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## An Evaluation of Five Perfluorinated Hydrocarbons as Tracers in Non-Aqueous Phase Liquids

Jennifer K. Bergin

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AN EVALUATION OF FIVE PERFLUORINATED HYDROCARBONS  
AS TRACERS IN NON-AQUEOUS PHASE LIQUIDS

by

Jennifer K. Bergin

A Thesis  
Submitted to the  
Faculty of The Graduate College  
in partial fulfillment of the  
requirements for the  
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Kalamazoo, Michigan  
December 1994

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Jennifer K Bergin

## AN EVALUATION OF FIVE PERFLUORINATED HYDROCARBONS AS TRACERS IN NON-AQUEOUS PHASE LIQUIDS

Jennifer K. Bergin, M.S.

Western Michigan University, 1994

Tracers are used in many facets of hydrogeological investigations. At this time, only tracers for aqueous phase liquids are known. The object of this investigation is to assess the viability of a suite of hydrocarbons as tracers in underground spills of non-aqueous phase liquids.

Laboratory experiments were performed to determine if the potential tracers were soluble in common petroleum hydrocarbons, non-volatile, differentiable and quantifiable by GC/MS, and conservative.

The first compound tested, perfluorokerosene, was detected but could not effectively be determined quantitatively with the GC/MS. Its use should be restricted to investigations in which only its presence, and not its concentration, needs to be determined. FLUTEC PP6, PP9, PP10, and PP11 were tested in soil columns, and found to be soluble in kerosene, conservative, and differentiable and quantifiable by GC/MS. The success of these compounds in a laboratory setting suggests that they may be effective in field studies as well.

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## INTRODUCTION

### Background Information on Tracers

This investigation is the most recent in a series aimed at developing a suite of compounds that can be used as tracers in non-aqueous phase liquids. At present, aqueous-phase tracers are widely used in the environmental industry, but there are no similar products for studies of non-aqueous phase environments. Hydrocarbon tracers would enable researchers to: (a) determine direction and speed of hydrocarbon flow, (b) delineate capture zones by mapping oil flow lines to wells, (c) assess the effectiveness of product recovery systems, (d) improve recovery system design and operation, (e) identify heterogeneities and stagnation areas in the aquifer materials, (f) locate spill sources, (g) predict contaminant plume movement, (h) verify and improve numerical models of oil flow, and (i) better understand oil flow processes. A suite of related compounds that could be used simultaneously would be still more useful, since they could provide more complete information on contaminant sources, multiple flow paths and mixing.

To be effective, a tracer must meet several requirements. It cannot react with the carrier fluid, which for non-aqueous phase studies would be a hydrocarbon such as gasoline, diesel, or kerosene. The tracer cannot sorb onto or react with the aquifer material through which it flows. Volatilization must be minimal, in order that the tracer may be detected for the duration of the field study. It should also dissolve in

the carrier fluid at high enough concentrations that it can still be detected after high-volume dilution under field conditions. In addition, for tracers that will be used concurrently, it is important that each be detectable under similar conditions, with similar solvents, injection amounts, etc. for ease in detection and to standardize experimental error.

For effective tracers to also be useful to the environmental industry, several other conditions should be met. They should be non-toxic to minimize the chance of government disapproval of their use. The tracers should also be economical: inexpensive, easily available, uncomplicated to use, and detectable with common field chemical analysis equipment. Finally, they should not prevent the recycling of product, should the contaminant eventually be recovered.

### Previous Work on Non-Aqueous Phase Tracers

Earlier studies of non-aqueous phase tracers found very few promising compounds. Oil-soluble fluorescent dyes, which are easily detected and quantified by fluorescence, were adsorbed strongly onto even trace quantities of organic matter in the soil, as was Beta Carotene (vitamin A). Water-in-oil emulsions of water-soluble fluorescent dyes were unstable on passage through soils. Even the less volatile Freons, such as Freon 113, were lost due to excessive volatilization. Anthracene proved to be an effective, non-sorbing, conservative fluorescent compound, but it is a known carcinogen and an EPA priority pollutant. Diphenyl anthracene and 9-phenyl anthracene also showed potential, but, as derivatives of anthracene, these may pose

problems for governmental approval, even at already gravely contaminated sites. Perfluorodecalin, detected by GC/MS, appeared to be conservative, but also very volatile. (Bratsburg, 1992)

### Purpose of the Investigation

The focus of this study was primarily on the effectiveness of a suite of potential tracers. The tracer compounds are five perfluorinated hydrocarbons (PFC's) also known as PFK and FLUTEC PP6, PP9, PP10, and PP11. It was anticipated that the FLUTEC chemicals would eliminate problems with soil sorption, breakdown, volatility and toxicity experienced in prior studies. It was further hoped that the laboratory investigations could establish that the PFC's were soluble in kerosene, sufficiently non-volatile to use, conservative in kerosene, and differentiable and quantifiable by GC/MS. The study was limited to evaluating the performance of the PFC's in a laboratory setting.

### A Description of the Perfluorinated Hydrocarbons

The five hydrocarbons are all perfluorinated compounds, meaning that all hydrogen atoms have been replaced with fluorine. This makes the molecules more massive. Their boiling points and vapor pressures are higher, and they are generally less reactive and less volatile than their non-fluorinated relatives. In addition, they have low water solubilities, (Golding, 1992) reducing the chances that they would contaminate groundwater when used in a field study. FLUTEC PP6 (perfluorodecalin)

is also being tested by the U.S.F.D.A for use as a human blood substitute, implying it is completely non-toxic.

The five chemicals tested are listed below in Table 1. The four FLUTEC compounds are proprietary; no chemical information other than their formulas was provided when they were shipped. They were obtained from ISC Chemicals, Ltd. in Bristol, England.

Table 1  
The Five Potential Tracers

Name	Chemical Formula	Molecular Weight (g/mol)
Perfluorokerosene (PFK)	$C_9F_{20} - C_{16}F_{34}$	488.059-838.108
FLUTEC PP6 (Perfluorodecalin)*	$C_{10}F_{18}$	462.074
FLUTEC PP9 (Perfluoromethyldecalin)*	$C_{10}F_{20}$	500.07
FLUTEC PP10	$C_{13}F_{22}$	574.099
FLUTEC PP11 (Perfluorophenanthrene)*	$C_{14}F_{24}$	624.106
*indicates best guess at chemical name & structure		

## MATERIALS AND METHODS

### Instrumentation

The instruments used, courtesy of the Western Michigan University Institute for Water Sciences (IWS) water quality lab, were a HP 5890A Gas Chromatograph connected to a HP 5970B Mass Selective Detector. Data were analyzed using HP 59970 Mass Spectrometry ChemStation Processing software. Gas Chromatography/Mass Spectrometry (GC/MS) was chosen over GC alone, because of the high precision required for differentiation of the perfluorinated chemicals. In addition, GC/MS increased the precision of quantitative analyses of the tracers. The general setup can be seen in Figure 1.

Gas chromatography is a type of partition chromatography. Compounds are dissolved in solute and injected into the GC instrument. The substances are then vaporized, and the mobile phase is forced to flow through a column. The vaporized solutes interact to differing degrees with the stationary phase that coats the column and thus travel along the column at different rates. Each compound has a unique travel time, or retention time ( $R_t$ ), and is generally reported as a peak, as seen in Figures 2 and 3. The area under the peak can, with careful calibration, provide quantitative data. The resolution, or accuracy and precision with which a peak can be detected and quantified, depends on two factors. The first is the separation of the

