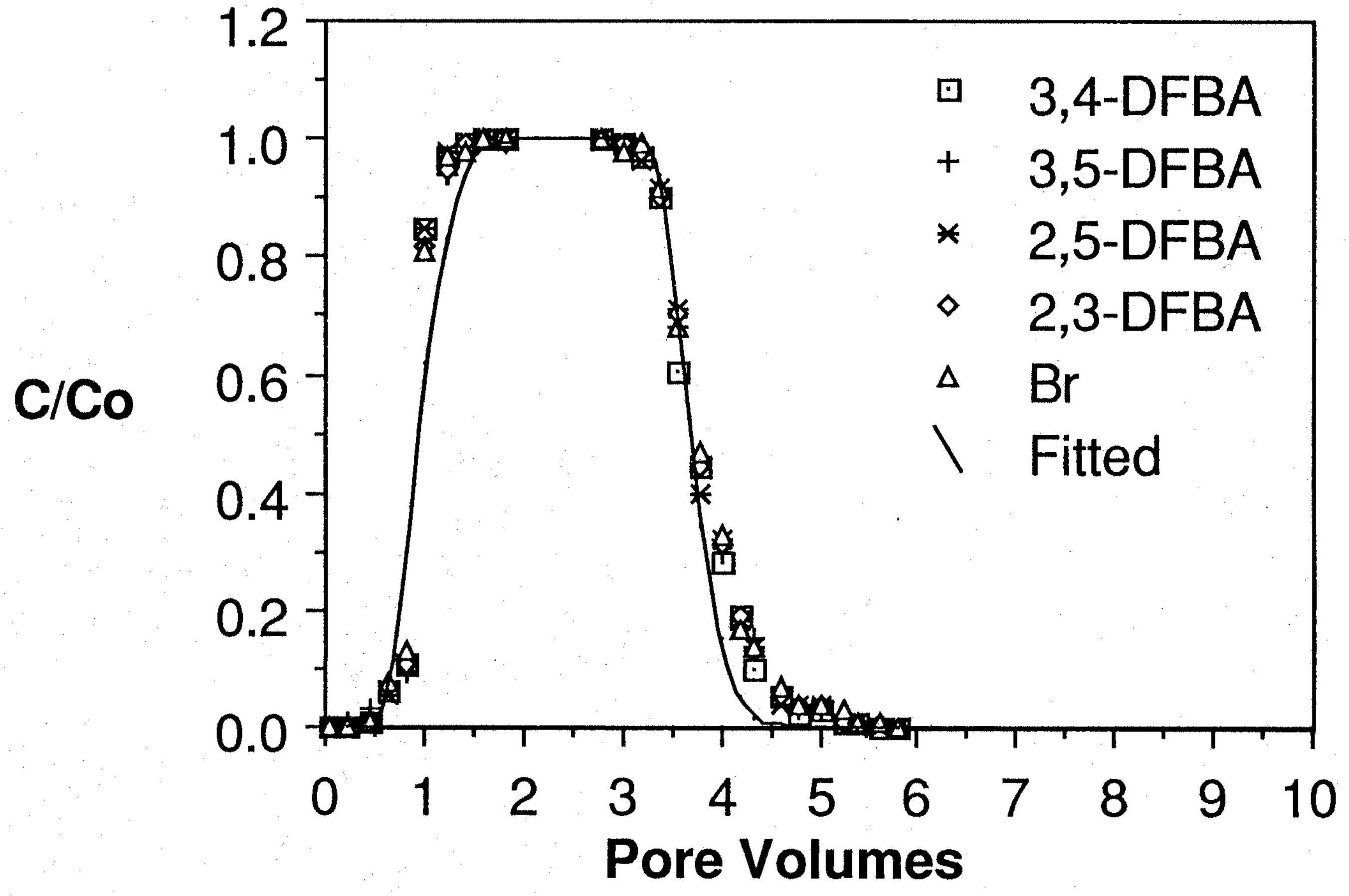


Figure 25. Observed and fitted breakthrough curves for the four fluoro-organics and bromide from column 2 under ponded flow conditions.

Table 8. Mean and standard deviation values of the difference between the measured tracer concentrations and the fitted curves for bromide.

	3,4-DFBA	3,5-DFBA	2,5-DFBA	2,5-DFBA	Br
Column 1-saturated	0.021(0.06)	0.021(0.06)	0.018(0.06)	0.019(0.07)	0.018(0.07)
Column 2-saturated	0.020(0.08)	0.019(0.07)	0.031(0.07)	0.030(0.07)	0.031(0.07)
Column 1-unsaturated	0.006(0.04)	0.005(0.04)	-0.002(0.03)	0.003(0.03)	0.003(0.02)
Column 2-unsaturated	0.027(0.03)	0.015(0.03)	0.012(0.03)	0.011(0.03)	0.014(0.02)

fluoro-organic compounds are similiar to those for the observed bromide data versus the fitted curve. At the 95% confidence interval, the mean values for the residuals of the observed fluoro-organic and bromide relative concentrations compared to the fitted curve did not differ statistically from 0.

For each fluoro-organic compound the residuals between the observed relative concentrations and the observed bromide relative concentrations were determined and the mean and standard deviations of these values are presented in Table 9. At the 95% confidence interval, the mean values for the residuals of the observed fluoro-organic data versus bromide did not differ statistically from 0.

The tailing of the breakthrough curves observed from column 1 and column 2 could be due to mixing of fluids which took place in void spaces at the bottom of the column, or it could be the result of mixing which may have occured when the flow of the tracer pulse was replaced with flow of tap water.

The stability of the four fluoro-organics under these column conditions can be evaluated using the mass recovery determined for each compound. The mass recovery for each compound in each column was measured by using the breakthrough curve of each compound. For each sample on the curve, the concentration of that sample was multiplied by the volume of column outflow that sample represents. This produces a value of mass, and the cumulative mass of each sample on the curve is determined, and compared to the mass of the compound in the original pulse to determine if any mass was lost during flow though the column. The mass recoveries for the four fluoro-organics and bromide for each column under saturated flow conditions are given in Table 10. Mass recoveries at or near 100% for all five compounds seem to indicate that the four fluoro-organics have stability characteristics similar to bromide under these conditions.

Table 9. Mean and standard deviation values of the difference between the fluoro-organic and the bromide concentrations for each experiment conducted.

		3,4-DFBA	3,5-DFBA	2,5-DFBA	2,3-DFBA
Col 1-saturated		0.005(0.031)	0.005(0.025)	-0.002(0.028)	0.002(0.026)
Col 2-saturated		0.004(0.018)	-0.005(0.013)	0.004(0.021)	-0.005(0.013)
Col 1-unsaturated		0.003(0.015)	0.002(0.021)	-0.005(0.015)	-0.007(0.013)
Col 2-unsaturated		-0.001(0.018)	-0.001(0.021)	0.002(0.020)	0.006(0.016)
Seviletta field site tracer test		-0.00003(0.0005)	0.0002(0.0006)	0.00006(0.0004)	-0.0002(0.003)
Vadose Zone tracer test porous cup	1-A	0.011(0.07)	0.031(0.07)	0.025(0.057)	0.027(0.05)
	1-B	- 0.01(0.012)	-0.01(0.018)	0.01(0.017)	-0.03(0.03)
	1-C	0.004(0.018)	-0.006(0.02)	0.002(0.01)	0.003(0.01)
	4-A	0.01(0.01)	0.003(0.01)	0.01(0.01)	0.008(0.019)
	4-C	0.0(0.017)	0.007(0.013)	0.005(0.017)	0.006(0.014)

Table 10. Mass recoveries for the four fluoro-organics and bromide for each experiment conducted.

	3,4-DFBA	3,5-DFBA	2,5-DFBA	2,3-DFBA	Br
Column 1-saturated	101.4%	100.8%	99.3%	99.6%	99.6%
Column 2-saturated	100.4	99.4	100.4	99.7	101.0
Column 1-unsaturated	101.7	100.7	98.7	98.7	101.2
Column 2-unsaturated	101.0	101.5	99.5	99.5	102.0
Seviletta field site	105	112	104	102	106 *
tracer test	~~110.8~~	~~105.5~~	~~100.8~~	~~97.3~~	~~105.4~~
Vadose zone tracer test					
porous cup 1-A	93.0	96.2	87.7	94.1	90.5
1-B	24.3	24.0	24.1	25.6	23.7
1-C	35.0	36.2	33.6	33.5	32.8
4-A	19.5	19.0	16.9	17.3	16.3
4-C	52.4	53.1	51.8	46.1	46.5

24 July 1990

* Pencilled values recalculated from App. G data: % recovery = $100 * \frac{(5 min)(56L/min)}{20L} * \Sigma C/Co$

3.5 Trickle Flow Column Study Results

All samples of column outflow from both columns under trickle flow conditions were analysed for fluoro-organic and bromide concentrations using the HPLC technique. The percent error of the HPLC analysis was determined using the response values for the standards which were run during the analysis of these trickle flow column study samples. For these samples the coefficient of variation was 3.0%. The resulting breakthrough curves for each compound are shown in Figure 26 for column 1 and Figure 27 for column 2. This data is plotted as C/Co versus cumulative column pore volumes.

The CXTFIT program was used to fit a curve for the bromide data from each column for the trickle flow tracer tests as well. Model 2 was again run with normalized flux concentrations, a pore water velocity of 0.024 cm/min, a 2.0 pore volume pulse injection, no first order decay, no zero-order production, no bromide present in the column prior to the pulse injection and an initial pulse concentration of 100 ppm. The program estimated the retardation and dispersion of bromide using 15 iterations from an estimated value of 1 for each. This program was not strictly applicable since the moisture content within the columns was not constant with depth, but the conditions present in the columns approximated those for which the CXTFIT model was designed. The fitted breakthrough curve for bromide for column 1 is also given in Figure 26, and that for column 2 is included in Figure 27. This computer analysis generated an estimated retardation of 0.96 and a dispersion coefficient of 0.09 cm^2/day for bromide for column 1 and an estimated retardation of 0.99 and a dispersion coefficient of 0.05 cm^2/day for bromide for column 2.

For each fluoro-organic compound and bromide, the residuals between the observed relative concentrations and the fit values were determined and the

