HPFF Cable Leak Location Using Perfluorocarbon Tracers

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REPORT SUMMARY

Traditionally, leaks from high-pressure, fluid-filled (HPFF) cables have been high-cost occurrences, primarily due to the difficulty in detecting leak locations. In this project, researchers developed methods using perfluorocarbon tracers (PFT) to quickly and accurately locate underground leaks.

Background

Cable fluid leaks emanating from pipe-type circuits are difficult to locate. With such systems traditionally under major city streets, leak location can often involve identifying “false” targets or locations. Utility personnel typically investigate these findings by excavating the area and trying to pinpoint a leak with conventional freezing techniques. PFT technology, used in other fields over the past ten years, offers a benign and environmentally acceptable method for pinpointing leaks— even very small leaks that could not otherwise be detected. By “tagging” the cable fluid with PFT, personnel can detect leaks via above-ground testing, reducing the costs of excavation and speeding repair time.

Objectives

To develop and demonstrate a feasible PFT method for underground cable leak location.

Approach

The project team implemented a four-phase approach to meeting their objective. Initially, researchers investigated the viability of using PFT with HPFF cable fluids. In the second phase, they developed a PFT sampling protocol by studying the soil and atmospheric transport characteristics of PFTs. In subsequent testing phases, researchers conducted both staged tests and actual field tests. Project members first released a known quantity of PFT-tagged cable fluid into the ground at the field site and gathered samples for analysis. Final testing, conducted in cooperation with Consolidated Edison Company of New York, Inc. (Con Edison), involved detection of actual HPFF cable fluid leaks in two locations.

Results

Project testing demonstrated that PFT methods are a viable means of locating underground fluid leaks. Researchers determined that a two-part detection strategy seemed most effective. First, they isolated a leak target to within one city block by measuring PFT concentrations in the ambient air along the feeder. Then, they further pinpointed the location via subsurface concentration measurements using borehole sampling equipment. This latter step identified leak targets to within 10 feet of their actual location. Moreover, the technology developed in the project was successful in analyzing very small concentrations. As a result, small leaks once thought impossible to locate can now be detected and more easily repaired.

EPRI Perspective

The PFT technology demonstrated in this project is far more sensitive and accurate than previous techniques tested over the past 20 years. Industry participants expect its application to save utilities hundreds of thousands of dollars in avoided downtime, leak location expenses, and environmental impacts. To further this technology, developed through collaborative efforts of EPRI, Con Edison, the Empire State Electric Energy Research Corporation (ESEERCO), and Brookhaven National Laboratory, EPRI has sponsored additional PFT research. For instance, earlier this year, EPRI and Con Edison collaborated to successfully demonstrate a mobile PFT system that will speed sample analysis.

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ABSTRACT

Perfluorocarbon tracers (PFTs) have been widely used to tag air movements in the atmosphere and buildings and as an indicator of underground fluid and natural gas movements. This paper reports on the use of PFTs to locate underground leaks in high pressure, fluid-filled (HPFF) electric feeder lines. The method involves tagging the fluid with a volatile PFT which, after a leak occurs, can be detected at or above the street surface to isolate the leak location. The demonstration of the feasibility of using PFTs in this application was investigated in this four phase program. Phase 1 investigated the physical properties of the PFTs with respect to the HPFF cable fluids and found the PFT technique to be potentially viable. Phase 2 studied the soil and atmospheric transport of PFTs so as to develop a sampling protocol. The third phase applied and refined this protocol in the performance of two urban field tests in commercial streets in Queens, New York. In both experiments thirty gallons of fluid containing 0.03% by weight of a PFT was released six feet under the road surface and its emissions monitored by various PFT sampling equipment and real-time instrumentation. In the first experiment the experimental release site was known and in the second unknown, that is, the fluid release site was unknown to the personnel developing the search protocol so as to test the proposed protocol.

The results indicated that the PFT method may be a viable means of locating underground fluid leaks provided a two part leak detection strategy is employed. First, the leak is isolated to within one city block (~200 feet) by measuring the concentration of the PFT in the ambient air along the feeder. Further isolation of the leak to within ~10 feet requires the use of subsurface concentration measurements provided by borehole sampling equipment. Ultra-sensitive flux measurements at the street surface showed that, at this site, no perceptible amount of PFT was emitted through small and/or invisible cracks in the street surface with the large majority of the emissions emanating from the nearby utility manholes and sewers.

The fourth phase was the application of the refined sampling protocol to the determination of an actual leak at another site in Queens, NY. These results are given in attached appendices to this report. Further instrumental development is needed to cultivate this method for routine operation.