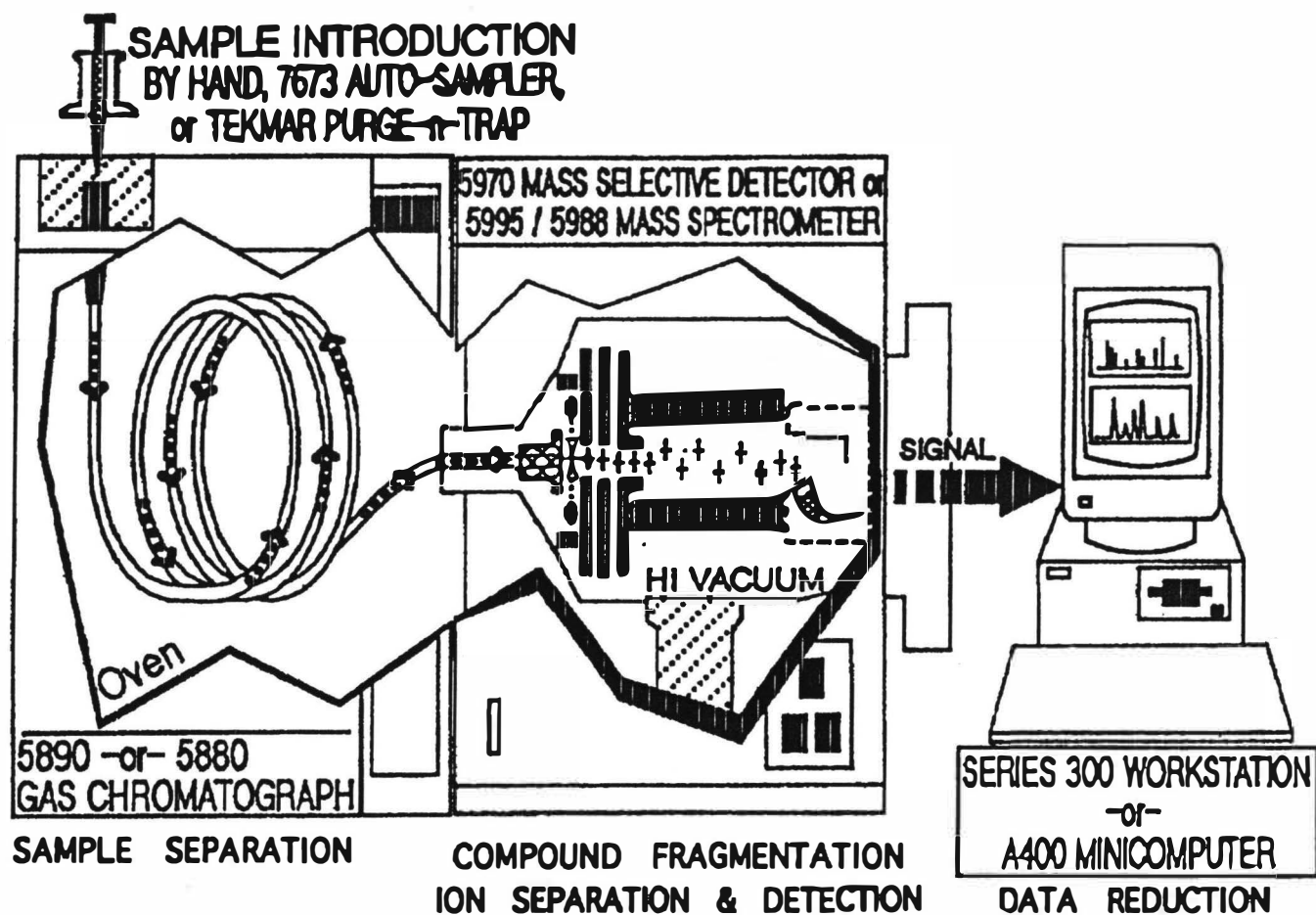


Figure 1. Basic Sections of a GC/MS System.

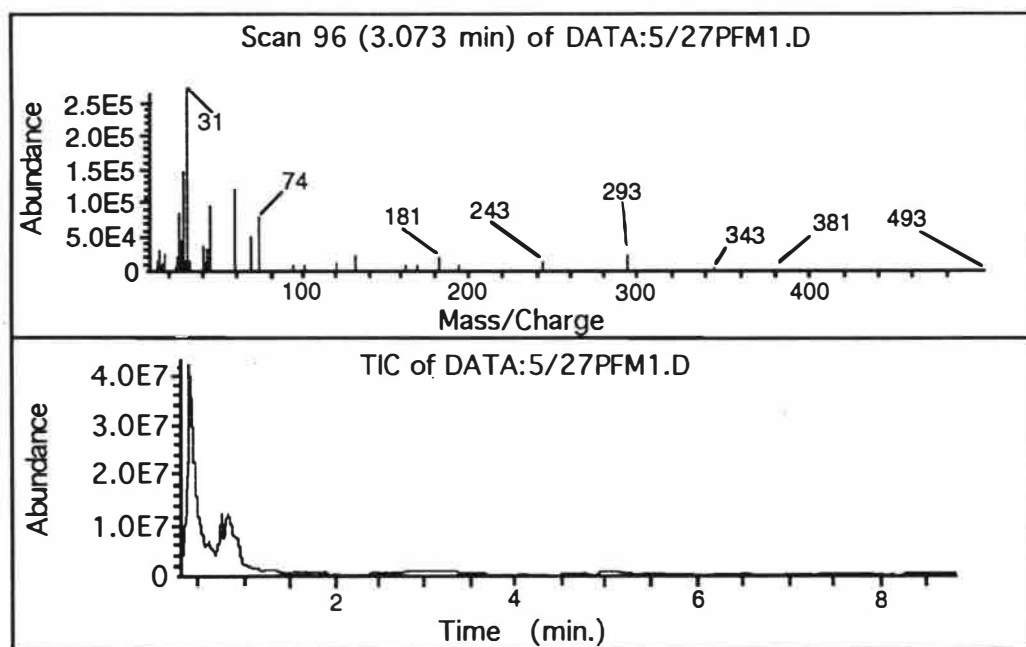
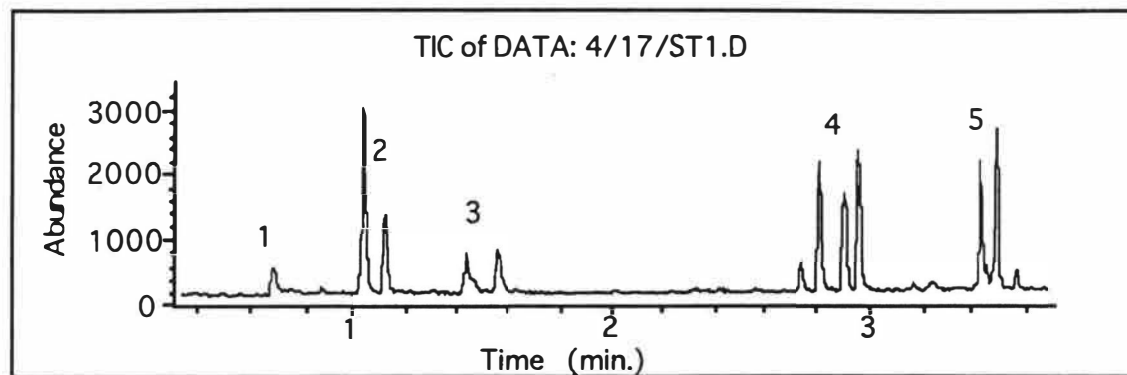


Figure 2. An Example of a Multiple Ion Scan - FLUTEC PP9.



<u>Peak Number</u>	<u>Chemical</u>
1	Kerosene
2	FLUTEC PP6
3	FLUTEC PP9
4	FLUTEC PP10
5	FLUTEC PP11

Figure 3. An Example of a Single Ion Scan - Ion 131.

peaks; the second is the average peak width at baseline.

Several different detectors are commonly used with a GC; the IWS set-up uses a Mass Spectrometer for very sensitive and precise data acquisition. The GC separates the solutes, which are then analyzed in the MS.

In the IWS set-up, the analytes are already vaporized when they reach the MS. They are analyzed by bombarding them with high energy electrons, producing unstable ions which fragment into lower mass daughter ions. These are accelerated, separated according to their mass/charge ratio, and each ion that hits the detector is recorded. All the ions of different mass/charge ratios are shown, along with their relative abundances. In this investigation both multiple and single mass/charge ratios (SIMS) were used. The SIMS output gave much better peak resolution, hence better detection and quantitative analysis. The resulting plot is rather like that from a GC, except one knows not only the retention time of a compound, but also the exact mass/charge ratio of the ion producing the peak. Figure 3 shows the result of a single ion scan at a mass/charge ratio of 131 in which the chemicals eluted through the column in order of increasing molecular weight. The five peaks are: (1) a minor kerosene peak, (2) FLUTEC PP6, (3) FLUTEC PP9, (4) FLUTEC PP10, and (5) FLUTEC PP11.

## Soil

The soil used in these experiments came from a sand and gravel quarry in the Indian Fields Kame located on Portage Rd. in Kalamazoo. The soil had no discernable amounts of organic material, as it was gathered from a zone well below soil horizon formation. The soil was sieved to remove gravel greater than 0.5" in diameter before it was used, and a Grain Size Distribution Curve was prepared (Figure 4).

Prior to all but one of the experiments, the soil was dried in a 95°C oven for two days to remove any water film that might adhere to the grains. Such extremely dry soil would be rare in nature; it was necessary, however, in order to optimize laboratory conditions. Grains surrounded by this thin layer of water might not be wet by kerosene, and could prevent saturated, homogeneous flow. Because of the large volume of soil required and the preliminary nature of the trough test of FLUTEC PP6, the soil was not dried in this case.