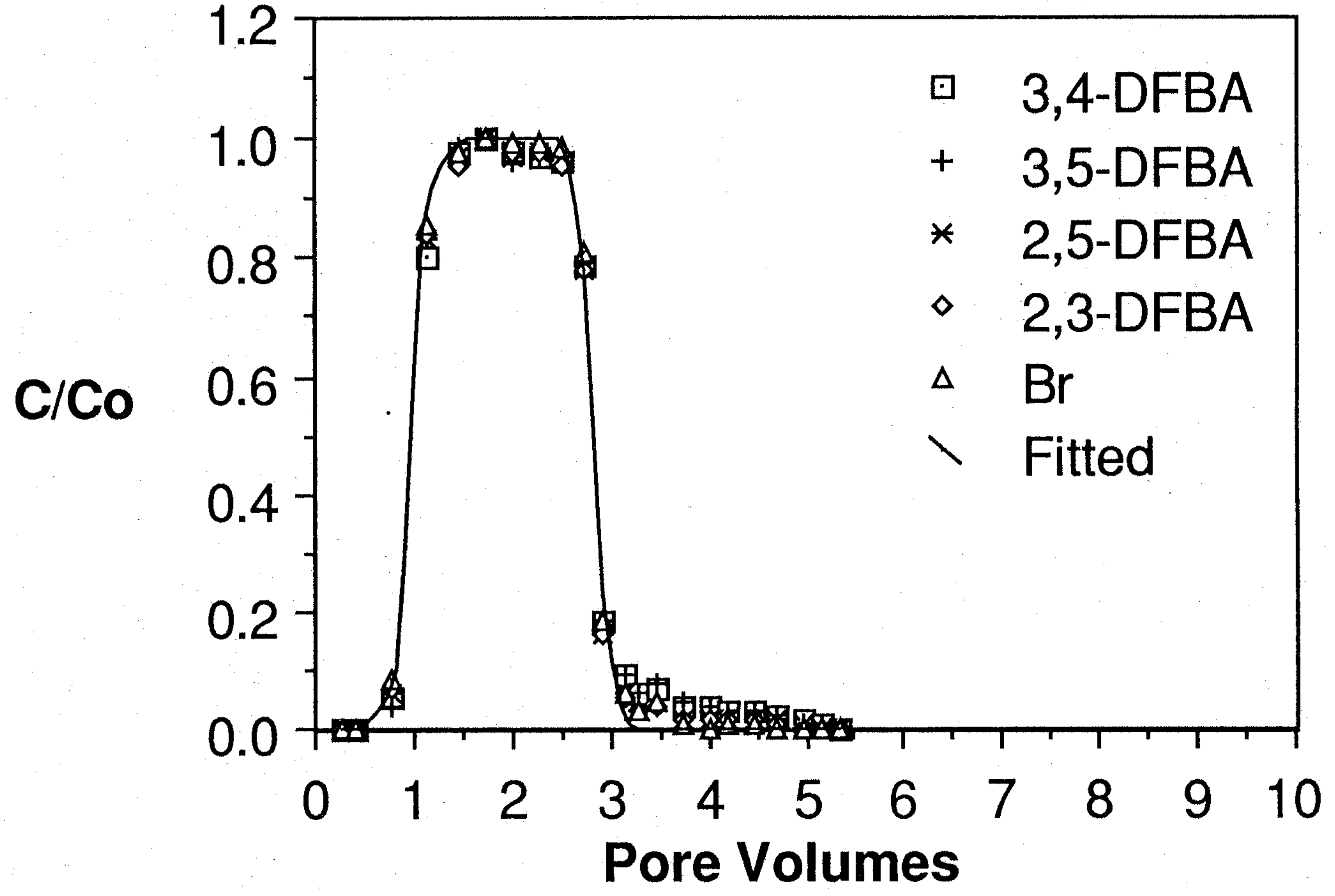


Figure 26. Observed and fitted breakthrough curves for the four fluoro-organics and bromide from column 1 under trickle flow conditions.

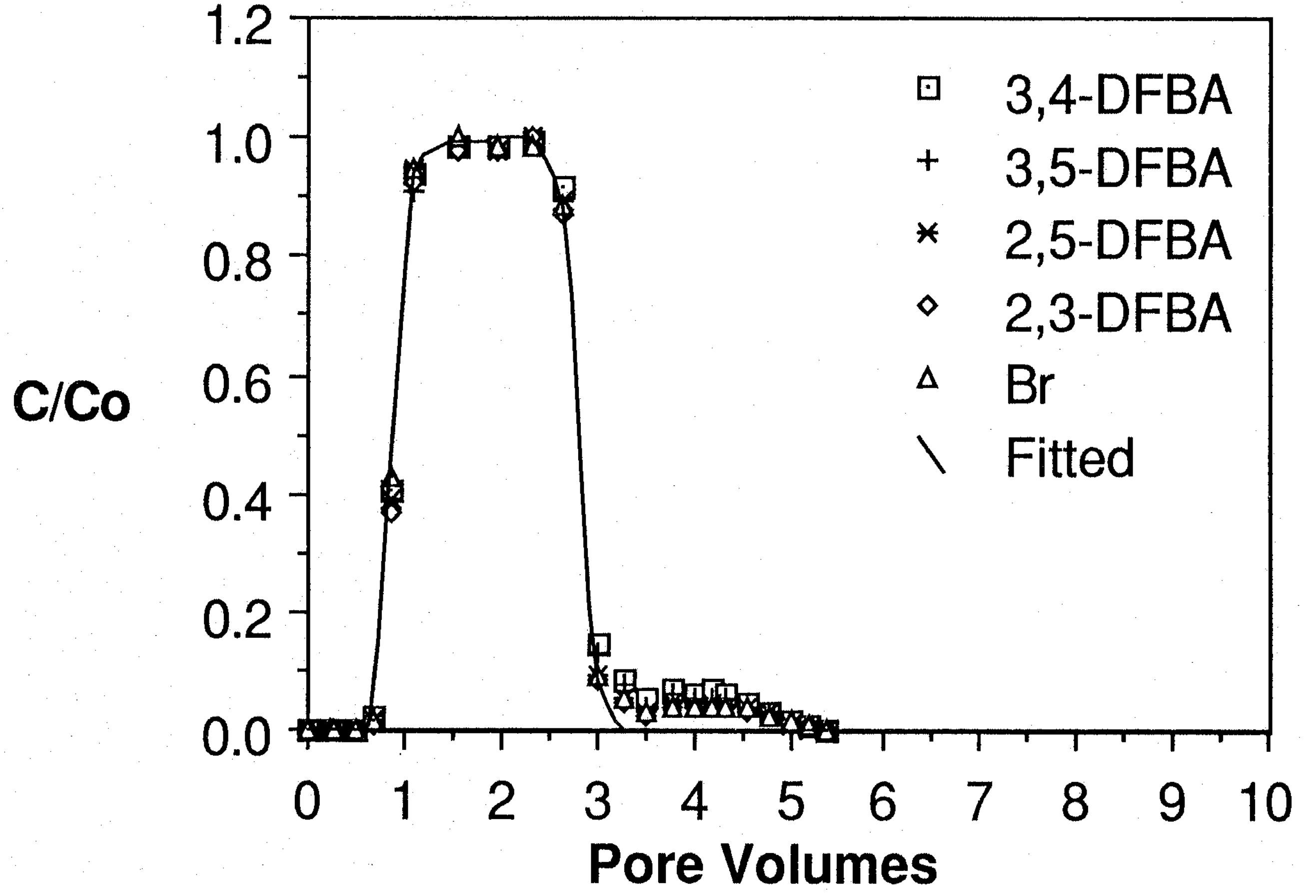


Figure 27. Observed and fitted breakthrough curves for the four fluoro-organics and bromide from column 2 under trickle flow conditions.

mean and standard deviations of these residuals were calculated. This was done for both columns and these values are presented in Table 8. At the 95% confidence interval, the mean values for the residuals of the observed fluoro-organic and bromide relative concentrations compared to the fitted curve did not differ statistically from 0.

For both columns under trickle flow conditions the standard deviation values for the observed fluoro-organic residuals tended to be higher than the deviations for the observed bromide from the fitted curve. The largest deviations from the fitted data were seen for the earliest eluting compounds, 3,4-DFBA and 3,5-DFBA. These deviations may have been caused by interference from compounds present in the samples which elute early and increase the baseline and the response for the early eluting fluoro-organics.

For each fluoro-organic compound the residuals between the observed relative concentrations and the observed bromide relative concentrations were determined and the mean and standard deviations of these values are presented in Table 9. At the 95% confidence interval the mean values for the residuals of the observed fluoro-organic data versus bromide did not differ statistically from 0.

The tailing of the breakthrough curves observed from both columns 1 and 2 could be the result of mixing which took place at the bottom of the columns during the flow experiment, or it could be due to mixing which occured when the tracer pulse flow was replaced with flow of tap water.

The stability of each fluoro-organic was compared to that of bromide using the mass recovery technique described previously. The mass recoveries for the four fluoro-organics and bromide for each column under trickle flow conditions are given in Table 10. Recoveries at or near 100% for all five compounds indicate that all four fluoro-organics have stability characteristics similiar to bromide under these column flow conditions. The increased recoveries seen for the early eluting fluoro-organics 3,4-DFBA and 3,5-DFBA may be due to the interference in the baseline described above.

3.6 Aquifer Tracer Test Results

All of the samples which had been collected from the pumping sequence designed to recover the pulse placed in the aquifer at the Seviletta field site were analysed for fluoro-organic and bromide concentrations via the HPLC technique. The percent error of the HPLC analysis was determined using the response values for the standards which were run during the analysis of the aquifer tracer test samples. For these samples the coefficient of variation was 8.0%. The results of this analysis are plotted as relative concentrations versus time in Figure 28. The extremely low tracer concentrations observed, less than 1% of the injected concentration, may have been due to dilution caused by the pumping episodes.

To quantify the behavior of each fluoro-organic versus that of bromide during this test the mean and the standard deviation of the residuals of the relative concentrations for each compound versus bromide were determined. (Table 9). At the 95% confidence interval the mean values of the residuals determined for the four fluoro-organics versus bromide did not differ statistically from 0.

The relative concentrations for each fluoro-organic were plotted versus the relative concentrations for bromide and a linear least-squares procedure determined the equation of the best least-squares fit line for each set of fluoro-organic data. Using the standard deviation the confidence interval of the slope of each line was determined. If each fluoro-organic behaved similiarily to bromide the slope of a line through the relative concentrations for each compound plotted versus that of bromide should be 1.0. The slopes of the regression lines for each fluoro-organic versus bromide did not differ statistically from 1.0 at the 95% confidence level. All four graphs for the relative

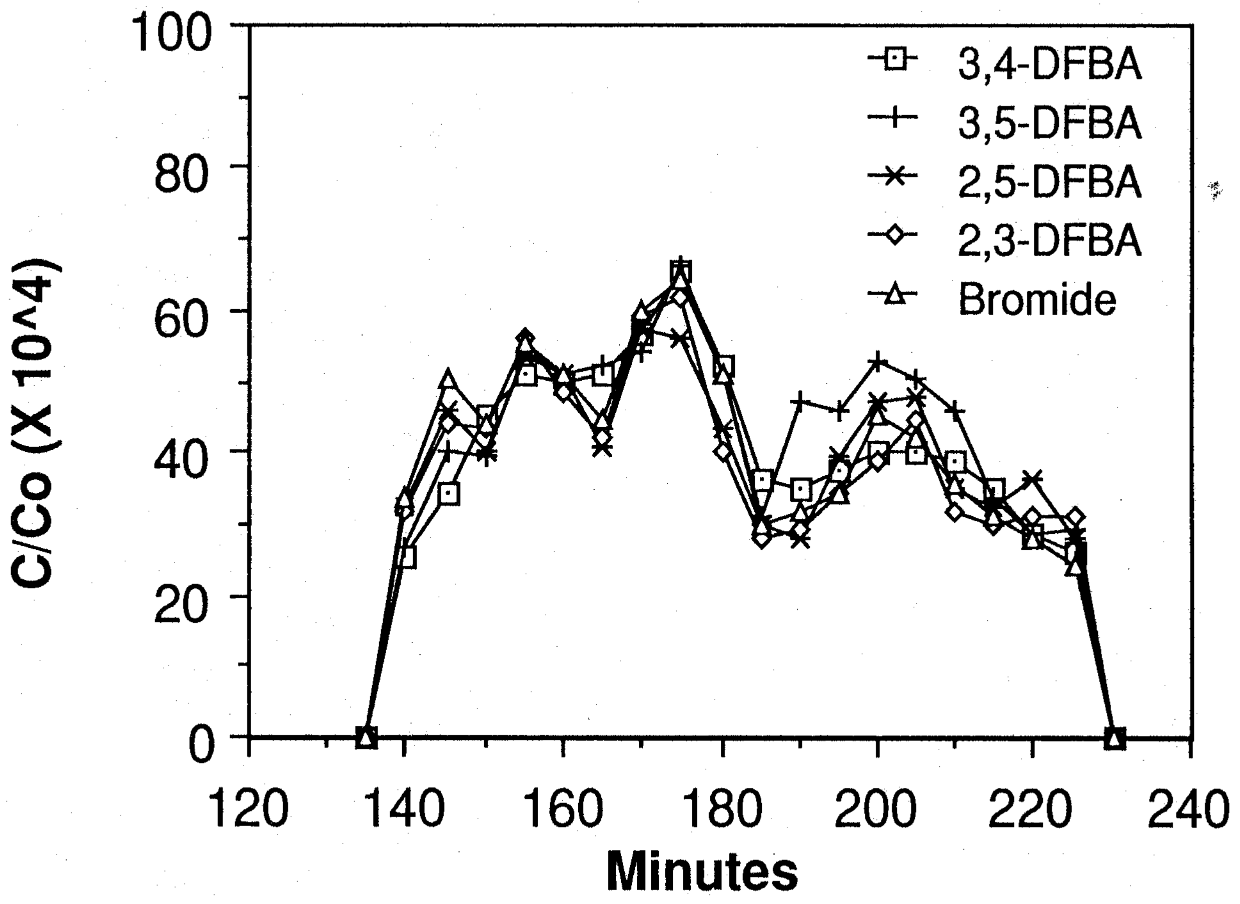


Figure 28. Breakthrough curves for fluoro-organics and bromide from aquifer tracer test.

concentrations of the fluoro-organics versus bromide were combined as Figure 34a.

