This manuscript has been prepared for

presentation at HAZMAT West'88

Long Beach, CA, November 8-10, 1988

This copy is to provide information

prior to publication.

MEASUREMENT OF RETARDATION FACTORS
FOR CONTAMINATED AQUIFER MATERIALS

by

M.W. Priddle[1], R.E. Jackson[1]
and R.J. Patterson[2]

[1]National Water Research Institute
Canada Centre for Inland Waters
Burlington, Ontario, L7R 4A6

[2]Woodward-Clyde Consultants
203 N. Golden Circle Drive
Santa Ana, CA 92705

EXECUTIVE SUMMARY

Groundwaters beneath the Federal Special Waste Compound at the Gloucester, Ontario landfill became contaminated due to the disposal of laboratory solvents by EPS during the period 1972-80. A plume of contaminated groundwater is now moving away from the site. This plume of toxic organic chemicals has been well defined by Environment Canada scientists over the last eight years. These chemicals have been found to migrate at widely varying rates depending upon their retardation factors.

This paper describes a laboratory procedure that has been developed to simulate the migration of organic chemicals in groundwater. Aquifer material from the Gloucester Landfill is repacked in laboratory columns and contaminated water is passed through. By monitoring the concentration of these contaminants in the effluent, retardation factors can be derived. It is these factors that determine how fast a particular contaminant will travel with respect to the average groundwater flow velocity.

It may be possible to determine how fast contaminants will proceed from any type of groundwater pollution event (e.g., leaking underground storage tanks, landfills, spills, etc.), using this procedure. Further applications may be found in optimizing groundwater remediation schemes that involve purge wells. Flow rates can easily be increased using this column apparatus in order to simulate the high groundwater flow rates encountered during "pump and treat" operations.

RÉSUMÉ DE L'ÉTUDE

Les eaux souterraines qui se trouvent sous le site fédéral d'enfouissement des déchets à Gloucester, en Ontario, ont été contaminées par les solvants de laboratoire déversés par le SPE durant la période de 1972-1980. Un panache d'eau contaminée est en train de se déplacer actuellement loin du site. Ce panache de produits chimiques organiques toxiques a été bien défini par les scientifiques d'Environnement Canada au cours des huit dernières années. On a constaté que ces substances migrent à des vitesses très différentes selon leurs facteurs de ralentissement.

Ce rapport décrit une procédure de laboratoire qui a été mise au point pour simuler la migration des produits chimiques organiques dans la nappe souterraine. Les matières aquifères de la décharge de Gloucester sont regarnies dans des colonnes de laboratoire et on y fait passer de l'eau contaminée. En surveillant la concentration de ces contaminants dans l'effluent, on peut en déduire les facteurs de ralentissement. Ce sont ces derniers qui déterminent à quelle rapidité un contaminant particulier se déplacera par rapport à la vitesse moyenne de l'écoulement de l'eau souterraine.

Grâce à cette méthode, il est possible de déterminer avec quelle vitesse les contaminants vont se déplacer à la suite de n'importe quel événement entraînant la pollution de la nappe aquifère (par exemple des fuites souterraines dans les réservoirs de stockage, décharges, déversements accidentels, etc.). On peut trouver d'autres

applications pour améliorer au maximum les plans d'épuration de la nappe souterraine faisant appel à des puits de vidange. En utilisant cet appareil à colonne, on peut facilement accroître les débits pour simuler les grandes vitesses d'écoulement des eaux souterraines que l'on observe durant les opérations de "pompage/traitement".

ABSTRACT

Retardation factors for four organic chemicals found in ground-waters beneath the Gloucester waste disposal site have been determined by laboratory tracer tests. The four chemicals, tetrahydrofuran (THF), diethyl ether (DEE), 1,2-dichloroethane (1,2-DCA) and benzene (BENZ), are all found in plumes of varying lengths emanating from the site in which they were originally disposed. The retardation factors (R_f) for these compounds vary in proportion to their octanol/water partition coefficients (K_{ow}).

Laboratory tracer experiments were undertaken using columns of repacked aquifer sediments in order to compare retardation factors with those estimated by Patterson et al. (1985) from field data. Pristine groundwater, spiked with these four contaminants and a non-reactive tracer, was pumped through a glass column filled with aquifer sediment. This apparatus was set up in a cold room (8°C) to simulate groundwater conditions at the site. Column effluent samples were collected sequentially in Tedlar bags and analyzed for the tracer as well as the four contaminants. Results indicate that the laboratory column experiments can be useful predictive tools in the study of the migration of organic solutes in groundwater, providing that precautions are taken to prevent the loss of contaminants by volatilization or sorption on the experimental apparatus.

RÉSUMÉ

Grâce à des essais de dépistage effectués en laboratoire au moyen de traceurs, on a déterminé les facteurs de ralentissement de quatre produits chimiques organiques trouvés dans les eaux souterraines en-dessous du site d'évacuation des déchets de Gloucester. Les quatre substances chimiques, à savoir le tétrahydrofuranne (THF), l'éther éthylique (DEE), le 1,2-dichloroéthane (1,2-DCA) et le benzène (BENZ), se trouvent toutes dans des panaches de différentes longueurs émanant du site dans lequel elles ont été initialement évacuées. Les facteurs de ralentissement (R_f) de ces composés varient en proportion de leurs coefficients de distribution octanol/eau (K_{OW}).

Pour entreprendre en laboratoire ces expériences au moyen de traceurs, on a utilisé des colonnes de sédiments aquifères regarnis en vue de comparer les facteurs de ralentissement avec ceux estimés par Patterson et al. (1985) à partir de données recueillies sur le terrain. De l'eau souterraine propre, dopée avec ces quatre contaminants et un traceur non réactif, a été pompée et introduite dans une colonne de verre remplie de sédiment aquifère. Cet appareil a été placé dans une chambre froide (8 °C) pour simuler les conditions prévalant dans les eaux souterraines du site étudié. Le traceur ainsi que les quatre contaminants ont été dosés dans des échantillons de l'effluent de la colonne recueillis en série dans des sacs Tedlar. D'après les résultats, les expériences menées en laboratoire au moyen de colonnes peuvent servir d'outils de prévision dans l'étude de la migration des soulutés organiques dans les eaux souterraines, pourvu que des précautions soient

prises pour éviter que l'appareil utilisé pour l'expérience ne laisse échapper des contaminants par volatilisation ou sorption.