It was also necessary to determine the average porosity of the soil, which was measured by two methods. First, a 100mL graduated cylinder was filled to the top with water, and filled again to the 100mL mark with dry soil. The volume displaced from the graduated cylinder was measured and assumed to be equal to the total non-void volume of the soil.

$$(1) \quad \text{Total Volume}(100\text{mL}) - \text{Non-Void Volume} = \text{Void Volume}$$

$$(2) \quad \text{Void Volume}/\text{Total Volume}(100\text{mL}) * 100\% = \text{Porosity}$$

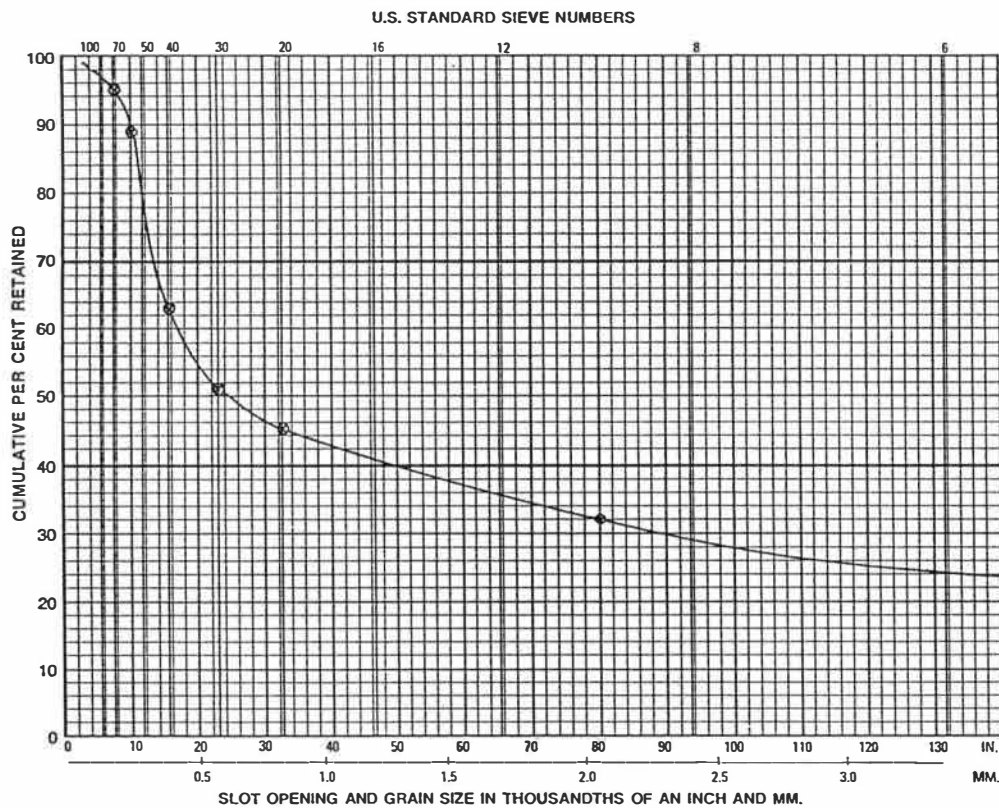


Figure 4. Grain Size Distribution Analysis.

This was done three times and the average porosity was used for calculations.

The second method was less successful. In this case, the graduated cylinder was filled to 100mL with dry soil, and the amount of water needed to fill the pores was measured. In each of four measurements there were many pockets where air was trapped, making the void volume appear smaller than it was.

### Volatility

The volatility of the PFC's was a concern, since previous tests (Bratsburg, 1992) indicated that when a 10% solution of perfluorodecalin (FLUTEC PP6) in kerosene was exposed to air in a 50 ml beaker, it took only 3.5 hours for it to evaporate completely. Such a high evaporation rate would preclude PP6's use as a tracer, since it would not exist long enough for a field study to be conducted. In order to test this, the apparatus in Figure 5 was used to simulate product floating on the water table.

A one-liter glass cylinder was filled with soil, the bottom 1 to 1.5 in. of which was water-saturated. This was followed by a 6 in. layer saturated by a standard 1:200 solution of FLUTEC PP6 in kerosene, and topped with dry soil. A glass tube with a nylon screen at the bottom was inserted into the kerosene-saturated layer to allow sampling of the kerosene/PP6 solution. Into the glass tube fit either a glass rod (to prevent direct evaporation of the standard), or a smaller glass tube which was used to take samples. The test was run three times, in which the kerosene layer was sampled over 26, 30, and finally 188 hours, and the concentration of PP6 was charted.

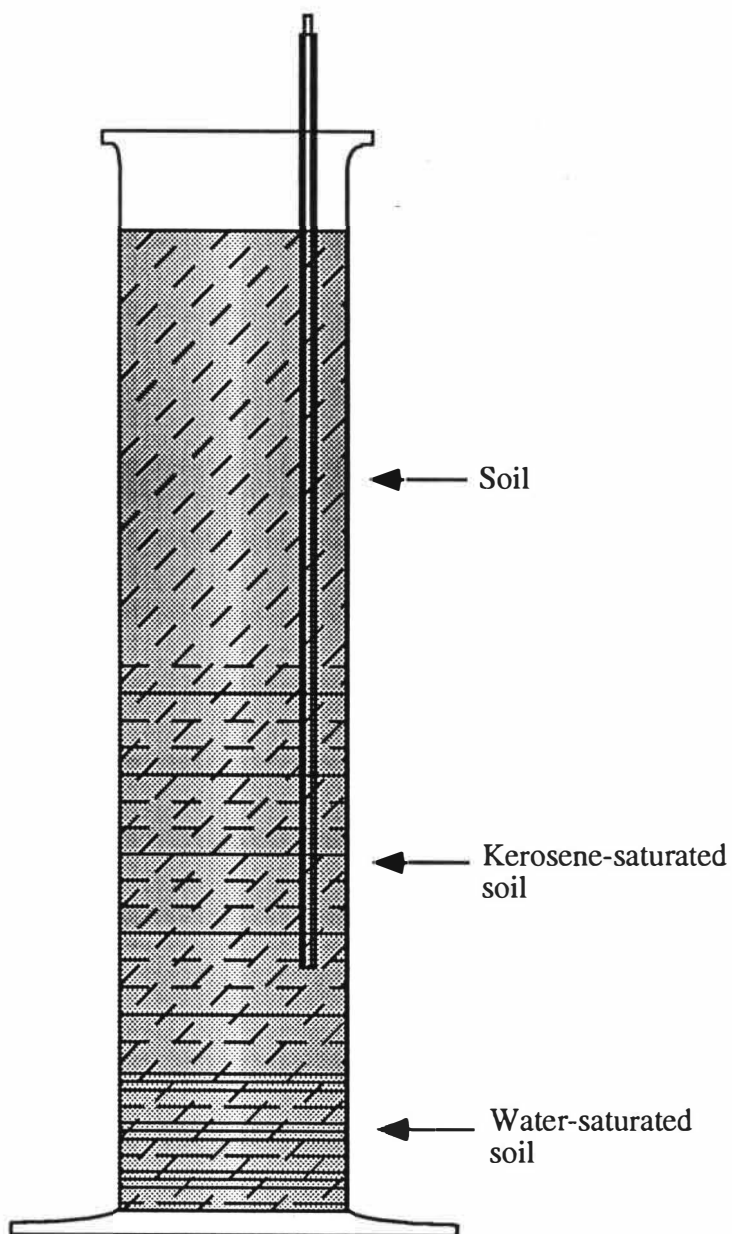


Figure 5. Apparatus for Testing FLUTEC PP6 Volatility.

Another test was run to determine whether chilling the kerosene mixture might reduce both the volatility of PP6 and experimental error. In this test, a standard solution of 1mL PP6 diluted to 100mL with kerosene was divided between two vials. One was kept at room temperature, the other stored in the freezer. Both mixtures were sampled, and the concentration of FLUTEC PP6 was tracked over the course of 22 days.

### Preliminary Testing

At the beginning of the study, there were only two potential tracers readily available: perfluorokerosene (PFK) and perfluorodecalin (FLUTEC PP6). It was decided that before more chemicals were purchased, a preliminary run should be performed to assess whether further study was warranted. First, 0.1mL of a 1:250 standard solution of PFK in kerosene was diluted to 10mL with diethyl ether. Upon injection into the GC/MS, it produced very broad peaks, and so was not used for the preliminary test.