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INTRODUCTION

In many major cities, electric power is transmitted by under-ground, high voltage electric cables. Most of these cables are surrounded by an fluid-filled jacket which serves both as a dielectric insulator and a coolant to dissipate the heat generated within the cables. Cracks and pits caused by stray currents and old age, often develop in the metal pipes which confine the fluid and lead to leaks which must be repaired. Currently, the most time consuming and expensive part of repairing a fluid leak is the job of estimating the leak location precisely enough so that a trench can be dug and the pipe repaired.

A fluid leak is detected by a perceptible reduction in the level of fluid in the pot head used to supply a high pressure, fluid-filled (HPFF) electric feeder line. Current methods permit the detection of leaks as small as one gal/h. Feeder lines range from less than a mile in length up to ten miles of length. If one is fortunate, the leak may be close enough to a manhole, sewer, or subway so that a visual inspection of these openings can locate the leak to within a city block. A more typical scenario involves using various pressure and flow measurement techniques to isolate the leak to progressively smaller lengths of the feeder line. These methods have proved to be time consuming and expensive and they are unable to locate leaks that have leak rates much below 10 gal/h.

A promising new method of locating fluid leaks from under-ground transmission cables is to tag the fluid with a volatile perfluorocarbon tracer (PFT), which can be detected above ground should a leak develop. A version of this method has already been tested with some success using the tracer, sulfur hexafluoride [16]. However, not only is the ambient tropospheric background concentration of sulfur hexafluoride 2 to 4 orders of magnitude higher than those for PFTs, but local usage can make urban back-ground levels even higher, which makes detection of sulfur hexa-fluoride taggant in the ambient air above a fluid leak difficult at reasonable fluid tagging levels.

Prior work at BNL has shown that the PFTs are soluble to about 4% by weight in the polybutene fluid used in these high voltage cables. Diffusion modeling indicated that a leak could be detected in as little as six hours and that the tracer emission rate at the surface directly above the leak site would come to steady state in about two days for a release one meter below the surface. Laboratory tests showed that there were no physical or chemical losses of the PFTs on the sand used to fill the cable trenches as long as the relative humidity of the sand is above 25%. A PFT-tagged fluid release one meter below the surface of an open field at BNL confirmed that a pure diffusion model could be used to estimate the underground dispersion of the PFT vapors from the release site and was also used to test various release and sampling equipment subsequently used in the experiment reported here.

This paper will report on an experiment designed to test the feasibility of detecting and locating an underground fluid leak using PFT-tagged fluid. The experiment was conducted by the staff of the Tracer Technology Center at Brookhaven National Laboratory (BNL) with the help and cooperation of the Consolidated Edison Company (Con Edison) and was sponsored by the Electric Power Research Institute (EPRI) and the Empire State Electric Energy Research Corporation (ESEERCO).

This report is divided into three sections, being:

I. Preliminary laboratory experiments to verify feasibility

II. Field demonstration experiment

III. Urban Leak location experiments, with a known and unknown leak site

Preliminary Laboratory Experiments to Verify Feasibility

This initial phase of the program had as its purpose to evaluate the feasibility of using PFT for HPFF leak location. The task was divided into four phases.

Phase 1: Solubility and Compatibility of PFTs in Cable Fluid

This phase explored the interaction of the PFTs with the cable fluid as specifically determined by laboratory experiments, i.e., the solubility of PFTs in the cable fluid, the vapor pressure of the PFTs above the cable fluid and the respective temperature dependence for each of these processes. This phase also included a literature review of all material pertinent to this project including compatibility of the PFT with all materials encountered in HPFF as presently implemented.

Phase 2: Effects of Soil Interaction and Atmospheric Transport on PFT Vapor Detection

This phase addresses the following questions: 1) What amount of PFT will be emitted from the surface at steady state? 2) How long will it take to reach steady state? 3) What is the spatial distribution of the PFT emission at the surface?, and 4) What is the spatial and temporal atmospheric PFT concentration in an urban environment after emission from a leaking subsurface HPFF cable?

When tagged fluid leaks from an HPFF subsurface cable, a portion of the fluid will diffuse into the soil and a portion may pool, depending on the soil conditions and leak rate. The tagged fluid that has diffused into the soil will quickly provide a source of PFT vapor which will interact with the soil, e.g., some soils may have adsorption capacity for the PFT and possibly impede the transport of the PFT vapors to the surface. In general, however, it is expected that the overburden of soil will simply act as a transport restriction, i.e., providing numerous small paths for the PFT vapors to be transported to the air. These assumptions will be experimentally examined in this phase. Laboratory experiments and models pertaining to gaseous diffusion through soil will be used to determine and estimate the expected PFT emission rates above ground. Similarly, experiments will be performed to determine the potential adsorption capacity of various soil on various PFTs. Diffusion measurements for PFTs will be made in various soil columns. This phase will be culminated by a simulated trench experiment designed to verify the models and laboratory determined parameters and to develop the PFT sampling scenarios for the optimal detection of the emitted PFTs in an HPFF leak situation.

