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Enhancement of residual aviation gasoline removal from sandy aquifer material

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ENHANCEMENT OF RESIDUAL AVIATION GASOLINE REMOVAL
FROM SANDY AQUIFER MATERIAL

by

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ABSTRACT

Release of residual aviation gasoline saturation from field contaminated sandy aquifer material was investigated using six soil columns. Addition of a biodegradable non-ionic surfactant (5g/L) to the flushing solution produced an immediate increase in concentrations of methylated alkanes which declined over 20 pore volumes to below initial levels. 15g/L of surfactant produced higher effluent concentrations over 6 pore volumes. Adding 50% (v/v) 2-propanol caused a spike release of contaminants in less than 2 pore volumes.

Methanol at 50% released contaminants at fairly low concentrations over 30 pore volumes. At 20% neither alcohol produced much increase in effluent concentrations. Combination of 20% 2-propanol and 5g/L Triton X-100 did not improve the performance of surfactant alone. Soil analysis showed more than 96% of the residual saturation was removed in all six columns.

Solvophobic theory, including the effects of reduction in interfacial surface tension, predicted the relative results of both concentrations of alcohols.

ACKNOWLEDGEMENTS

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Chapter 1. INTRODUCTION

1.1 Problem Statement

Ground water provides a large supply of drinking, irrigation and industrial water throughout the world. Leaks and spills of toxic material from waste pits and storage tanks constitute a serious threat to the quality of the groundwater. Large numbers of underground gasoline tanks have leaked part of their contents into the subsurface and gasoline may be one of the most common causes of ground water pollution (Hoag and Marley 1986). After the gasoline has reached the water table, the more soluble components diffuse into the groundwater and create plumes of contamination the size of which depends on the properties of the soil and contaminants and the groundwater velocity. However, much of the gasoline remains floating on the water table, trapped in the soil pores by capillary forces.

One of the most common methods of remediation of contaminant plumes is the pump and treat process in which groundwater is pumped to the surface and the contaminants removed prior to reinjection. Such pumping does not have a significant effect on the trapped residual gasoline, unless an extremely high hydraulic gradient is used, and so the source of contamination remains in the soil. As a result, the pump and treat method may take tens or hundreds of years to remediate a spill with residual product

saturation, which is a very expensive endeavor (Travis and Doty 1990).

1.2   Research Objective and Approach

This research was undertaken to determine whether certain additives to the injected water in the pump and treat scheme would enhance the mobilization of the trapped residual hydrocarbons. Similar tests have been made on laboratory-contaminated soils (Boyd and Farley 1990a, Tuck, Jaffe et al. 1988) but in this study soil from a field-contaminated well core was used.

Both surfactants and alcohols have been used in tertiary oil recovery with some success (Bansal and Shah 1977, Taber, Kamath et al. 1961) and so both were tried in this work to compare their effectiveness. The individual surfactant and alcohols were selected because of prior use in similar processes and because in low concentrations they are biodegradable by resident soil biological populations. This latter factor is significant because it is vital not to introduce further contamination into the groundwater supply.

A soil column system was used which simulated the hydrologic conditions at the contaminated site. Sample collection, extraction and analysis techniques were developed in order to estimate the effect of the flushing additives in releasing the residual saturation. Following the flushing of the columns, the soil was removed, extracted and

analyzed to determine how much contamination remained. The effects of the additives were modeled using solvophobic theory developed by Rao, Hornsby et al. (1985).

Chapter 2. PREVIOUS RESEARCH

2.1 Contaminants in the Subsurface

2.1.1 Sorption and Transport

Considerable research has been carried out on the sorption and transport of contaminants soluble in ground water. The advection-dispersion theory is used to predict the arrival of contaminants at a particular location. One-dimensional advective - dispersive transport can be described by

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \tag{1}$$

where D is the dispersion coefficient, v is the ground water velocity determined by Darcy's Law, C is the concentration of the solute, x is distance and t is time.

Retardation of contaminants by processes such as precipitation, adsorption, ion exchange, partitioning with soil organic matter or organic solvents must also be accounted for in predicting contaminant transport. A constant retardation factor (R) can be incorporated into equation (1) by dividing both D and v by R. In unretarded transport R is equal to one. The value of the retardation factor is equivalent to the increased time it will take the contaminant to reach a fixed point (Palmer and Johnson 1989b) or the velocity of the water divided by the velocity of contaminant.

2.1.2   Gasoline in Ground Water

Contamination of major ground water sources by gasoline spills or leaks has only been documented since 1968. The following processes affecting the behavior of gasoline components in the ground water were discussed by Brookman, Flanagan et al. (1985) in a review of pertinent literature.

The solubility of many hydrocarbons, including paraffins, increases between 25°C, at which most laboratory measurements are made, and 0°C. In general, the increase is not more than a factor of two. Hydrocarbon solubilities tend to decrease by about one-third from distilled water to sea water, which suggests that high ionic strength ground water might have a similar but smaller effect. Solubilities of individual hydrocarbon components may differ from those of the same components in a mixture. Research indicates that solubilities can be either increased or decreased. pH does not seem to affect the solubility of neutral hydrocarbons in water of low ionic strength.

Biodegradation of gasoline components was investigated in laboratory culture studies (Jamison, Raymond et al. 1976). No biodegradation of 2,4-dimethyl hexane was reported whereas 2,3,4- and 2,3,3-trimethyl pentane were degraded by 13% and 16% respectively by a mixed culture of bacteria. Houzim (1978) observed that alkanes are the least adsorbed by soil of all gasoline components. Higher molecular weight alkanes are adsorbed more

than lower molecular weight alkanes which is to be expected as adsorbability is inversely related to aqueous solubility.

2.2   Non Aqueous Phase Liquids

2.2.1   Residual Saturation

Liquids which can exist as a separate fluid phase are known as non-aqueous phase liquids (NAPL's) and are divided into two classes (Light and Dense) by their density with respect to that of water. Aviation gasoline is an example of an LNAPL which tends to "float" on the capillary fringe above the water table (Palmer and Johnson 1989a). Farr, Houghtalen et al. (1990) showed that the concept of a capillary fringe is not truly applicable in the presence of LNAPL because the water table is actually above the LNAPL-water interface.

When large quantities of such an LNAPL are spilled the liquid tends to flow vertically through the soil pores under the influence of gravity towards the water table. Initially the saturation of the LNAPL may be 100% and the relative permeability for the liquid is equal to one. However, as the LNAPL saturation decreases so does the relative permeability until the latter reaches zero at the residual NAPL saturation (which consists of pendular rings and small blobs or ganglia). This residual saturation cannot be removed from the soil, under natural conditions, except by dissolution into ground water (Palmer and Johnson 1989a). Given the low solubilities of many

gasoline components, residual saturation can continue to act as a source of contamination for many years and can affect large water volumes.

Infiltration by rainfall through residual oil has been shown to enhance concentration of moderately soluble aromatic gasoline components in the ground water (Chang, Wise et al. 1990, Wise, Chang et al. in press). These authors demonstrate, in a field study, how the residual NAPL acts as a continuous source for ground water contamination.

2.2.2   Capillary Number

Several factors have been identified as important in the trapping of residual gasoline including the interfacial tension and density and viscosity ratios of the fluids, soil wetting behavior of the fluids, the geometry of the soil pores, the hydraulic gradient and gravity. The ratio of the capillary forces causing trapping to the viscous forces which can overcome it is known as the Capillary Number Nc, which is given by

$$N_c = \frac{k\rho gJ}{\sigma} = \frac{V\mu_w}{\sigma} \tag{2}$$

where k is the intrinsic permeability of the soil (cm^2), ρ is the soil density (g/cm^3), σ is the interfacial tension (dyne/cm), g is the

gravitational acceleration (cm/s^2), J is the hydraulic gradient, V is the Darcy velocity (cm/sec) and μ_w is the dynamic viscosity of the water (g/cm-s) (Wilson and Conrad 1984, Connor, Newell et al. 1989). The capillary number can be used to estimate the residual saturation.

Hunt, Sitar et al. (1988a) discuss the physics of residual oil trapping and mobilization in detail and note that displacement of residual oil generally is initiated at Nc > 2 * 10^{-5} and complete displacement is achieved when Nc > 5 * 10^{-3}. It is apparent from the expressions for the capillary number that the mobility of the residual oil can be enhanced by increasing the Darcy velocity or hydraulic gradient or decreasing the interfacial tension. There is a limit to the practical increase possible in field velocities and hydraulic gradients so the most effective way to mobilize the residual NAPL is by lowering the interfacial tension.

2.2.3   Removal of Residual Saturation

Aqueous dissolution of residual NAPL saturation is mass transfer limited (Hunt, Sitar et al. 1988a) and the rate of mass transfer is a function of the water velocity and NAPL saturation (Miller, Poirier-McNeill et al. 1990). Experimental flushing of a soil column (95cm^3) containing 10 ml of unleaded gasoline (Borden and Kao 1989) took about 500 pore volumes to reduce 10mg/L m- and p-xylene and 15mg/L toluene to 100μg/L levels. Borden and Piwoni (in press)

provide an expression for estimating the retardation in aqueous flushing

$$R_i = 1 + \frac{\rho}{\theta} (K_{d_i} + \frac{TPH}{S_i})$$ (3)

where ρ is the aquifer bulk density (g/cm³), K_{d_i} is the solid-water partition coefficient (cm³/g), TPH is the total petroleum hydrocarbon concentration (mg/kg), S_i is the aqueous solubility (mg/L), θ is the water-filled porosity and R_i is the linear equilibrium retardation factor for compound i.

These factors lead to the conclusion that aqueous flushing is a very unsatisfactory way of removing NAPL from the soil. Several alternative techniques have been suggested for displacing the oil ganglia including steam injection (Hunt, Sitar et al. 1988b). Boyd and Farley (1990b) note that mobilization of residual hydrocarbons has been achieved in tertiary oil recovery from petroleum reservoirs by injecting surfactants, alcohols, carbon dioxide or alkaline solutions to reduce interfacial tensions.

2.3 Cosolvents

2.3.1 Use in Petroleum Recovery

Research in the use of alcohols as cosolvents in enhanced oil recovery indicates that their effect depends on the particular alcohol, oil and

water in a given system (Taber, Kamath et al. 1961). The effects can be explained using ternary phase diagrams and are affected by the position of the plait point on the binodal curve, which separates the miscible and immiscible regions. Some alcohols (e.g. tertiary butyl alcohol) will lead to disappearance of the aqueous phase with increasing alcohol content whereas some (e.g. 2-propanol) will lead to disappearance of the oil phase. Some control can be exerted over the position of the plait point and, hence, the system behavior by adding specific amounts of oil or water to the alcohol (Taber and Meyer 1964).

2.3.2   Use in Mobilizing Residual Saturation in Soil

Study of the effects of alcohols as cosolvents in ground water contamination resulted from concern about the presence of waste solvents, including alcohols, in landfills and hazardous waste sites. Until recently all the research has focused on the consequences on the sorption and transport of hydrophobic organic contaminants (Rao, Hornsby et al. 1985, Nkedi-Kizza, Rao et al. 1985, Nkedi-Kizza, Rao et al. 1987, Munz and Roberts 1986, Woodburn, Rao et al. 1986, Staples and Geiselmann 1988).

Rao, Hornsby et al. (1985) developed a solvophobic theory based on sorbate solubilities, hydrocarbonaceous surface areas and octanol-water partition coefficients (K_{ow}), and the difference in interfacial

tensions between the sorbate and water and the cosolvent respectively. This theory is described in more detail in section 4.3.1. Experimental verification of the theory was provided by Nkedi-Kizza, Rao et al. (1985), Nkedi-Kizza, Rao et al. (1987), and Woodburn, Rao et al. (1986) who showed that the effect of cosolvent was independent of soil type and that the sorption coefficient (Rm - 1) for each sorbate decreases log-linearly as the fraction of organic cosolvent increases.

Low levels of cosolvent (1 to 10%) were investigated by Staples and Geiselmann (1988) who found that 1% alcohol produced no effect but at 10% by volume 2-propanol, ethanol and methanol reduced the equilibrium soil-water partition coefficient of the contaminant (kepone) by factors of 19.1, 4.3 and 3.9 respectively with 100mg/L soil. This indicates that even low volumes of cosolvent could decrease travel times of some contaminants by reducing the amount of sorption. Mihelcic (1990) determined that 10% of MTBE or ethanol (two common gasoline additives) increased aromatic hydrocarbon solubility by approximately 100%.

Greater hydrophobicity of the cosolvent was observed to increase the effect on a given contaminant. Similarly, the more hydrophobic the contaminant the greater the effect of a particular cosolvent (Munz and Roberts 1986). These authors found that for chemicals with aqueous mole fraction solubilities less than 0.001 the infinite dilution

activity coefficient is a constant. They noted that for a significant increase in contaminant solubility to occur a cosolvent with high aqueous solubility must be used, and that the effects in systems with multiple contaminants should not differ substantially from binary contaminant-water systems.

Groves (1988) developed a rapid method for estimating hydrocarbon solubility in the presence of a cosolvent based on the activity coefficients of the contaminant in the hydrocarbon and water phases and the concentration of the contaminant in the hydrocarbon phase. A technique for predicting partition coefficients for components of hydrocarbon mixtures with cosolvents in the presence of water was presented by El-Zoobi, Ruch et al. (1990). They showed, in addition, that these partition coefficients could be correlated with the cosolvent concentration in the water phase and related their discussion to the alcohol-hydrocarbon-water ternary phase diagram as used in the petroleum recovery literature (Taber, Kamath et al. 1961).

The use of alcohol cosolvents for mobilizing NAPLs was discussed by Boyd and Farley (1990a) who successfully flushed residual trichloroethylene (DNAPL) from a column filled with glass beads using pure 2-propanol.

2.4   Surfactants

2.4.1   Nature of Surfactants

Surfactants (surface-active agents) are substances which, at low concentrations, adsorb onto interfaces within a system and considerably alter (usually reduce) their interfacial free energies (the minimum amount of work required to create an interface). The interfacial free energy per unit area is the interfacial tension between two phases.

The molecular structure of surfactants is amphipathic as it consists of both a hydrophilic and hydrophobic group. Surfactants are classified by the nature of the hydrophilic group which may carry a negative charge (anionic), a positive charge (cationic) or no charge (non-ionic). Non-ionic surfactants are soluble in water and organic solvents, including hydrocarbons.

At a certain, fairly low, concentration (the critical micelle concentration) surfactants form micelles or colloidal-sized clusters in which the hydrophobic tails point towards the center. Properties of a surfactant solution, such as conductivity, surface and interfacial tensions, detergency and refractive index show marked changes at the critical micelle concentration (CMC). CMCs are much lower for non-ionic than ionic surfactants for comparable hydrocarbon chain lengths (Miller and Neogi 1985).

The spontaneous dissolution of a substance (solubilization) by interaction with the micelles is an important property of surfactants at concentrations above the CMC. This process can render water-insoluble substances soluble and is thought to be a major mechanism in the removal of oil from soil (Rosen 1989). The solubilization capacity of the micelle (or moles of solubilizate per mole of micellized surfactant) often remains constant over a wide range of concentration above the CMC. Nonpolar materials, including aliphatic hydrocarbons, are solubilized in the inner core of the micelle and show increased solubility with increasing temperature for non-ionic surfactants such as Triton X-100. The rate of solubilization is directly proportional to the surfactant concentration above the CMC and decreases with increasing molecular weight of the oil (Rosen 1989). It also increases in the presence of dissolved calcium ions.

Reduction in interfacial tension by a surfactant depends on the surface excess concentration of the surfactant. The efficiency and effectiveness of such reduction is enhanced when a second phase is present if that phase is a saturated hydrocarbon (nonpolar) in which the surfactant has almost no solubility.

2.4.2   Use in Petroleum Recovery

Surfactant-polymer flooding is a proven technique for tertiary oil recovery. Use of an appropriate surfactant can reduce interfacial

tension (and, hence, the capillary number) from 20 or 30 dynes/cm to 0.001 or 0.0001 dynes/cm and thus mobilize the oil trapped in the reservoir (Ling, Lee et al. 1987). The surfactant is injected as a slug consisting of brine, surfactant, alcohol as cosurfactant (to reduce interfacial tension and viscosity) and sometimes oil; and causes the oil ganglia to coalesce as an oil bank due to low interfacial viscosity. Owing to the cost of surfactants, a small volume of solution is used followed by a polymer solution and then brine. This sequence is designed to have increasing viscosity in order of injection to control oil mobility (Ling, Lee et al. 1987).

2.4.3   Use in Mobilizing Residual Saturation in Soil

Kile and Chiou (1989) investigated enhanced aqueous solubility of DDT and trichlorobenzene by surfactants (including Triton X-100) and found that above the CMC the effect of non-ionic surfactants is proportional to the nonpolar chain content of the surfactant. The solubility of DDT was slightly increased below the CMC which they attributed to the micellization process.

Solubilization of polycyclic aromatic compounds by four non-ionic surfactants (including Triton X-100) was found to be proportional to the concentration of surfactant above the CMC (Edwards, Luthy et al. 1991). The logarithm of the mole fraction micelle phase/aqueous

phase partition coefficient (log K_m) appears to be a linear function of log K_{ow} for each surfactant solution.