The first trial was designed to test FLUTEC PP6 in an environment loosely approximating field conditions. The set up (Figure 6) consisted of a 120"x3"x3" steel trough, slightly tilted (0.5 in.) to provide some elevation head. Two 12 in. sections were reserved: one at the high end as a reservoir for kerosene and water, and one at the low end for drainage. Two separatory funnels dripped kerosene and water into the reservoir at a fairly constant rate. The center of the trough was filled with soil. The bottom 3 in. of soil was saturated with water, followed by approximately 6 in.

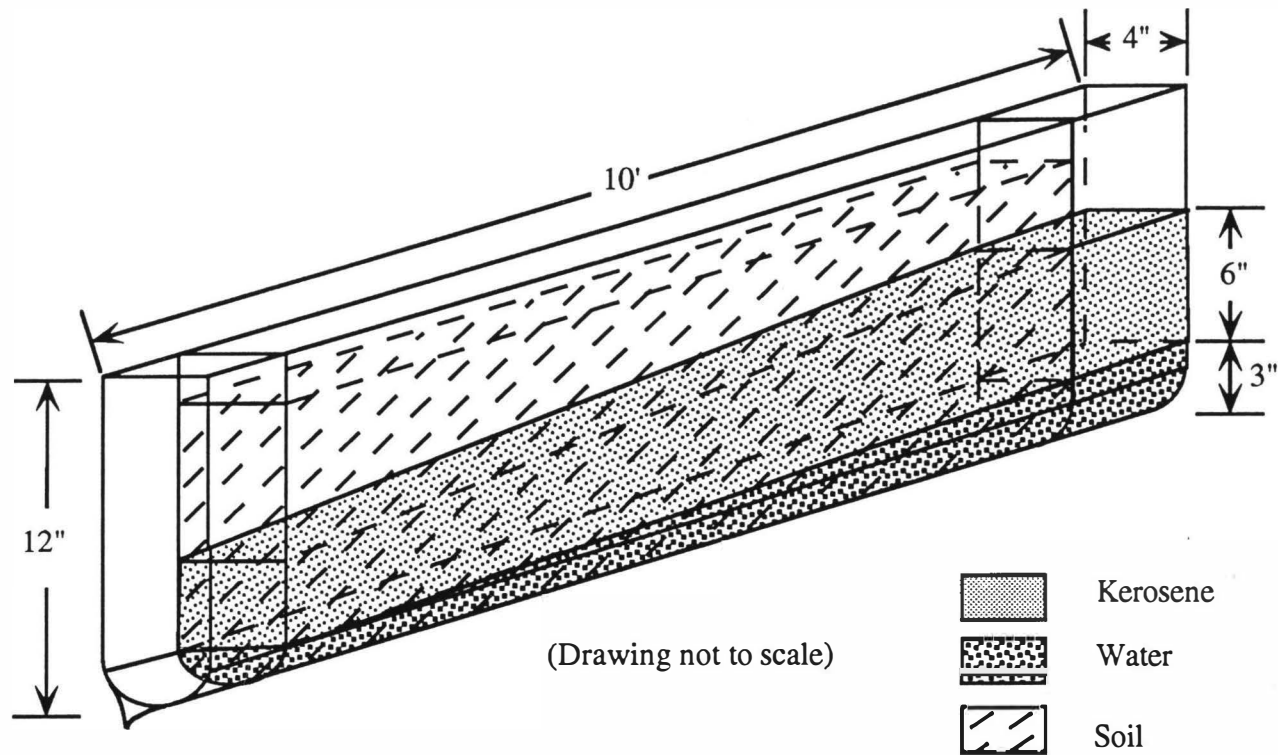


Figure 6. Sand Trough Apparatus for Preliminary Test of FLUTEC PP6.

of kerosene-saturated soil, and another 3 to 5 in. of dry soil. This mimicked the top of a gently dipping water table, covered by a floating plume of kerosene, and topped with uncontaminated soil.

To start the test, 10mL of approximately 1:200 PP6 in kerosene was injected 5 in. from the input end of the trough. Samples were taken from the draining kerosene approximately every twenty minutes until the majority of the PP6 had eluted through the trough, and every one to two hours after that. Immediately after each sample was taken, a 200 $\mu$ L aliquot of sample was diluted to 1mL with diethyl ether and put on ice. Then 1 $\mu$ L of diluted sample was injected into the GC/MS for analysis.

A rough estimate of the volume of kerosene-saturated soil was made, and having estimated a value for porosity of the soil, the pore volume was calculated.

#### Differentiation by GC/MS

In order to determine if the four tracers were differentiable by GC/MS, each was diluted 1:200 with diethyl ether and injected into the instrument. The data gathered included the time at which each would elute through the column, and a "fingerprint" (distinctive arrangement of peaks) for future identification.

All four FLUTEC tracers were run, looking at both single ions and a composite of all ions, to determine which mass/charge ratio was the most abundant for each tracer. The most abundant ion should be easiest to detect, especially at low concentrations.

## Solubility

During the course of the above experiments, the solubility of FLUTEC PP6 was far lower than expected. Previous work (Bratsburg, 1992) indicated that a 1:10 dilution of PP6 in kerosene had been used as a standard; whereas it was actually impossible to make a 1:10 solution, and very difficult to make even a 1:100 dilution. This reduced solubility was a cause for concern, since a tracer only barely soluble in non-aqueous phase liquids in a lab setting would be very difficult to detect when further diluted by free product in a contaminant plume.

To determine the solubility of each of the tracers, the following method was used. Four erlenmeyer flasks, each containing 50mL of kerosene and a stir bar were stoppered to minimize volatilization and placed on stir plates. Each tracer was added to a specific flask in 100 $\mu$ L increments, and the resulting mixture stirred until the tracer dissolved. When the additions stopped dissolving, the previous total volume of tracer added was taken to be the maximum volume soluble in kerosene. During the first trial, the stir plate motors heated the kerosene in the flasks, giving artificially high solubilities for the tracers. During the second trial, flasks were placed in water baths to keep the solutions at room temperature.

## Test for Conservative Nature of FLUTEC Chemicals

To determine whether or not the four FLUTEC chemicals were conservative, the set-up shown in Figure 7 was used. A glass column 48 in. long and 1 in. in

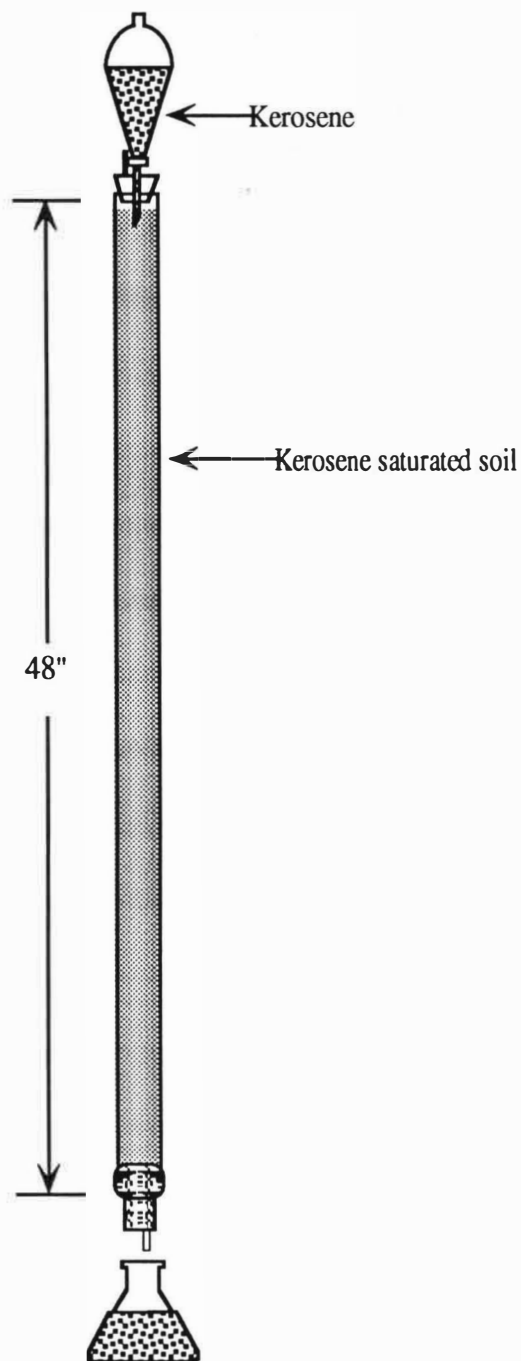


Figure 7. Soil/Kerosene Column for Testing the Conservative Nature of FLUTEC Chemicals.

diameter was fitted with a rubber stopper at the top and with a screw-on teflon plug at the bottom, and filled with kerosene-saturated soil. Silicone caulk was piped around the bottom plug to prevent leaking. The caulk was tested to make sure it would not affect the experiment by soaking it in kerosene for several days, then running the kerosene on the GC/MS and looking for extraneous peaks. Kerosene was fed into the column using a separatory funnel, and exited the column via a thin nylon tube. The set-up procedure was repeated for the second run, to make sure no residual tracers would skew concentration measurements.