INTRODUCTION

Many researchers (e.g., Curtis et al., 1986, McCarty et al., 1981 and Schwarzenbach and Westall, 1981) have studied the migration of some of the numerous volatile organic compounds that may pollute groundwater. These compounds - such as chlorinated one and two carbon solvents, aromatics and oxygenated solvents - do not behave identically in groundwater. Previous studies at field sites have shown that these compounds migrate at widely varying rates in the subsurface (e.g., Patterson et al., 1985). Each compound has a different retardation factor depending on its chemical characteristics and the properties of the matrix through which it is flowing.

The most significant property that influences the rate of organic contaminant migration in groundwater is the organic carbon content of the aquifer material (Karickhoff et al., 1979). It has been shown that organic carbon in unconsolidated material is preferentially associated with the smaller grain sizes (i.e., <125 μm) and therefore these fractions account for most of the sorption (Schwarzenbach and Westall, 1981). The various chemicals exhibit sorption properties that depend on their octanol-water partition coefficient (K_{ow}) (Chiou et al., 1983). Compounds with large K_{ow}'s are more strongly sorbed and consequently their migration is more strongly retarded.

In the case of a disposal site where a multitude of organic chemicals have percolated to the water table and begun migrating in groundwater, the compounds will undergo 'chromatographic dispersion',

i.e., aqueous-phase solute transport coupled with sorption. This process occurs because each compound has a different affinity for the sorbent (organic carbon) and will travel at a different rate just as compounds do in a packed chromatographic column. At the Gloucester site near Ottawa, Ontario, this phenomenon has been observed (see Figure 1). The oxygenated solvents (diethyl ether, THF and 1,4-dioxane) with low K_{OW} values, have migrated much farther than the chlorinated or aromatic compounds (e.g., 1,2-dichloroethane, carbon tetrachloride and benzene) which have higher K_{OW} values (Patterson et al., 1985).

Schwarzenbach and Westall (1981) have derived equations to predict retardation factors for various compounds on the basis of K_{OW} values and the fraction of organic carbon present in sediments. These correlations, based on linear free energy relationships, provide first approximations of field retardation factor (R_f) values (Patterson et al., 1985 and Curtis et al., 1986).

The objective of this present study was to develop a laboratory simulation technique that could be applied to investigate field retardation processes occurring at the Gloucester site (see Jackson et al., 1985). Samples of aquifer sediment from the Gloucester site were repacked in a glass column and groundwater containing four of the compounds that had been studied in the field by Patterson et al. (1985) was pumped through under simulated field conditions. The results from these experiments have been compared with the field data and retardation factors predicted from the Schwarzenbach and Westall equation.
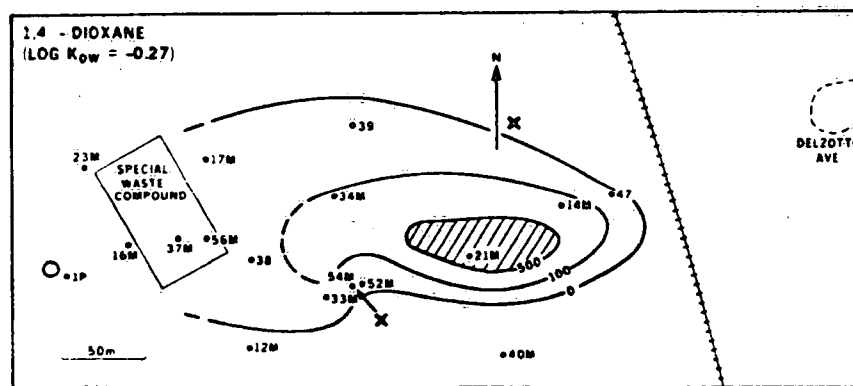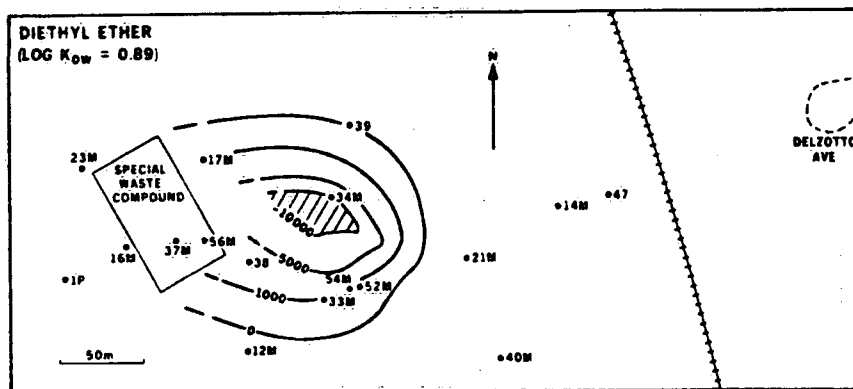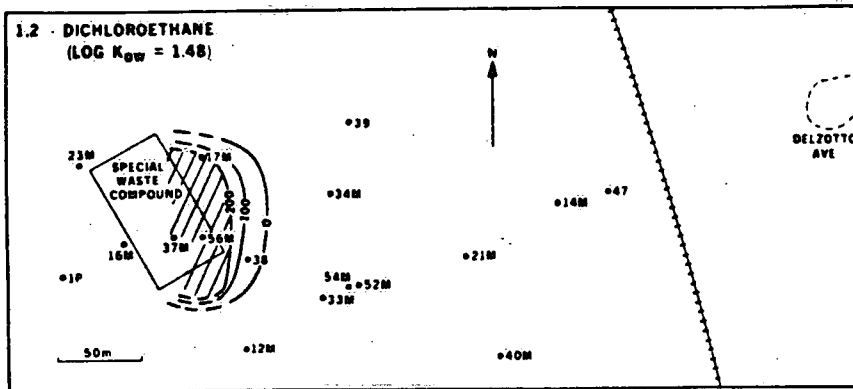
LEGEND

- **MULTILEVEL SAMPLER OR PIEZOMETER**

—500— **CONTOUR OF MAXIMUM CONCENTRATION (PARTS PER BILLION) ENCOUNTERED IN SECTION (1982)**

AREA OF MAXIMUM CONCENTRATION

O **COLUMN WATER**

X **COLUMN AQUIFER MATERIAL**

Figure 1. Plan views of diethyl ether, 1,2-dichloroethane and 1,4-dioxane plumes and sample locations of column aquifer materials and water.