The mass recoveries for all five compounds are presented in Table 10. These results indicate that the four fluoro-organics exhibited similiar stability as bromide under these conditions. The higher recoveries for 3,4-DFBA and 3,5-DFBA may be due to interference from compounds present in the samples which elute early and raise the baseline in the vicinity of these two compounds. The lower recoveries for 2,3-DFBA and 2,5-DFBA compared to bromide may be due to the relatively poor separation between these two compounds. Accurate quantitation of compounds which elute close together becomes more difficult at the low concentration levels seen in this aquifer tracer test.

3.7 Vadose Zone Tracer Test Results

All of the samples which had been collected from the porous cup samplers over the time period of the vadose zone tracer test were analysed for fluoro-organic and bromide concentrations via the HPLC technique. The percent error of the HPLC analysis was determined using the response values for the standards which were run during the analysis of the vadose zone tracer test samples. For these samples the analytical error was 5%. The results from porous cup 1-A are shown in Figure 29, results from porous cup 1-B are shown in Figure 30, and results from porous cup 1-C are shown in Figure 31. Results from sampling location 4 are presented in Figure 32 for porous cup 4-A and in Figure 33 for porous cup 4-C. All of the breakthrough curves generated from this experiment are presented as C/Co versus hours since the pulse was applied to the site.

To quantify the behavior of each fluoro-organic versus that of bromide during this test the mean and the standard deviation of the residuals of the relative concentrations for each compound versus bromide were determined. (Table 9). At the 95% confidence interval the mean values of the residuals determined for the four fluoro-organics versus bromide did not differ statistically from 0.

The relative concentrations of each fluoro-organic are plotted versus bromide in Figure 34b for porous cup 1-A, in Figures 35a & b for porous cups 1-B and 1-C. The best fit linear least squares technique used previously indicated that the slopes of the regression lines for each set of fluoro-organic relative concentrations versus bromide did not differ from 1.0 at the 95% confidence inteval for porous cups 1-A, 1-B and 1-C. The relative concentations of each fluoro-organic are plotted versus bromide in Figures 36a & b for porous cup

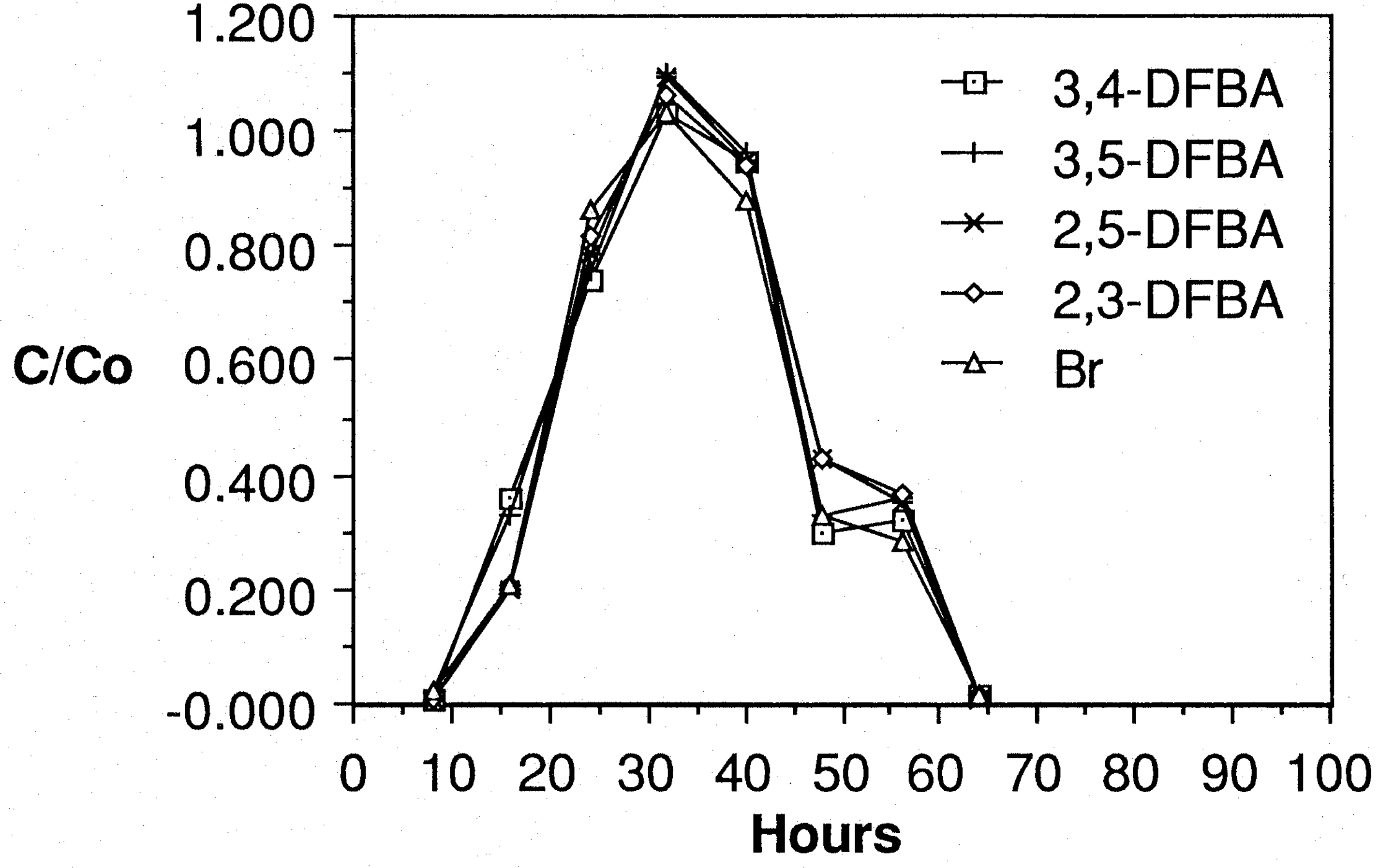


Figure 29. Breakthrough curves for the four fluoro-organics and bromide from vadose zone tracer test sampler 1-A.

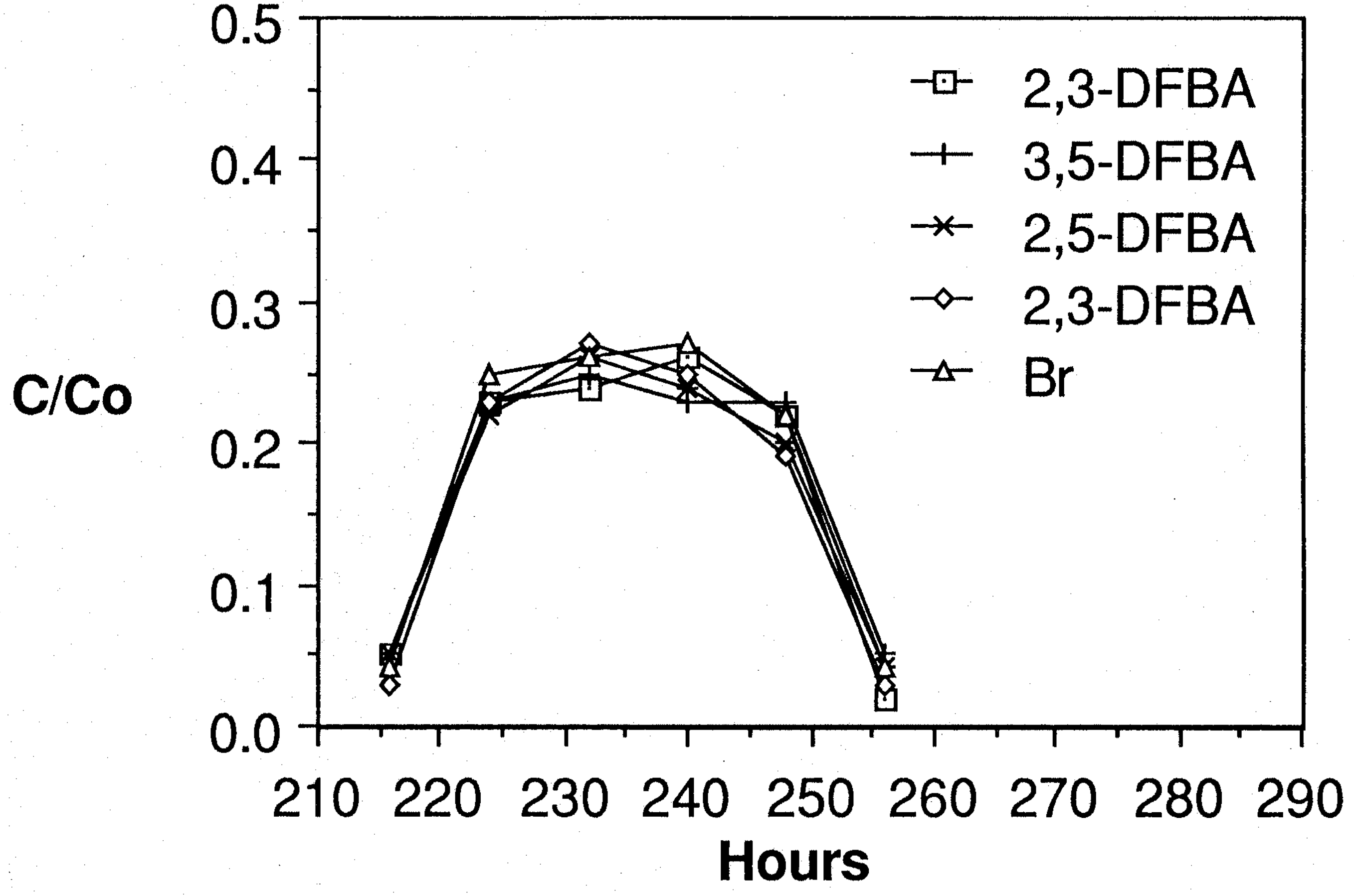


Figure 30. Breakthrough curves for the four fluoro-organics and bromide from vadose zone tracer test sampler 1-B.