For each run, a 10mL slug of standard (250 $\mu$ L of each tracer diluted to 50mL with kerosene, or a concentration of between 9000ppm and 9400ppm, depending on the tracer's density) was injected through the rubber stopper into the column. Samples were taken approximately every five minutes until the concentrations started to level off, and then every 10-40 minutes for the following hour. Samples were capped with aluminum foil and stored in a freezer until they were analyzed.

For each trial, the GC/MS was calibrated with three solutions of the four tracers at concentrations of approximately 9000ppm, 90ppm, and 1ppm. Although peaks were measurable at 1ppm, they were only barely above background levels. Thus, 1ppm is the detection limit for the FLUTEC chemicals using the IWS GC/MS system. With injection volumes of 1 $\mu$ L, the GC/MS was detecting tracers at the nanogram level or  $10^{-9}$ g. Because the concentrations did not have a linear relation with peak area, two lines were used to convert integrated peak area counts into concentrations: one for values between 90 and 9000ppm and one for values between

1 and 90ppm. This introduced considerable uncertainty into computed concentration values. In the future, more than three solutions should be used to calibrate the instrument in order to obtain a better best fit line and more accurate concentrations.

While setting up the column, it was possible to very accurately measure the volume of kerosene used to saturate the soil. This value was assumed to be equal to the pore volume, and was used to calculate the breakthrough time for each of the two runs.

### Sources of Error

There were many possible sources of error in this investigation. Perhaps the most noticeable problem was the variation in the amount of diluted sample injected into the GC/MS. Since the syringe used would not draw a perfect vacuum, it was impossible to develop a consistent technique for getting 1 $\mu$ L of sample. Averaging the results of multiple runs was possible during the tests to determine volatility, and some tests to quantify error, but not in the final experiments. During the tests to determine whether or not the PFC's were conservative, there was time for only one run of each sample; the entire analysis and cooldown process taking approximately 20 min. for each sample. Even for the minimum number of fifteen samples, it took five hours to run them all just once. Running the samples three times to get acceptable statistical information would take far too long. It is hoped that running multiple samples and quantifying the error at other times will be sufficient. The technique did grow more consistent with repetition. After considerable practice, the injection error

was reduced to approximately  $\pm 5\%$ , or  $\pm 10\%$  at a 95% confidence level.

Another source of error was the volatility of the diethyl ether used to dilute the kerosene/tracer samples. Due to the sensitivity of the instruments, even a small amount of solvent evaporation between runs on the GC/MS was enough to cause wild fluctuations in the concentration of tracer in the sample. To reduce this problem, diluted samples were kept in an ice bath until after they were run on the GC/MS.

Although the volatility of kerosene is low, and that of the FLUTEC chemicals even lower, test tubes were capped with foil and placed in a freezer between the time of collection and the time they were diluted and placed in the ice bath mentioned above. In addition, the total volume of sample removed from the column (5-10mL) was much larger than the volume diluted for testing (200 $\mu$ L). This ensured that any evaporation of kerosene or tracers would not have a significant effect on the measured tracer concentration.

A source of error inherent to the GC/MS instruments influences quantitative measurements. The strength of the signal coming from the detector depends on the voltage of the ion multiplier, which varies from use to use. So the same solution of tracer, on different days, may show a variation of 30% or more. This made it difficult to compare concentrations measured during an experiment that lasted several days or weeks. As a control measure, a standard solution of 1:200 FLUTEC PP6 in kerosene was stored in the freezer, and run before any samples. Since the concentration of the standard should remain constant, tracking its variations provided an estimate of how much variance in readings was due to the instrumentation.

## RESULTS AND DISCUSSION

### Soil

A value for soil porosity was needed in order to calculate the pore volume of the soil saturated with kerosene for the column test, and especially for the sand trough test, so it could be determined whether the tracers were conservative. The mean porosity calculated was 38%. According to Davis (1969) and Johnson and Morris (1962), the porosity ranges for the major constituents of the soil are: (a) fine gravel, 25-38%, (b) coarse sand, 31-46%, and (c) fine sand, 26-53%. The calculated porosity correlates well with these values.

### Volatility

High volatility for any compound would eliminate it from the roster of potential tracers. Since FLUTEC PP6 had the lowest molecular weight, it was assumed that it would be the most volatile of the FLUTEC chemicals and that it was generally representative of their characteristics.

The concentration of PP6 remained relatively constant throughout each of the three tests of evaporation from a soil column. These data indicated that volatility might not be as great a problem as previously thought. Table 2 shows that the average peak area, which is proportional to concentration, over 188 hours did not vary significantly. The variation among different samples was about the same as the

variation among different runs of the same sample.

Table 2  
Data for Evaporation of FLUTEC PP6 From a Soil Column

Date	Time	Mean Peak Area*	sm $\Phi$	sm as % of mean
1/23/93	1:45pm	34142	1173	3%
1/23/93	3:05pm	33329	1077	3%
1/23/93	4:35pm	27717	581	2%
1/23/93	5:30pm	29461	914	3%
1/28/93	8:30pm	37898	898	2%
1/31/93	10:45am	23674	1345	6%
Average over the 6 samples:		31275	1311	4%
* average of three trials for each sample $\Phi$ standard deviation of the mean				

The second means of testing the volatility of PP6 was to store a standard solution both in a freezer, and at room temperature, and see how the concentration of PP6 varied. As can be seen in Figure 8, peak areas for FLUTEC PP6 varied in both the chilled vial of solution and that kept at room temperature. Some of this variation must be due to changes in the ion multiplier voltage, and some due to experimental error. However, both the concentration of FLUTEC PP6, and the difference between