Phase 3: Development and Urban Field Test of the Leak Detection Protocol

The purpose of this phase is to find the best way to sample the urban air in order to detect and quantify the extent of a PFT-tagged HPFF cable leak buried under city streets. The feasibility of this experiment will be derived from Phase 1 and 2 experiments which will be useful to determining the potential capability and/or necessity of both above ground, i.e., atmosphere, PFT sampling and in ground or surface detection for determining the presence, location and magnitude of a fluid leak. The urban field experiment will make use of an existing Con Edison buried pipe, previously used for simulated leaks, located in a manhole near an actual cable. PFT tagged fluid will be leaked from this pipe at a detectable rate as determined from Phase 2, probably at a leak rate between 0.25 and 10 gal/h. A second PFT will be released into the air from the same manhole to provide a measure of the subsurface transport time and losses.

The performance of this Phase 3 task will occur in the following steps:

1. Preliminary site visit

2. Plan sampling protocol and perform background measurements

3. Procure, fabricate and test tracer release equipment

4. Perform field experiment
5. Interpret field data
6. Prepare Phase 4 protocol

Phase 4: Demonstrated Detection of an Actual (Intentional) Buried HPFF Cable Fluid Leak

The purpose of this phase is two-fold, namely (1) to develop the method of adding PFT to live feeder and verify that a homogeneous PFT/fluid mix can be created in a reasonable time, and (2) to test the strategy developed in Phase 3 for pinpointing HPFF cable fluid leak locations. Consequently, the tasks in this phase are:

1. Adding PFT to a cable
2. Detecting an intentional leak
3. Development of a final leak dilution protocol

2

PRELIMINARY LABORATORY EXPERIMENTS TO VERIFY FEASIBILITY

The experiments will be discussed according to phase and task description.

Phase 1: Solubility and Compatibility of PFTs in HPFF Cable Fluid

Perfluorocarbon tracers, PFTs, are a family of perfluorinated alkylsubstituted cycloalkane compounds developed as tracers for various applications by the Tracer Technology Center at Brookhaven National Laboratory. These PFTs are liquid at room temperature, totally non-toxic, thermally inert and have limited commercial use. A sample of the PFT physical properties is given in Table 2.1.

Table 2-1
PFT Characteristics

PFT[a]	Vapor Pressure at 25°C, atm	Background Ambient Conc., fL/L[b]	Liquid Density, g/mL	Molecular Weight	Boiling Pt., °C
PDCH	0.046	25.6	1.85	400	103
PMCH	0.14	3.6	1.79	350	73
PMCP	0.44	2.8	1.70	300	49
PDCB	0.50	0.35	1.67	300	45

[a] PDCH (perfluorodimethylcyclohexane), PMCH (perfluoromethylcyclohexane), and PMCP (Perfluoromethylcyclopentane) are available from Manchem, Inc., Princeton, NJ; PDCB (perfluorodimethylcyclobutane) is available from PCR Research Chemicals, Gainesville, FL.
[b] Concentrations Units: fL/L = femtoliters/liter (i.e., parts-per-quadrillion or 10^{-15}); pL/L = picoliters/liter (i.e., parts-per-trillion or 10^{-12}).

These PFTs also have very good dielectric properties, as given in Table 2.2.

Consequently, their introduction into the presently used HPFF cable fluid will not degrade the dielectric properties of the fluid. Conderc (1) explored the long-term compatibility of perfluorocyclobutane and tetrafluoromethane tracers used as tracers on HPFF cable properties. His results are given in Table 2.3, as taken from his paper. The two tracers, similar to the PFTs used by the Tracer Technology Center were concluded to be as compatible as Nitrogen, which has a long history of use in the field.