APPARATUS

The apparatus for the laboratory column tracer studies was designed to satisfy the following criteria:

1. The apparatus should be constructed from inert materials, i.e., those recommended for sampling volatile organics in groundwater.

2. The aquifer sample should be representative of the site as a whole and should be repacked in the column to duplicate field conditions as closely as possible.,

    - representative organic carbon content

    - repacked with similar bulk density, porosity and uniformity

3. Sampling procedures to prevent loss or gain of any analytes should be at least as rigorous as those normally performed during field sampling, i.e.,

    - samples collected with minimal headspace, kept cool and analyzed promptly (within 36 hours).

The apparatus shown in Figure 2 was designed to comply with these criteria. The sediment samples used to pack the columns were from cores of aquifer materials about 100 m and 200 m downgradient from the Special Waste Compound (see Figure 1). They were analysed for organic carbon and grain size distribution. Porosity and bulk density were calculated for each field sample. After drying, the sediments were carefully repacked in glass columns (see Figure 3) to minimize
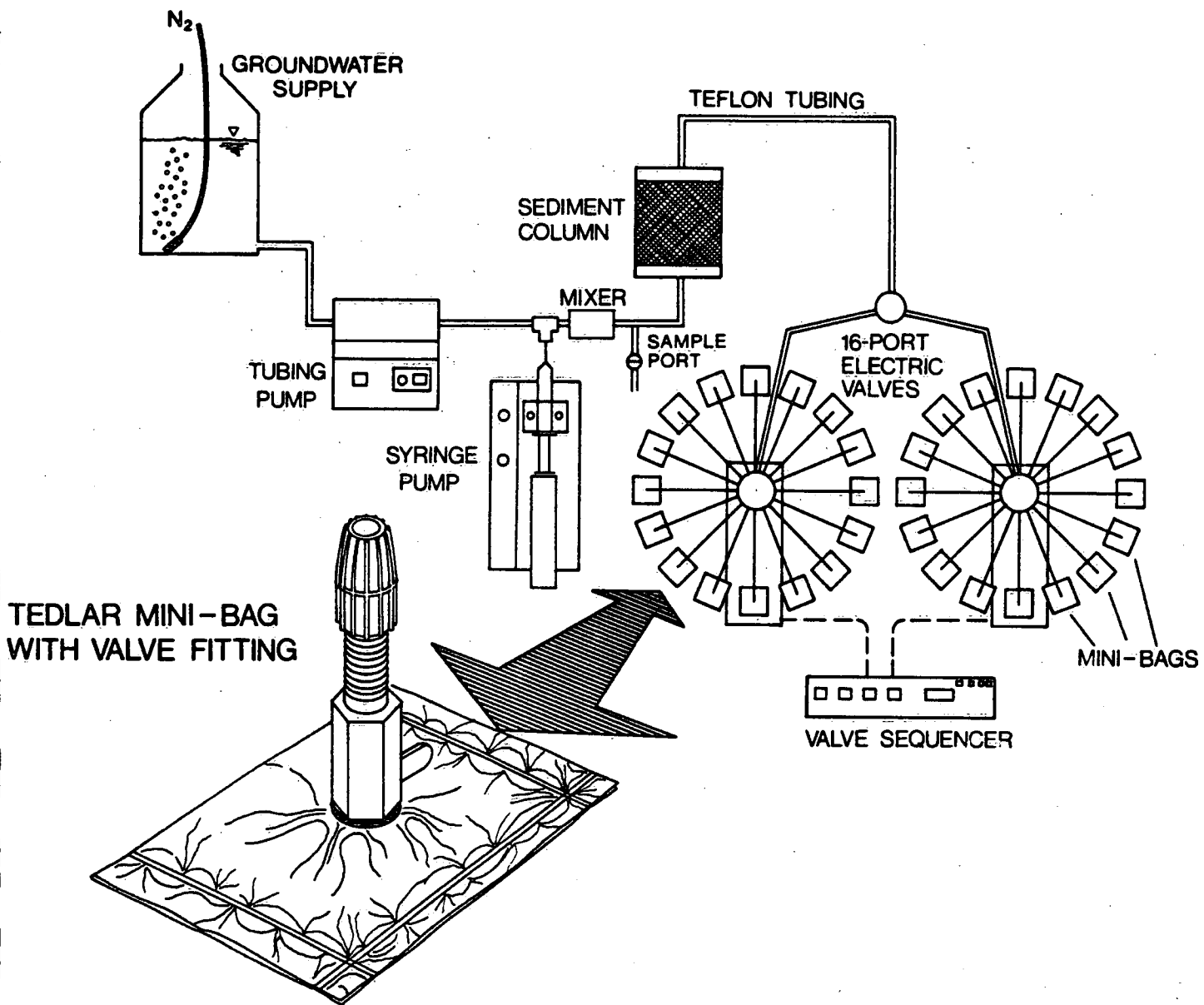
N₂

GROUNDWATER
SUPPLY

TEFLON TUBING

SEDIMENT
COLUMN

MIXER

SAMPLE
PORT

16-PORT
ELECTRIC
VALVES

TUBING
PUMP

SYRINGE
PUMP

TEDLAR MINI-BAG
WITH VALVE FITTING

MINI-BAGS

VALVE SEQUENCER

Figure 2. Simplified diagram of complete column apparatus.