The removal of residual hydrocarbon saturation from the unsaturated zone can be considerably enhanced by use of a surfactant (Tuck, Jaffe et al. 1988). Tetrachloroethylene was flushed from a column of glass beads using an anionic surfactant (0.5g/L). Smith, Tuck et al. (in press) observed that although anionic surfactant solutions may enhance removal by decreasing interfacial tension, cationic surfactants may have the opposite effect and increase contaminant sorption.

Soil washing with one anionic and one non-ionic surfactant at concentrations of 0.01 to 4.0 wt% was found not to increase the removal of residual gasoline as compared with water flushing (Ziegenfuss 1987). Use of a water-insoluble surfactant resulted in the recovery of 40% of the residual gasoline but formed a high viscosity emulsion which reduced the relative permeability of the sand by an order of magnitude (Texas Research Institute 1979). In combination with a soluble non-ionic surfactant the oil recovery remained at 40% but the relative permeability was only reduced by 63%. Multiple application of the same surfactants to a sand-filled tank removed more than 75% of the residual gasoline (Texas Research Institute 1985). The choice of surfactant is, therefore, of considerable importance in soil flushing.

Surfactant treatment of soils will probably be most effective when the contamination is spread over a large volume (greater than 100 m^3) and is not greater than 10,000 ppm or the source of contamination has been removed (Ellis, Payne et al. 1985). Batch and column tests using a surfactant pair with gasoline (and other contaminants) achieved 93% removal with ten pore volumes of 4.0% total surfactant. The optimum concentration of surfactant for petroleum hydrocarbon contaminated soils was found to be 1.5%; above this value no improvement is observed and below 0.5% acceptable removal was not attained. The authors also attempted to remove the surfactant for reuse, but were only able to remove the surfactant with the contaminants.

Chapter 3. EXPERIMENTAL METHODS

3.1 Materials

3.1.1 Reagents and Supplies

All chemicals used in this research were ACS reagent grade or better. Solvents and reagents were supplied by Aldrich Chemical Company (Milwaukee, WI), Fisher Scientific (Fair Lawn, NJ), Mallinckrodt (Paris, KY), and Burdick and Jackson (Muskegon, MI). ^{14}C-labeled toluene was obtained from Pathfinder Laboratories, Inc. (St. Louis, MO), and tritiated water from Amersham Corporation (Arlington Heights, IL). A pseudo cumene-based scintillation cocktail, Ready-Solv™HP (Beckman Instrument Company, Fullerton, CA), was used.

Rice University well water was deionized using a system provided by Ionpure Water Systems (Houston, TX) including a $10\mu m$ prefilter, one cationic, one anionic and two mixed bed cartridges. It was further purified using an Ultrapure Ion Exchange cartridge (Barnstead D0809) to remove silica and carbon dioxide, an Organic Removal cartridge (Barnstead D0813) to remove chlorine and organic and odor-causing impurities and a 0.2 μm general purpose final filter (Barnstead D3749) to remove particulates and bacteria.

Blank feed solution containing 0.01M calcium chloride ($CaCl_2$) to stabilize clay minerals, and 0.01M formaldehyde (CH_2O) to prevent biological activity was prepared in the purified water. Two pH

buffers were used: 0.025 M sodium tetraborate ($Na_2B_4O_7$) for the surfactant experiments and 0.05 M Tris Hydroxymethyl Aminomethane (THAM) for the alcohol and combined alcohol-surfactant experiments. In both cases the pH was adjusted to 8.0 using hydrochloric acid. According to Nkedi-Kizza, Rao et al. (1985) and Clark (1990), 0.01M formaldehyde will have negligible cosolvent effects on the solubility of organic compounds in the water.

Collection bags were made with Tedlar (#TST20SG4) film from Dupont (Wilmington, DE), 2-way bulkhead mountable valves from Omnifit (#001104; Atlantic Beach, NY), and Viton O-rings (V0747) from Parker Seal Co., (Houston, TX).

The surfactant used was Triton X-100 (obtained from Aldrich Chemical Co.), which is the trade name for octyl-phenyl polyoxyethylene ethers, $C_{14}H_{21}(OCH_2CH_2)_n$ OH where n = 5 - 15 (average molecular weight = 628). It is a polydisperse, non-ionic surfactant with a critical micellar concentration of 207mg/L (Mukerjee and Mysels 1970) and the micelle has a molecular weight of about 90,000.

3.1.2. Soil

The soil used in these experiments was collected in August 1989 from a well core at the site of aviation gasoline and JP-4 jet fuel spills on a U.S. Coast Guard base in Traverse City, MI. The well (M31)

was drilled 200 meters down gradient from the original location of the spill which is thought to have occurred in 1969 (Chang, Wise et al. 1990). Ostendorf, Kampbell et al. (1989) reported that free oil product and/or residual oil was detected 220m from the source. A 3 ft thick section across the water table (16'1") was cored and divided into 4 inch segments which were placed in Mason jars. The jars were sealed and taped and stored in a refrigerator until use. Much of the residual oil was in the sample from 15'8" to 16'0" but biological growth had occurred in this sample. Therefore, the sample used for the experiments was that taken from 16'0" to 16'4", which, from its texture and odor was also thought to contain considerable residual oil.

Previous researchers have determined that the upper part of the Traverse City aquifer (in which the water table occurs) is a well sorted, uncemented, fine/medium sandy sediment (Twenter, Cummings et al. 1985) with a dominant size fraction of 177-500 μm (Clark 1990). The sand has a fairly low organic carbon content of 0.008% and, therefore, a low sorption capacity for hydrophobic organic chemicals (Thomas, Clark et al. 1988). This soil was used because it has been successful in previous column experiments (Clark 1990), contaminated samples were available and the spill site was well characterized.

3.2.   Experimental System

3.2.1.   Soil Columns

The system used was based on one developed by Dr. Kan and Dr. Tomson at Rice University to study one-dimensional contaminant flow (Kan and Tomson 1990a).

A borosilicate precision glass chromatography column (0.9 cm 1.D x 15 cm long, Spectrum Inc., Houston, TX), held in a vertical position, was used to contain the soil with stainless steel plungers and Viton O-rings to seal the system (Fig 3.1).   Stainless steel screens (10 µm Valco, Inc., Houston, TX) separated the soil from the 316 stainless steel tubing (1/16" O.D. x 0.03" I.D.), which formed the core of the plungers.   Feed solution was pumped from 30ml or 50ml glass syringes (Multifit, Becton-Dickinson, Rutherford, NJ; Perfectum, Popper & Sons, Inc., New Hyde Park, NY), which were connected to the tubing by Luer-lok fittings, using a Harvard Apparatus Syringe Infusion Pump (#22).   Apparatus dispersion of this soil column system was determined to be insignificant (Kan and Tomson 1990a).

The effluent tubing passed through a hole in the top of a Styrofoam chest which was filled with crushed ice in order to maintain the collection system at a low temperature and minimize diffusion losses. For the tritium breakthrough runs a fraction collector (ISCO Isis
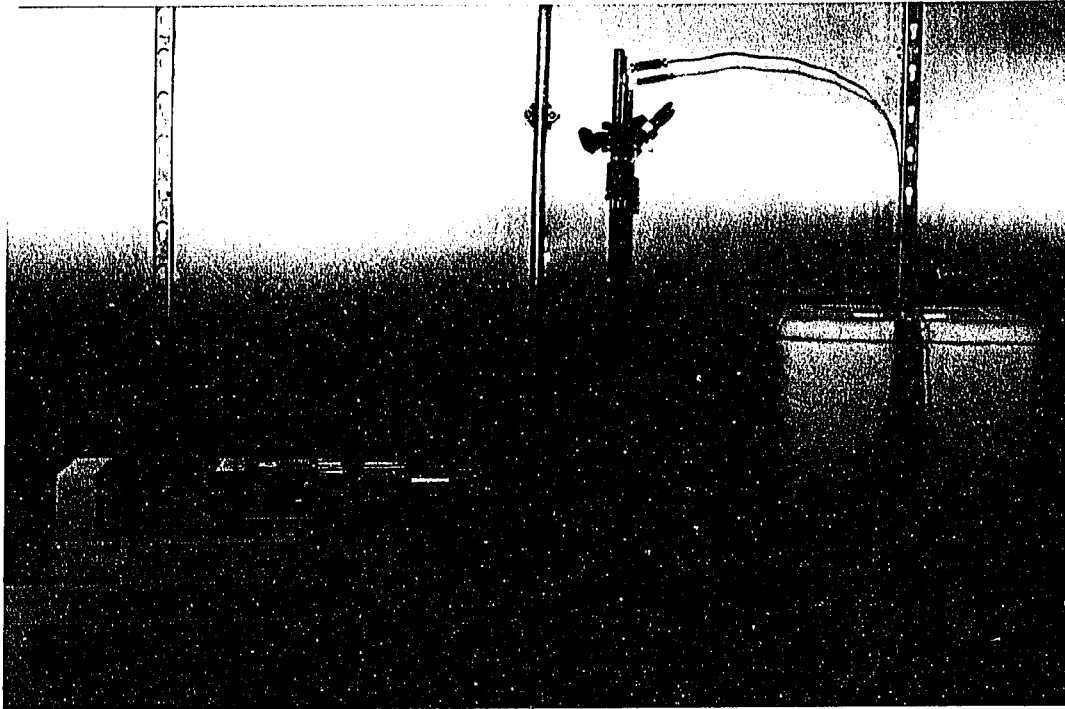
Fig 3.1   Photograph of soil column apparatus
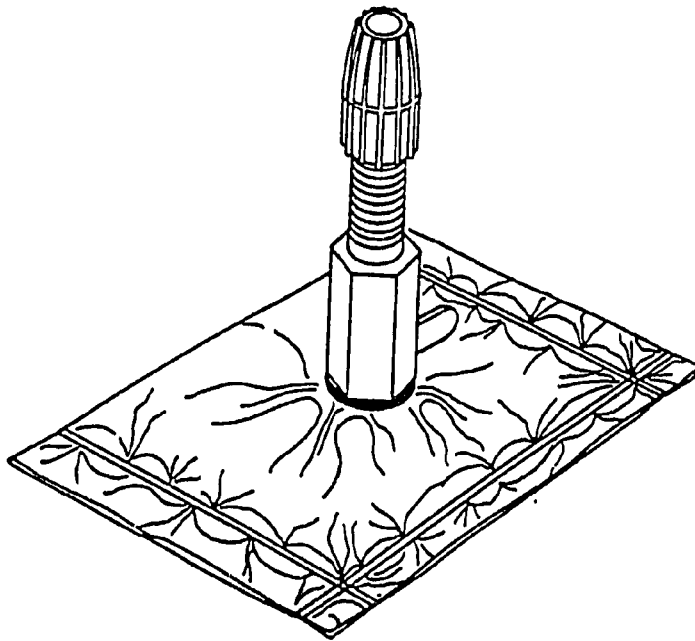
Fig 3.2   Tedlar collection bag (from Priddle & Jackson, in press)

Autosampler), containing 25 ml. scintillation vials, was used to collect the samples.

All the experiments were run in a 12°C $\pm$ 1°C constant-temperature room in order to simulate the ground conditions at the Traverse City site (S. Fiorenza, pers. comm.).

The pressure head within the columns was determined using Darcy's Law $(Q = KA\frac{dh}{dl})$ to ensure that it was fairly close to the field hydraulic gradient. According to Wilson and Conrad (1984) high hydraulic gradients in soil columns can mobilize some residual oil which would not be affected under field conditions. The column gradient was 0.0124 compared to a field gradient of 0.004 - 0.007 (Twenter, Cummings et al. 1985). The value of hydraulic conductivity (K) was taken from Twenter, Cummings et al. (1985) as 120 ft/day or 0.042 cm/s. This calculated column gradient is a low estimate as the sand packing was less dense in the columns than in the field (effective porosity of 15%). A higher K value would reduce the calculated column pressure head. The flow rate used in the calculation was the pumped rate of 1.2ml/hr and the area was computed from the column internal diameter (0.9 cm).

3.2.2.   Sample Collection

The samples of effluent were collected in small bags made of Tedlar PVC film (Fig 3.2), which were based on a design used by Priddle and Jackson (in press). The bags were constructed by punching a small hole (4-5 mm diameter) in the film, sealing two sides of the bag with a heat sealer, (Cole-Parmer, Chicago, IL), inserting the shortened bulkhead mountable end of the valve, with a Viton O-ring (1/4" I.D. x 3/32" wall), through the hole, attaching a nut to the valve inside the bag and tightening it to form an airtight seal. The open end of the bag was then heat sealed and a vacuum created in the bag using an aspirator mounted on a faucet. The completed bag was attached to the effluent 1/16" tubing of the experimental system inside the ice-filled Styrofoam chest. A seal was created by the O-ring inside the proximal end of the valve. The valve was then opened so that sample collection could begin.

The bags were tested to ascertain their efficiency. Initial tests were performed at room temperature using ^{14}C-labeled toluene (Specific Activity 10·9 μCi/μmole) at 250 ppb in feed solution. Six bags were filled with 5.5 ml of the solution and samples of 0.5 ml were removed through the valve at varying intervals. For the first four bags (A-D) samples were withdrawn only after 3 and 6 hours (plus 120 hours for C & D), but for bag E samples were taken every hour for the first six hours to plot the loss of toluene in greater detail. Bag F was sampled once or twice daily for five days. Samples were also

taken from the volumetric flask in which the solution was made. For bags A-D these samples were taken after the bags had been filled, apparently allowing time for some volatilization. In the case of bags E and F, the initial samples were taken prior to filling the bags.

A large loss of toluene occurred within the first few hours (Fig. 3.3). For bags E and F the total loss during the first six hours is approximately 25%, of which 20% occurred during the first three hours. The loss in the flask was 22% in 3 hours and 31% in 6 hours. Such a large loss of toluene from the bags at room temperature was not acceptable so collection over ice in the constant temperature room (12°C) was tried. Two bags (G & H) were attached to the effluent end of syringes filled with 50 ppb of benzene, toluene, ethyl benzene and o-, m- and p-xylene (BTEX). This solution was pumped at 20μl/min into the bags, which rested on crushed ice in beakers, for 4 1/2 hours. Approximately 5.5 ml was decanted from both bags into small vials (1·5 drams) with no headspace and the vials were stored in the refrigerator overnight.