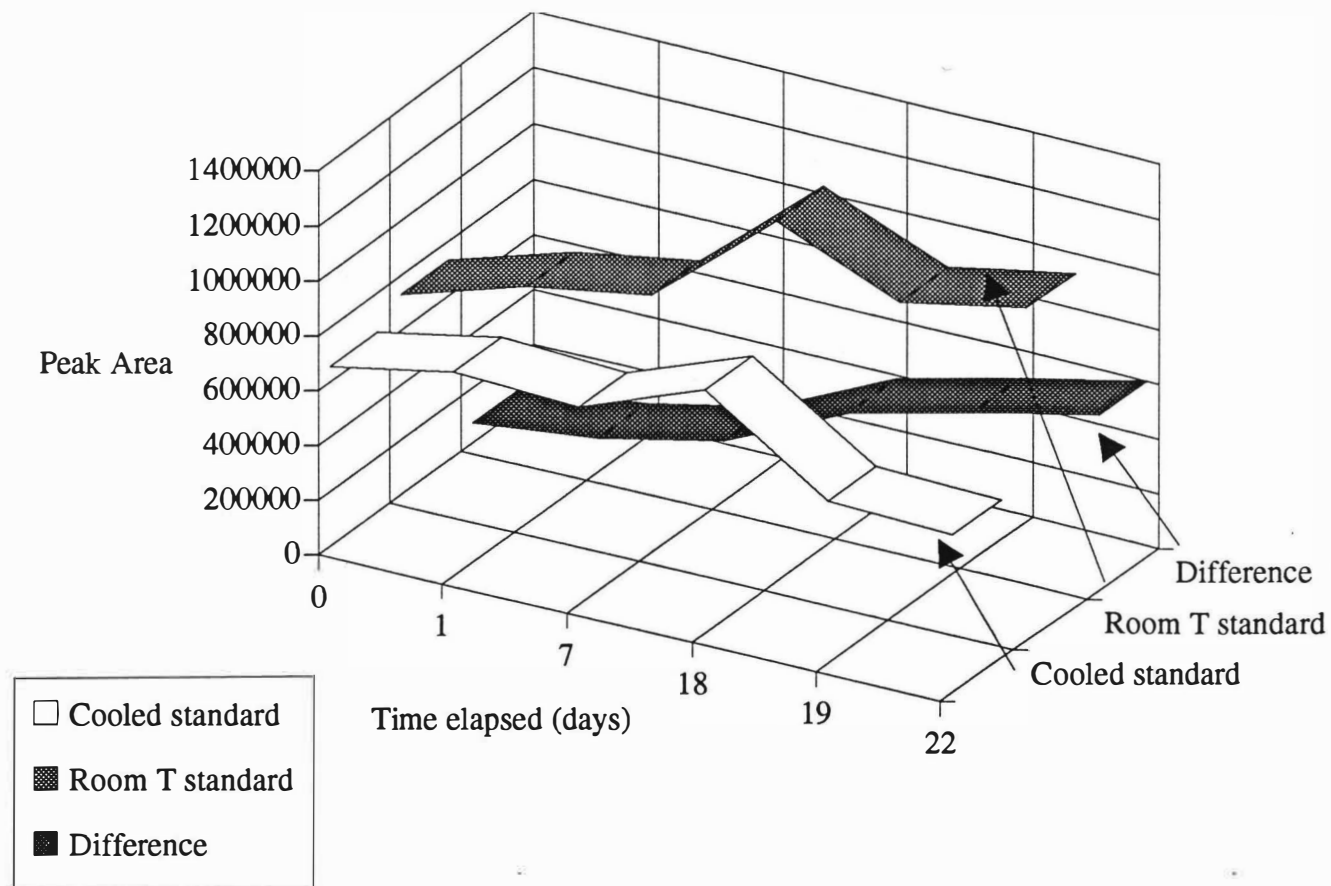


Figure 8. FLUTEC PP6 Standard Concentration - Room Temperature vs. Cooled.

the two solutions increased continuously over the three-week period. This implies that kerosene was evaporating faster than FLUTEC PP6 in the room temperature solution, concentrating the PFC, and also increasing the difference between the solutions. This suggests not only that FLUTEC PP6 is less volatile than kerosene, but also that excessive evaporation is unlikely to be a problem in field studies. Samples should, however, be kept chilled until they can be analyzed to preserve field concentrations of the tracers.

### Preliminary Test of a Potential Tracer

When perfluorokerosene (PFK) was run on the GC/MS, the peaks were very broad. A high value for average peak width at baseline will reduce the resolution of the peaks, and prohibit precise or accurate detection and quantitative analysis. The PFK peaks were so broad, in fact, that they would probably also have interfered with or completely masked peaks from other tracers.

If FLUTEC PP6 was conservative then, as mentioned above, the most concentrated level of PP6 should elute through the soil at the same velocity as the kerosene. As can be seen in Figure 9, the peak concentration of PP6 did elute near one pore volume. Knowing that the volume of kerosene-saturated soil was only approximated, and that the actual peak value of PP6 may have occurred slightly before or after the highest concentration of PP6 was measured, it seemed reasonable to assume that PP6 was, in fact, conservative, and to subject it and the three other FLUTEC chemicals to more rigorous testing.

Pore Volume vs. Peak Area (Concentration of FLUTEC PP6)

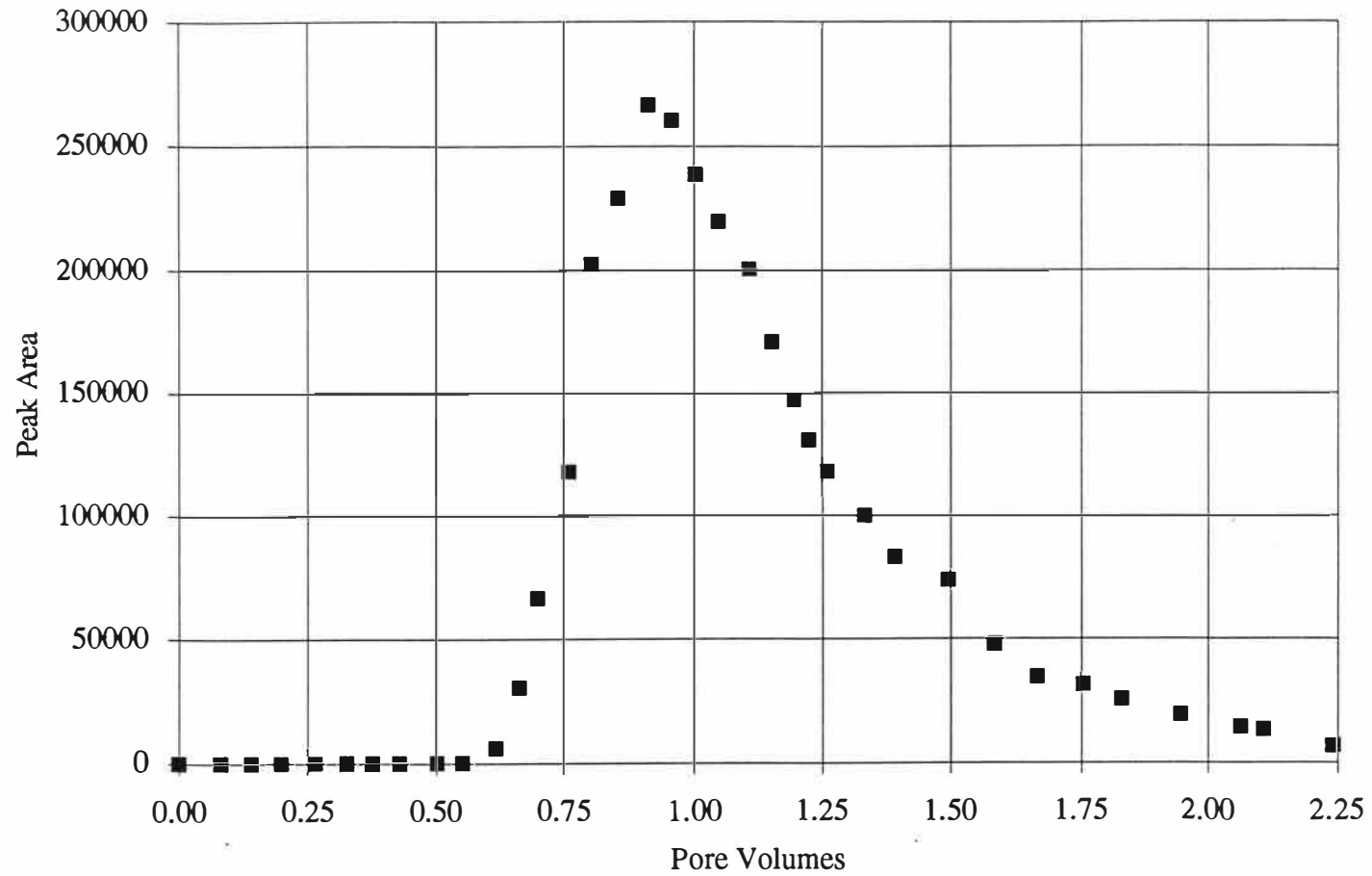


Figure 9. Breakthrough Curve for FLUTEC PP6 in Preliminary Test.

## Differentiation by GC/MS

Ion fragment 69 ( $\text{CF}_3$ ) was most abundant for FLUTEC PP9, PP11, and PP6, followed by ion fragment 131 ( $\text{C}_2\text{F}_5$ ). FLUTEC PP10 produced primarily mass/charge (m/e) 131 ions, with m/e 69 being next most abundant. The spectra of the tracers at 131 and 69 were compared by using a SIMS program to single out only one mass/charge ratio. The peaks for the run at m/e 69 were somewhat broader, and although peak overlaps were observed at both mass/charge ratios, there was more overlapping at 69, so 131 was the ion fragment chosen for lab determination of the tracers. Where peaks did overlap at ion 131, the peak of interest was two orders of magnitude larger than the conflicting peak, making the potential variation well within the general experimental error of  $\pm 5\%$  (see Figure 10).

When the tracers were diluted with kerosene as well as diethyl ether, the retention time was slightly delayed due to additional chemical interactions. An unexpected peak was also observed around 0.6 min once the peak area threshold was set low enough. This was most likely a product of the kerosene, since the peak's area remained essentially constant at 10,000 peak area units through successive dilutions of the standard solution, while the tracer peaks decreased in size by a factor of 1000.