GLASS COLUMN

SUPPORT ROD

SEDIMENT SAMPLE

FRITTED GLASS DISC

STAINLESS STEEL
END CAP

'O'- RING
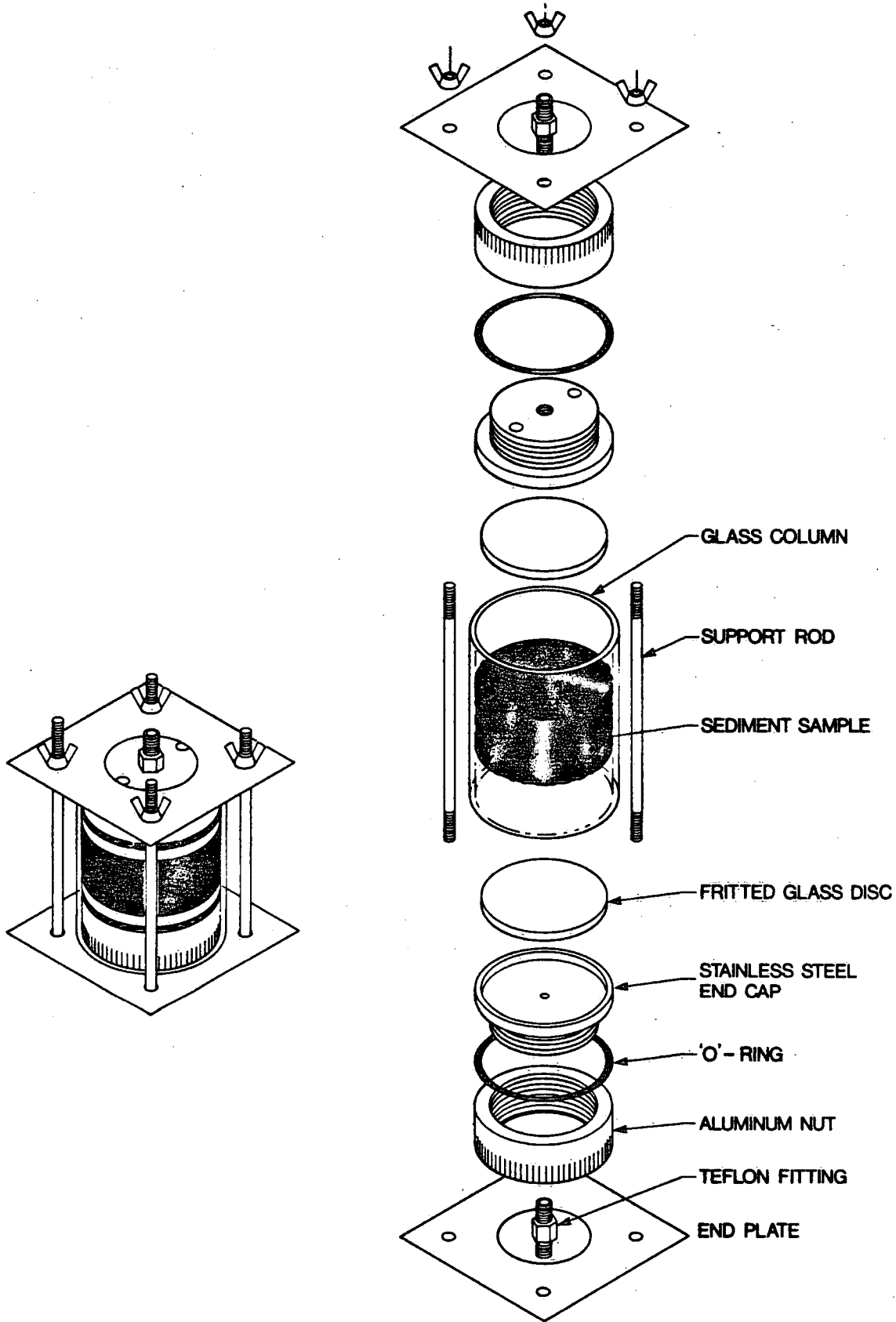
ALUMINUM NUT

TEFLON FITTING

END PLATE

Figure 3. Exploded view of column.

stratification and reproduce as closely as possible, the field parameters of porosity (0.3) and bulk density (1.8).

During initial tests of the apparatus, the supply source was a large Tedlar (polyvinyl fluoride) bag filled with groundwater that had been spiked with iodide (a conservative tracer) and the organic compounds of interest. Tests showed that up to 95% of some organic compounds (e.g., benzene) was lost as the water passed through the silicone tubing of the small peristaltic pump. As a result, the system was modified to include a syringe pump that added a more concentrated solution of the four organic compounds and the iodide tracer after the pump. Kuhn et al. (1985) describe a similar column apparatus for the study of microbial transformations in groundwater.

The column effluent had to be collected at regular intervals in order to determine breakthrough of the tracer and contaminants. Two 16-port valves with a sequencer were used for this purpose. A major problem was the collection of relatively small water samples without loss of organic compounds by volatilization or sorption. This problem was overcome by using small Tedlar bags to collect effluent samples. Tedlar can easily be heat-sealed and thus bags of almost any size can be made. Tests showed that even though some sorption or biodegradation may have occurred – up to 18% of benzene was lost while storing a standard – the Tedlar bags are suitable sample collection containers.

The bags were constructed with a hole that accommodated a small Teflon on/off valve. In this way, the bags could be evacuated prior to being attached to the sampling ports of the valves. Consequently water was collected with only a very small headspace. The work of Pankow (1986) suggests such small bubbles are unlikely to cause significant losses of the volatile organic compounds. Once the bags were filled, they were removed from the valve and the water was withdrawn using a syringe and injected directly into a sparging tube on a purge and trap unit connected to a gas chromatograph with a mass selective detector (GC/MSD).

The apparatus was constructed from the four materials noted in Table 1. With the exception of Tedlar, the other three materials are recommended for sampling water contaminated with volatile organics (Barcelona et al., 1983). Preliminary tests indicated that the standard solutions being pumped through the system may lose some organic compounds through sorption. Therefore, C_0 values (standard solution concentration) were taken to be the concentration in a Tedlar bag after the standard had been pumped through the whole system without the column. Later, a pre-column port was added (see Figure 2) to alow direct measurement of C_0 in water entering the column.

Table 1. Column materials.

TEFLON	– all tubing, fittings and syringe
STAINLESS STEEL	– mixer, column ends and valve
GLASS	– syringe and column walls
TEDLAR	– sample bags

Uncontaminated groundwater for use in these experiments was collected from a monitoring well (84M-6) near the Gloucester site (see Figure 1). It was passed through a 0.20 μm filter in order to remove any microorganisms that might biodegrade the organic contaminants and stored in a 4 L glass bottle prior to use. Several tests were run to ensure that no major geochemical changes occurred during passage through the column.

COLUMN TESTS

Two column tests were performed under different sets of conditions. Table 2 lists the column characteristics and operating conditions for each test.

Table 2. Column characteristics and test conditions (P.V. = pore volume).