Table 2-2
Dielectric Properties of PDCB versus Con Edison Fluid

	PDCB	Con Edison Fluid
Breakdown Voltage, liquid KV (rms)[a]	42	35
Breakdown Voltage, vapor, KV (rms)[b]	32 (1 atm, 44°C) 55 (2 atm, 66°C)	
Resistivity[c], ohm/cm	$>4 \times 10^{14}$	$>1.0 \times 10^{14}$
Dielectric constant, at 10^2–10^5 Hz at 3 GHz	1.85 1.85	
Dissipation factor, at 10^2–10^5 Hz at 3 GHz	<0.00006 0.0041	>0.0005

[a] ASTM D 877, 0.1″ gap between planes, one atm, 25°C
[b] Modification of ASTM D 2477, 0.1″ gap, sphere to plane
[c] ASTM D 257

Table 2-3
AC Breakdown of Aged Cable Models (Aging Test 1)

Gas	Model No.	Breakdown Voltage (kV)	Breakdown Stress (kV/mm)	Average Breakdown Stress (kV/mm)
N_2	1	25.5	46.1	43.0
	2	22.0	39.8	
CF_4	3	25.0	45.2	42.8
	4	22.0	39.8	
	5	24.0	43.4	
$c\text{-}C_4F_8$	6	25.5	46.2	46.6
	7	26.2	47.4	
	8	25.5	46.2	

750 hr test, 120°, 70% low viscosity polybutene with 20% 5 mm SunXX;
Paper: Good quality kraft paper, 124 µm thick with d = 1.02 g/cc.
Tracer at 2.4 atm saturation.

Connsell and Boardman (2) examined the swelling of polypropylene by PFD, perfluorodecalin, and found it to be negligible. Polypropylene polymer is used in the newer PPP tape used to wrap cables for use in HPFF cable systems.

Previous work (3) indicated that the PFT should have a small solubility in the HPFF cable fluid in the 1–10% range. This work is summarized in Table 2.4.

Table 2-4
Solubility of PDCB in Various Oils

Solvent	T(°C)	Solubility of PDCB in wt%
Mineral oil	24	1
Paraffin oil	24	1
Naphthetic oil	24	3
Silicone oil	24	11
Transformer oil	24	5
Rohm and Haas Plexol 79	29	1.2
Monsanto OS-124	29	1.3
Sunoco 18H Bottoms	29	1.7
Union Carbide UCON SO-HB-5100	29	1.9
Mobil XRM 109F	29	2.5
Sinclair Turbo S1408	29	3.2
Esso 4040 Turbo Oil	29	6.3
DuPont PR 143	29	50.3

However, the actual HPFF cable fluids being used have not been examined previously for PFT solubility and therefore were investigated in this program. Four samples of HPFF cable fluids were received from Con Edison for use in the determination of their PFT solubility and other properties. They are summarized in Table 2.5, along with their measured density.

Table 2-5
HPFF Cable Fluid and Their Measured Density at 25°C

Fluid	Density (gm/cc)
71th Street FDR Feeder	0.78
51th Street FDR Feeder	0.79
New Low Viscosity Polybutene (NLVP)	0.82
Sun No. 6	0.80

The solubility of two PFTs, PMCH and m-PDCH (see Table 2.1 for abbreviations) was determined by three various techniques:

a) A gas chromatographic technique which is an efficient reliable technique allowing for solubility determination at temperatures other than room temperature;

b) An infrared (IR) spectroscopic technique for verification;

c) A visual technique, examining how much PFT would dissolve into a cable fluid solubility by adding small aliquots until no more dissolved.

The gas chromatographic technique for solubility determination is based on two requirements: 1) the expected solubility must be less than 10% by weight; and 2) the solvent, in this case the cable fluid, must be relatively non-volatile, which is true of HPFF cable fluids. The chromatographic technique is then based on preparing the cable fluid as the liquid phase on an inert support, a diatomaceous earth. This was prepared by dissolving a measured amount of cable fluid in an inert solvent, hexane, adding the diatomaceous earth and evaporating the solvent to form a 10% cable fluid on diatomaceous earth mixture. The resulting cable fluid-earth mixture is packed into a 6′ x 1/8″ O.D. stainless steel column and inserted into an HP-5890A gas chromatograph with a thermal conductivity detector. Each PFT under examination is chromatographed and the specific retention volume, V, is calculated from

$$V_g = \frac{f(t_r - t_o)}{m} \qquad \text{(eq. 1)}$$

in which t is the retention time of the specific PFT on the specific cable fluid, t is the dead-volume transit time, f is the flow rate of carrier gas through the cable fluid-diatomaceous earth column and m is the total mass of cable fluid on the column. Once the specific retention volume, V, has been calculated, the solubility can be calculated from

$$\text{S (gm of PFT per liter of cable oil)} = \frac{100\,P_o(\text{atm})M_w d(\text{gm/cc})V_g(\text{cc/gm})}{RT} \qquad \text{(eq. 2)}$$

in which P is the vapor pressure of the PFT; M is its molecular weight; d, the density of the cable fluid; V, the specific retention volume; R, the gas constant, 82.06 cc-atm/K-mole; and T, the absolute temperature of the measurement. Eq. (2) can be best understood after a discussion of the Henry's law constant which will follow. The resulting solubilities, S, are tabulated in Table 2.6.