The samples were analyzed by purge and trap gas chromatography at Hanby Analytical Laboratories (Houston, TX), and the results compared with those from two vials filled directly with the feed solution. The bag concentrations for all six chemicals were between 80% and 90% of those from the vials (Fig. 3.4). This percentage recovery for semi-volatile chemicals was considered adequate.
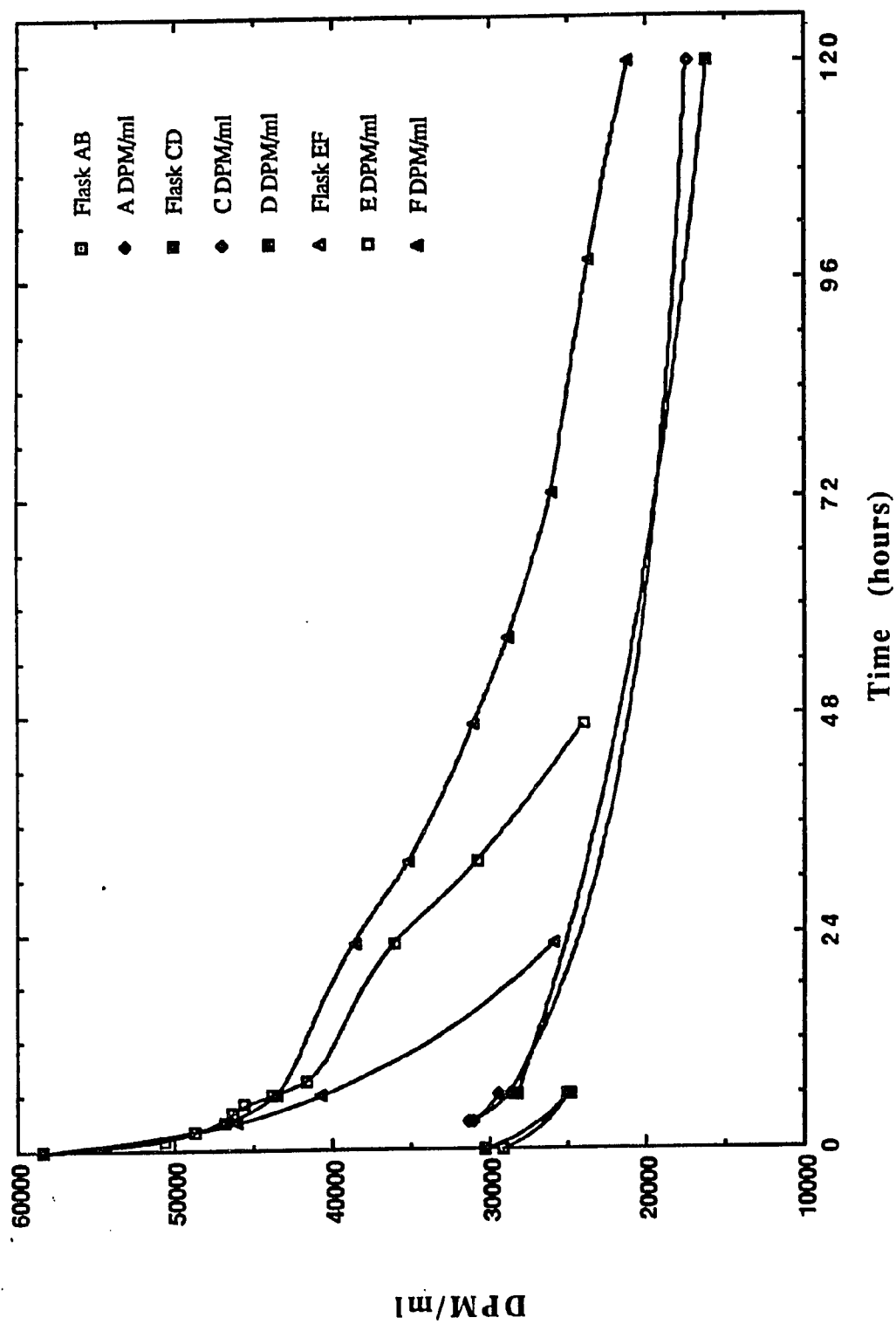
Figure 3.3   Tedlar bag toluene retention at room temperature
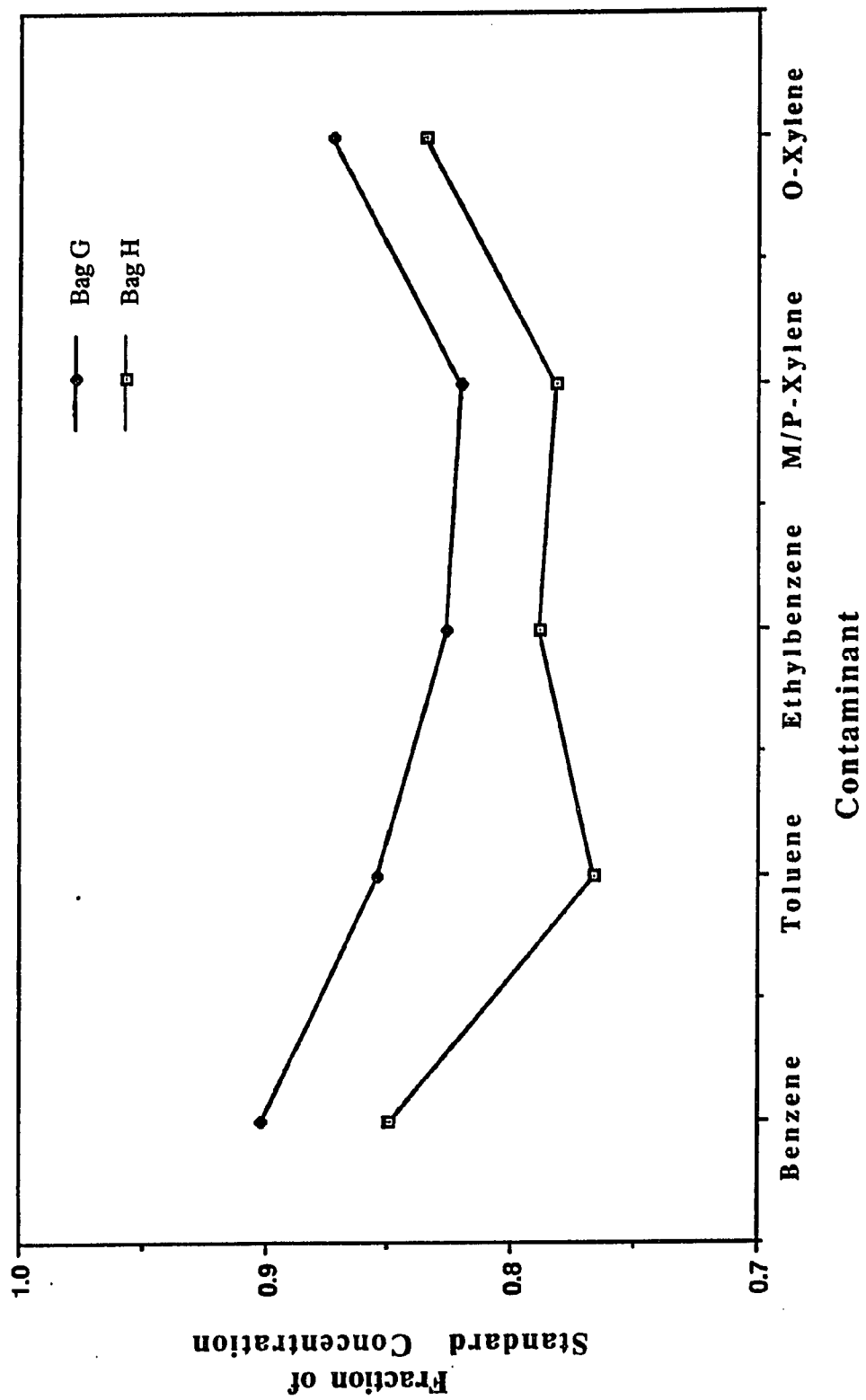
Fig 3.4 Tedlar bag contaminant retention at 12°C

When the column experiments were run, the chemicals collected were found to be less volatile methylated alkanes for which the losses through the bags were expected to be lower and so the collection mechanism was thought to be the most acceptable method for these experiments.

3.2.3. Sample Extraction

In order to analyze the effluent concentrations using direct injection gas chromatography it was necessary to extract the chemicals from the effluent and concentrate them in a solvent. This process had to be rapid, flexible and reproducible to ensure that samples could be extracted soon after the bags were removed from the effluent tubing, that a variable sample size could be extracted and that the results would be representative, in a consistent manner, of the true concentrations. For these reasons the Mixxor™ (Genex, Gaithersburg, MD) System was used.

The Mixxor consists of a graduated glass mixing reservoir, a glass mixer-separator piston with an axial channel which leads to a collecting container, a screw cap to the mixer-separator and a plastic spacer (Fig 3.5). The latter prevents the mixer-separator being forced too far into the reservoir and facilitates phase separation. The two liquids to be extracted are placed in the reservoir and the piston, with the spacer, is fitted into the top of the reservoir. The screw cap
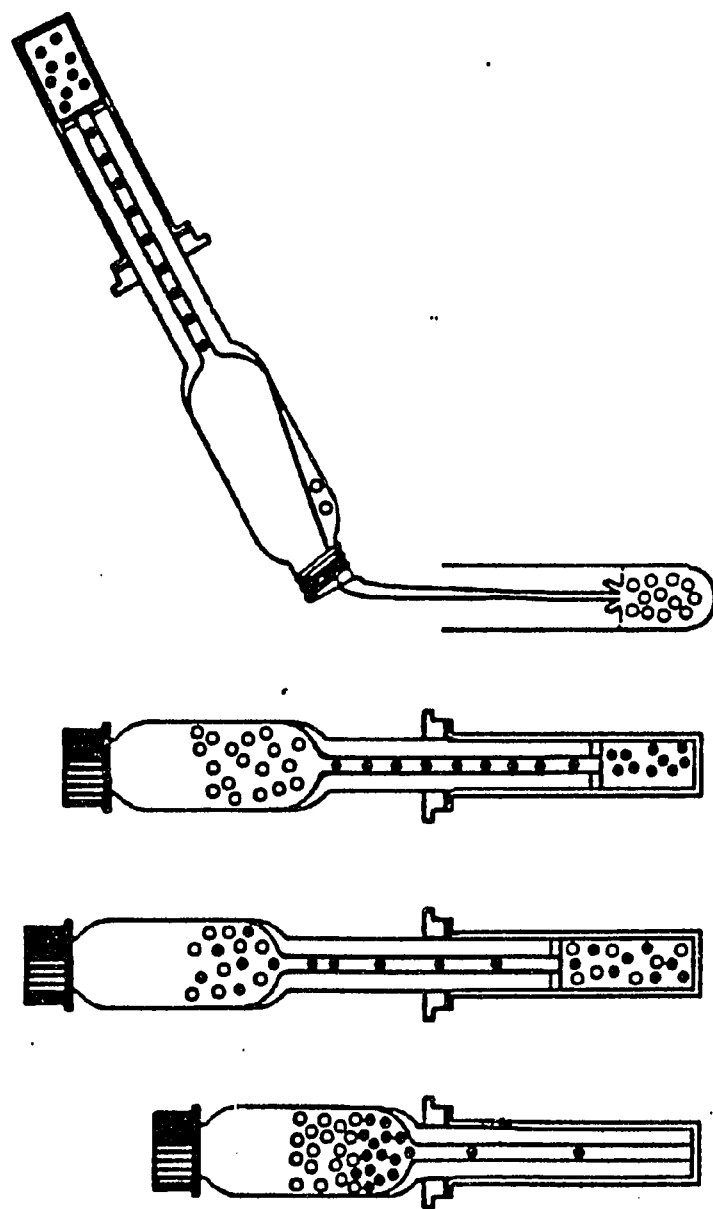
Fig 3.5 Mixxor Extraction System - the process of mixing and separating the two liquids proceeds from left to right. Open circles represent sample, filled circles represent solvent.

is tightened to produce a closed system and the piston is pushed into the reservoir. The screw cap is tightened to produce a closed system and the piston is pushed into the reservoir in an up and down motion several times. The two liquids are forced back and forth through the axial channel between the reservoir and mixing chamber, which causes the mass to be broken into very small droplets and allows an intimate mixing of the two phases. The spacer is then adjusted to hold the piston above the level of the liquid in the reservoir and the phases are allowed to separate. The piston is then pushed into the reservoir and the upper phases flows into the upper chamber. When the lower phase reaches the top of the axial channel, the screw cap is removed and the upper phase decanted into a vial. The mixer can then be removed and the lower phase poured out of the reservoir.

Methylene chloride was used as the extraction solvent in all the extractions because its high density (1.3266 g/cc) enabled it to separate rapidly from the aqueous phase in the Mixxor.

The extraction efficiency of the Mixxor was examined using solutions of aviation gasoline (diluted in methanol), and BTEX. For the latter the recovery for the contaminants was 71% for toluene and 94-97% for the other aromatic hydrocarbons. For the aviation gasoline the recovery varied between 88 and 99% for the different components. The computed concentrations were not adjusted for this extraction efficiency.

The effect of alcohol and surfactant in the effluent on the methylene chloride extraction was unknown. Therefore extractions were made from solutions containing aviation gasoline and 2-propanol or Triton X-100 in order to quantify this effect. With 5g/L Triton X-100 areas of four peaks ranged from 83 to 90% of the aviation gasoline standard with one at 62%. With 50% 2-propanol recoveries were lower, ranging from 65 to 75%. When the amount of solvent was too large compared to the volume of sample an emulsion of the 2-propanol and methylene was formed which reduced recoveries. Attempts were made during the column flushing to avoid this situation by selecting appropriate solvent volumes. Extracts from stock solution containing the flushing additives were also performed to ensure that they had no effect on the baseline and, indeed, none was observed.

3.3 Experimental Procedures

3.3.1 Soil Column Loading

Several factors were important in the loading of the contaminated soil into the glass columns. Rapid loading was necessary to avoid the loss of any remaining volatile or semi-volatile constituents. The intention was also to maintain the integrity of the soil, as much as possible, so that the structure of the soil and residual oil would be preserved. Lastly, the elimination of air spaces in the column was attempted so that saturated flow conditions would prevail in the

experimental runs and parts of the column would not evade being flushed by feed solution.

To take account of these factors, a specific loading procedure was developed. A glass syringe was filled with feed solution and the plunger was coated with hydrophilic Phynal grease (Reliance Glass Works, Inc., Bensenville, IL) to avoid fluid loss and ensure smooth flow. The plunger was inserted into the syringe and air bubbles were removed. The syringe was then connected to the 1/16" O.D. (x 0.03" I.D.) tubing and the syringe was mounted on the syringe pump. Solution was pushed through the tubing until a few millimeters appeared at the base of the glass column and a screen was then dropped into the column and centered over the hole in the stainless steel plunger. At this time the tape and lid were removed from the Mason jar of soil and a spatula was used to transfer large clumps of soil from the jar into the top of the column. These were allowed to drop to the bottom of the column and the side of the column was tapped vigorously to make soil settle into the feed solution. This process was continued, ensuring that the fluid level was maintained at or just above the soil surface, until the soil was about 10 cm thick. The fluid level was then adjusted so it was at the soil surface. A second screen was centered on top of the soil and the upper plunger was gently pushed down into the column until it fit tightly over the screen and soil at which point it was secured in position with the

Teflon nut. The height of soil was measured to allow calculation of the volume.

The syringe pump was then switched on and allowed to flow until fluid was observed at the effluent end of the tubing. Next, a sample bag was attached to the tubing, inside the ice-filled chest, and collection commenced.

3.3.2. Flushing Regimes

In all experiments the feed solution flow rate was $20\mu l/min$ (1.2 ml/hr). This flow rate can be converted to a field velocity of 4.2 to 5.7 feet/day (0.0015 - 0.0020 cm/s), over the range of porosities present in the columns (26 - 35%), which is within the velocity range of 3 to 6 ft/day (0.0011 - 0.0021 cm/s) measured at the spill site (Twenter, Cummings et al. 1985). The pH of the solution was maintained at 8.0 which is the pH of uncontaminated groundwater around the Traverse City spill (Thomas, Clark et al. 1988), as this would be a probable source of water for remedial pumping schemes.

The general system was the same for each of the six experimental runs with the only differences being the amount of each type of fluid which was passed through the column and the additive(s) to the feed solution (Table 3.1). Initially several pore volumes of blank feed solution were flushed through the column to assess the contaminant

Column	Stock Solution	Additive	Cleanup*
TC2	Borate buffer (26PV**)	5g/L Triton X-100 (24.7PV)	10
TC3	THAM buffer (28PV)	50% (v/v) 2-propanol (8.9PV)	9
TC4	THAM buffer (6PV)	20% (v/v) 2-propanol (10PV); followed by 50% (v/v) 2-propanol (5PV)	8
TC5	Borate buffer (16PV)	15g/L Triton X-100 (21.3PV)	10
TC7	THAM buffer (16PV)	5g/L Triton X-100 + 20% (v/v) 2-propanol (24.5PV)	13
TC8	THAM buffer (14PV)	20% (v/v) methanol (6.8PV); followed by 50% (v/v) methanol (40.8PV)	9

** PV represents the number of soil column pore volumes
* Clean-up represents the number of pore volumes of stock solution flushed through the soil column prior to the tritiated water breakthrough (3-5PV) and subsequent flushout (3-5PV).

Table 3.1: Column experiments - specific flushing regimes.

Column	Length (cm)	Volume (cm3)	PV from sand (ml)	Porosity (sand)	PV from tritium data (ml)	Porosity (tritium)
TC2	10.2	6.49	2.27	35.0	2.3	35.4
TC3	9.90	6.30	1.67	26.5	1.9	30.1
TC4	10.0	6.36	2.24	35.2	1.8	28.3
TC5	9.60	6.11	1.69	27.7	2.2	36.0
TC7	9.85	6.27	1.70	27.1	2.2	35.1
TC8	9.55	6.08	1.79	29.5	1.8	29.7

Table 3.2 Column porosity estimates from sand masses and tritiated water breakthrough data.

release which was achieved with water alone. This was followed by flushing with the feed solution plus a known concentration of surfactant, 2-propanol, methanol or a combination of 2-propanol and surfactant. In two of the experiments two different concentrations of alcohol were used sequentially. The column was then again flushed with blank feed solution to remove the additive and assess the residual aqueous concentrations of contaminants. A tritium breakthrough curve was run and finally the blank solution was pumped through the column to remove the tritium prior to dismantling of the column and soil analysis.

The first experiment run used the sodium tetraborate buffer in the feed solution with surfactant as the additive. However, when 2-propanol was added to this feed solution for the second column a white precipitate formed. Experiments showed that this precipitate was calcium borate which was caused by the reduced solubility of the ions in alcohol compared to water. Therefore, a different buffer (THAM) was used to achieve the same pH for the alcohol and alcohol-surfactant combination experiments. The solubility of gases in alcohol is much greater than that in water and when the alcohol was added to the feed solution and poured into the syringe many small bubbles formed. As many of these as possible were removed by tapping before the syringe was attached to the column influent tubing. Unfortunately, small bubbles continued to develop both in the syringe and the column as the solution passed through the latter.

This does not seem to have caused a problem in the flush-out part of the experiment. However, it has created a discrepancy between the pore volumes of column TC4 which were calculated from the tritium breakthrough curve and from the soil mass - column volume ratio (Table 3.2). The column which was flushed with 50% 2-propanol only (TC3) did not develop as much air space, probably because only a few pore volumes of alcohol solution were passed through this column. In the combination 2-propanol - surfactant experiments the surfactant appeared to prevent the formation of most of the small gas bubbles and the soil column remained saturated throughout the experiment.

3.3.3.   Sample Collection, Extraction and Analysis

As a result of using field-contaminated soil there were many unknowns in these experiments. The amount of soil in the column and, therefore, the porosity or pore volume could not be computed until after the experiments when the tritium breakthroughs were run and the columns dismantled to extract the soil. Also the initial concentrations of aviation gasoline and the individual contaminants were not known and may have varied between columns although every attempt was made to load them in an identical manner. The distribution of residual saturation within the Mason jar was assumed to be relatively uniform but the validity of this assumption is uncertain.