	TEST 1	TEST 2
Diameter	7.0 cm	7.0 cm
Length	4.65 cm	16.2 cm
Sample	303 g	1108 g
Bulk density	1.69	1.80
Porosity	0.36	0.31
f_{oc}	0.00026	0.0005
Flow rate	10 cm/day	44 cm/day
Slug input	2 P.V.	0.66 P.V.
Water	0.2 μm filtered	N_2 purged 0.2 μm filtered
C_o-Iodide (mg/L)	55	36
C_o-THF (μg/L)	1100	210
C_o-DEE (μg/L)	370	200
C_o-1,2-DCA (μg/L)	440	470
C_o-BENZ (μg/L)	220	200

Test 1 was conducted with a very short column so the average groundwater velocity of the Gloucester aquifer could be employed (10 cm/day) without the test taking an inordinate amount of time. Conversely, Test 2 was conducted with a much longer column and a higher groundwater velocity (44 cm/day). In Test 2, the water was purged with N_2 to remove oxygen in an effort to prevent aerobic degradation of the benzene.

RESULTS

Breakthrough curves for Test 1 for the four organic chemicals and the iodide tracer are shown in Figures 4, 5, 6, 7 and 8. The point at which $C/C_{max} = 0.5$ on each curve was used to calculate a retardation factor for comparison with field and theoretical values (Table 3). C_{max} is the maximum concentration detected in the column effluent during the test. The retardation factor for a given compound is calculated from:

retardation factor (R_f) =

$$\frac{\text{number of pore volumes to reach } C/C_{max} = 0.5 \text{ for organic compound}}{\text{number of pore volumes to reach } C/C_{max} = 0.5 \text{ for iodide}}$$
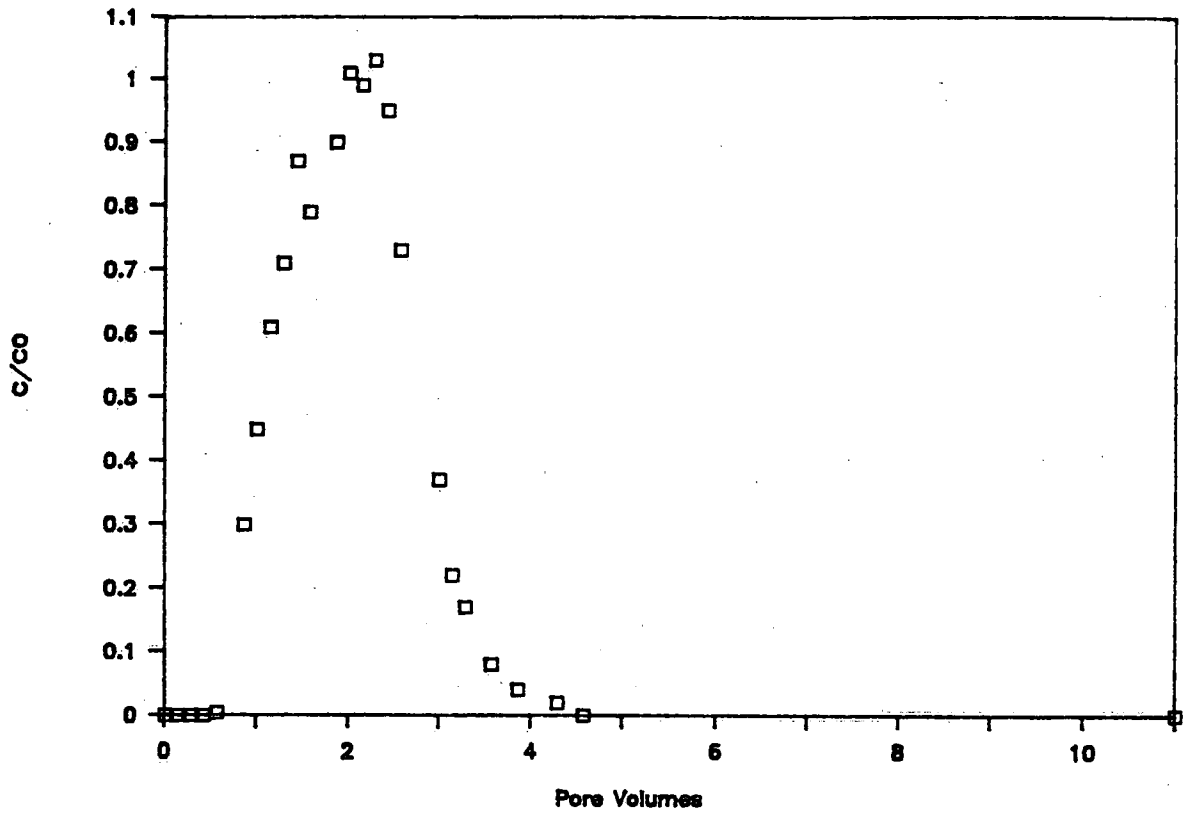
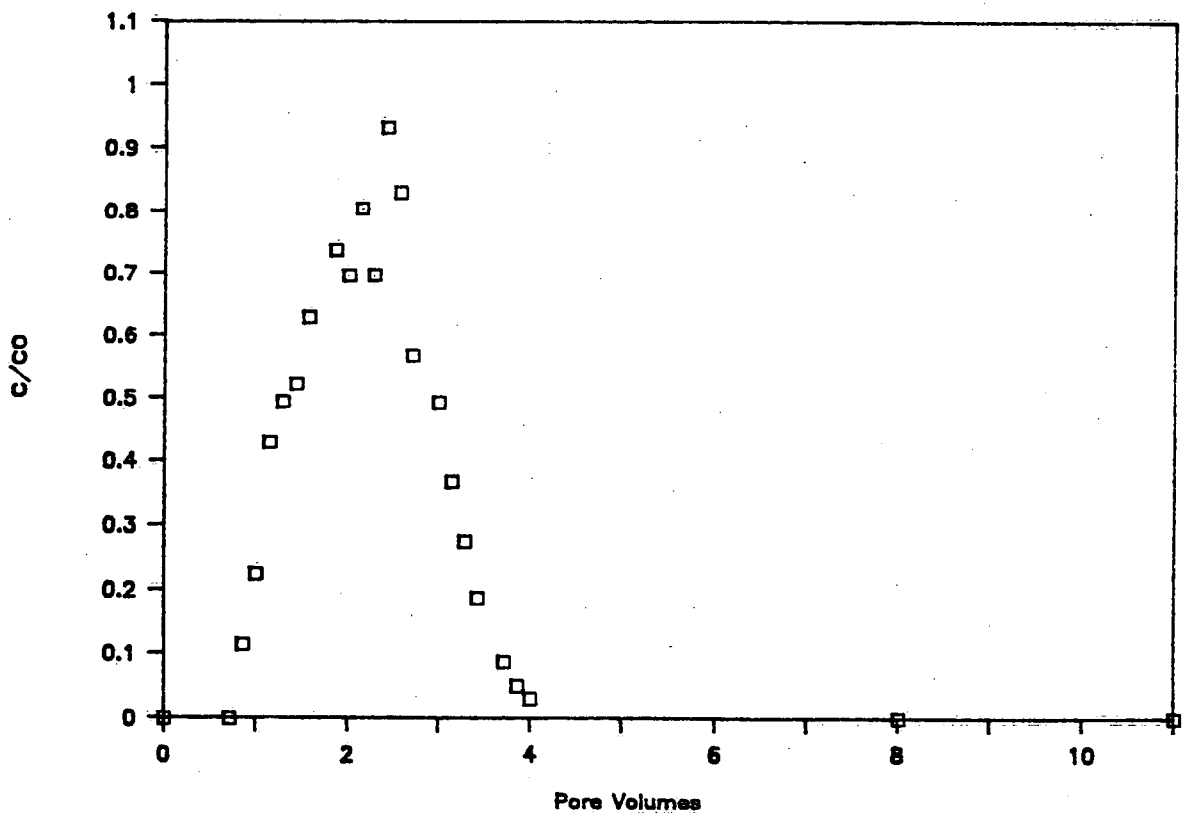Figure 4. Iodide breakthrough curve (Test #1).