## Solubility

Solubilities were far lower than expected, but still high enough to be useful in

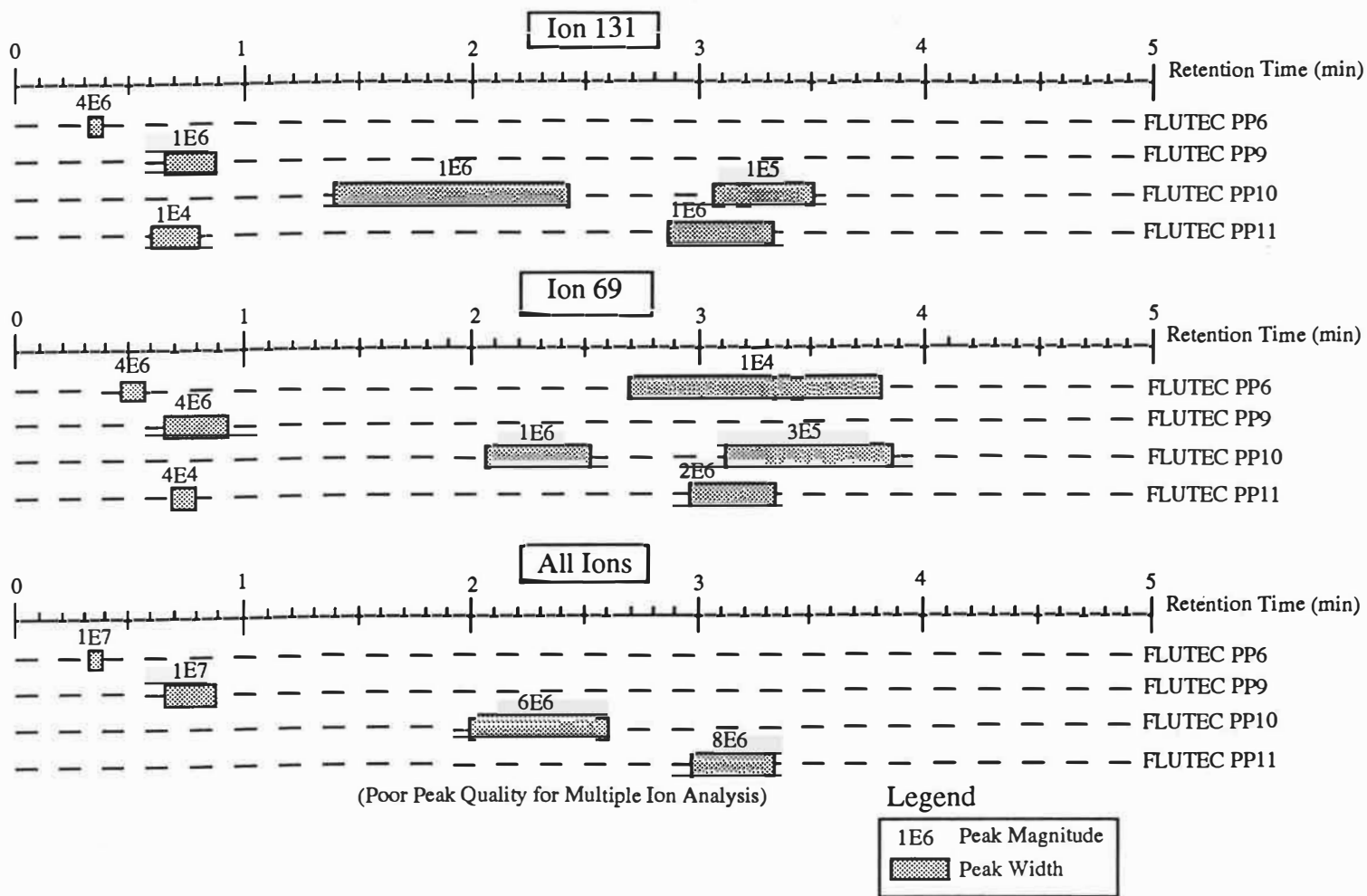


Figure 10. Peak Widths and Retention Times for FLUTEC Chemicals.

field studies. Table 3 shows the results of the test.

Table 3  
Experimental Solubilities for FLUTEC PP6, PP9, PP10,  
and PP11 in Kerosene at 22°C

Name	Solubility (g/L)
FLUTEC PP6	51
FLUTEC PP9	44
FLUTEC PP10	44
FLUTEC PP11	32

#### Test for Conservative Nature of FLUTEC Chemicals

A conservative tracer should move at the same velocity as the kerosene into which it is injected. One would thus expect the highest concentration of tracer to be observed as one pore volume of kerosene is eluted. This maximum or "breakthrough" concentration would be less than the original concentration, since some tracer would be expected to move away from the slug by diffusion and dispersive advection.

Figures 11 and 12 show the results of soil column runs one and two, respectively. The maximum concentration of all four tracers appears in both tests at 1.1 pore volumes. For the preliminary run using the sand trough, the pore volume was not well known; this was used to partially explain the breakthrough apparently

# Concentration vs. Pore Volume for FLUTEC PP6, PP9, PP10, & PP11

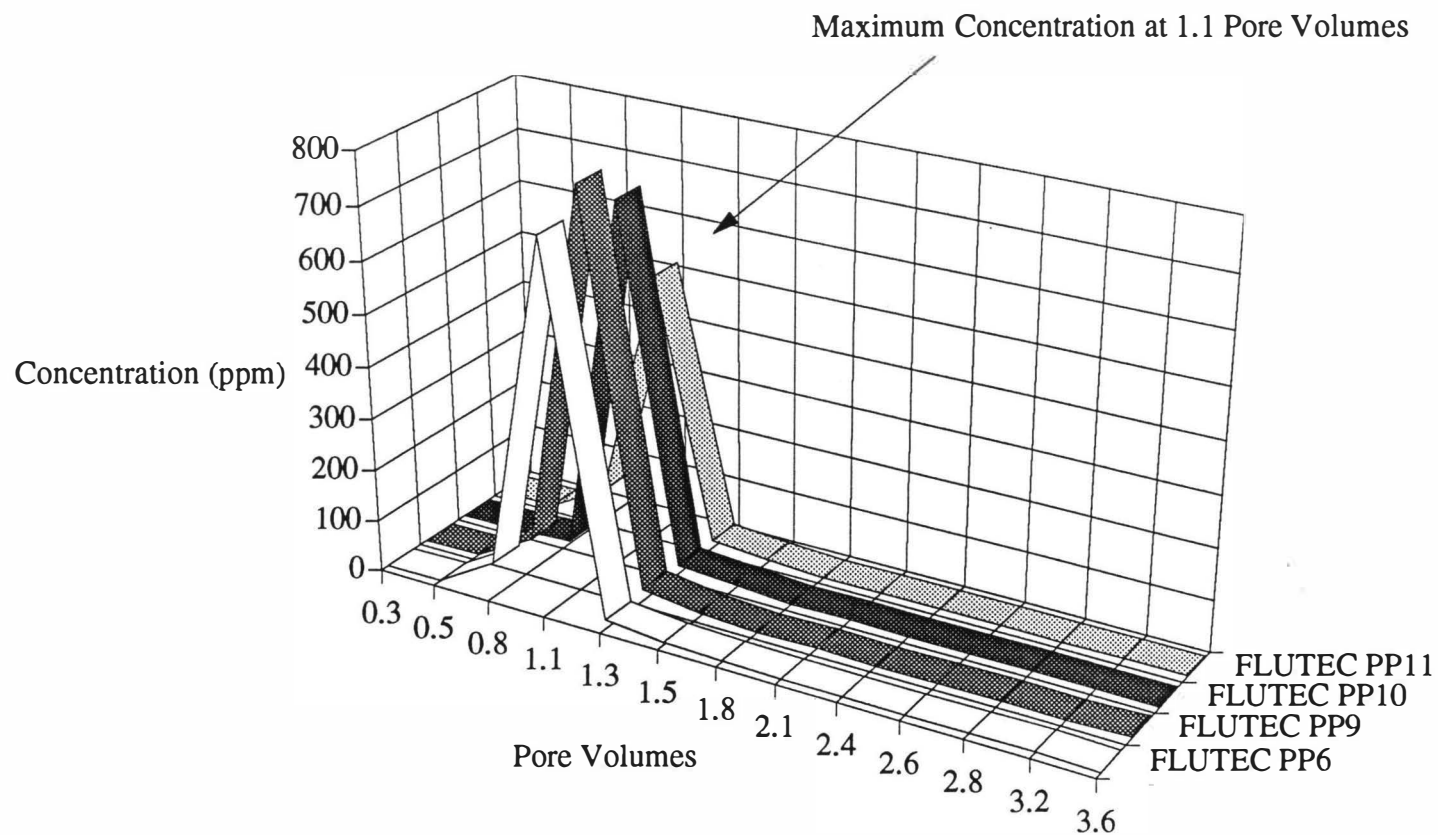


Figure 11. Breakthrough Curves for FLUTEC Chemicals - Column Test 1.