Table 2-6
Solubility (gm/l) of PFT in Various Cable Fluids as a Function of Temperature

t (°C)	FDR 71	FDR 51	NLVP Fluid	Sun No. 6
PMCH				
40	51.8	46.2	50.4	48.5
50	56.1	50.0	57.3	49.4
60	53.7	52.7	60.1	51.0
70	55.0	53.0	63.8	52.7
80			67.0	
PDCH				
30	38.6	44.7	46.1	52.2
40	41.9	49.2	45.0	46.8
50	43.8	51.4	47.4	48.8
60	45.4	52.4	48.7	52.2
70	46.6	53.9	53.0	50.8
80	48.6	59.5	54.6	48.2
90				55.7
100				48.7

The above solubilities can be converted into approximate weight percent by dividing by eight. As can be seen from the above results, the PFTs are amply soluble (4.5 to 6% by weight) in the cable fluid, far in excess of the nominal 0.1%; as specified as a minimum solubility.

The solubility of the PFTs has been verified by IR spectrometry. A solution of FDR 51 cable fluid was saturated with PDCH and 3 standards of 1%,2%, and 3% PDCH in FDR 51 were prepared. The IR spectra of the four solutions were recorded by a Nicolet 7100 Fourier transform infrared spectrometer(FT-IR) and two peaks of PDCH were chosen for the analysis. The results are given in Table 2.7.

Table 2-7
PDCH Peak Analyses

	Measured Peak Area at 24°C	
Concentration (% PDCH) in FDR 51	**Peak No. 1**	**Peak No. 2**
1%	1.95	1.23
2%	3.73	2.61
3%	5.78	4.05
Saturated Solution	8.39	6.00

From these measurements a solubility of 34.6 g PDCH/liter of cable fluid is calculated which is in reasonable agreement with the results obtained by gas chromatography in Table 2.6.

A third, less accurate, verification of these solubilities has been obtained by visually observing that 10 mL of FDR 51 cable fluid can dissolve 200–250 µL of PTCH (perfluorotrimethylcyclohexane) at room temperature, which is equivalent to a PTCH solubility of 34–44 gm PTCH/liter of cable fluid.

Related to the solubility (for solubilities below 10%) is the Henry's law coefficient, H*, from which the equilibrium partial vapor pressure of PFT over the cable fluid can be calculated. It has been shown above that it is possible to prepare cable fluids with up to 5% PFT dissolved in them. Once this tagged fluid is leaked from HPFF cable line, the dissolved PFT will have a tendency to escape the fluid phase into the surrounding air spaces. The measure of this tendency is the equilibrium PFT partial pressure, P, over the cable fluid. This is a necessary quantity which is needed in the further transport modeling calculations since this is the concentration of the PFT above the fluid given a certain percentage of PFT in the fluid.

The partial pressure, P, of a solute (i.e., the PFT) over a solvent(i.e., the cable fluids) is conventionally described by two limiting laws: Raoult's law [solute (PFT) concentration near 100%, or more precisely, solute mole fraction nearing one] and Henry's law [solute (PFT) concentration near 0%, or solute mole fraction nearing zero]. Raoult's law is the "easier" of the limiting laws, i.e.,

$$P_i = P_o X_i \qquad \text{(eq. 3)}$$

since the proportionality constant between the solute partial pressure and solute mole fraction is simply the solute vapor pressure, P. Henry's law is

$$P_i = H^* X_i \qquad \text{(eq. 4)}$$

in which H* is an experimentally determined constant, almost impossible to predict. This is due to the very non-ideal situations which arise as $X \rightarrow 0$, where Henry's law takes effect. Figure 2.1 illustrates the transition between Raoult's law and Henry's law and a "real measurement", depicted by a heavy line. Another important quantity is γ, defined as the ratio of H* to Po, for most solute/solvent systems. If $\gamma\infty = 1$, then Raoult's law fully describes the partial pressure. This is the case if the solute and solvent are very similar, e.g., hexane in heptane. But if the solute is very dissimilar from the solvent, then $\gamma\infty$ can range up to the thousands, as is seen in Table 2.8, a selection of $\gamma\infty$ for various systems (15). In the case of a PFT solute in a hydrocarbon solvent, we can expect to be large, which must be experimentally measured.