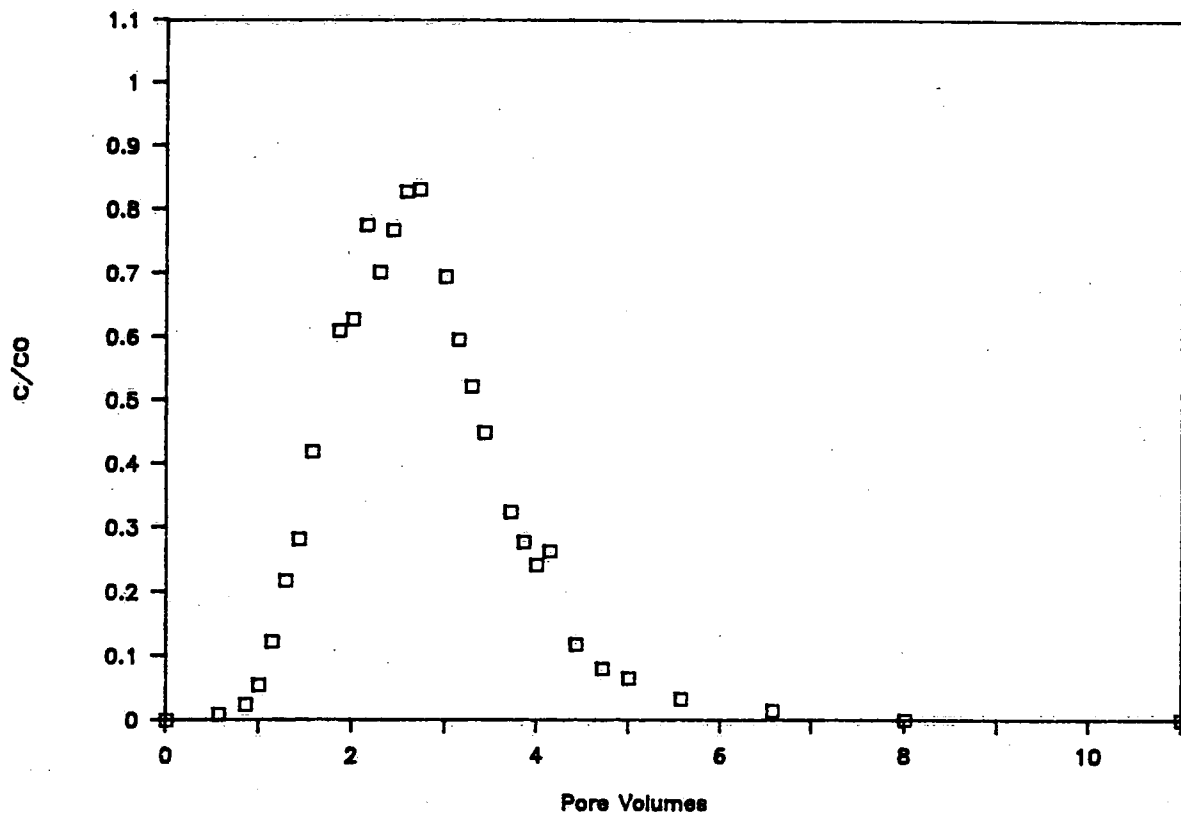Figure 5. Tetrahydrofuran breakthrough curve (Test #1).