Concentration vs. Pore Volume for FLUTEC PP6, PP9, PP10, & PP11

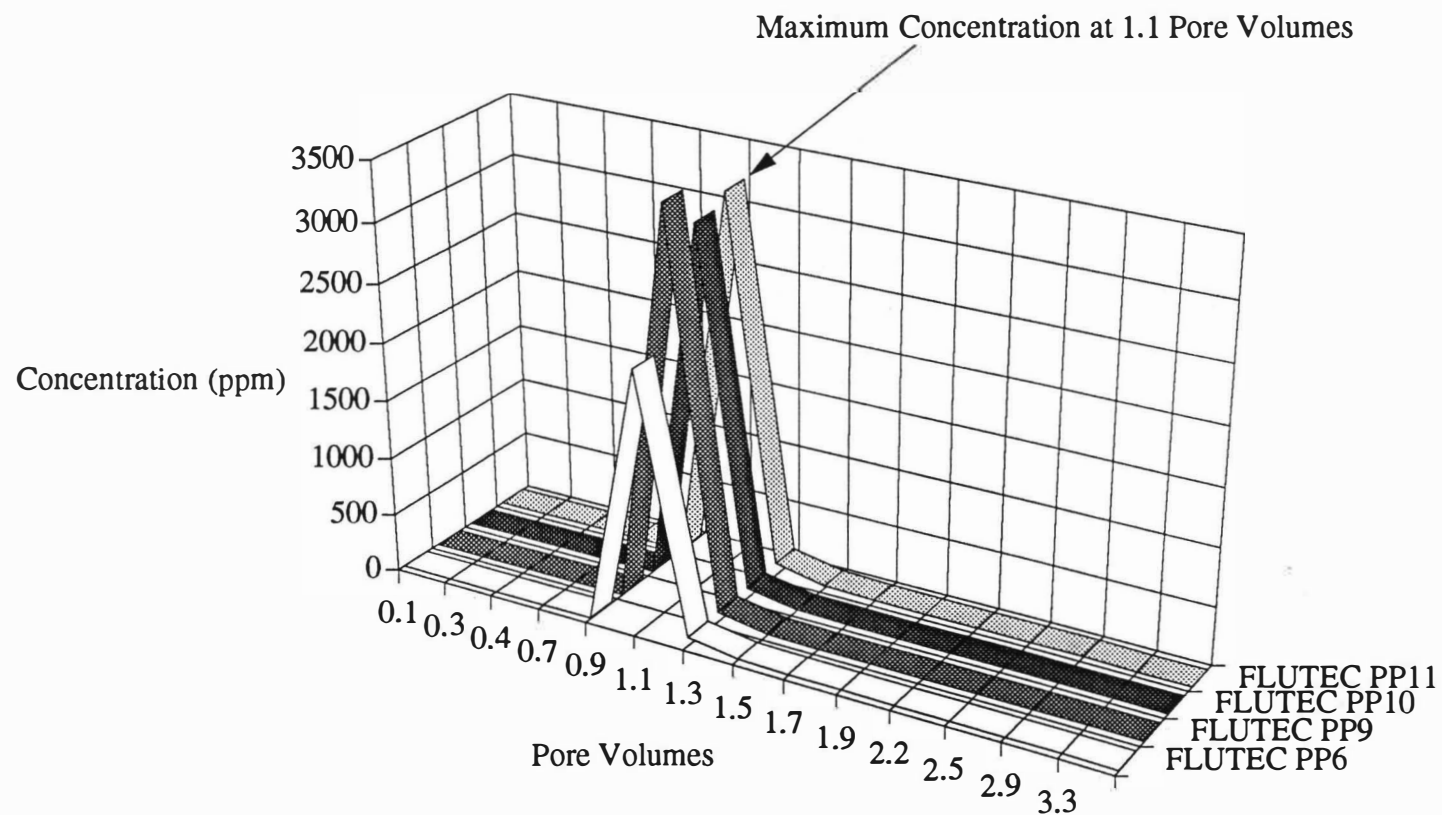


Figure 12. Breakthrough Curves for FLUTEC Chemicals - Column Test 2.

occurring near, but not exactly at one pore volume. The pore volume is known much more accurately for the column. It is still probable, though, that since no sample was taken at one pore volume, the actual maximum concentration may have occurred then. Of course, it is also possible that all four tracers were retarded 0.1 pore volumes as they eluted through the column.

In order to make sure all the PFC's eluted through the column and were not adsorbed, the total mass injected and eluted was calculated for each tracer. For both trials, the mass injected was approximately 90mg for each of the four FLUTEC chemicals. To calculate the mass eluted, the average concentration for each segment of the breakthrough curve was multiplied by the volume eluted at that concentration.

In the first column trial, the mass of tracer eluted was calculated to be approximately half the mass injected. It is believed this is because no sample was taken at the actual concentration maximum, which eluted through the column between 0.9 and 1.1 pore volumes. Additional evidence for unmeasured higher concentrations is the fact that the maximum concentration for column trial two (Figure 12) is one order of magnitude greater than that for column trial one (Figure 11).

In the second column trial, the mass of tracer eluted averaged approximately 1.5 times the volume injected. This is most likely due to the uncertainties in the calibration curves noted previously. Tracers that adsorb onto soil materials should cause a tail of fairly constant tracer detections after the slug passes as they dissolve back into the flowing kerosene. In both trials, by 1.9 pore volumes, concentrations had sharply decreased to the 1ppm level, where they stayed essentially constant for

the remaining 1.5 pore volumes. An average of only 1 mg of each tracer was eluted after the concentrations leveled off. This implies that adsorption is not significant.

Despite the uncertainties in tracer concentration, it is clear that the breakthrough time for the four chemicals is very close to one pore volume, and it does not seem likely that the tracers are being adsorbed significantly. The evidence suggests that the tracers are conservative, and that they warrant further study under field conditions.

### Implications for Future Use

Before using these chemicals in the field, several issues must be addressed. First, and most important is the potential mass balance problem. Given the detection limits and solubilities of the FLUTEC chemicals, how could one get enough tracer into a plume to survive many volumes of dilution?

The lowest solubility was 32g/L (PP11 in kerosene). This would decrease to about 8g/L if all four tracers were dissolved in the same slug of kerosene. The detection limits were approximately 1ppm or 1mg/L for all four FLUTEC chemicals. These values imply that four FLUTEC tracers in a 1L slug of kerosene could be diluted about 8,000 times, to 8,000L, and still be detected by GC/MS. At the upper limit, a product spill of 100,000 gallons would require approximately 50L of kerosene/tracer, or about 500g of each tracer, if the tracer were to be diluted throughout the whole plume. Tracers, however, are generally used to delineate a

single flow line, which would be only a fraction of the volume of a plume, requiring far less tracer. Five to ten liters would probably be sufficient.

It would be convenient to keep costs down by analyzing kerosene/tracer samples on site. Unfortunately, GC/MS is too expensive and bulky to be used routinely in the field. Both Golding (1992) and Bratsburg (1992) suggest that a standard GC with an electron capture detector would be more than sufficiently sensitive for differentiation of PFC's. Electron capture detectors are common accessories on field GCs, and should be evaluated in future investigations. This study makes it clear that laboratory analyses are also possible, so long as the samples are kept chilled until analyzed.

There is also a question of possible retardation by biomechanisms. A preliminary trial of FLUTEC PP6 was attempted using the sand trough apparatus and old soil. The soil had been used two or three months prior to the trial to conduct similar experiments with kerosene and FLUTEC PP6. In this case, the sand trough did not elute any kerosene, even though several liters were placed in the recharge chamber. Something was blocking fluid flow through the soil. One possible explanation is that bacteria were consuming the residual kerosene/tracer and that either they or their byproducts were plugging up the interstices. If this is the case, biomechanisms could have an impact on tracer studies conducted in areas with spills in warm, well aerated soil like that in the sand trough. However, this is an example of successful identification of a stagnated area; exactly the sort of product flow question it was hoped the tracers could answer.

In what sort of field problem might the tracers appropriately be used? Ideally, the tracers would be utilized first in an area with non-organic sand and gravel soils similar to those used in the laboratory investigation. This would minimize potential problems with adsorption to organics, and provide high porosity and permeability for easy flow and emplacement of the kerosene/tracer slug. The spilled contaminant must be kerosene, since other types of product were not tested, and should be of limited extent (less than 100,000 gallons), so as not to require large quantities of tracer. It might be easiest to get the special approval from government agencies that will be required for injection of the tracers if they were used on an already highly contaminated site. Hopefully, if these guidelines are followed, the field tests will prove as successful as the laboratory investigations.

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