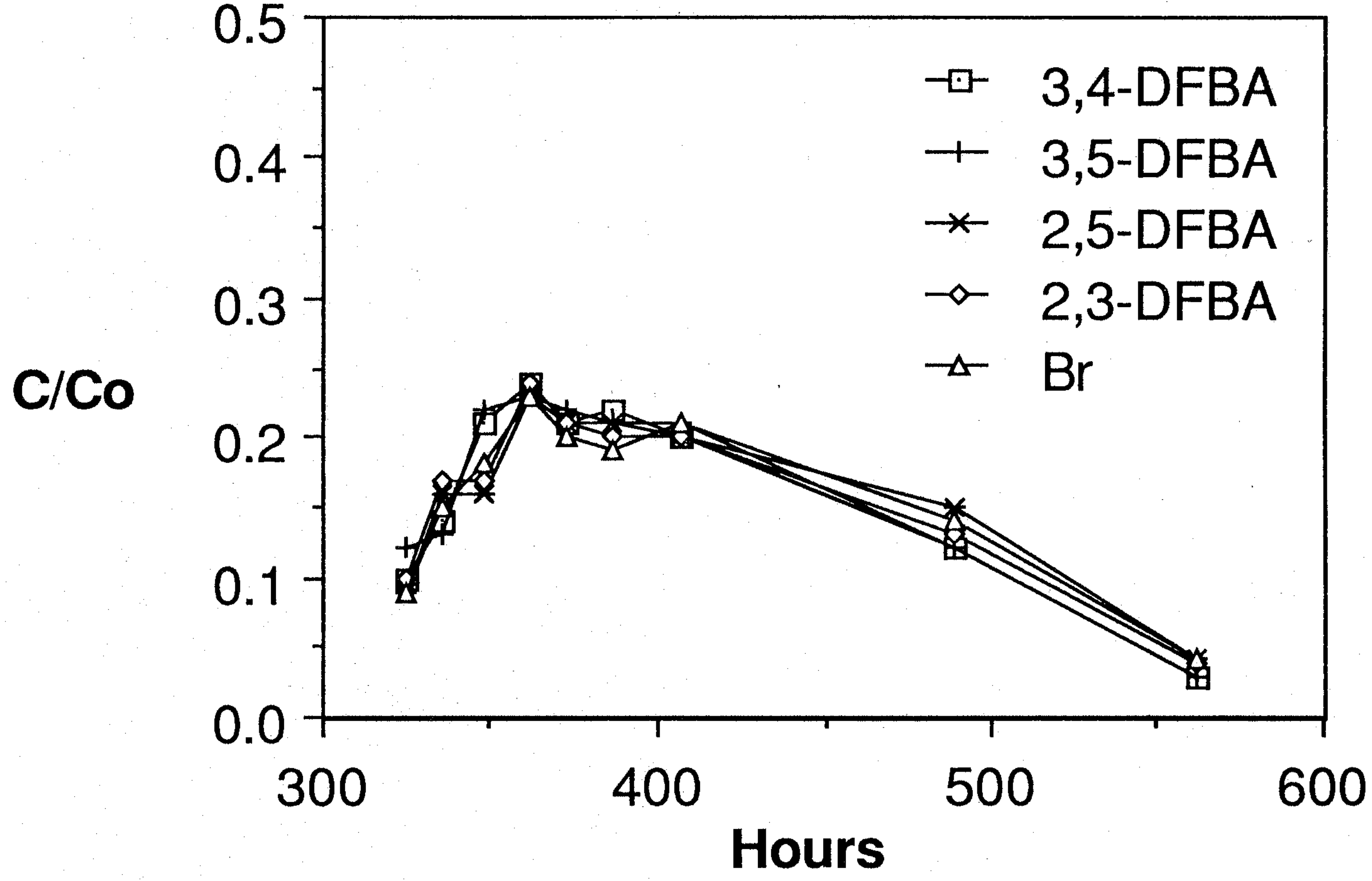


Figure 31. Breakthrough curves for the four fluoro-organics and bromide from vadose zone tracer test sampler 1-C.

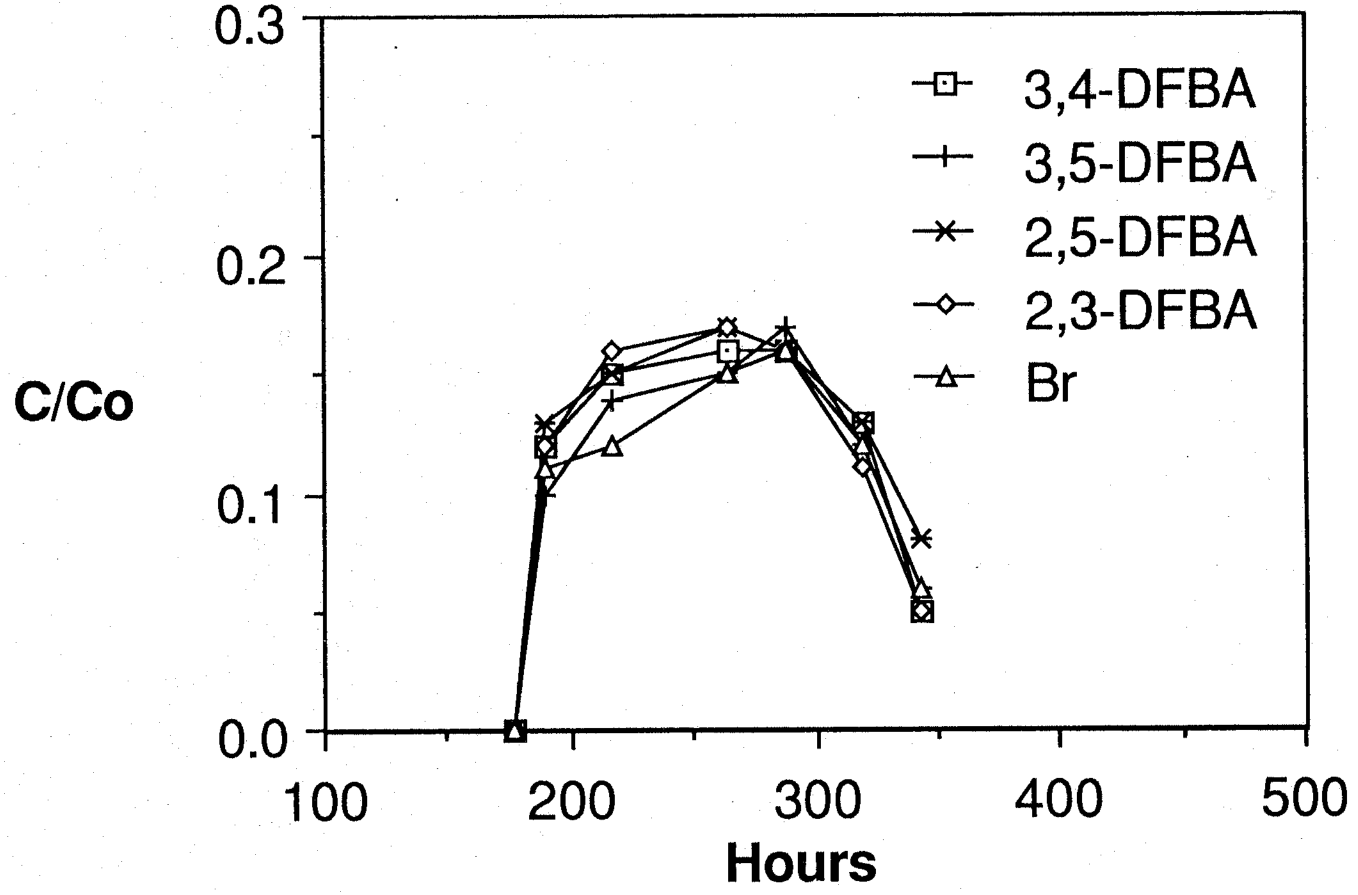


Figure 32. Breakthrough curves for the four fluoro-organics and bromide from vadose zone tracer test sampler 4-A.

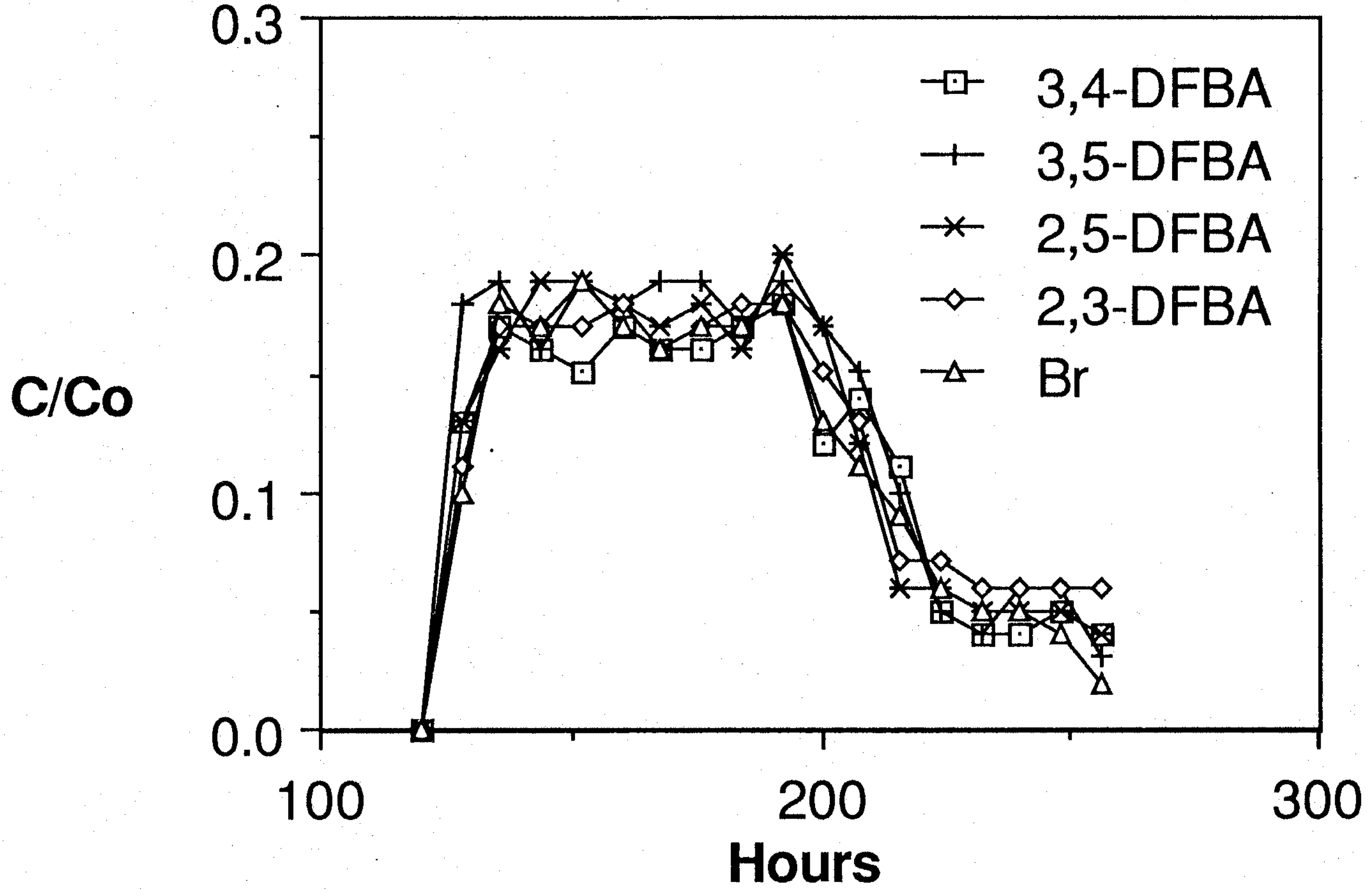
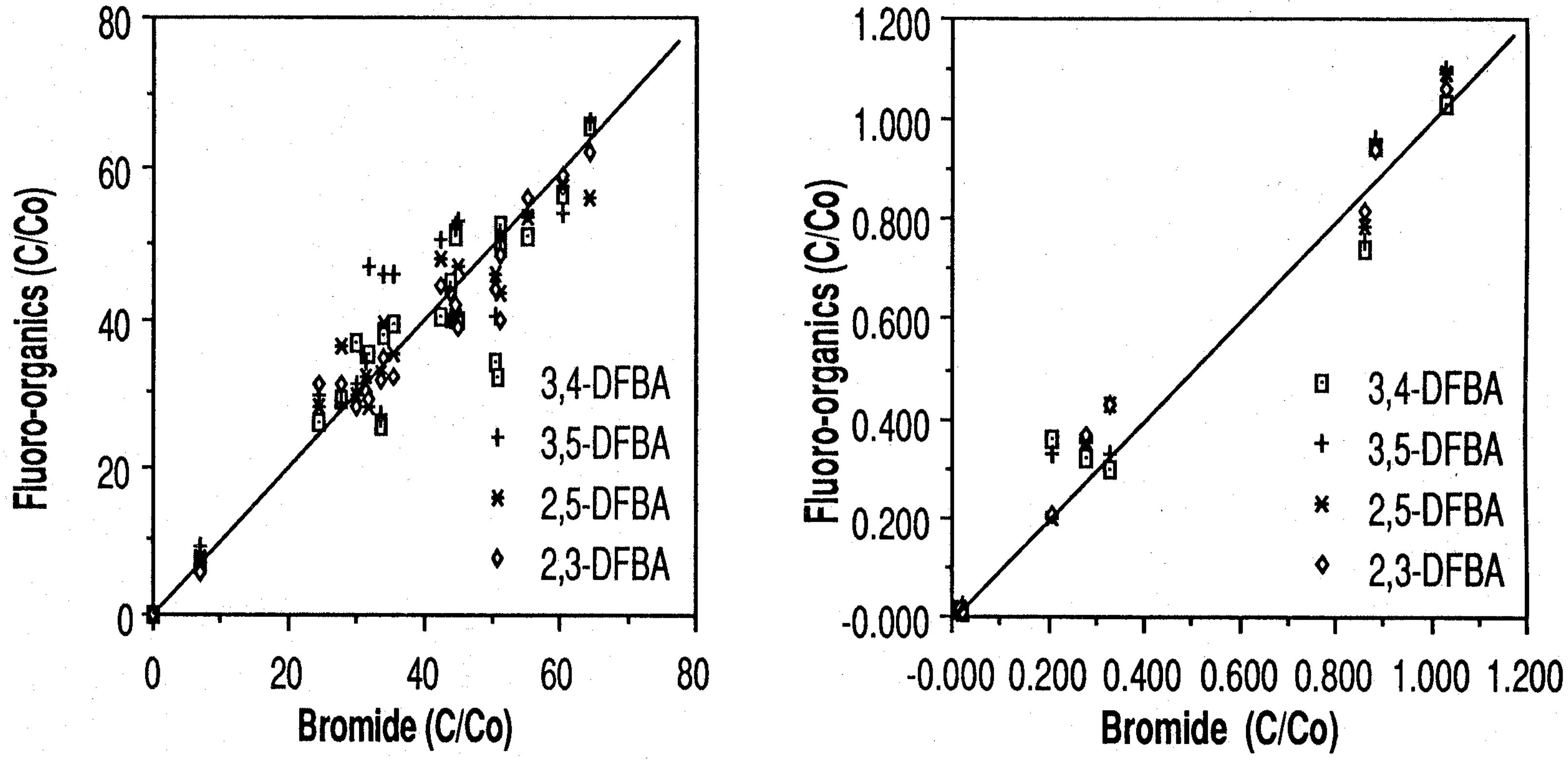