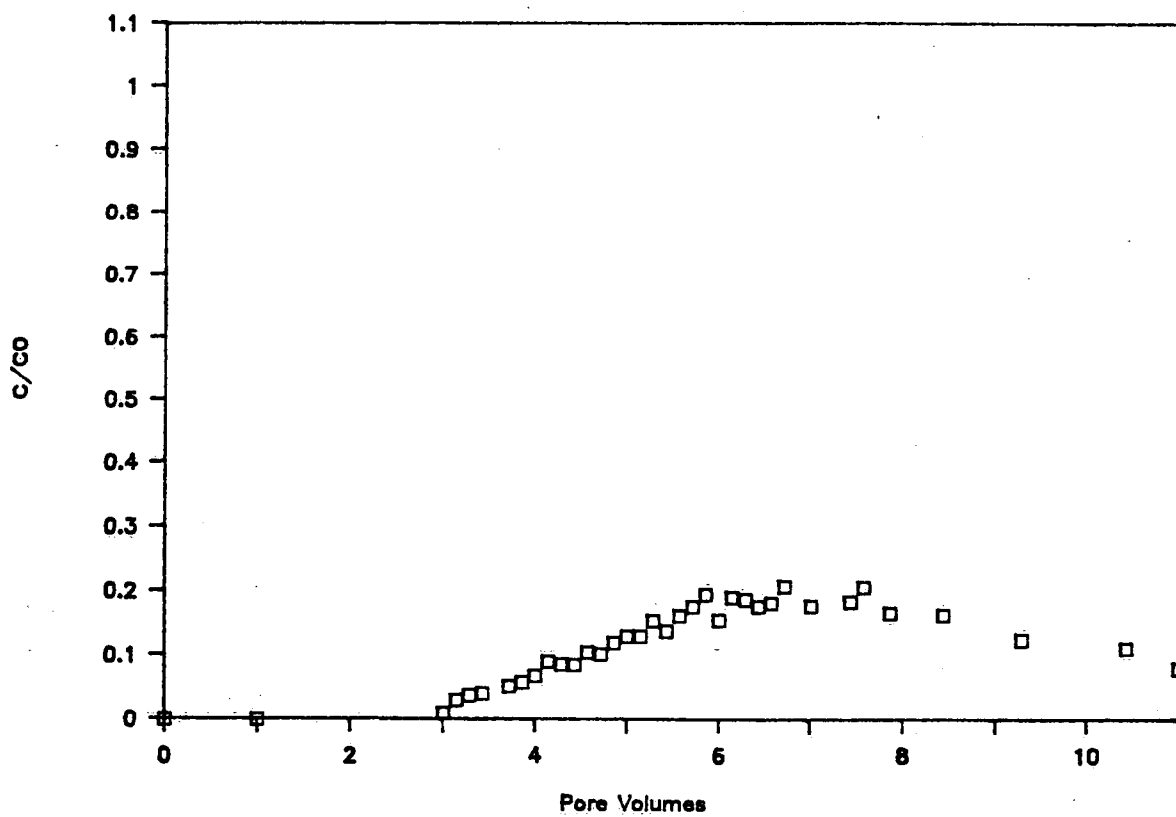Figure 6. Diethyl ether breakthrough curve (Test #1).

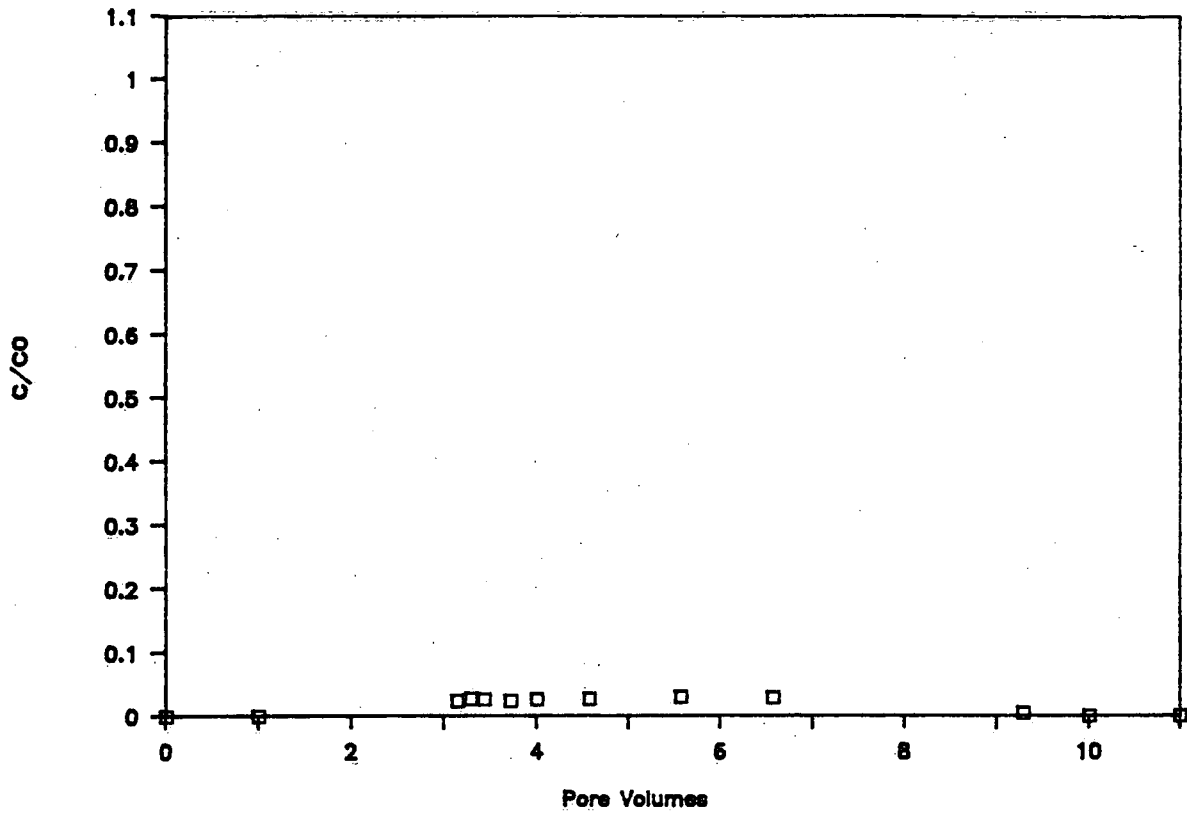Figure 7. 1,2-dichloroethane breakthrough curve (Test #1).

Figure 8. Benzene breakthrough curve (Test #1).

Table 3. Comparison of Retardation Factors

| Chemical | log K_{ow} | Retardation Factors | | | | |
		A	B	C	D	E
tetrahydrofuran	0.46	2.2	2.2	1.3	1.1	1.01
diethyl ether	0.89	3.3	3.0	1.6	1.5	1.02
1,2-dichloroethane	1.48	7.6	n.p.	4.4	n.d.	1.05
benzene	2.04	8.8	n.p.	n.d.	n.d.	1.1

n.p. - not present in test section; n.d. - not possible to determine

A - determined from plume lengths (see Patterson et al., 1985)
B - determined from purge well evaluation test (see Whiffin and Bahr, 1985)
C - determined from breakthrough curves in column test #1
D - determined from breakthrough curves in column test #2
E - calculated from the equations of Schwarzenbach and Westall (1981)

R_f = 1 + bulk density/porosity x K_p where K_p = 3.2 f_{oc} $(K_{ow})^{0.72}$
    (using f_{oc} = 0.00026)

It appears that the results from the column experiments fall between the high retardation factors calculated from field observations and the low ones calculated by equations. The field values and columns results differ by about a factor of 2. The plot of C/C_0 vs. pore volumes (or time) for benzene (Figure 8) indicates that this compound only broke through nominally and the small area beneath the curve indicates a definite mass loss. This could be due to irreversible sorption on the sediment and/or apparatus or biodegradation in the column. McCarty et al. (1981) attribute the shape of a similar breakthrough curve to the effects of dispersion, sorption and biodegradation. Benzene is susceptible to biodegradation and it remains in the system for the longest time. Also, the complete system

(i.e., valves, tubing, fittings) was not sterilized prior to the run. Even with the feed water purged with N_2 to remove oxygen (Test #2), there was still a significant loss of benzene.