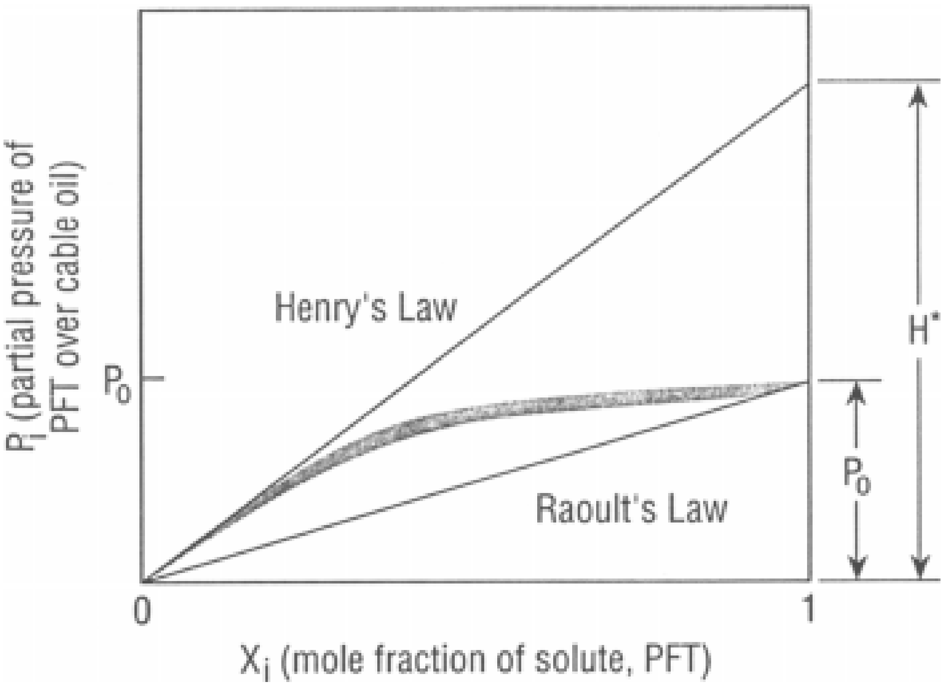


Figure 2-1
The transition (gray shaded line) from Henry's law to Raoult's law for a real solute in a solvent. P_o is the solute vapor pressure and H* is the Henry's law coefficient.

Table 2-8
Infinite Dilution Activity Coefficients, $\gamma\infty = H^*/P_o$

	Solvent			
Solute	**H_2O**	**Benzene**	**Heptane**	**CH_3CN**
CCl_4	6300	1.13	1.20	6.67
$CHCl_3$	1000	0.81	1.47	1.49
CH_2Cl_2	370	0.92	2.20	—
CH_3CN	—	3.5	30	—
CH3OH	—	—	51	—
Toluene	4500	—	—	—
Hexane	—	—	1.00	—

The best way to measure or equivalently H*, is by gas-liquid chromatography (GLC). In this case, the solute is the injected sample and the solvent is the liquid phase. Standard GLC theory (14) expresses this as

$$\gamma\infty = \frac{RT}{P_o V_g M} \qquad \text{(eq. 6)}$$

in which P is solute vapor pressure, M is the solvent molecular weight, V the specific retention volume of the solute and R the gas constant. Consequently, to measure, a column is prepared with the solvent as the liquid phase and the solute chromatographed to obtain V. That is, the cable fluid as the liquid phase with the PFT being chromatographed. However, there is a small problem here; the cable fluid molecular weight, M, which is unknown since the fluid probably is a mixture. But, if we realize that what is wanted is the Henry's law coefficient, this problem is overcome, i.e.,

$$\begin{gathered} H(M - atm^{-1}) = \frac{d(gm/cc)V_g(cc/gm)}{RT} \\ (R = .082061 - atm/{}^\circ K\ mole) \end{gathered} \qquad \text{(eq. 7)}$$

and d is the cable fluid density. This form of Henry's law

$$P_i = (1/H)[X] \qquad \text{(eq. 8)}$$

requires the molarity of the PFT in the cable fluid, again not a convenient unit. A final form

$$P_i = \tilde{H}(wt\%) \qquad \text{(eq. 9)}$$

in which the PFT concentration is expressed as weight percent (wt%), defines H as

$$\begin{aligned} \tilde{H} &= (10\,M_w H(M - atm^{-1}))^{-1} \\ &= \frac{RT}{10\,m_w d V_g} \end{aligned} \qquad \text{(eq. 10)}$$

in which M is the solute (PFT) molecular weight.