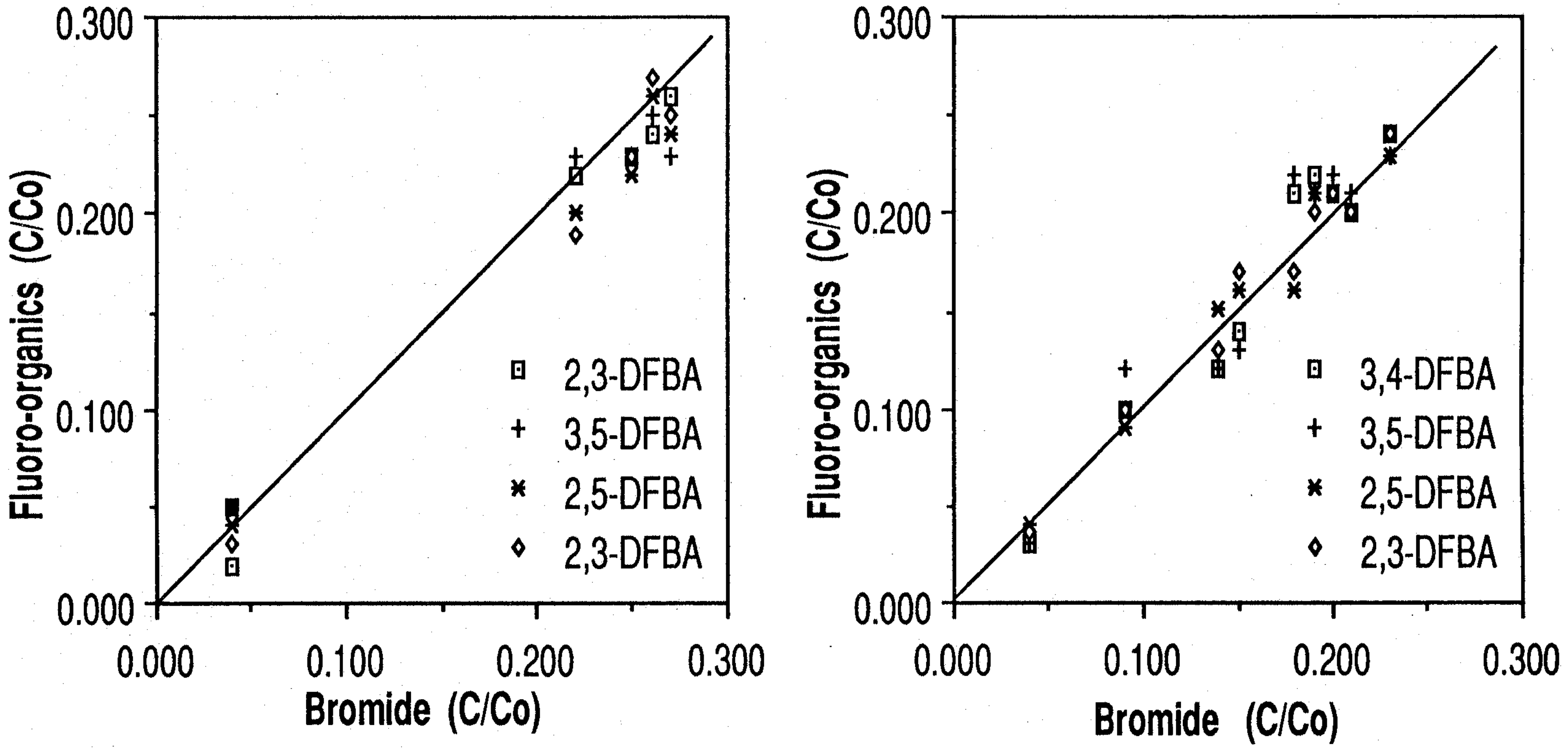
Figure 33. Breakthrough curves for the four fluoro-organics and bromide from vadose zone tracer test sampler 4-C.



a

b

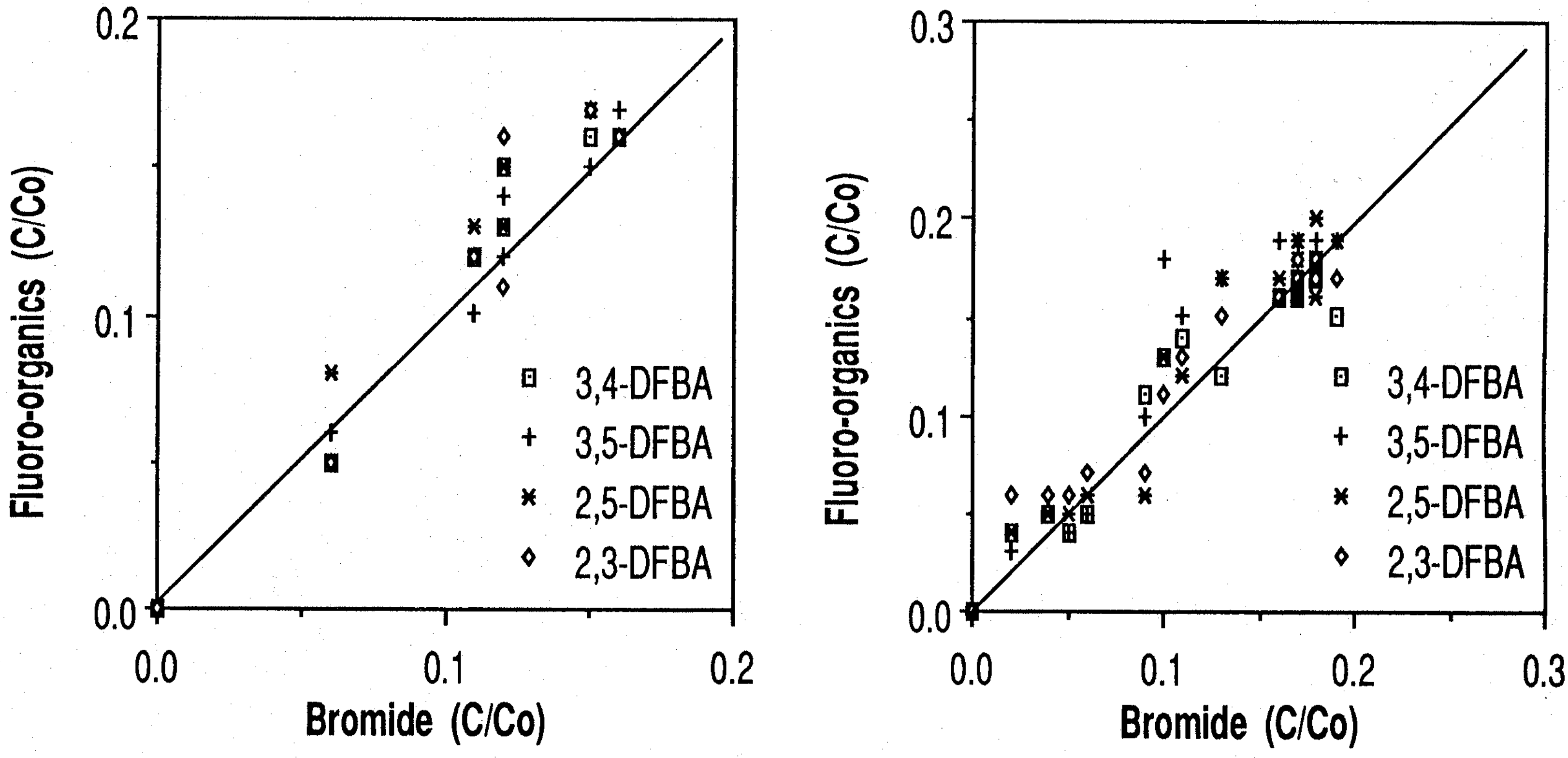
Figure 34. Relative concentrations for the four fluoro-organics versus bromide for the aquifer tracer test (a) and vadose zone tracer test sampler 1-A (b).



a

b

Figure 35. Relative concentrations for the four fluoro-organics versus bromide for vadose zone tracer test samplers 1-B (a) and 1-C (b).



a

b

Figure 36. Relative concentrations for the four fluoro-organics versus bromide for vadose zone tracer test samplers 4-A (a) and 4-C (b).

samplers 4-A and 4-C. The best fit linear least squares technique indicated that the slopes of the regression lines for each set of fluoro-organic relative concentrations versus bromide did not differ from 1.0 at the 90% confidence inteval for porous cups 4-A and 4-C. Nitrate levels were higher at these two sampling locations than at porous cups 1-A, 1-B and 1-C, and there may have been other compounds present in addition to nitrate which inteferred with the chromatography and skewed the results.

The relative recoveries of each fluoro-organic and bromide for each porous cup were determined using the flux, time, and the concentration for each sample. Multiplication of these produced a value of mg/cm^2, and this was multiplied by the area of the site over which the tracer pulse was applied. This value was divided by the total mass of each compound applied to the site to determine the relative recovery for each. This data is presented in Table 10. All the fluoro-organic compounds show higher recovery values than bromide for each porous cup sampler, with the earliest eluting peaks having the highest recoveries. This may be due to interference from compounds present in the samples which elute early and alter the baseline for the early eluting fluoro-organics and thus increase the concentration values reported. The strong deviations from 100% recovery seen in Table 10 are assumed to reflect spatial variability in water flow paths at this highly heterogeneous site.