Owing to these problems and the unknown effects of the various flushing solutions the sample size varied depending on the contaminant concentrations in the previous sample or experience from prior experiments. Each sample was extracted and analyzed in a process which took approximately one hour and if effluent concentrations were high another sample would be taken at once.

An attempt was made to take a sample of one estimated pore volume (or a little less) after the attachment of the syringe of flushing solution containing the additive(s). This was done so that the next sample would be primarily of the additive-containing solution. However, this could not be done accurately because the pore volumes were not known, so the concentrations in this sample in each experiment may not represent a true initial effluent concentration but may be somewhat diluted.

In the sampling procedure the valve on the collection bag was closed and the bag removed and immediately replaced with a new bag. The sample bag was wiped, to remove any water drops from melted ice, and immediately weighed. The sample was removed using a syringe and put into the Mixxor with a small amount of methylene chloride. The extraction was performed in an appropriate size Mixxor (2, 5, 10, and 50 ml sizes were used). The extract was then transferred by syringe to a 5.5 ml vial and a measured amount of cumene internal standard (400mg/L) was added with a 25μl syringe.

The extract was then analyzed on a Tracor 560 gas chromatograph (Austin, TX) with a 30 meter DB-5 megabore column (J and W, Folsom, CA) and flame ionization detector. The injector port temperature was 200°C and the detector was maintained at 250°C. The initial oven temperature was 50°C which was held constant for five minutes followed by a ramp increase of 6°C/minute to a final temperature of 180°C, held for two minutes.

3.3.4 Tritium Breakthrough Runs

A few microlitres of tritiated water (specific activity 250 μCi/ml) were added to a syringe containing 20 ml of blank feed solution and mixed. This solution was passed through the column at 20 μl/min and samples were collected every ten minutes (0.2 ml) in preweighed scintillation vials. The vials were reweighed and 10 ml of scintillation cocktail was added to each vial. They were then capped and vibrated for a minute or two, to mix the sample and cocktail, and analyzed on a Beckman LS3801 liquid scintillation counter using a five minute count time per vial.

The breakthrough curves were plotted from the data and the volume at which $C/C_0 = 0.5$ was taken to be the pore volume (Table 3.2). The pore volumes for the columns ranged from 1.8ml (TC4 and TC8) to 2.2ml (TC5 and TC7).

3.3.5   Soil Extractions

After the tritiated water solution had been flushed from the column the equipment was dismantled. The soil was transferred with a spatula from the column to a pre-weighed 40 ml vial. Three ml of methanol was used to wash the remaining soil from the sides of the column into the vial. The vial was sealed with a teflon-lined septum and cap and was shaken for approximately 3 hours in a Lab-Line Instruments, Inc. Supermixer (Melrose Park, IL). It was then spun for 15 minutes at 1500 rpm in a Sorvall RC2-B Superspeed Automatic Refrigerated centrifuge. The supernatant fluid was removed by syringe into a preweighed 1.5 dram vial, reweighed and analyzed by gas chromatography. Approximately 1 to 1.4 ml of methanol was added to the vial and the shaking, centrifuging, decanting and analysis repeated.

This soil extraction process, and particularly the solvent used, was selected after performing three similar extractions on contaminated soil from the sample jar. The process was used because it was relatively simple and could be performed fairly rapidly. Methanol, 2-propanol and methylene chloride were tested as extraction solvents and methanol was the most successful in removing the contaminants from the soil. The density of the methylene chloride appeared to be a problem because the sand remained in clumps and did not separate into individual grains in the solvent. Both the methylene chloride and 2-propanol extracts had very poor baseline

resolution on the gas chromatogram due to severe tailing of the solvent peak. Methanol produced the best chromatogram resolution and gave the highest concentrations and was selected for these reasons.

3.3.6. Soil Analysis

Following the soil extractions the vials were opened and the methanol allowed to evaporate in a fume hood. The vials were then reweighed so that the weight of the dry sand could be calculated. From these values and the total volume of each column the porosity was estimated (Table 3.2). The porosities calculated in this manner range from 26.5% to 35.2% and the variation is thought to be due to the natural grain size fluctuations in each sample and some non-uniformity in the packing density resulting from the column loading technique.

There is considerable discrepancy between the pore volumes calculated from the sand masses and the tritium breakthrough curves in four of the columns. TC4 has a higher pore volume from the sand mass because of the large amount of exsolved gas in the column affected the tritium breakthrough. However three of the columns (TC3, 5 and 7) have higher pore volumes from the tritium data. The only common factor in these columns was that they were all constructed using the same pair of stainless steel plungers in the

ends of the column (two sets were available and the other set was used for columns TC2, 4 and 8). Losses of sand during the dismantling of the columns would have resulted in higher pore volumes being calculated by that method than actually existed. The pore volumes calculated from the sand masses have been used for all the graphs and data tables. They were selected because of the previously discussed problems with the tritium breakthrough data and of the lower probability of errors in the mechanical weighing of the sand than in the tritiated water procedure.

3.4 Data Analysis

3.4.1. Calculation of Effluent Concentrations

Five peaks on the gas chromatograms were selected as representative of the change in contaminant concentrations during the flushouts. The retention times for these peaks were approximately 6.2, 6.9, 7.1, 8.1 and 15.0 minutes (Fig 3.6). The peak for the cumene internal internal standard had a retention time of 13.7 minutes.

The area of each contaminant peak was divided by the area of the cumene peak and multiplied by the extraction ratio of the effluent to solvent, the ratio of the internal standard to the extract and the concentration of the internal standard.
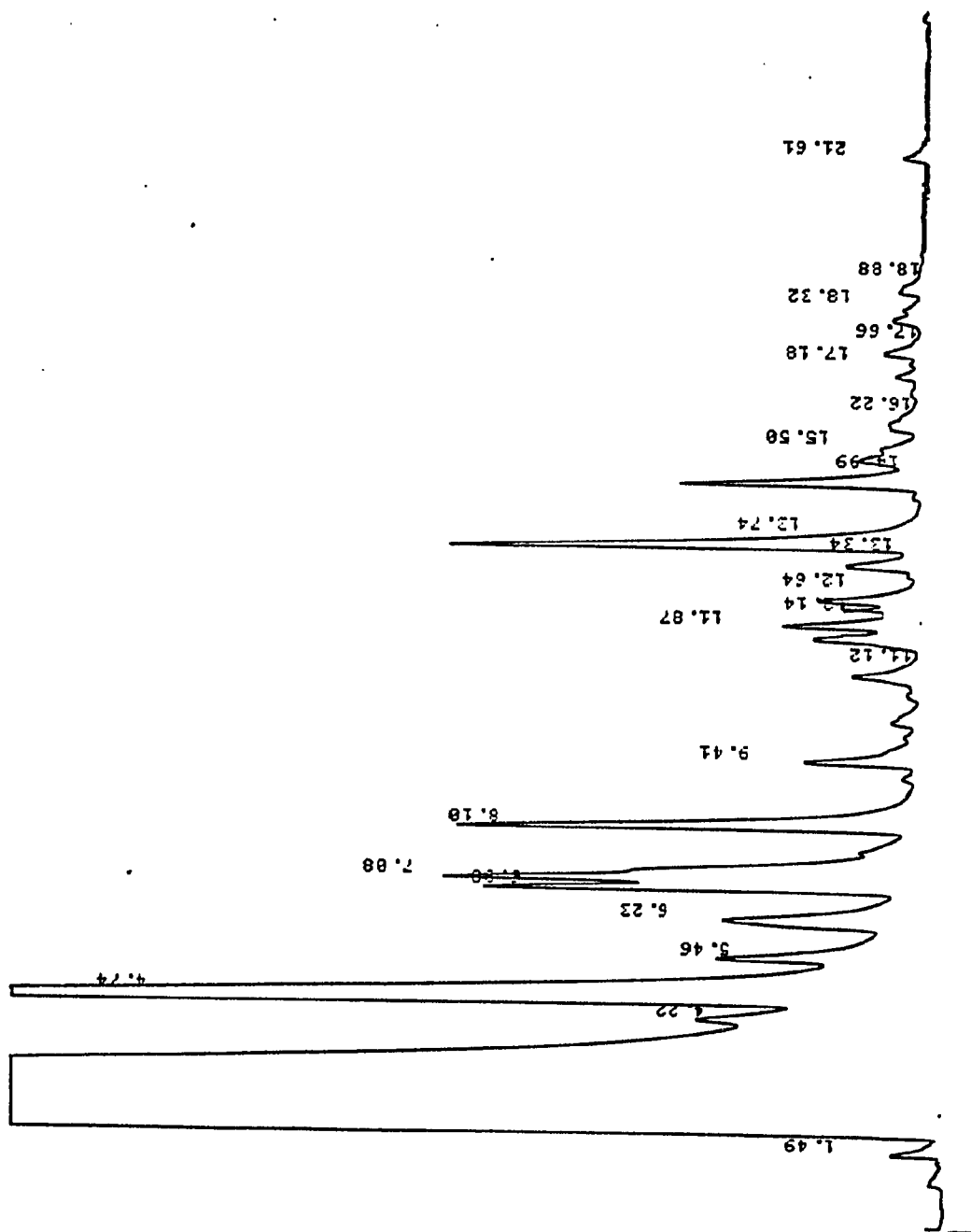
Fig 3.6 Representative gas chromatograph from sample TC2.14.

$$\text{Concentration} = \frac{\text{Peak area} * \text{Extraction ratio} * \text{Internal Standard Ratio}}{\text{Internal standard peak area}}$$

where

$$\text{Extraction ratio} = \frac{\text{Volume solvent}}{\text{Volume effluent}}$$

and

$$\text{Internal standard ratio} = \frac{\text{Volume of internal standard} * 400\text{mg/L}}{\text{Volume of extract}}$$

This produced a final concentration for each peak, which was plotted against the number of pore volumes of total flow at which the sample was removed from the effluent tubing.

3.4.2. Identification of Contaminant Peaks

In order to determine the identity of the selected peaks gas chromatography-mass spectrometry analysis was performed on three samples. All the samples had a high concentration of contaminants (TC2.15, TC3.10 and TC3.11) and were from the 5g/L Triton X-100 and 50% 2-propanol experimental runs.

All the peaks identified by the GC-MS analysis were methylated alkanes, apart from the cumene internal standard (Fig 3.7). All three
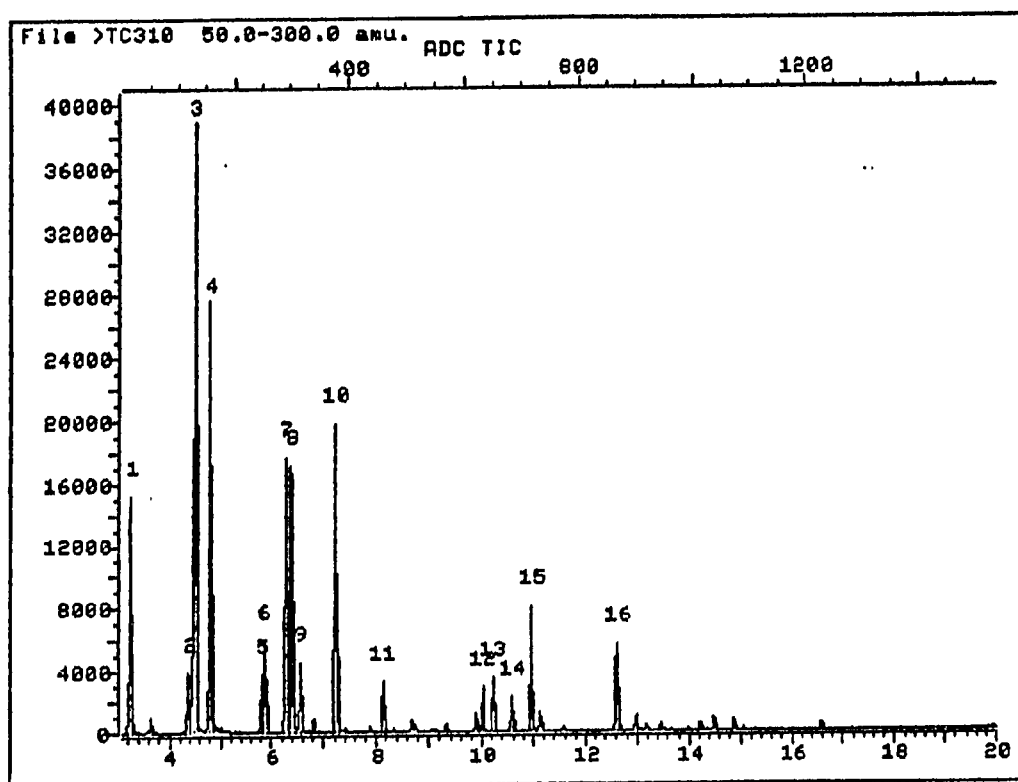
Fig 3.7   Representative GC-MS chromatogram with peak identity as follows

Peak Number	Peak Identity
1	Chloroform
2	2,3-dimethyl pentane
3	Cyclohexane (solvent additive)
4	2,2,4-trimethyl pentane
5	2,5-dimethyl hexane
6	2,4-dimethyl hexane
7	2,3,4-trimethyl pentane
8	2,3,3-trimethyl pentane
9	2,3-dimethyl hexane
10	2,2,5-trimethyl hexane
11	2,3,5-trimethyl hexane
12	4-ethyl 2,2-dimethyl hexane
13	2,2,4-trimethyl heptane
14	3,3,5-trimethyl heptane
15	Cumene
16	2,5,6-trimethyl octane

analyses produced similar results in terms of most likely peak identification. However the resolution of the instrument was insufficient to distinguish between different isomers of the same chemical. As the specific identity of the contaminant was not crucial to this research no steps were taken to resolve this question.

The retention times and associated most likely chemical isomers determined by the GC-MS analysis are listed in Table 3.3. The five monitored peaks were 2,4-dimethyl hexane, 2,3,4-trimethyl pentane, 2,3,3-trimethyl pentane, 2,2,5-trimethyl hexane and 2,5,6-trimethyl octane. The first four of these are the same as those determined by Vandegrift and Kampbell (1988) from Traverse City aviation gasoline. These authors also analyzed a trimethyl octane (and heavier molecular weight alkanes including decane, undecane, dodecane, tridecane and tetradecane) in a JP-4 jet fuel sample from Traverse City. This suggests that the residual saturation at well M31 may be a combination of the aviation gasoline and jet fuel spills from which the volatile and semi-volatile aromatic components have escaped.

3.4.3.   Dispersion analysis from tritium breakthrough curves

The tritium breakthrough data were analyzed using the CXTFIT modeling program (Parker and Genuchten 1984). They were modeled with a local equilibrium model to determine the pore velocities and values of column dispersion, which are given in Table

GC Retention	GC-MS Chemical Identification
6.2	2,4,-dimethyl hexane
6.9	2,3,4-trimethyl pentane
7.1	2,3,3-trimethyl pentane
8.1	2,2,5-trimethyl hexane
13.7	Cumene
15.0	2,5,6-trimethyl octane

Table 3.3 GC-MS Identification of Monitored GC Peaks

Column	Velocity (cm/hr)	Dispersion (cm^2/hr)	r^2
TC2	4.72	0.115	0.998
TC3	4.53	0.171	0.995
TC4	5.25	0.281	0.994
TC5	3.54	0.084	0.996
TC7	3.72	0.099	0.999
TC8	5.26	0.112	0.950

Table 3.4 Column pore velocities and dispersions from tritium breakthrough analysis

3.4 with their associated correlation coefficients (r^2). The pore velocities in the six columns varied between 3.5 to 5.3 (cm/hr) and the dispersions ranged from 0.084 to 0.281 (cm^2/hr). The largest dispersion value is from the column with the most severe bubble problem (TC4). The variation in these values suggests that channel flow probably occurred in these columns rather than plug flow.

Chapter 4. RESULTS AND DISCUSSION

4.1   Experimental Column Runs

4.1.1   5 g/l Triton X-100 (TC2)

The effluent concentrations were uniformly low (<160 ppb) during the period of flushing with stock solution. In fact, only the two trimethyl pentanes were above the gas chromatography detection limit for the sample size and extraction ratios used.

However, the effluent concentrations increased rapidly to a maximum of 7.2 mg/L (Table 4.1) when the surfactant solution was passed through the soil column (Fig. 4.1). All five contaminants reached maximum concentrations within the first two pore volumes of Triton X-100 solution collected from the column. The concentrations decreased to a quarter of the maximum within five pore volumes and then declined more slowly over the next 15 pore volumes collected until they were close to the stock solution effluent concentrations, although the di- and tri-methyl hexane and trimethyl octane peaks were still detectable.

Upon reintroduction of the stock solution all five contaminants became undetectable. A total of sixty pore volumes of fluid were passed through the column, twenty-four of surfactant solution and thirty-six of stock solution.