The flattened curve for 1,2-dichloroethane was difficult to interpret since decreasing but detectable levels were still present in the effluent after 13 pore volumes. Future work is planned to examine these problems in detail by changing flow rates, sediment composition, contaminants, water supply and other variables.

DISCUSSION

Laboratory column tracer experiments can be useful predictive tools in the study of the migration of organic solutes in groundwater. However, precautions must be taken to prevent the loss of these contaminants during such experiments. The column apparatus developed for this study minimizes the problems of sorption and volatilization. Using the procedure described, representative retardation factors for various organic chemicals can be determined for unconsolidated aquifer materials. The effect of experimental variables (column packing, flow rates, water composition, column dimensions, etc.) will be assessed in more detail in future simulations.

As Patterson et al. (1985) and Curtis et al. (1986) have shown, the Schwarzenbach and Westall (1981) equation underestimates actual retardation. Retardation factors calculated by this equation using values for f_{oc} and K_{ow} for the aquifer material and organic chemicals of Test #1 are shown in Table 3 (column E). These retardation factors are very low compared to those determined from both column experiments and field plume lengths. The low values may be attributed in part to the fact that the empirical expressions do not account for sorption on mineral surfaces (Curtis et al., 1986). Therefore, it seems necessary to alter the predictive equation to account for other variables (e.g., surface area) before it can be applied to a broader range of environments. The column experiments also appear to underestimate retardation compared to field values but to a lesser extent. This difference may reflect the longer contact time between sediments and contaminants in the aquifer (i.e., diffusion into dead end pores) or non-equilibrium sorption-desorption.

There is great potential for using column experiments to evaluate the performance of remedial measures (e.g., purge wells, etc.) since flow rates can easily be raised to simulate those that will occur during remediation. Using a purge well test (injection-withdrawal) at the Gloucester site, Whiffin and Bahr (1985) were able to determine how many pore volumes had to be pumped in order to remove 90% of three oxygenated solvents (DEE, THF and 1,4-dioxane) present in the test section. This test was conducted at a groundwater velocity of about 3 m/day.

From the column breakthrough curves for DEE and THF (Figures 5 and 6) similar pore volume values can be derived. In the purge well evaluation test 90% decontamination was reached after 4 and 7 pore volumes for THF and DEE respectively. In the first column test, it took about 3 and 4 pore volumes respectively for THF and DEE to drop to 10% of their maximum concentrations. The more efficient removal (fewer pore volumes) of the contaminants in the column test probably reflects a lower groundwater velocity (10 cm/day vs. 3 m/day) and possibly reduced contact time for the contaminants and sediments. At higher flow velocities reversible sorption/desorption does not proceed at a rate sufficient to reach local equilibrium, therefore increasing the volume of water that must be purged to reach a desired concentration (Bahr et al., 1984). This fact is important in designing efficient purging operations that minimize both time and volume pumped while ensuring effective decontamination of the aquifer.

REFERENCES

Bahr, J.M., Pickens, J.F., Jackson, R.E., and Whiffin, R.B. 1984. Non-equilibrium desorption of volatile organics during a field test of aquifer decontamination. EOS, 65(16):206.

Barcelona, M.J., Gibb, J.P. and Miller, R.A. 1983. A Guide to the Selection of Materials for Monitoring Well Construction and Ground-water Sampling. ISWS Contract Report 327, Illinois State Water Survey, Champaign, Illinois.

Chiou, C.T., Porter, P.E. and Schmedding, D.W. 1983. Partition equilibria of nonionic organic compounds between soil organic matter and water. Environ. Sci. Technol. 17(4): 227-231.

Curtis, G.P., Roberts, P.V. and Reinhard, M. 1986. A natural gradient tracer experiment on solute transport in a sand aquifer: 4. Sorption of organic solutes and its influence on mobility. Water Resources Res. 22(13): 2059-2067.

Jackson, R.E., Bahr, J.M., Belanger, D.W. and Walbridge, S. 1985. The Gloucester project: A study in organic contaminant hydrogeology. In Proceedings of the Second Canadian/American Conference on Hydrogeology, National Water Well Association, Dublin, Ohio.

Karickhoff, S.W., Brown, D.S. and Scott, T.A. 1979. Sorption of hydrophobic pollutants on natural sediments. Water Res. 13: 241-248.

Kuhn, E.P., Colberg, P.J., Schnoor, J.L., Wanner, O., Zehnder, A.J.B., and Schwarzenbach, R.P. 1985. Microbial transformations of substituted benzenes during infiltration of river water to groundwater: Laboratory column studies. Environ. Sci. Technol. 19(10):961-968.

McCarty, P.L., Reinhard, M. and Rittmann, B.E. 1981. Trace organics in ground water. Environ. Sci. Technol. 15(1): 40-51.

Pankow, J.F. 1986. Magnitude of artifacts caused by bubbles and headspace in the determination of volatile compounds in water. Anal. Chem. 58(8): 1822-1826.

Patterson, R.J., Jackson, R.E., Graham, B.W., Chaput, D. and Priddle, M. 1985. Retardation of toxic chemicals in a contaminated outwash aquifer. Wat. Sci. Tech. 17: 57-69.

Schwarzenbach, R.P. and Westall, J. 1981. Transport of nonpolar organic compounds from surface water to groundwater. Laboratory sorption studies. Environ. Sci. Technol. 15(11): 1360-1367.

Whiffin, R.B. and Bahr, J.M. 1985. Assessment of purge well effectiveness for aquifer decontamination. Proceedings of the Fourth National Symposium on Aquifer Restoration and Groundwater Monitoring. National Water Well Association, Worthington, OH.