SUMMARY AND CONCLUSIONS

4.1 Summary

A laboratory and field evaluation was undertaken to determine the suitability of 2,3-DFBA, 2,5-DFBA, 3,4-DFBA and 3,5-DFBA as soil and groundwater tracers. Batch studies, saturated and unsaturated column studies and a field aquifer and field vadose zone tracer test were conducted in order to gather enough information to make a determination of these compounds' suitability. Bromide ion was used as the standard against which the fluoro-organics were measured. An HPLC separation technique was also developed to detect and quantify the fluoro-organics and bromide in samples taken throughout this evaluation.

The liquid chromatographic separation technique used throughout this evaluation performed adequately, with both cartridge and conventional type analytical SAX columns being utilized. While the separation of the fluoro-organics and bromide was similar on both types of columns, the cartridge type column seemed more susceptible to leakage because of the greater number of fittings required to place it in line. The higher standard deviations for the measured detection limits of 2,3-DFBA and 2,5-DFBA may have been due to the close proximity of these two peaks. The differences in analytical error seen in each experiment may have been due to deterioration of the HPLC equipment, primarily the U6K injector. After a year of heavy use, the U6K injector seemed to wear out seals quickly and was prone to leakage, requiring frequent inspections and repair. As the equipment grew older the analytical error associated with it increased.

None of the four fluoro-organics selected for evaluation exhibited any decrease in concentration under batch conditions with two widely varying soils. Sorption of the compounds to the polypropylene tubes used was not observed. There was no trace of any fluoro-organic compounds present in the two soils used for these batch studies.

All four compounds exhibited similar mobility and stability characteristics as bromide during flow through porous media under saturated conditions. The mean values for the residuals of the observed fluoro-organic and bromide data versus the fitted data for bromide did not differ statistically from 0.0 at the 95% confidence interval, nor did the mean values for the residuals of the observed fluoro-organic data versus the observed bromide data. Mass recoveries of the four fluoro-organics were very close to the mass recovery determined for the bromide.

In the unsaturated column study, the four fluoro-organics exhibited increased standard deviation values of the mean residuals from those seen for bromide versus the fitted data. While the mean values for the residuals for the fluoro-organics and bromide versus the fitted data did not differ statistically from 0.0 at the 95% confidence interval this pattern can still be seen. The possible difference in behavior of the fluoro-organics may be due to differences in microscopic pore water velocities which result in mobile and immobile zones within the column. The higher diffusion coefficient for bromide versus the four fluoro-organics may result in bromide diffusing into the immobile zones and then back into the mobile zones later, while the fluoro-organics may remain in the mobile water zones. This might cause the behavior of the bromide to differ from that of the fluoro-organics in an unsaturated environment. The higher relative recoveries for the fluoro-organics may have been due to interference from compounds present in the samples which elute early and alter the baseline for the early eluting fluoro-organics and thus increase the concentration values reported. This may also have caused the higher standard deviation values seen for the observed fluoro-organic data versus the fitted data.

The stability characteristics of the four fluoro-organics determined after three months in the phreatic aquifer at the Seviletta field site were very similar to those of bromide under the same conditions. The high analytical error seen for this experiment may have been due to a combination of leakage problems with the U6K injector and low concentrations levels of the samples measured. At the 95% confidence interval the mean values of the residuals determined for the relative concentrations of the four fluoro-organics versus bromide did not differ statistically from 0. The slopes of the regression lines for each fluoro-organic versus bromide did not differ statistically from 1.0 at the 95% confidence level.

The data from the vadose zone tracer test indicated that the four fluoro-organics behaved in a manner close to that of bromide. At the 95% confidence interval the mean values of the residuals determined for the relative concentrations of the four fluoro-organics versus bromide did not differ statistically from 0. The best fit linear least squares technique indicated that the slopes of the regression lines for each set of fluoro-organic relative concentrations versus bromide did not differ from 1.0 at the 95% confidence interval for porous cups 1-A, 1-B and 1-C and at the 90% confidence interval for porous cups 4-A and 4-C. The higher relative mass recoveries for the fluoro-organics seen in this experiment may have been due to interference from compounds present in the water samples which altered the baseline for the early eluting compounds. This may also explain the deviation of the slopes of the the regression lines for porous cups 4-A and 4-C. Several of the porous cup samplers exhibited levels of nitrate higher than would be expected. It is thought that the hay which had been used to insulate the water emitters was the source of this nitrate and that holes in the plastic liner allowed the nitrate to reach the porous cup samplers. High nitrate levels in the samples would tend to alter bromide concentration readings and skew the fluoro-organic to bromide ratio.

4.2 Conclusion

Based on the results of these batch studies, saturated and unsaturated column studies and aquifer and vadose zone tracer tests, it is concluded that 2,3-DFBA, 2,5-DFBA, 3,4-DFBA and 3,5-DFBA exhibit characteristics of acceptable soil and groundwater tracers in environments similar to those used for this evaluation.

The relatively poor separation of 2,3-DFBA and 2,5-DFBA leads to increased error of measurement and difficulty of detection at low concentration levels. If only a few tracer compounds are required, it may be best to select just one of them.

Care must be taken when selecting these compounds for use in field situations. Because they are weak acids, they will become uncharged species in waters having a low pH value. The exact pH level at which each compound will become neutral depends on the pKa value determined for that compound. In environments having low pH values such as mill tailings or mine drainage waters, these fluoro-organics may not be suitable tracer compounds. The pH of the water should be at least one unit higher than the pKa for the compound being utilized. If tracer testing is to be conducted in waters with slightly low pH levels, fluoro-organics compounds may be selected which have the lowest pKa values.

If a very concentrated solution of any of these fluoro-organics is required, the solubility can be increased by raising the pH of the solution by adding a base. After the fluoro-organics have dissolved the pH of the solution can be lowered to the neutral range with the addition of acid without precipitation of the fluoro-organics.

Cost can be an important factor when choosing which fluoro-organics compounds to use as tracers. The prices of these compounds vary widely depending on the company selling them and the amount which is purchased. These range from \$14.00/gram for 2,5-DFBA down to \$4.46/gram for 3.4-DFBA when purchased in 10g units or less. (Aldrich Chemical Company, Milwaukee, WI). The price of 3,4-DFBA drops to \$3.43/gram when purchased in 50 gram units. (Yarsley Chemicals, London, England).

Toxological testing has not been conducted on these compounds, so they should not be used in situations where they may enter water meant for human consumption.

4.3 Future Work

Future work which may be undertaken to further evaluate these compounds could include toxicity tests to determine if these compounds are safe to be used in situations where they may end up in human drinking water supplies and to insure that they are not a health hazard to researchers working with them.

Studies involving the use of micro-organism rich environments could also be conducted to further evaluate the stability of these compounds in various natural environments.

Chromatographic techniques could be refined so that these four fluoro-organics could be used simultaneously with the four other fluoro-organics already used as groundwater tracers. A separation technique that would separate these 8 fluoro-organics, bromide, chloride and nitrate could be useful.

Trace enrichment techniques could be refined to lower the detection limits of these four compounds, increasing the amount of dilution acceptable, and thus increasing the time and distance scales of the tracer tests. This would increase the effectiveness of these four fluoro-organics as soil and groundwater tracers.

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APPENDIX A. Equations used throughout this evaluation.

Beers Law:

$A = (E)\,(d)\,(c)$

with: A = absorbance
E = extinction coefficient
d = length of detector cell
c = concentration (moles/liter)

Acid dissociation constant expression used to determine pKa values for fluoro-organic compounds:

$pH = pKa - \log [HA/A^-]$

with pH = pH of titration solution
pKa = acid dissociation constant
HA= amount of acid present as neutral species
A^- = amount of acid present in anionic form

Darcy's Law:

$Q = KA\, dh/dl$

with: Q = flow rate out of column (vol/time)
K = hydraulic conductivity (length/time)
A = cross-sectional area ($length^2$)
dh/dl = hydraulic gradient (length/length)

Specific discharge:

$q = Q/A$

q = specific discharge (length/time)

Pore water velocity:

$v = q/0$

with: v = pore water velocity (length/time)
0 = volumetric water content

Porosity

$n = 1 - P_b/P_s$

with P_b = bulk density
P_s = particle density

APPENDIX B. Chromatography data measured during evaluation.

B.1. Normalized detector response versus wavelength for the four fluoro-organics, bromide, chloride, nitrite and nitrate.

Wavelength	3,4-DFBA	3,5-DFBA	2,3-DFBA	Br	2,5-DFBA	$N0_3$	NO_2	Cl
190	0.88	1.0	0 .69	0.41	0.67	0.03	0.002	0 .32
195	0.78	0.79	0.56	0.39	0 .53	0.04	0.002	0.17
200	0.51	0.44	0.34	0.33	0 .33	0.05	0.003	0.08
205	0 .27	0.23	0.22	0.24	0.21	0 .05	0.003	0.01
210	0.16	0.18	0.14	0.12	0 .14	0.047	0.003	0.003
215	0.17	0.21	0.16	0.08	0.17	0.04	0.002	0
220	0.21	0.27	0.18	0.03	0.18	0	0	0
225	0.27	0.33	0.2	0	0.19	0	0	0

B.2. Detector response versus injected mass for the four fluoro-organics and bromide.

Mass	3,4-DFBA	3,5-DFBA	2,3-DFBA	2,5-DFBA	Br
100	0.48541	0.40259	0.36976	0.35976	
200					0.83088
500	1.96035	1.56835	1.48405	1.53120	3.45613
2000					6.46269
2500	9.57006	7.93468	7.29699	7.72295	
5000	19.13331	15.79634	14.54699	15.41570	15.86850
10000					31.48700

APPENDIX C. Data from determination of acid dissociation constants for the fluoro-organic compounds.

C.1. Titration curve data for 2,3-DFBA.

pH	ml 0.01 NaOH added	pH	ml 0.01M NaOH added
2.53	0	3.47	17
2.57	0.5	3.51	17.5
2.63	1	3.56	18
2.65	1.5	3.61	18.5
2.68	2	3.66	19
2.7	2.5	3.72	19.5
2.72	3	3.78	20
2.74	3.5	3.86	20.5
2.76	4	3.95	21
2.79	4.5	4.05	21.5
2.82	5	4.18	22
2.84	5.5	4.4	22.5
2.86	6	4.69	23
2.88	6.5	5.24	23.5
2.90	7	5.73	24
2.93	7.5	6.36	24.5
2.96	8	6.95	25
2.98	8.5	8.06	25.5
3	9	9.01	26
3.01	9.5	9.38	26.5
3.03	10	9.62	27
3.06	10.5	9.79	27.5
3.09	11	9.91	28
3.12	11.5	10.03	28.5
3.15	12	10.01	29
3.17	12.5	10.18	29.5
3.19	13	10.21	30
3.23	13.5	10.23	30.5
3.26	14	10.24	31
3.29	14.5	10.25	31.5
3.32	15	10.26	32
3.36	15.5	10.27	32.5
3.4	16	10.28	33
3.43	16.5	10.28	33.5
		10.28	34
		10.28	34.5

C.2. Titration curve data for 2,5-DFBA.

pH	ml 0.01 NaOH added	pH	ml 0.01M NaOH added
2.62	0	3.54	15.5
2.65	0.5	3.56	16
2.67	1.0	3.62	16.5
2.69	1.5	3.68	17
2.72	2.0	3.75	17.5
2.74	2.5	3.82	18
2.76	3.0	3.92	18.5
2.79	3.5	4.03	19
2.81	4.0	4.15	19.5
2.84	4.5	4.34	20
2.86	5.0	4.73	20.5
2.88	5.5	5.54	21
2.92	6.0	8.04	21.5
2.93	6.5	9.33	22.5
2.96	7.0	9.75	23
2.99	7.5	10.02	23.5
3.02	8.0	10.21	24
3.05	7.5	10.27	24.5
3.07	8.0	10.38	25
3.1	8.5	10.47	25.5
3.13	10.0	10.50	26
3.16	10.5	10.53	26.5
3.18	11.0	10.54	27
3.22	11.5	10.55	27.5
3.25	12	10.56	28
3.28	12.5	10.57	28.5
3.32	13	10.57	29
3.35	13.5	10.57	29.5
3.39	14	10.57	30
3.43	14.5	10.57	30.5
3.47	15	10.57	31