Fig 4.1 Effluent concentrations of the monitored peaks from TC2 column

Sample	Pore Volume	2,4-dimethyl hexane	2,3,4-trimethyl pentane	2,3,3-trimethyl pentane	2,2,5-trimethyl hexane	2,5,6-trimethyl octane
TC2.1	1.0	ND	ND	ND	ND	ND
TC2.2	3.2	ND	ND	ND	ND	ND
TC2.3	6.4	ND	0.0502	0.1063	ND	ND
TC2.4	10.4	ND	0.0742	0.1588	ND	ND
TC2.5	13.2	ND	0.0309	0.0676	ND	ND
TC2.6	16.3	ND	0.0625	0.128	ND	ND
TC2.7	16.3					
TC2.8	19.8	ND	0.0458	0.1065	ND	ND
TC2.9	20.9	ND	ND	ND	ND	ND
TC2.10	22.3	ND	ND	ND	ND	ND
TC2.11	23.6	ND	ND	ND	ND	ND
TC2.12	25.9	ND	0.0748	ND	ND	ND
Add 5g/L Surfactant						
TC2.13	25.9	ND	ND	ND	ND	ND
TC2.14	26.7	1.5164	2.2880	4.7960	3.4079	1.7678
TC2.15	27.6	3.6535	3.3923	7.2048	5.4185	2.1513
TC2.16	28.5	2.7065	2.4669	5.0085	3.6447	1.2296
TC2.17	29.5	1.2563	1.6228	3.3396	2.2453	0.6714
TC2.18	30.4	0.8586	1.2453	2.5092	1.8313	0.6174
TC2.19	31.3	0.7417	0.8580	1.6348	1.3576	0.4761
TC2.20	32.2	0.5724	0.6336	1.1923	1.0490	0.3845
TC2.21	33.2	0.4489	0.5346	0.9510	0.9021	0.3411
TC2.22	36.0	0.2212	0.2830	0.5323	0.4858	0.2106
TC2.23	38.7	0.1675	0.1758	0.3237	0.3245	0.1059
TC2.24	41.4	0.1317	0.0557	0.1131	0.1626	0.0643
TC2.25	45.1	0.0999	0.0252	0.0516	0.0773	0.0352
TC2.26	49.7	ND	ND	ND	ND	ND
	50.6					
Stock sol'n	50.6	ND	ND	ND	ND	ND
TC2.27	51.6	ND	ND	ND	ND	ND
TC2.28	52.6	ND	ND	ND	ND	ND
TC2.29	54.3	ND	ND	ND	ND	ND
TC2.30	60.4	ND	ND	ND	ND	ND

Table 4.1 Effluent concentrations (mg/L) from TC2 column

4.1.2   15 g/l Triton X-100 (TC5)

During the flushing with stock solution all the effluent concentrations were below the detection limit of the gas chromatograph. Upon introduction of the more concentrated surfactant solution the concentrations increased dramatically (Fig. 4.2, Table 4.2) to a maximum of about 135 mg/L (2,3,3-trimethyl pentane). This is about twenty times the peak effluent concentration resulting from the more dilute surfactant solution. The concentrations of all five contaminants again decreased exponentially and within ten pore volumes were each less than 1 mg/L.

When stock solution was flushed through the soil again the concentrations dropped even further. However, they remained detectable in the cases of the dimethyl hexane and trimethyl hexane.

4.1.3   50% 2-propanol (TC3)

Almost thirty pore volumes of stock solution were passed through this soil column, and effluent concentrations of the five monitored contaminants were fairly low (Table 4.3) and did not exceed 1.6 mg/L.

When the alcohol solution was passed through the soil column the increase in effluent concentrations was dramatic and short-lived (Fig. 4.3). They reached a maximum of 90 mg/L for the 2,3,3-trimethyl

Fig 4.2　Effluent concentrations of the monitored peaks from TC5 column

5 2

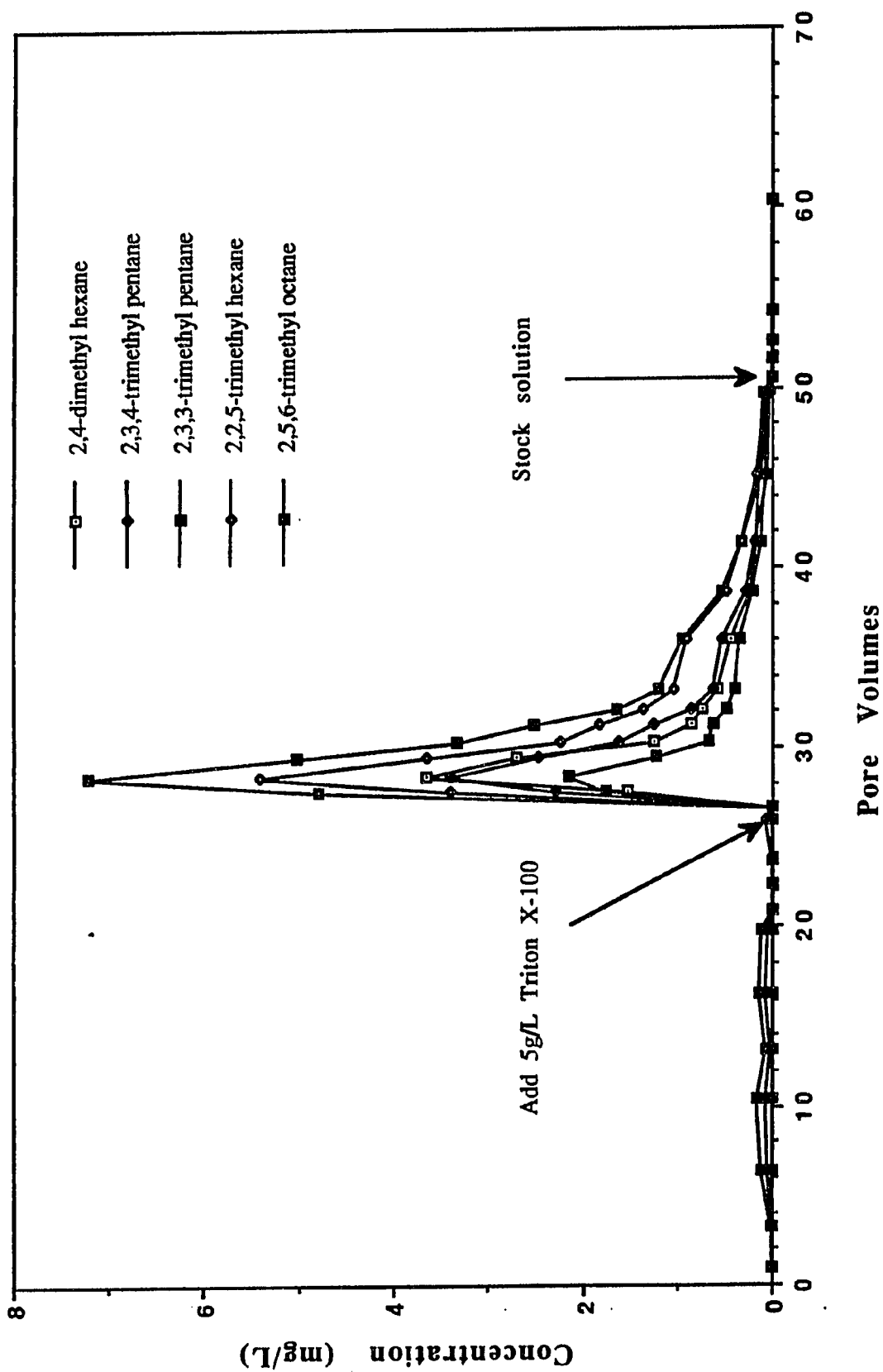| Sample	Pore Volume	2,4-dimethyl hexane (mg/L)	2,3,4-trimethyl pentane	2,3,3-trimethyl pentane	2,2,5-trimethyl hexane	2,5,6-trimethyl octane
TC5.1	3.7	ND	ND	ND	ND	ND
TC5.2	9.0	ND	ND	ND	ND	ND
TC5.3	15.1	ND	ND	ND	ND	ND
Add 15g/L Surfactant	16.0					
TC5.4	17.2	ND	ND	ND	ND	ND
TC5.5	17.8	18.0286	20.8470	50.8660	26.8732	14.2082
TC5.6	18.1	54.5729	51.6250	134.6000	99.3306	25.0877
TC5.7	18.6	36.5050	31.3010	85.1056	57.9149	19.3977
TC5.8	19.1	29.9548	26.5780	67.6693	50.6300	12.7571
TC5.9	19.7	17.8792	11.3240	34.0341	17.2707	10.7132
TC5.10	20.5	10.0809	9.9656	24.1141	12.9234	6.4952
TC5.11	21.5	9.1094	7.7628	15.7602	10.4604	4.4678
TC5.12	22.5	3.6611	4.7455	9.9873	6.3410	3.0033
TC5.13	23.7	2.3016	2.8414	5.9043	3.9523	2.1744
TC5.14	25.3	1.2167	1.3999	2.7763	2.1092	1.3085
TC5.15	27.6	0.6031	0.4929	0.8986	0.8764	0.5488
TC5.16	30.8	1.5122	0.3037	0.4856	0.4245	0.1280
TC5.17	37.3	0.8059	0.0195	0.1200	0.1238	0.0178
Stock Solution	37.3					
TC5.18	47.1	0.028	ND	ND	0.026	ND

Table 4.2 Effluent concentrations (mg/L) from TC5 column

Fig 4.3   Effluent concentrations of the monitored peaks from TC3 column

2,4-dimethyl hexane
2,3,4-trimethyl pentane
2,3,3-trimethyl pentane
2,2,5-trimethyl hexane
2,5,6-trimethyl octane

Concentration (mg/L)
Pore Volumes

Stock solution

Add 50% 2-propanol

Sample	Pore Volume	2,4-dimethyl hexane (mg/L)	2,3,4-trimethyl pentane	2,3,3-trimethyl pentane	2,2,5-trimethyl hexane	2,5,6-trimethyl octane
TC3.1	3.3	0.1159	0.0492	0.1346	0.2852	0.5432
TC3.2	8.6		0.1094	0.2365	0.5483	0.8653
TC3.3	14.1	0.3509	0.0811	0.1891	0.4441	0.7318
TC3.4	18.9	0.5756	0.0733	0.1621	0.4314	0.7756
TC3.5	20.6	0.2854			0.3438	0.8947
TC3.6	22.6	0.2505	0.0574	0.1774	0.4912	1.0431
TC3.7	24.6	0.2108	0.0626	0.1640	0.4844	1.5584
TC3.8	28.1	0.2100	0.0418	0.1081	0.5699	1.4195
Add 50% 2-propanol	28.1					
TC3.9	29.2	0.2100	0.0400	0.1000	0.5700	1.4100
TC3.10	30.6	34.7095	37.3160	90.0958	46.4524	12.9377
TC3.11	31.5	6.2434	6.6819	16.5354	9.3719	3.9236
TC3.12						
TC3.13	33.1	0.1697	0.1024	0.2635	ND	ND
TC3.14	37.3	0.0791	0.0253	0.5130	ND	ND
Stock solution	37.9					
TC3.15	41.7	0.0875	0.1591	0.4089	ND	ND
TC3.16	46.9	ND	ND	ND	ND	ND

Table 4.3   Effluent concentrations (mg/L) from TC3 column

pentane and within four pore volumes were less than 500 ppb or undetectable. The alcohol appears to have effected a "spike" release of the aviation gasoline residual saturation.

This was the second column which was run and the effects of the alcohol were not expected to be this dramatic. For this reason a large sample was taken and, therefore, the true maximum concentration is unknown. In the subsequent 2-propanol experiment smaller samples were taken to improve the definition of the contaminant release.

When stock solution was flushed through the column again all five contaminants became undetectable.

4.1.4 20% and 50% 2-propanol (TC4)

Owing to the effect of the previous 2-propanol run a new soil column was flushed with over eleven pore volumes of stock solution and then with a 20% solution of 2-propanol (Fig 4.4). Only the trimethyl pentanes were detectable, at concentrations less than 200 ppb (Table 4.4), in the effluent from the stock solution flush. With addition of the 20% 2-propanol a slow and small increase was observed in the concentration of four of the monitored contaminants, all except the trimethyl octane, to a maximum of 800 ppb. As a result of this very slight effect of the lower concentration of alcohol the flushing
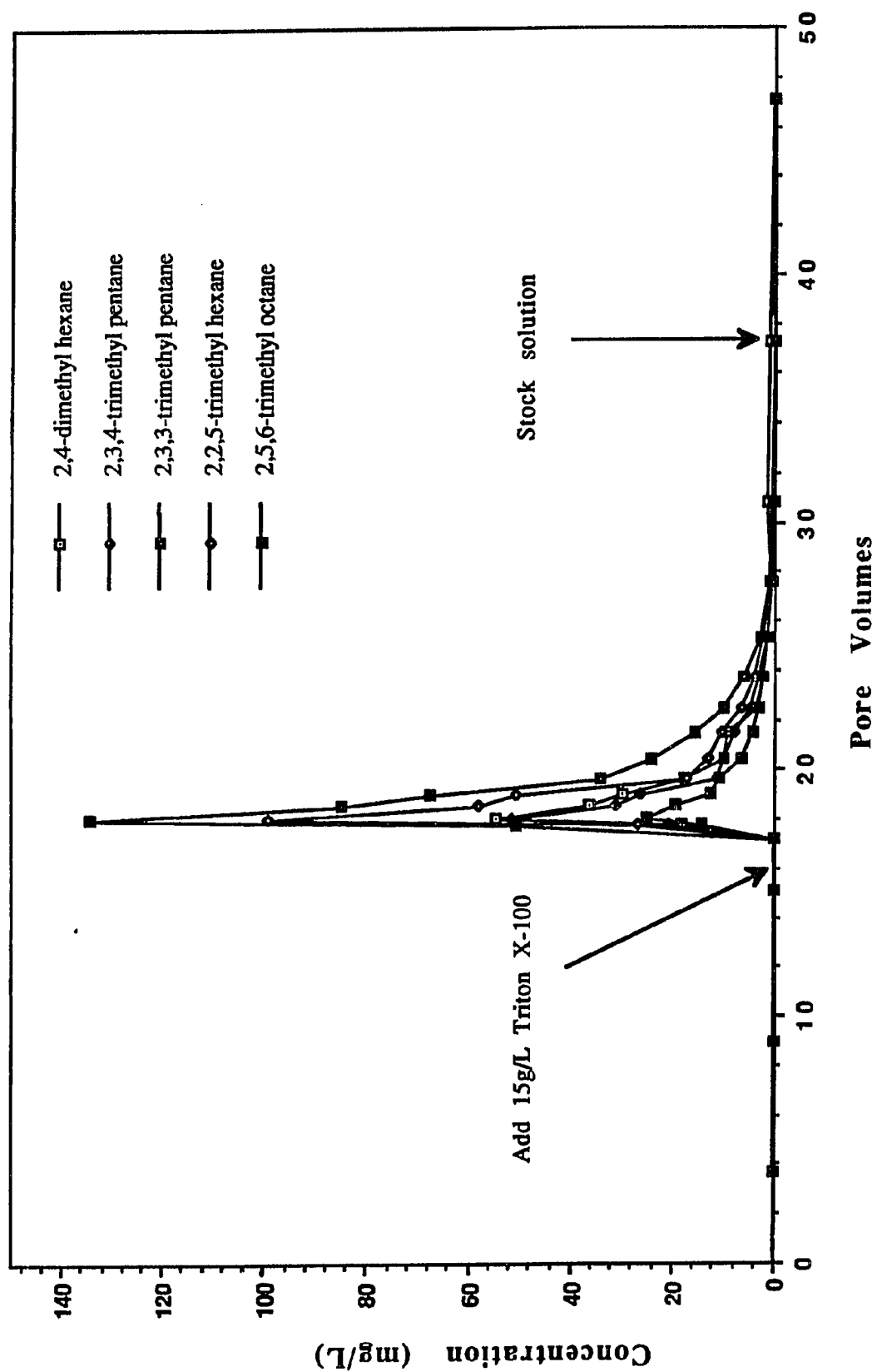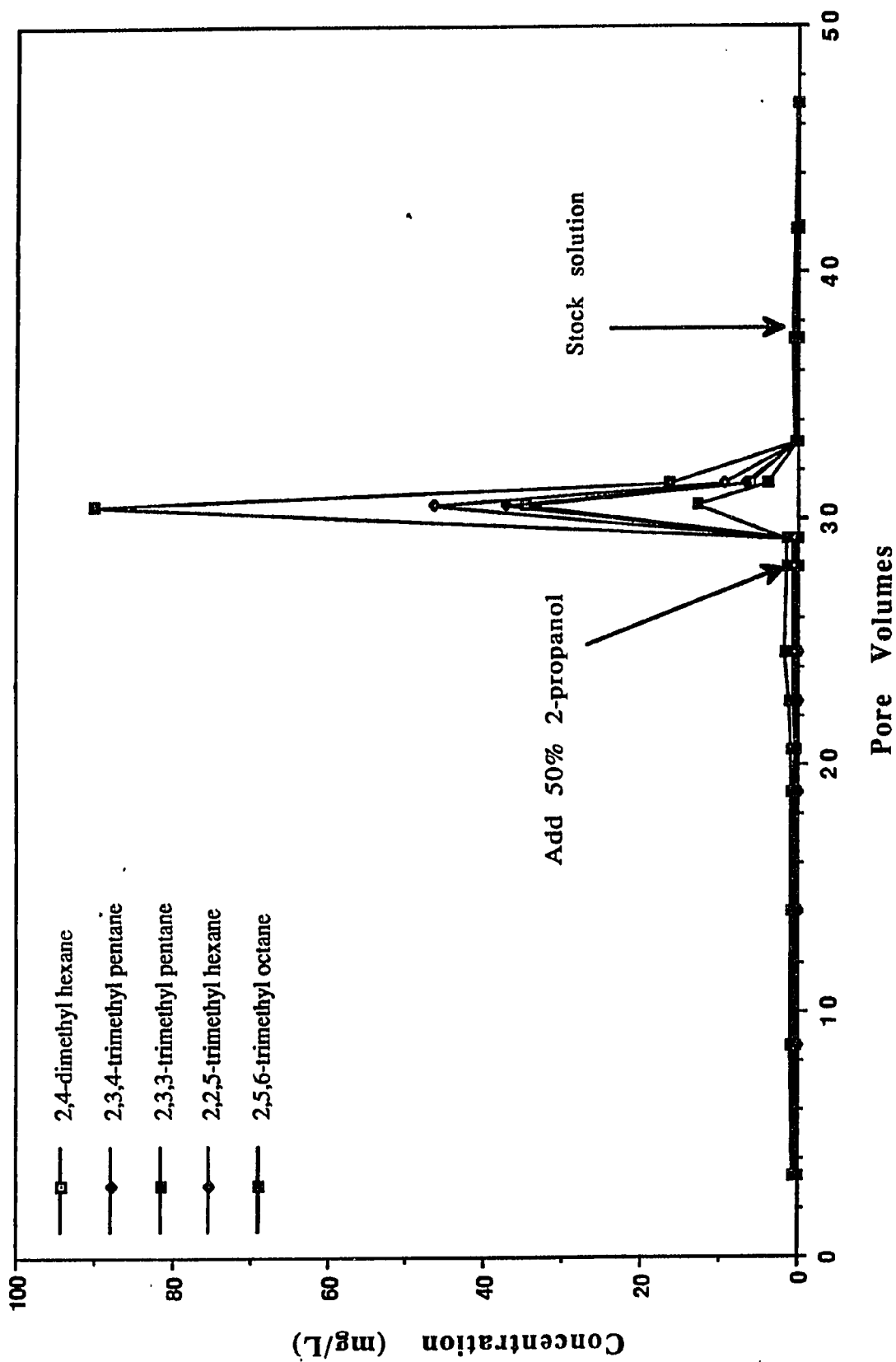
Fig 4.4 Effluent concentrations of the monitored peaks from TC4 column