Consequently, from a measurement of the specific retention volume, V, one can calculate these wt% Henry's law coefficients, and these are tabulated in Table 2.9.

Table 2-9
Henry's Law Coefficients in Fluid Oil (atm/wt%)

Fluid				
PMCH				
t (°C)	**FDR 71**	**FDR 51**	**NLVP Oil**	**Sun No. 6**
40	5.1×10^{-4}	5.8×10^{-4}	5.3×10^{-4}	5.5×10^{-6}
50	7.2×10^{-4}	8.1×10^{-4}	7.0×10^{-4}	8.1×10^{-4}
60	1.1×10^{-3}	1.1×10^{-3}	9.4×10^{-4}	1.1×10^{-3}
70	1.5×10^{-3}	1.5×10^{-3}	1.3×10^{-3}	1.5×10^{-3}
80	—	—	1.7×10^{-3}	—
PDCH				
30	1.7×10^{-4}	1.5×10^{-4}	1.4×10^{-4}	1.2×10^{-4}
40	2.5×10^{-4}	2.1×10^{-4}	2.3×10^{-4}	2.2×10^{-4}
50	3.6×10^{-4}	3.1×10^{-4}	3.4×10^{-4}	3.3×10^{-4}
60	5.2×10^{-4}	4.6×10^{-4}	4.9×10^{-4}	4.6×10^{-4}
70	7.4×10^{-4}	6.4×10^{-4}	6.5×10^{-4}	6.8×10^{-4}
80	1.0×10^{-3}	8.3×10^{-4}	9.1×10^{-4}	1.0×10^{-3}
90	—	1.2×10^{-3}	1.2×10^{-3}	1.2×10^{-3}
100	—	1.6×10^{-3}	1.8×10^{-3}	1.9×10^{-3}

Consequently, to obtain the partial pressure of the tracer above the cable fluid, simply multiply the weight percentage PFT concentration in the fluid by the appropriate wt% Henry's law constant to get the partial pressure in atmospheres.

The solubilities can be calculated by understanding that a completely saturated solution occurs when the partial pressure is equal to the vapor pressure. From this definition one calculates (and adjusting for units)

$$S(\text{gm}/1) = P_o(\text{atm}) M_w H(M - \text{atm}^{-1}) \qquad \text{(eq. 11)}$$

making use of Eq. (7) which expresses H(M-atm-1) in terms of the specific retention volume we get Eq. (2) with appropriate unit conversion factors.

Task 1.2 Literature Review of PFT Compatibility

During the course of using PFTs as a leak detection method for HPFF, the PFT will be introduced into the length of HPFF cable line, most likely as a 0.1% or less PFT solution in fluid. The PFT will potentially then be in contact with other materials which are part of the transmission line. BNL had requested that Con Edison supply a list of materials, especially elastomeric materials used in seals and pumps. Table 2.10 gives the list supplied by Con Edison (4) to BNL.

Table 2-10
Elastomeric Materials used in HPFF Transmission Lines

Location	Material
Needle Valves	Buna N “O” rings
Insulating Coupling	Buna N “O” rings
Ball Valves	Teflon seats, Viton seals
Check Valves	Flexstallic gasket, stainless steel, asbestos, or teflon
Differential Pressure Switch	Viton “O” rings
Relief Valve	Viton “O” rings
Filter	Buna N “O” ring
Pumps	Ball bearing seals, Buna N, Viton, Silicone, Tungsten
Gauges	Copper Tubes

Interactions of these elastomeric seals, etc., with PFTs have been explored by the PFT manufacturers and Table 2.11 gives a typical listing. Note that: (1) there is no effect on PFT on Buna N under the extreme experimental conditions used in the study tabulated in Table 2.10, and (2) there is an effect of PFT on Viton, and correspondingly Teflon (of a similar chemical composition).

The interaction manifests itself as a saturation of the Viton by PFT but only if the Viton is in contact with 100% PFT. The situation is different with a 0.1% PFT solution in HPFF, then the earlier experiments performed at BNL on the change in tensile strength and hardness for PFT saturated Viton are given in Table 2.12 as adapted from reference 5. A negligible change in these parameters is shown. Consequently, if pure PFT were contacted to these Viton elastomeric seals and seats, one could expect after a sufficient amount of time, the Viton and Teflon to saturate to 5 to 10% with PFT. However, to accomplish this saturation requires diffusion of the PFT into the Viton and the rate of diffusion of PFT into Viton is extremely small, i.e., D # 10^{-10} cm/sec; consequently, since the time required to diffuse a distance x into an elastomer is