C.3. Titration curve data for 3,4-DFBA.

pH	ml 0.01 NaOH added	pH	ml 0.01M NaOH added
2.91	0	4.07	15.5
2.94	0.5	4.12	16
3.0	1	4.16	16.5
3.03	1.5	4.21	17
3.08	2	4.27	17.5
3.11	2.5	4.33	18
3.14	3.0	4.4	18.5
3.18	3.5	4.49	19
3.22	4.0	4.57	19.5
3.26	4.5	4.68	20
3.3	5.0	4.8	20.5
3.34	5.5	4.99	21
3.37	6	5.27	21.5
3.4	6.5	5.79	22
3.44	7	6.24	22.5
3.48	7.5	6.86	23
3.51	8	9.18	24
3.54	8.5	9.57	24.5
3.57	9	9.79	25
3.6	9.5	9.99	25.5
3.64	10.0	10.1	26
3.68	10.5	10.23	26.5
3.71	11	10.28	27
3.75	11.5	10.31	27.5
3.79	12	10.33	28
3.82	12.5	10.34	28.5
3.85	13	10.35	29
3.89	13.5	10.35	29.5
3.84	14	10.35	30
3.99	14.5	10.35	30.5
4.04	15	10.35	31
4.07	15.5	10.35	31.5

C.4. Titration curve data for 3,5-DFBA.

pH	ml 0.01 NaOH added	pH	ml 0.01M NaOH added
2.69	0	3.87	16.5
2.74	0.5	3.93	17.0
2.78	1.0	3.97	17.5
2.84	1.5	4.03	18
2.87	2.0	4.09	18.5
2.90	2.5	4.17	19
2.92	3.0	4.26	19.5
2.95	3.5	4.37	20
2.98	4.0	4.48	20.5
3.02	4.5	4.68	21
3.05	5.0	4.87	21.5
3.08	5.5	5.87	22.5
3.11	6.0	6.53	23
3.15	6.5	7.87	23.5
3.18	7.0	8.98	24
3.21	7.5	9.47	24.5
3.24	8.0	9.72	25
3.27	8.5	9.89	25.5
3.30	9.0	10.03	26
3.33	9.5	10.09	26.5
3.36	10.0	10.13	27
3.40	10.5	10.20	27.5
3.43	11.0	10.24	28
3.46	11.5	10.27	28.5
3.49	12	10.30	29
3.53	12.5	10.32	29.5
3.57	13	10.34	30
3.60	13.5	10.35	30.5
3.63	14	10.36	31
3.69	14.5	10.36	31.5
3.73	15	10.36	32
3.77	15.5	10.36	32.5
3.81	16	10.36	33
		10.36	33.5

C.5. Titration curve data for *m*-TFMBA.

pH	ml 0.01 NaOH added	pH	ml 0.01M NaOH added
3.03	0	4.7	20.5
3.05	0.5	4.84	21
3.07	1	5.04	21.5
3.11	1.5	5.31	22
3.15	2.0	5.62	22.5
3.19	2.5	5.83	23
3.22	3.0	6.13	23.5
3.24	3.5	6.36	24
3.27	4	6.72	24.5
3.29	4.5	7.07	25
3.31	5.0	7.93	25.5
3.34	5.5	8.43	26
3.37	6	8.73	26.5
3.4	6.5	8.94	27
3.43	7	9.07	27.5
3.46	7.5	9.17	28
3.49	8	9.26	28.5
3.52	8.5	9.34	29
3.56	9	9.41	29.5
3.59	9.5	9.45	30
3.62	10	9.5	30.5
3.65	10.5	9.55	31
3.68	11	9.6	31.5
3.71	11.5	9.63	32
3.74	12	9.65	32.5
3.77	12.5	9.67	33
3.8	13	9.7	33.5
3.83	13.5	9.72	34
3.86	14	9.75	34.5
3.9	14.5	9.77	35
3.95	15	9.79	35.5
4	15.5	9.81	36
4.04	16	9.82	36.5
4.09	16.5	9.83	37
4.13	17	9.84	37.5
4.19	17.5	9.85	38
4.25	18	9.85	38.5
4.31	18.5	9.85	39
4.38	19	9.85	39.5
4.47	19.5	9.85	40
4.58	20		

C.6. Titration curve data for *o*-TFMBA.

pH	ml 0.01 NaOH added	pH	ml 0.01M NaOH added
2.45	0	3.35	18
2.45	0.5	3.42	18.5
2.46	1	3.49	19
2.47	1.5	3.58	19.5
2.49	2.0	3.68	20
2.51	2.5	3.86	20.5
2.52	3.0	4.05	21
2.54	3.5	4.52	21.5
2.55	4	5.4	22
2.57	4.5	5.74	22.5
2.59	5.0	5.98	23
2.6	5.5	6.45	23.5
2.62	6	6.92	24.5
2.64	6.5	7.73	25
2.67	7	8.05	25.5
2.69	7.5	8.46	26
2.7	8	8.87	26.5
2.73	8.5	8.99	27
2.75	9	9.19	27.5
2.77	9.5	9.41	28
2.79	10	9.55	28.5
2.81	10.5	9.68	29
2.83	11	9.78	29.5
2.85	11.5	9.88	30
2.88	12	9.96	30.5
2.91	12.5	10.03	31
2.94	13	10.11	31.5
2.97	13.5	10.18	32
3	14	10.22	32.5
3.03	14.5	10.28	33
3.07	15	10.32	33.5
3.12	15.5	10.36	34
3.16	16	10.39	34.5
3.2	16.5	10.42	35
3.24	17	10.43	35.5
3.29	17.5	10.44	36
		10.44	36.5
		10.44	37
		10.44	37.5

C.7. Titration curve data for PFBA.

pH	ml 0.01 NaOH added	pH	ml 0.01M NaOH added
2.26	0	3.13	21
2.26	0.5	3.18	21.5
2.26	1	3.25	22
2.27	1.5	3.35	22.5
2.29	2.0	3.46	23
2.3	2.5	3.61	23.5
2.32	3.0	3.82	24
2.33	3.5	4.28	24.5
2.35	4.0	5.38	25
2.36	4.5	6.0	25.5
2.37	5.0	6.6	26
2.39	5.5	7.07	26.5
2.41	6	8.4	27
2.42	6.5	8.96	27.5
2.44	7	9.26	28
2.45	7.5	9.46	28.5
2.46	8	9.57	29
2.47	8.5	9.72	29.5
2.49	9	9.83	30
2.51	9.5	9.92	30.5
2.53	10	10.01	31
2.55	10.5	10.09	31.5
2.57	11.0	10.13	32
2.59	11.5	10.17	32.5
2.61	12	10.22	33
2.63	12.5	10.27	33.5
2.64	13	10.31	34
2.66	13.5	10.35	34.5
2.67	14	10.38	35
2.7	14.5	10.40	35.5
2.72	15	10.42	36
2.74	15.5	10.43	36.5
2.76	16	10.44	37
2.78	16.5	10.45	37.5
2.81	17	10.46	38
2.84	17.5	10.46	38.5
2.87	18	10.46	39
2.91	18.5	10.46	39.5
2.95	19	10.46	40
2.99	19.5	10.46	40.5
3.03	20	10.46	41

C.8. Titration curve data for 2,6-DFBA.

pH	ml 0.01 NaOH added	pH	ml 0.01M NaOH added
2.36	0	3.09	18.5
2.36	0.5	3.14	19
2.36	1	3.19	19.5
2.37	1.5	3.25	20
2.38	2.0	3.33	20.5
2.39	2.5	3.4	21
2.4	3.0	3.52	21.5
2.41	3.5	3.63	22
2.43	4	3.87	22.5
2.44	4.5	4.14	23
2.46	5.0	5.01	23.5
2.48	5.5	5.75	24
2.49	6	6.17	24.5
2.5	6.5	6.6	25
2.52	7	7.43	25.5
2.54	7.5	8.55	26
2.56	8	9	26.5
2.58	8.5	9.27	27
2.59	9	9.45	27.5
2.61	9.5	9.58	28
2.62	10	9.7	28.5
2.65	10.5	9.82	29
2.67	11	9.91	29.5
2.68	11.5	9.99	30
2.7	12	10.04	30.5
2.73	12.5	10.11	31
2.76	13	10.17	31.5
2.77	13.5	10.22	32
2.79	14	10.28	32.5
2.81	14.5	10.3	33
2.84	15	10.32	33.5
2.88	15.5	10.33	34
2.91	16	10.34	34.5
2.95	16.5	10.34	35
2.97	17	10.34	35.5
2.99	17.5	10.34	36
3.04	18	10.34	36.5

APPENDIX D. Batch study data expressed as relative concentrations.

D.1. Batch study data for the four fluoro-organics and bromide in fine-grained sand with initial concentrations of 50 ppm fluoro-organic and 100 ppm bromide.

Days	3,4-DFBA	3,5-DFBA	2,5-DFBA	2,3-DFBA	Br
1	1.00	1.00	1.00	1.00	1.00
3	0.99	1.0	1.0	1.0	1.0
5	0.99	0.99	0.99	0.98	1.0
7	1.0	1.0	1.0	1.0	1.0
14	1.01	1.02	1.0	1.01	1.01
21	1.01	1.02	1.01	1.01	1.01
28	1.02	1.01	1.01	1.02	1.02
35	1.01	1.01	1.01	1.01	1.01
42	1.0	1.0	1.01	1.0	1.01
49	1.01	1.0	1.0	1.0	1.0
56	1.0	1.0	1.0	1.0	1.0
63	1.0	1.0	1.0	1.0	1.0
70	1.01	1.01	1.02	1.01	1.0
77	1.01	1.0	1.01	1.0	1.0
84	1.0	1.01	1.0	1.0	1.0

15

D.2. Batch study data for the four fluoro-organics and bromide in silty clay loam with initial concentrations of 50 ppm fluoro-organic and 100 ppm bromide.

Days	3,4-DFBA	3,5-DFBA	2,5-DFBA	2,3-DFBA	Br
1	1.00	1.0	1.0	1.0	1.0
3	1.0	1.0	1.0	1.0	1.0
5	1.0	1.0	1.0	1.0	1.0
7	1.0	1.0	1.0	1.0	1.0
14	1.01	1.01	1.0	1.01	1.01
21	1.01	1.0	1.01	1.01	1.01
28	1.00	1.0	1.0	1.0	1.0
35	1.01	1.01	1.0	1.0	1.01
42	1.0	1.0	1.0	1.0	1.01
49	1.0	1.0	1.0	1.0	1.0
56	1.0	1.0	1.01	1.01	1.0
63	1.01	1.0	1.01	1.01	1.0
70	.01	1.0	1.01	1.0	1.0
77	1.01	1.0	1.01	1.01	1.0
84	1.0	1.01	1.0	1.0	1.0

15

APPENDIX E. Breakthrough curve data expressed as relative concentrations for the four fluoro-organics and bromide from saturated column study.

E.1. Breakthrough curve data for the four fluoro-organics, bromide and fitted curve from column 1, saturated column study.