Sample	Pore Volume	2,4-dimethyl hexane (mg/L)	2,3,4-trimethyl pentane	2,3,3-trimethyl pentane	2,2,5-trimethyl hexane	2,5,6-trimethyl octane
TC4.1	2.7	ND	0.0337	0.0863	ND	ND
TC4.2	6.6	ND	0.0659	0.1555	ND	ND
TC4.3	11.7	ND	0.0917	0.2112	ND	ND
Add 20% 2-propanol	11.7					
TC4.4	12.8	ND	0.0136	0.0352	ND	ND
TC4.5	13.3	ND	0.1202	0.3090	ND	ND
TC4.6	13.8	ND	0.1730	0.4454	ND	ND
TC4.7	14.4	0.0888	0.1476	0.3795	ND	ND
TC4.8	15.6	0.0800	0.2255	0.5798	ND	ND
Add 50% 2-propanol	16.0					
TC4.9	16.9	0.1304	0.3101	0.7977	0.0383	ND
TC4.10	17.4	57.9464	45.2609	127.243	57.0360	19.8846
TC4.11	17.8	17.1177	11.2410	31.8603	16.6710	10.6662
TC4.12	18.2					
TC4.13	19.0	9.2128	3.5283	7.1640	12.2829	0.0912
TC4.14	20.6	0.1407	0.1531	0.3938	ND	ND
Stock solution	21.0					
TC4.15	24.4	0.0938	0.1632	0.4196	ND	ND
TC4.16	27.1	ND	ND	ND	ND	ND
TC4.17	29.9	ND	ND	ND	ND	ND

Table 4.4   Effluent concentrations (mg/L) from TC4 column

solution was replaced by 50% 2-propanol solution after 4.3 pore volumes of the 20% solution.

The first half pore volume of effluent of the stronger solution produced concentrations of the contaminants as high as 127 mg/L The second pore volume gave much reduced concentrations such as 32 mg/L for the 2,3,3-trimethyl pentane. Unfortunately, an intermediate sample was lost due to leakage of the bag valve but by the next sample, 1.2 pore volumes later, the concentrations were less than 13 mg/L. After a further one and a half pore volumes the concentrations were less than 400 ppb or undetectable. When the alcohol solution was replaced with stock solution all the contaminants ceased to be detectable.

4.1.5.   Surfactant and 2-propanol (TC7)

The combination of 5 g/L Triton X-100 and 20% 2-propanol was used on a new soil column to see whether the alcohol would enhance the surfactant effect. Once again the effluent concentrations in the stock solution were low or undetectable (Table 4.5).

Flushing with the combination of alcohol and surfactant increased the effluent concentrations to a maximum of 2.5 mg/L (Fig. 4.5). Within ten pore volumes all the monitored contaminants had effluent concentrations of less than 1.2 mg/L. They then declined gradually
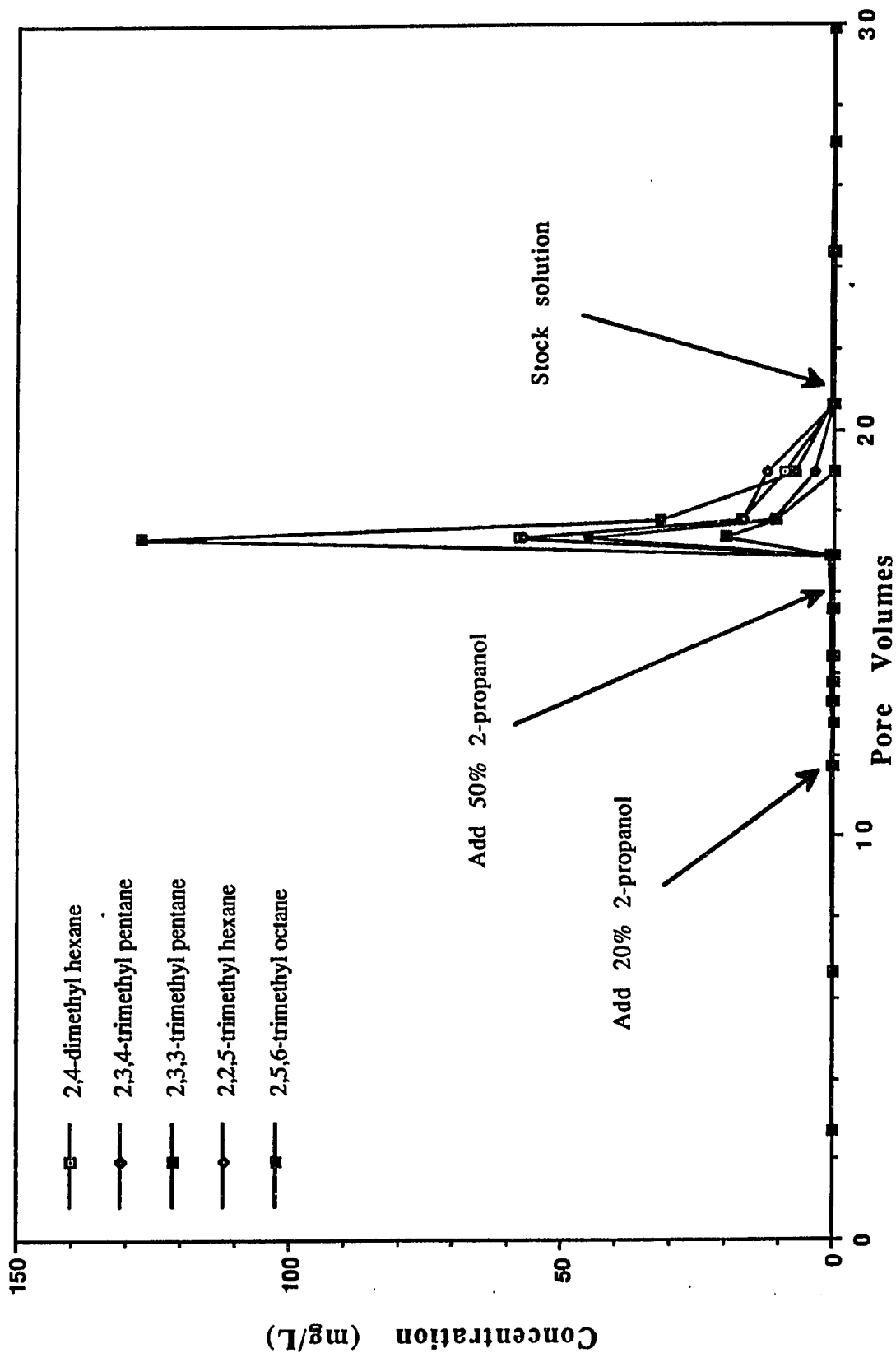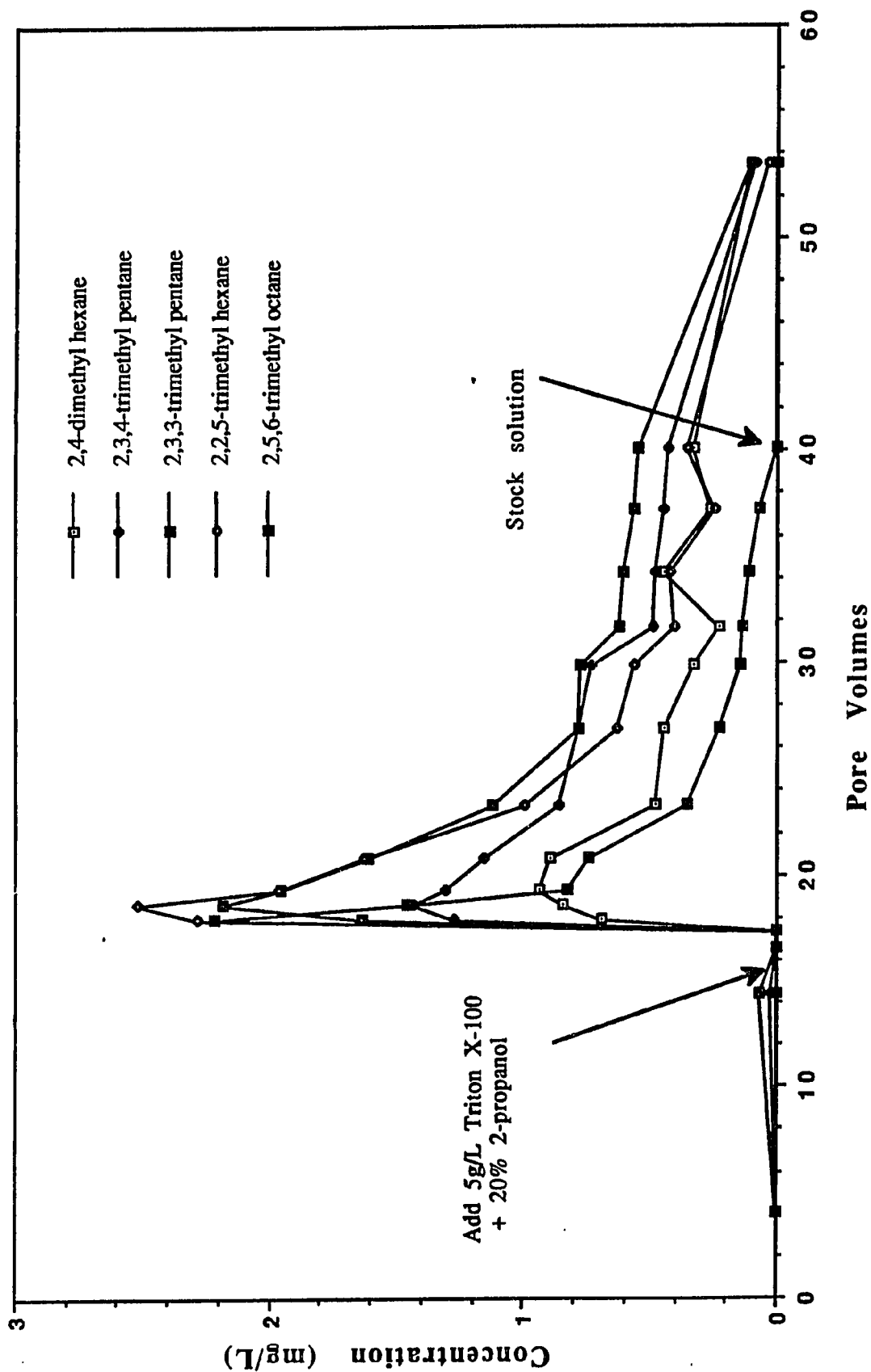
Fig 4.5   Effluent concentrations of the monitored peaks from TC7 column

Sample	Pore Volume	2,4-dimethyl hexane (mg/L)	2,3,4-trimethyl pentane	2,3,3-trimethyl pentane	2,2,5-trimethyl hexane	2,5,6-trimethyl octane
TC7.1	4.1	ND	ND	ND	ND	ND
TC7.2	14.4	ND	0.0275	0.0666	ND	ND
Add 5g/L Surfactant + 20% 2-propanol	15.6					
TC7.3	16.6	ND	ND	ND	ND	ND
TC7.4	17.4	ND	ND	ND	ND	ND
TC7.5	18.0	0.6950	1.2708	1.6373	2.2876	2.2148
TC7.6	18.7	0.8460	1.4350	2.1830	2.5230	1.4600
TC7.7	19.4	0.9330	1.3052	1.9575	1.9601	0.8295
TC7.8	20.9	0.8895	1.1520	1.6096	1.6230.	0.7401
TC7.9	23.3	0.4798	0.8630	1.1211	0.9976	0.3559
TC7.10	26.9	0.4478	0.7854	0.7857	0.6347	0.2268
TC7.11	29.9	0.3300	0.7340	0.7720	0.5610	0.1440
TC7.12	31.7	0.2287	0.4899	0.6235	0.4078	0.1316
TC7.13	34.3	0.4444	0.4776	0.6078	0.4204	0.1117
TC7.14	37.3	0.2652	0.4436	0.5646	0.2464	0.0640
TC7.15	40.1	0.3290	0.4321	0.5499	0.3513	ND
Stock solution	40.1					
TC7.16	53.5	0.1000	0.0815	0.1038	0.0303	ND

Table 4.5   Effluent concentrations (mg/L) from TC7 column

over the next thirteen pore volumes at which point the trimethyl octane became undetectable and the other contaminants were at less than 550 ppb.

The combination solution was then replaced with stock solution and concentrations declined to 100 ppb or lower.

In comparison with the surfactant alone the addition of 20% 2-propanol did not appear to greatly enhance the release of the contaminants.

4.1.6   20% and 50% Methanol (TC8)

The effluent concentrations produced by the stock solution were undetectable with the gas chromatograph.   Upon flushing with twenty percent methanol the two trimethyl pentanes were detected at less then 550 ppb but the other three contaminants remained undetected (Table 4.6).   As a result of this slight effect the 20% methanol solution was replaced with 50% methanol after 6.8 pore volumes of the dilute solution.

Effluent concentrations of the five contaminants increased to a maximum of 1.5 mg/L (Fig. 4.6a) during flushing with the 50% methanol solution.   In contrast to the other five columns the concentrations of three of the contaminants remained at a fairly

Fig 4.6a Effluent concentrations of the identified peaks from TC8 column
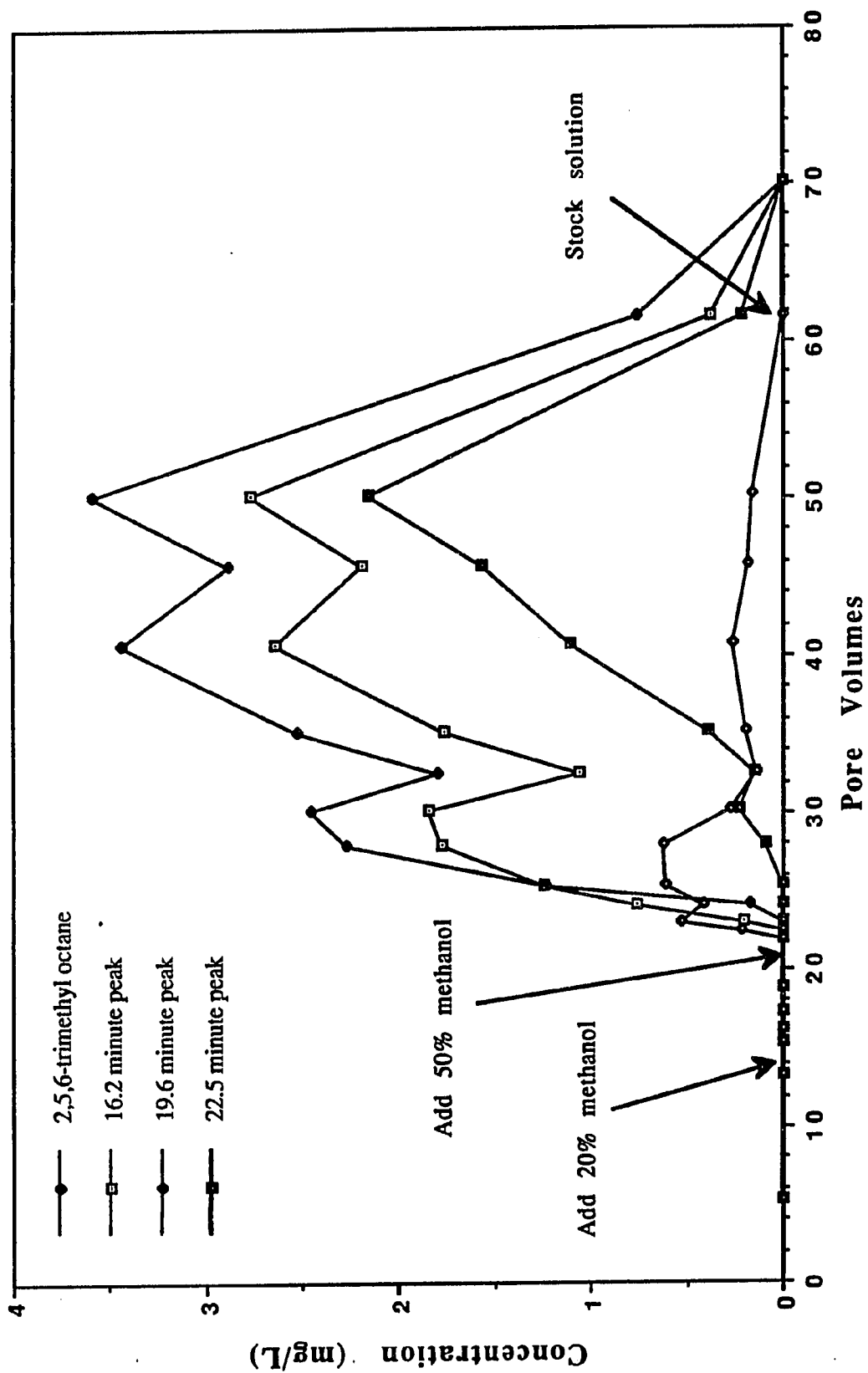
Fig 4.6b Effluent concentrations of three unidentified peaks from TC8 column
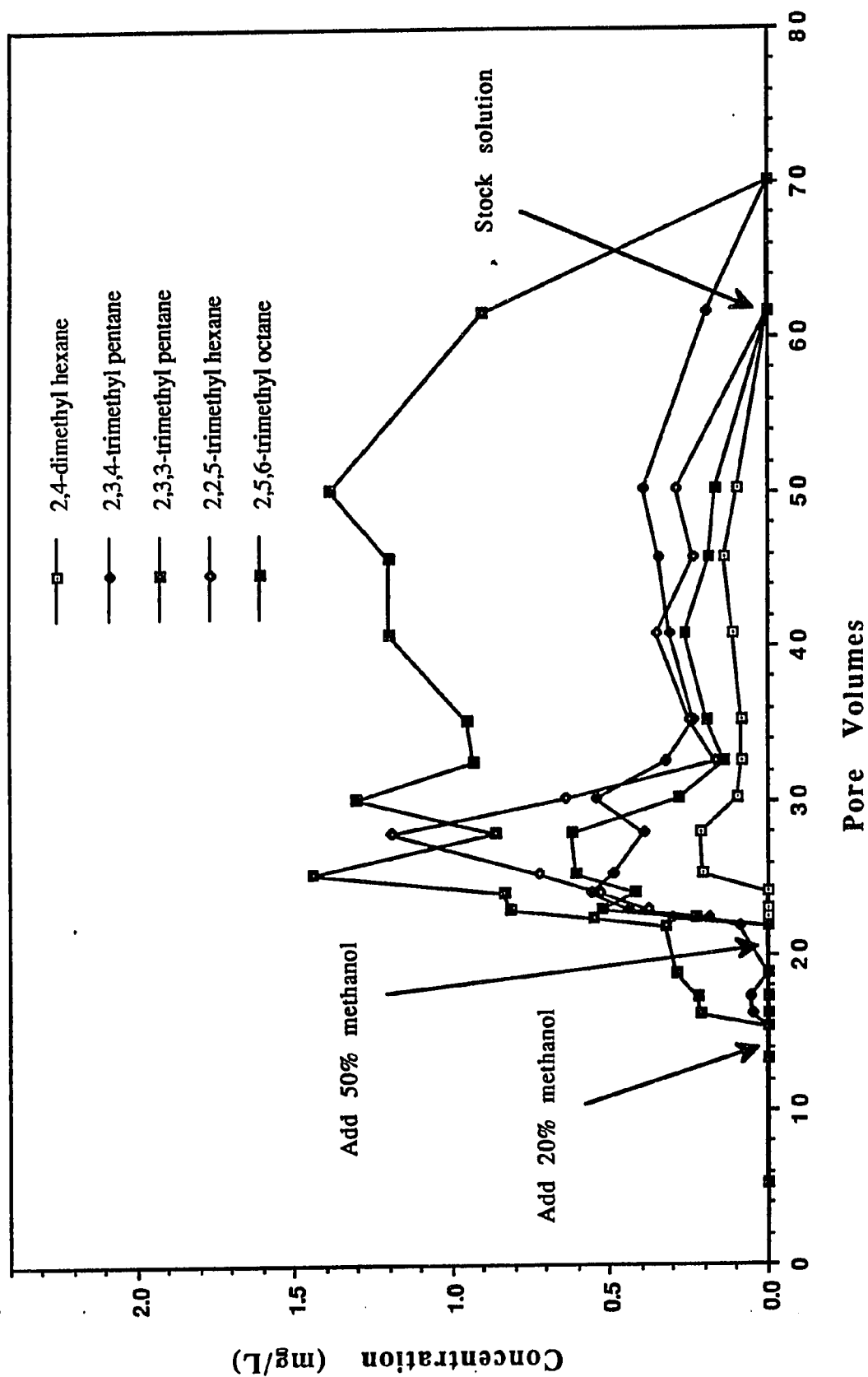with 2,5,6-trimethyl octane for comparison

Sample	Pore Volume	2,4-dimethyl hexane	2,3,4-trimethyl pentane	2,3,3-trimethyl pentane	2,2,5-trimethyl hexane	2,5,6-trimethyl octane	16.2 minute peak	19.6 minute peak	22.5 minute peak
TC8.1	5.3	ND	ND	ND	ND	ND	ND	ND	ND
TC8.2	13.4	ND	ND	ND	ND	ND	ND	ND	ND
Add 20% methanol	14.0								
TC8.3	15.4	ND	ND	ND	ND	ND	ND	ND	ND
TC8.4	16.3	ND	0.0516	0.2122	ND	ND	ND	ND	ND
TC8.5	17.4	ND	0.0534	0.2221	ND	ND	ND	ND	ND
TC8.6	18.9	ND	ND	0.2925	ND	ND	ND	ND	ND
Add 50% methanol	20.8								
TC8.7	21.9	ND	0.0894	0.3264	ND	ND	ND	ND	ND
TC8.8	22.5	ND	0.1869	0.5543	0.3059	0.2243	ND	ND	ND
TC8.9	23.1	ND	0.4407	0.8130	0.3786	0.5245	0.2114	ND	ND
TC8.10	24.1	ND	0.5611	0.8338	0.5293	0.4182	0.7655	0.1786	ND
TC8.11	25.4	0.2047	0.4908	1.4444	0.7218	0.6101	1.2397	1.2391	ND
TC8.12	28.1	0.2136	0.3908	0.8611	1.1932	0.6179	1.7800	2.2722	0.0884
TC8.13	30.3	0.0979	0.5434	1.3014	0.6391	0.2810	1.8388	2.4496	0.2255
TC8.14	32.6	0.0832	0.3244	0.9305	0.1647	0.1393	1.0588	1.8016	0.1527
TC8.15	35.3	0.0854	0.2330	0.9533	0.2481	0.1910	1.7614	2.5225	0.3875
TC8.16	40.8	0.1074	0.3112	1.1969	0.3518	0.2606	2.6358	3.4401	1.1086
TC8.17	45.8	0.1408	0.3426	1.1985	0.2328	0.1842	2.1940	2.8816	1.5685
TC8.18	50.3	0.0966	0.3905	1.3892	0.2921	0.1650	2.7631	3.5888	·2.1559
TC8.19	61.6	ND	0.1904	0.9050	ND	ND	0.3769	0.7601	0.2247
Stock sol'n	61.6								
TC8.20	70.2	ND	ND	ND	ND	ND	ND	ND	ND

Table 4.6   Effluent concentrations (mg/L) from TC8 column

constant level for almost thirty pore volumes before declining significantly. The exceptions were the trimethyl hexane and octane which declined somewhat over ten pore volumes before remaining constant during the next twenty pore volumes.

Another important difference from the other experiments is that three other contaminant peaks with longer retention times of 16.2, 19.6 and 22.5 minutes were detected in considerable amounts (Fig 4.6b). These peaks gave maximum concentrations of 3.6 mg/L and increased in amount as flushing continued for over twenty-five pore volumes. These peaks are thought to represent higher molecular weight methylated alkanes than the other five monitored contaminants. They were not released by the other flushing regimes in noticeable quantities or, possibly, were not present to the same extent in the layers of soil used in the other columns. The former is a more likely choice as traces of these contaminants were found in all the methanol extractions of the soil from the columns.

Again, subsequent flushing with stock solution caused the effluent concentrations to fall below the gas chromatography detection limit.

4.2 Soil Contaminant Analysis

Each of the three methanol extracts (section 3.3.5) of contaminated soil from the sample jar (TC188) were analyzed by gas

chromatography for the eight contaminants. The peak areas were converted to contaminant masses, summed for the three extracts and divided by the weight of soil (Table 4.7). This produced an estimate for initial contaminant mass per gram of soil. Residual contaminant concentrations of the soil in the columns were measured in the same way. The ratio of contaminant mass per gram of soil from the flushed columns to the estimated initial contaminant mass per gram of soil gives an indication of the removal efficiency of the various flushing solutions. These ratios are expressed as percentages in Table 4.7.

The uncertainty regarding the similarity of the initial contaminant mass in each column means that there is an unknown error in this calculation. However, owing to the detection limit (1ppm) of the gas chromatograph and the efficiency of the extraction system estimates of the initial contaminant masses produced by summing the concentrations in the effluents from the columns are subject to considerable error.

Both 2,2,5-trimethyl hexane and 2,5,6-trimethyl octane appear to have been completely removed by all of the flushing regimes. In each column more than 96% of the 2,4-dimethyl hexane and 2,3,4- and 2,3,3-trimethyl pentanes were flushed from the contaminated soil. 5g/L Triton X-100 was the least efficient removal method for flushing the three heavier molecular weight alkanes (retention times

Chemical Retention Time	TC188 (mg/g)	TC2 (%) 5g/L Triton X-100	TC3 (%) 50% 2-propanol	TC4 (%) 20 & 50% 2-propanol	TC5 (%) 15g/L Triton X-100	TC7 (%) 5g/L Triton X-100 & 20% 2-propanol	TC8 (%) 20 & 50% methanol
6.2	0.00231	3.86	2.07	0.87	0.58	0.32	0.71
6.9	0.00366	0.96	0.30	0.40	0.75	0.19	0.24
7.1	0.00785	1.37	0.88	1.03	0.99	0.67	0.95
8.1	0.00324	ND	ND	ND	ND	ND	ND
15.0	0.00094	ND	ND	ND	ND	ND	ND
16.0	0.00131	54.24	3.54	6.50	7.13	2.97	5.26
19.3	0.00243	7.16	6.38	8.97	9.88	4.61	9.18
22.3	0.00055	6.14	5.97	4.92	10.30	5.22	11.78

Table 4.7 Soil extract analysis data. TC188 column shows the estimated initial contaminant masses per gram of soil. Other columns show the amount of contaminant remaining in the soil from the flushed columns as a percentage of the values in the contaminated sample TC188. ND = not detected.

of 16.2, 19.6 and 22.5 minutes) as up to 54% of the contaminants remained in the soil. With the other solutions more than 88% of these contaminants were flushed from the soil. This lower removal efficiency for the heavier contaminants is commensurate with their low effluent concentrations in all but the methanol flushing experiment. It also suggests that methanol may extract these chemicals better than the methylene chloride used for the column effluent extracts.

Therefore all six solutions appear to have flushed more than 96% of the five lower molecular weight methylated alkanes and more than 88% of the heavier molecular weight contaminants (except for the 16.0 peak with 5g/L Triton X-100) from the soil columns. These removal efficiencies compare favorably with that of 93% obtained by Ellis, Payne et al. (1985) during soil washing with 4% surfactant solution to remove petroleum hydrocarbons (Murban crude oil fraction).

4.3   Facilitated Transport Analysis

4.3.1   Alcohol cosolvents

The solvophobic theory of Rao, Hornsby et al. (1985) and Nkedi-Kizza, Rao et al. (1987) was used to model the retardation factors which would be expected with 20% and 50% methanol and 2-propanol as cosolvents and the identified methylated alkanes. The

retardation factor (R) is a measure of the retention of the contaminant within the soil. For flushing with water $R = R^w$ and is given by

$$R^w = 1 + \frac{\rho(OC)P^w}{\theta} \tag{4}$$

where ρ is the mass of soil divided by the column volume, OC is the organic carbon content of the soil, P^w is the sorption coefficient normalized with the organic carbon content of the soil, and θ is the porosity or water content.

For a mixed solvent system the relation is similar with R^w and P^w replaced by R^m and P^m where

$$P^m = P^w \exp(-\alpha\sigma^c f^c) \tag{5}$$

and

$$\sigma^c = \frac{\Delta\gamma^c(HSA)}{kT} \tag{6}$$

In this expression f^c is the volume fraction of cosolvent ($0 < f^c < 1$), α is an empirical constant determined to be 0.83 (Karickhoff 1984), HSA is the hydrocarbonaceous surface area of the contaminant (A^2), k is the Boltzmann constant (erg/K), T is the ambient temperature (K) and $\Delta\gamma^c$ is the difference between the interfacial free energies at the aqueous and cosolvent interfaces with the hydrocarbonaceous surface area of the sorbate (erg/A^2).

Of these parameters it was necessary to calculate P^w, HSA and $\Delta\gamma c$ (Table 4.8). The hydrocarbonaceous surface area was computed by the method of Hermann (1972) which relates it to the molal solubility. In order to apply this method octanol-water coefficients (K^{ow}) for the methylated alkanes were obtained from values for alkanes in Hansch, Quinlan et al. (1968) with additions for the methyl groups from Hansch and Leo (1979). These were converted to molal solubilities (S) using the relation

$$\log \frac{1}{S} = 1.237 \log K^{ow} + 0.248 \qquad (7)$$

from Hansch, Quinlan et al. (1968). A linear relationship was observed by Hermann between the HSA and the negative logarithm of the solubility. The slope (46.25) and the intercept (122.94) were obtained using simultaneous equations from data presented in his discussion.

An expression for P^w is given by Rao, Hornsby et al. (1985):

$$\ln P^w = -\alpha \ln X^w - \frac{\Delta S_f}{RT}(T_m - T) - \beta \qquad (8)$$

but as all the methylated alkanes are liquid at the temperature of the experiments (285K) the middle term can be neglected. X^w is the mole fraction solubility, which was determined from the previously calculated molal solubility, $\alpha = 0.83$ and $\beta = 2.142$.

Chemical	log Kow	Solubility (mol/L)	HSA (A^2)	Xo	Xw	Pw	IT with water (erg/cm^2)
2,4-dimethyl hexane	4.12	4.52E-6	370.12	8.15E-8	1.69E-6	89823	38.14
2,3,4-trimethyl pentane	4.18	3.81E-6	373.55	6.87E-8	1.42E-6	103512	38.68
2,3,3-trimethyl pentane	4.18	3.81E-6	373.55	6.87E-8	1.42E-6	103512	38.68
2,2,5-trimethyl hexane	4.68	9.18E-7	402.16	1.65E-8	3.42E-7	337557	43.14
2,5,6-trimethyl octane	5.68	5.32E-8	459.37	9.58E-10	2.88E-7	3589692	43.82

Table 4.8   Input data for cosolvent analysis

The determination of the difference in interfacial energies (or interfacial tensions) was considerably more involved and also required some assumptions of questionable validity. Interfacial tensions with water were obtained from the following expression (Lyman, Reehl et al. 1982)

$$\gamma^{ow} = -3.33 - 7.21*\ln(X_o + X_w) \qquad (9)$$

in which Xo and X_w are the mole fraction solubilities of the organic in water and water in the organic respectively. This relation is only accurate at 25°C whereas this research was undertaken at 12°C. values for X_o were calculated previously but values for X_w were estimated from relations between X_o and X_w for two alkanes given in Lyman, Reehl et al. (1982). Calculated interfacial tensions range from 38 to 44 erg/cm² (Table 4.8) which is a rather small variation.