Pore Volumes	3,4-DFBA	3,5-DFBA	2,5-DFBA	2,3-DFBA	Br	Fitted
0.07	0.001	0.0008	0	0	0	0
0.25	0.002	0.001	0	0	0.001	0
0.44	0.02	0.03	0	0.0005	0.002	0.0012
0.63	0.08	0.08	0.07	0.09	0.0523	0.0613
0.81	0.12	0.13	0.12	0.10	0.074	0.2984
1.00	0.80	0.81	0.77	0.83	0.81	0.6229
1.18	0.95	0.96	0.97	0.93	0.92	0.8353
1.37	0.99	0.99	0.96	0.97	0.97	0.9426
1.56	1.00	1.00	0.99	0.99	0.99	0.9824
1.74	1.00	1.00	1.00	1.00	1.00	0.9947
2.86	1.00	1.00	1.00	1.00	1.00	1.0
3.04	0.99	0.99	0.99	0.99	0.99	1.0
3.24	0.98	0.97	0.96	0.96	0.97	0.9978
3.41	0.92	0.91	0.89	0.88	0.91	0.9383
3.60	0.66	0.64	0.62	0.63	0.60	0.6834
3.80	0.45	0.44	0.41	0.41	0.33	0.3466
3.97	0.29	0.27	0.28	0.26	0.30	0.1559
4.16	0.18	0.15	014	0.16	019	0.0539
4.34	0.11	0.12	0.10	0.11	0.13	0.0175
4.53	0.06	0.08	0.05	0.06	0.09	0.0049
4.72	0.02	0.03	0.02	0.01	0.06	0.0013
4.91	0.01	0.02	0.01	0.03	0.02	0.0003
5.12	0.02	0.01	0.02	0.01	0.01	0.0001
5.24	0.01	0.01	0.01	0.01	0.01	0
5.43	0.008	0.006	0.007	0.008	0.005	0
5.61	0.003	0.003	0.001	0.004	0.001	0
5.88	0.001	0.001	0.001	0.001	0.01	0

E.2. Breakthrough curves for the four fluoro-organics, bromide and fitted curve for column 2, saturated column study.

Pore Volumes	3,4-DFBA	3,5-DFBA	2,5-DFBA	2,3-DFBA	Br	Fitted
0.05	0	0	0	0	0	0
0.22	0.003	0.004	0.0005	0.0001	0.0008	0.0012
0.46	0.01	0.03	0.005	0.004	0.01	0.0613
0.62	0.06	0.07	0.05	0.07	0.08	0.2984
0.82	0.11	0.09	0.11	0.11	0.13	0.6229
1.02	0.85	0.82	0.850	0.82	0.81	0.8353
1.24	0.97	0.94	0.98	0.95	0.97	0.9426
1.41	0.99	0.99	0.98	0.99	0.98	0.9824
1.59	1.0	1.0	1.0	1.0	1.0	0.9947
1.81	1.0	1.0	0.999	0.99	1.0	1.0
2.79	1.0	1.0	1.0	1.0	1.0	1.0
3.0	0.99	0.98	0.99	0.99	0.98	0.9978
3.21	0.97	0.98	0.96	0.98	0.99	0.9383
3.39	0.90	0.91	0.92	0.90	0.92	0.6834
3.58	0.60	0.68	0.71	0.70	0.68	0.3466
3.81	0.44	0.46	0.40	0.44	0.47	0.1559
4.0	0.28	0.30	0.32	0.31	0.33	0.0539
4.19	0.19	0.17	0.18	0.19	0.10	0.0175
4.36	0.10	0.15	0.14	0.13	0.14	0.0049
4.61	0.05	0.06	0.04	0.05	0.07	0.0013
4.80	0.02	0.03	0.04	0.04	0.04	0.0003
5.01	0.03	0.03	0.04	0.04	0.04	0.0001
5.25	0.01	0.02	0.01	0.01	0.03	0
5.40	0.008	0.004	0.005	0.006	0.009	0
5.61	0.003	0.005	0.003	0.004	0.006	0
5.81	0.0	0.001	0.001	0.0	0.001	0

APPENDIX F. Breakthrough curve data expressed as relative concentrations for the four fluoro-organics, bromide and fitted curve for trickle flow column study.

F.1. Breakthrough curve data for the four fluoro-organics, bromide and fitted curve for column 1, trickle flow column study.

Pore Volumes	3,4-DFBA	3,5-DFBA	2,5-DFBA	2,3-DFBA	Br	Fitted
0.26	0.0	0.0	0.0	0.0	0.0	0
0.39	0.0	0.0	0.0	0.0	0.0	0
0.79	0.05	0.04	0.06	0.071	0.086	0.0842
1.12	0.80	0.833	0.831	0.838	0.855	0.8862
1.47	0.98	0.96	0.967	0.959	0.979	0.9994
1.73	1.0	01.0	1.0	1.0	1.0	1.0
1.99	0.979	0.964	0.971	0.977	0.992	1.0
2.28	0.973	0.970	0.976	0.976	0.994	1.0
2.50	0.960	0.957	0.962	0.958	0.984	0.9991
2.72	0.79	0.781	0.778	0.781	0.814	0.8064
2.94	0.18	0.185	0.162	0.158	0.185	0.1993
3.14	0.09	0.090	0.059	0.055	0.060	0.0170
3.31	0.06	0.062	0.031	0.033	0.029	0.0011
3.48	0.066	0.077	0.038	0.042	0.043	0
3.74	0.042	0.043	0.018	0.015	0.008	0
4.00	0038	0.038	0.017	0.013	0.001	0
4.22	0.034	0.031	0.018	0.012	0.01	0
4.49	0.033	0.028	0.019	0.012	0.01	0
4.71	0.021	0.020	0.015	0.006	0.001	0
4.96	0.014	0.011	0.010	0.003	0.001	0
5.14	0.008	0.004	0.002	0.001	0.001	0
5.36	0.002	0.002	0.001	0.001	0.001	0

F.2. Breakthrough curve data for the four fluoro-organics, bromide and fitted curve for column 2, trickle flow column study.

Pore Volumes	3,4-DFBA	3,5-DFBA	2,5-DFBA	2,3-DFBA	Br	Fitted
0	0.0	0.0	0.0	0.0	0.0	0
0.22	0.0	0.0	0.0	0.0	0.0	0
0.29	0.0	0.0	0.0	0.0	0.0	0
0.51	0.0	0.0	0.0	0.0	0.0	0
0.68	0.021	0.023	0015	0.010	0.012	0.018
0.85	0.403	0.372	0.386	0.367	0.429	0.4287
1.11	0.937	0.910	0.948	0.925	0.944	0.950
1.53	0.987	0.980	0.987	0.978	1.00	0.995
1.95	0.983	0.982	0.978	0.977	0.99	0.991
2.66	0.918	0.879	0.893	0.872	0.889	0.8865
3.01	0.146	0.127	0.094	0.087	0.092	0.0965
3.29	0.085	0.074	0.055	0.048	0.051	0.0017
3.51	0.055	0.041	0.031	0.021	0.032	0
3.77	0.068	0.059	0.046	0.039	0.041	0
4.04	0.064	0.055	0.041	0.035	0.036	0
4.20	0.065	0.056	0.044	0.037	0.042	0
4.36	0.059	0.051	0.040	0.035	0.040	0
4.58	0.046	0.040	0.037	0.031	0.035	0
4.80	0.032	0.029	0.029	0.022	0.021	0
5.02	0.019	0.015	0.011	0.010	0.019	0
5.21	0.010	0.008	0.002	0.005	0.009	0
5.40	0.002	0.001	0.0	0.001	0.002	0

APPENDIX G. Breakthrough curve data expressed as relative concentrations (x 10^{-4}) for the four fluoro-organics and bromide from aquifer tracer test at Sevileta field site.

Minutes	3,4-DFBA	3,5-DFBA	2,5-DFBA	2,3-DFBA	Br
135	0	0	0	0	0
140	25.3	26.8	32.4	31.8	33.5
145	34.1	40.1	46.0	44.0	50.4
150	45.0	39.5	40.0	43.1	43.8
155	51.2	54.0	53.5	56.0	55.1
160	49.5	51.0	50.9	48.4	51.0
165	51.2	52.3	40.5	42.0	44.5
170	56.5	54.0	57.6	59.2	60.1
175	65.8	66.0	56.1	62.0	64.2
180	52.5	51.0	43.4	40.0	51.0
185	36.5	31.0	29.7	28	30
190	35.2	46.9	27.8	29.0	31.9
195	37.5	45.7	39.3	34.4	34.1
200	39.9	53.1	47.1	38.8	45.0
205	40.4	50.4	48.0	44.5	42.3
210	39.1	46.1	35.2	31.9	35.4
215	35.3	34.0	32.2	30.2	31.5
220	26.9	28.5	36.4	31.0	27.9
225	25.8	29.6	28.0	31.2	24.3
230	0	0	0	0	0
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18 Ju

APPENDIX H. Breakthrough curve data expressed as relative concentrations for the four fluoro-orgnics and bromide from vadose zone tracer test at golf course field site.

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H.1. Breakthrough curve data for the four fluoro-organics and bromide from vadose zone tracer test - porous cup sampler 1-A.

Minutes	3,4-DFBA	3,5-DFBA	2,5-DFBA	2,3-DFBA	Br
8	0.01	0.02	0.01	0.01	0.02
16	0.36	0.33	0.20	0.21	0.21
24	0.74	0.76	0.79	0.82	0.86
32	1.03	1.1	1.09	1.06	1.03
40	0.95	0.96	0.95	0.94	0.88
48	0.30	0.33	0.43	0.43	0.33
56	0.32	0.36	0.35	0.37	0.28
64	0.014	0.017	0.011	0.012	0.019

H.2. Breakthrough curve data for the for fluoro-organics and bromide from vadose zone tracer test - porous cup sampler 1-B.

Minutes	3,4-DFBA	3,5-DFBA	2,5-DFBA	2,3-DFBA	Br
216	0.05	0.03	0.05	0.03	0.04
224	0.23	0.23	0.22	0.23	0.25
232	0.24	0.25	0.26	0.27	0.26
240	0.26	0.23	0.24	0.25	0.27
248	0.22	0.23	0.20	0.19	0.22
256	0.02	0.05	0.04	0.03	0.04

H.~~2~~3. Breakthrough curve data for the for fluoro-organics and bromide from vadose zone tracer test - porous cup sampler 1-C.

Minutes	3,4-DFBA	3,5-DFBA	2,5-DFBA	2,3-DFBA	Br
324	0.10	0.12	0.09	0.10	0.09
336	0.14	0.13	0.16	0.17	0.15
348	0.21	0.22	0.16	0.17	0.18
361	0.24	0.23	0.23	0.24	0.23
372	0.21	0.22	0.21	0.21	0.20
407	0.20	0.21	0.20	0.20	0.21
386	0.22	0.21	0.21	0.20	0.19
489	0.12	0.12	0.15	0.13	0.14
561	0.03	0.03	0.04	0.037	0.04

H.4. Breakthrough curve data for the for fluoro-organics and bromide from vadose zone tracer test - porous cup sampler 4-A.

Minutes	3,4-DFBA	3,5-DFBA	2,5-DFBA	2,3-DFBA	Br
177	0	0	0	0	0
189	0.12	0.10	0.13	0.12	0.11
217	0.15	0.14	0.15	0.16	0.12
265	0.16	0.15	0.17	0.17	0.15
289	0.16	0.17	0.16	0.16	0.16
319	0.13	0.12	0.13	0.11	0.12
343	0.05	0.06	0.08	0.05	0.06

H.5. Breakthrough curve data for the for fluoro-organics and bromide from vadose zone tracer test - porous cup sampler 4-C.

Minutes	3,4-DFBA	3,5-DFBA	2,5-DFBA	2,3-DFBA	Br
128	0.13	0.18	0.13	0.11	0.10
136	0.17	0.19	0.16	0.17	0.18
144	0.16	0.16	0.19	0.17	0.17
152	0.15	0.19	0.19	0.17	0.19
160	0.17	0.18	0.18	0.18	0.17
168	0.16	0.19	0.17	0.16	0.16
176	0.16	0.19	0.18	0.17	0.17
184	0.17	0.17	0.16	0.18	0.17
192	0.18	0.19	0.20	0.18	0.18
200	0.12	0.17	0.17	0.15	0.13
208	0.14	0.15	0.12	0.13	0.11
216	0.11	0.10	0.06	0.07	0.09
224	0.05	0.05	0.06	0.07	0.06
232	0.04	0.04	0.05	0.06	0.05
240	0.04	0.06	0.05	0.06	0.05
248	0.05	0.06	0.05	0.06	0.04
256	0.04	0.03	0.04	0.06	0.02
120	0	0	0	0	0

This thesis is accepted on behalf of the faculty of the Institute by the following committee:

Robert A. Bowman

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9 Sept., 1989

Date