In order to obtain mutual solubilities of the alkanes and cosolvents infinite dilution activity coefficients (Table 4.9) were calculated from formulae and constants, appropriate for this system, provided by Lyman, Reehl et al. (1982). Two methods, from the same reference, were used to obtain solubilities from these activity coefficients, and the most acceptable was chosen by inserting these values in the equation of a third, and most accurate method. The first set of values was taken from fig 3-3 (in the reference), which is usually accurate for activity coefficients between 50 and 1000, and the

Chemical	γ^{PinM}	γ^{MinP}	X^{PinM}	X^{MinP}	IT with Methanol (erg/cm^2)
Dimethyl Hexane	42.072	257.626	0.0238	0.0039	22.54
Trimethyl Pentane	42.072	257.626	0.0238	0.0039	22.54
Trimethyl Hexane	62.035	253.303	0.0161	0.0040	24.85
Trimethyl Octane	133.968	243.220	0.0075	0.0041	28.82

Chemical	$\gamma^{Pin2\text{-}p}$	$\gamma^{2\text{-}pinP}$	$X^{Pin2\text{-}p}$	$X^{2\text{-}pinP}$	IT with 2-propanol (erg/cm^2)
Dimethyl Hexane	13.094	127.668	0.0764	0.0078	14.51
Trimethyl Pentane	13.094	127.668	0.0764	0.0078	14.51
Trimethyl Hexane	14.803	126.094	0.0676	0.0079	15.30
Trimethyl Octane	18.792	122.172	0.0532	0.0082	16.79

Table 4.9 Data for interfacial tensions between cosolvents and contaminants. (P = paraffin; 2-p = 2-propanol; M = methanol; IT = interfacial tension; X = mole fraction solubility; γ = infinite dilution activity coefficient).

second set were obtained by using the reciprocal of the activity coefficient, which is applied to activity coefficients greater than 1000. The infinite dilution activity coefficients calculated for this system ranged from 13 to 258, but when the solubilities computed by the two methods were put into equation 3-13 those from the reciprocal data gave the least error.

The solubilities were put into the expression used to determine the organic-water interfacial tensions, which is extending this relation beyond its known validity. However, the resulting values seem reasonable (Table 4.9) with interfacial tensions ranging from 22 to 29 erg/cm^2 for methanol and 14 to 17 erg/cm^2 for 2-propanol, which are again fairly narrow ranges.

The calculated values were used to obtain retardation factors for water and 20% and 50% of the two cosolvents (Table 4.10, Fig 4.7). R^w's ranged from 45 to 1772 for the five contaminants. Adding 20% methanol reduced the retardation to 4.8 to 98 while 20% 2-propanol gave retardations of 2.1 to 10.4. 50% methanol lowered the R^m's even further to 1.07 to 2.24 whereas all five contaminants had retardations of less than 1.005 with 50% 2-propanol. Bearing in mind the approximations and assumptions used in obtaining the input parameters for the calculation of these numbers the exact values are not as relevant as the overall differences between the two cosolvents and the two concentrations of each alcohol.

Chemical	R^w	$\sigma^c_{Methanol}$	$\sigma^c_{2\text{-prop}}$	R^m 20% Methanol	R^m 50% Methanol	R^m 20% 2-propanol	R^m 50% 2-propanol
Dimethyl Hexane	45.3	14.67	22.23	4.88	1.1004	2.107	1.0044
Trimethyl Pentane	52.1	15.32	22.95	5.01	1.0884	2.132	1.0037
Trimethyl Hexane	167.5	18.69	28.45	8.48	1.0712	2.480	1.0012
Trimethyl Octane	1771.9	17.51	31.56	97.7	2.2359	10.40	1.0036

Table 4.10   Calculated retardation factors with varied fluid composition.

Fig 4.7a Retardation factor vs. fraction of methanol

Fig 4.7b Retardation factor vs. fraction of 2-propanol
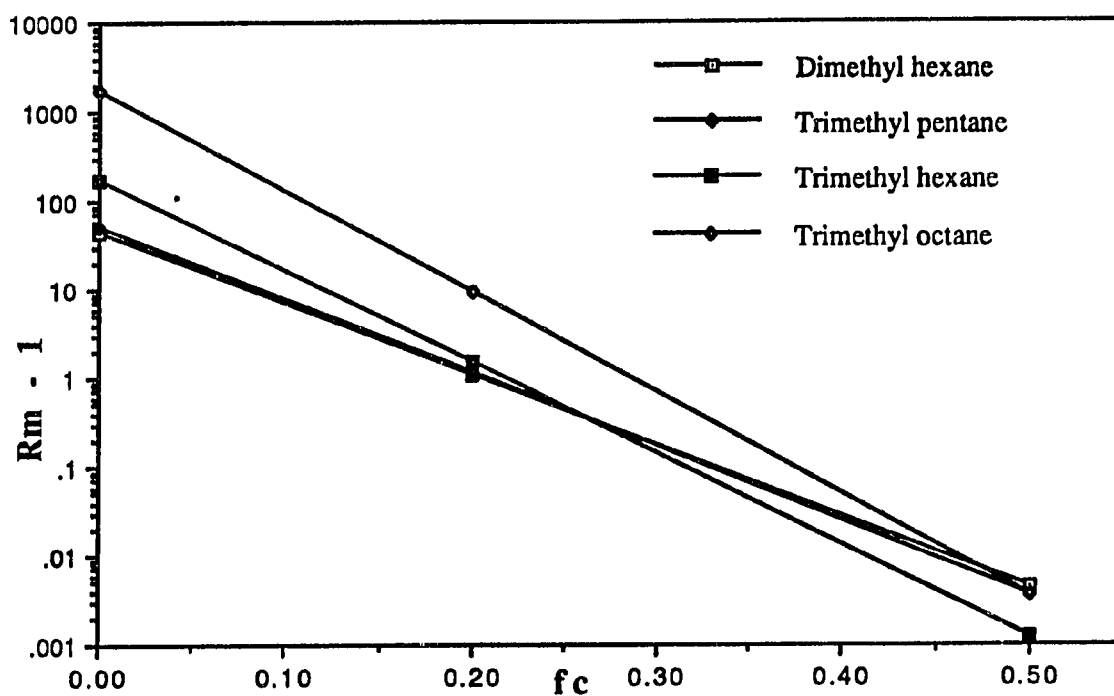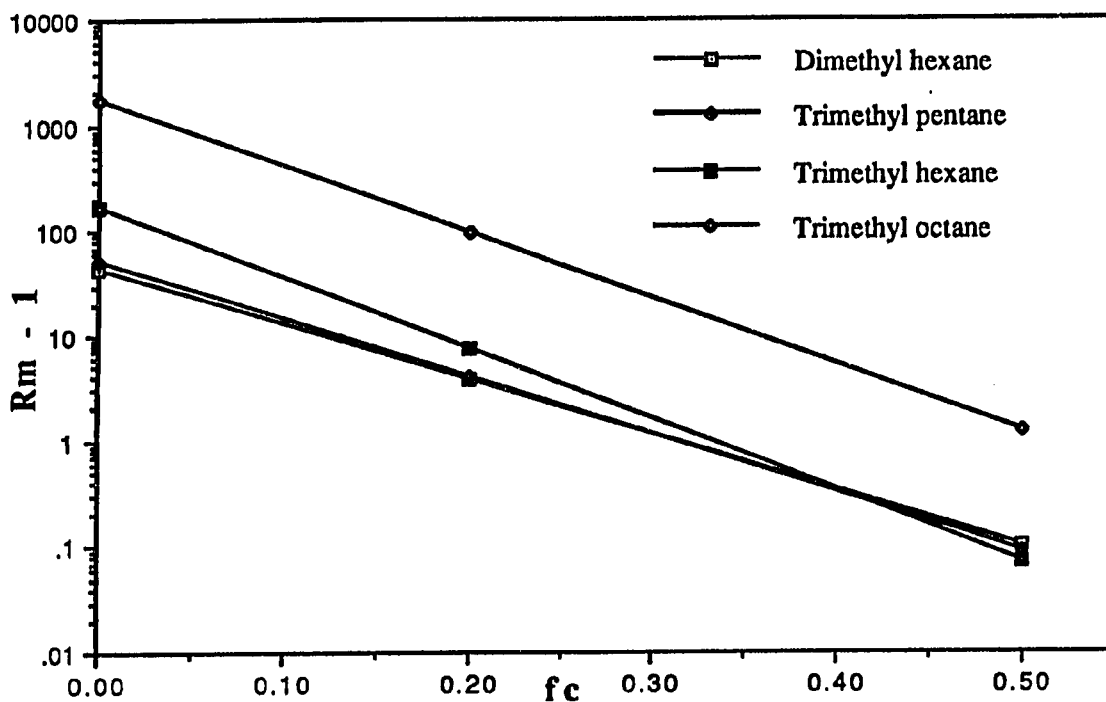
These results indicate that the low concentrations from aqueous flushing could have been predicted from the high R^w factors. The considerably enhanced effect of 2-propanol as a cosolvent, when compared with methanol, is also demonstrated by the fact that at 20% by volume the methanol retardation factors are 2.3 to 9.4 times greater than those of 2-propanol (1.07 to 2.23 times greater at 50% by volume).

4.3.2 Surfactants

Triton X-100 was used, as synthetic dissolved organic carbon, to study facilitated transport in soil columns (Kan and Tomson 1990b). Theory was developed to explain the effect of such dissolved organic carbon in flushing solutions on the retardation of organic contaminants. The retardation factor (R) can be expressed as

$$R = 1 + \frac{0.63K_{ow}OC\rho_b/n}{1 + 0.63K_{ow}DOC} \tag{10}$$

for a linear isotherm, where n is the porosity, ρ_b is the bulk density of the soil (g/cm^3), K_{ow} is the octanol-water partition coefficient and DOC is grams of dissolved organic carbon in a milliliter of water.

For highly hydrophobic compounds (i.e. large K_{ow}), as in this study, or high DOC water $0.63K_{ow}DOC$ will be much greater than one and the expression will reduce to

$$R = 1 + (\frac{\rho_b}{n} * \frac{OC}{DOC})$$ (11)

Applying this equation to the two concentrations of surfactant used in this research (5g/L and 15g/L) produced retardation factors of 1.141 and 1.047 respectively. This would suggest that the alkanes should have been flushed from the column very rapidly if they were all sorbed to organic carbon in the soil. However, the soil contained residual hydrocarbons in pore spaces which could explain why the flushing took several pore volumes more than predicted by this equation.

The theory discussed and applied above is only correctly applicable to soils with organic carbon contents greater than 0.001, which is 12.5 times the content of the Traverse City soil. Karickhoff (1984) mentioned the contribution of non-hydrophobic bonding in cases where the contaminants are highly polar or the organic carbon content is low. Although the amount of data regarding sorption to the mineral phase are small, a tentative method is suggested for calculating its effect. The total partition coefficient, K_v, is given by

$$K_v = K_m CMf^m + K_{oc}OCf^{oc}$$ (12)

where K_m and K_{oc} are the partition coefficients to mineral and organic components, CM and OC are the fractional masses of mineral and organic carbon in the whole sediment, and f^m and f^{oc} are the

active (available) fractions of the respective components. fm can be estimated from

$$f^m = \frac{1}{(1 + \frac{bOC}{CM})} \qquad (13)$$

where b is the "effectiveness" of the mineral blockage by organic matter at low surface coverage which is estimated as 50 from experiments and theoretical considerations. From calculations using the K_{oc} of trimethyl pentanes it is observed that as the ratio of CM to OC increases from 50 to 1000 the contribution of the mineral phase to the partition increases from 23% to 92%. Given the very small amount of organic carbon in the Traverse City soil this latter ratio is not unlikely. The effect of the increased sorptive area raises the retardation factor to 2.7 for 5g/L of surfactant which corresponds better to the observed data than does 1.14.

4.4 Comparison of Retardation Factors

Estimates of retardation factors were made from the experimental results by determining the number of pore volumes, from the initial injection of the additive-containing solution, taken for approximately 75% of the contaminants to be flushed from the column. This value was chosen because of the slow decline in concentrations in the surfactant experiments after the initial rapid drop. In columns TC3 and TC4 the retardation factors for 2-propanol were less than 2 and

between 1.5 and 2 respectively. In columns TC2 and TC5 with 5 and 15g/L Triton X-100 the retardation factors were 7.5 and 4.5 respectively. In column TC7 with the surfactant-alcohol combination the value was about 11 and in column TC8 with 50% methanol the retardation factor varied from about 15 to 30 for the different contaminants.

These values are all considerably larger than those calculated in the previous section (Table 4.11). This discrepancy probably results from errors in estimation of parameters in the equations as discussed earlier. However, the general pattern of results with a significantly larger retardation factor for methanol than 2-propanol and the value for the surfactant also greater than that for 2-propanol is common to the two methods of determination. The main difference is that the calculation methods for the surfactant and methanol retardation factors give a larger value for the surfactant than for methanol. The calculated retardation factor (R-1, i.e. greater than that of water) for 50% 2-propanol for 2,4-dimethyl hexane (0.0044) is 1/170 of the experimental value (about 0.75) and if the calculated retardation factor for methanol is multiplied by the same factor the resulting value is 17, which is close to that determined experimentally.

Additive	Estimated Experimental Retardation Factor	Calculated Retardation Factor
5g/L Triton X-100	7.5	2.7
15g/L Triton X-100	4.5	1.6
20% Methanol	Not determined	4.9 - 97.7
50% Methanol	15 - 30	1.1 - 2.24
20% 2-propanol	Not determined	2.1 - 10.4
50% 2-propanol	1.5 - 2	1.001 - 1.004
5g/L Triton X-100 + 20% 2-propanol	approx. 11	Not determined

Table 4.11 Comparison of experimentally determined and calculated retardation factors (R).

4.5   Recommendations and Applications

Further laboratory studies should be undertaken to determine the minimum amount of flushing solution containing the additive that can be used to remove residual gasoline saturation from the soil. Refinements that could be made to the research described herein include using a larger column, which would enable samples of smaller fractions of the pore volume to be taken. Fresh samples of cores from the area of residual saturation should be used. A larger variety of concentrations of the surfactant and alcohols and more hydrophobic alcohols should be tested. In addition the effect of using a small volume of the flushing solution containing the additive and then switching to water should be investigated.

It will also be necessary to carry out a test at a well-monitored contaminated field site. In order to estimate the quantities and approximate costs of field use of these additives calculations were based on a fairly large hypothetical contaminated volume of soil 100 meters long by 50 meters wide by 5 meters deep. This gives a total volume of 25000 m^3 which at a porosity of 30% has a pore volume of 7,500,000 liters.

With a concentration of 15g/L Triton X-100, 112,500 kg of the surfactant would be required per pore volume. For six pore volumes of this solution at a current bulk price of $2.40/kg the cost would be $1.63 million. For one pore volume of 50% 2-propanol solution at a

current bulk price of $0.50/liter the cost would be $1.86 million. For twenty pore volumes of 50% methanol solution at a current bulk price of $0.15/liter the cost would be $11.25 million. These approximate costs reflect only the price of the additive and do not include the costs of water, well installation and operation and processing the effluent to remove the contaminants.

Chapter 5. CONCLUSIONS

1.   Triton X-100 at 5g/L was effective in flushing more than 96% of most of the methylated alkanes from the soil in 20 pore volumes. Three times the concentration of surfactant achieved a slightly more effective cleaning of the soil in 6 pore volumes. This ratio of three to one in volume required for contaminant removal is expected from the fact that solubilization by a surfactant is proportional to its concentration in micelle form.

2.   Flushing with 2-propanol at 50% by volume was extremely effective in removal of the contaminants in less than 2 pore volumes (a spike release). At 20% by volume flushing had very little effect on contaminant removal.

3.   20% by volume methanol was found to affect only one contaminant. With 50% methanol the concentrations rose and remained fairly high for considerable volume of flow resulting in a slug release rather than a spike. Continued flushing with methanol removed increasing concentrations of higher molecular weight alkanes.

4.   Use of alcohol in flushing contaminated field sites is limited by the composition of the groundwater. If large quantities of dissolved ions are present, addition of alcohol could cause precipitation of salts and possible blocking of pore throats.

5. The solvophobic theory of Rao et al. (1985) predicted the relative effect of the two fractions of each cosolvent and the greater efficiency of 2-propanol than methanol in removal of the methylated alkanes. This theory is designed solely for sorbed hydrophobic organic contaminants but appears to have been effective for residual saturation removal in this case.

6. The different effects of 50% methanol and 50% 2-propanol were confirmed by Hung Nguyen (pers. comm.) in video-taped flushing experiments of residual toluene saturation, in a thin glass bead-filled column, using solutions supplied by this author. Methanol appeared to increase the solubility of the toluene at the edges of the ganglia while 2-propanol had both a solubility enhancement and seemed to flush the blobs of oil from the pores.

7. All of the soil column extracts had higher concentrations of the longer retention time contaminants than of the identified chemicals. However, as the concentrations of the former in the 50% methanol experiment were increasing with time, it is possible that with a greater volume of flushing by this solution a higher removal efficiency could have been achieved.

8. These results from experiments with field-contaminated soil show similar effects to those experiments performed, by other researchers, with laboratory- contaminated soils.

9. Flushing with water failed to remove detectable amounts of most of the contaminants confirming very poor removal efficiency for low aqueous solubility chemicals observed in other studies.

10. From the pattern of effluent concentrations the retardation factors of the surfactant-flushed columns appear to be in between those of the two alcohols.

11. The Tedlar bags with two-way valves were a successful method of collecting effluent without exposing it to the air. However, their use should be limited to low temperature experiments to minimize diffusion losses.

12. The Mixxor extraction system proved to be a quick, efficient and reproducible method of extracting and concentrating the contaminants in the effluent.

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