$$t \approx x^2/D \qquad \text{(eq. 12)}$$

Thus, to diffuse 0.1 cm into the Viton elastomer would require 10^8 sec or 3 years of time. Now, if there is only 0.1 to 1% of PFT in the cable fluid, then the maximum saturation of PFT into Viton from the fluid is

$$X_{PFT}^{Viton} = K_D X_{PFT}^{oil} \qquad \text{(eq. 13)}$$

in which X is the equilibrium mole fraction of PFT in the Viton in contact with tagged fluid, KD is the Nernst Distribution constant for this system, and X is the mole fraction of PFT in the cable fluid. Now the Nernst coefficient, KD can be expressed as

$$K_D \left(H_{PFT}^{oil} / H_{PFT}^{Viton} \right) \qquad \text{(eq. 14)}$$

i.e., a ratio of the Henry's law coefficient for PFT in fluid (H) to PFT in Viton. Nonetheless, these are quantities which have to be measured in the laboratory before this estimate can be made, i.e., Eq. (13). However, this is an equilibrium and it is kinetics, i.e., Eq. (12) which will control the rate of diffusion of PFT into the Viton from the tagged cable fluid, and it would take several years of constant contact before the Viton would start to become saturated according to Eq. (13). Consequently, it can be expected that the effect of PFT tagged cable fluid should be negligible on the elastomeric seals and seats present in HPFF cable transmission lines.

Table 2-11
Effect of PDCB on Elastomers*

		Length Change[1], (%)		Weight Change[2], (%)			
Elastomer	**Test Cond.**	**Temp.**	**Final**	**Temp.**	**Final**	**Extractibles[3], (%)**	
“Adiprene” C	A	<0.1	<0.1	<0.1	<0.1	<0.1	polyurethane
Urethane Rubber	B	<0.1	-0.3	0.3	-0.2	0.2	
“Adiprene” L	A	0.2	0.2	0.1	<0.1	0.2	
Urethane Rubber	B	<0.1	-0.4	0.8	<0.1	<0.1	
Buna N	A	<0.1	<0.1	<0.1	<0.1	0.2	
	B	0 .6	0.3	0.4	<0.1	0.4	
Buna S	A	1.0	<0.1	<0.1	<0.1	0.1	
	B	0.8	0.6	3.7	0.5	0.2	
Butyl	A	1.2	-0.3	0.1	0.2	0.6	
	B	0.5	0.7	4.7	1.3	0.6	
“Hypalon” 40	A	0.3	<0.1	-0.2	-0.2	0.6	
Synthetic Rubber	B	0.7	0.5	1.6	<0.1	0.6	
Natural Rubber	A	<0.1	<0.1	0.4	<0.1	0.1	
	B	0.4	<0.1	3.3	<0.1	0.2	
Neoprene W	A	0.2	- 0.4	-0.5	-0.6	0.7	
	B	0.5	0.3	1.0	-0.2	0.4	
“Nordel” Hydro-	A	-0.1	-0.5	5.2	-0.2	0.2	
carbon Rubber	B	0.8	0.2	4.3	-0.3	0.3	ethylene
Silicone Rubber	A	1.6	<0.1	6.5	<0.1	0.1	
(SE-361)	B	0.6	0.3	1.0	0.2	0.1	
“Thiokol” FA	A	<0. 1	0.1	<0.1	<0.1	<0.1	
Polysulfide	B	0.4	0.3	<0.1	-0.2	0.1	
“Vi ton” A	A	4.3	0.4	3.6	2.0	<0.1	polysulfide
Fluoroelastomer	B	1.9	-0.5	8.7	7.9	<0.1	

*Test Conditions: A) 7 days at 113°F (45°C), 15.2 psia (1.08 atm); B) 7 days at 212°F (100°C), 74 psia (5 atm).

[1] Determined by measuring the length of the elastomer: a) Before immersion in the liquid; b) Just prior to removing it from the liquid at the end of the liquid immersion time; c) After 21 days of drying in air at 75°F.

[2] Determined by weighing the elastomer: a) Before immersion in the liquid; b) Immediately after removal from the liquid at the end of the immersion time when the surface first appeared liquid free, etc.; c) After 21 days of drying in air at 75°F.

[3] Determined by evaporating the liquid from the high-boiling residue in a tared vial on a hot plate.

Table 2-12
Change in Tensile Strength and Hardness PDCB Solubilized Elastomers

Elastomeric Material	Taggant	Percent Solubilized	Tensile Strength (psi)	Hardness (Durometer A)
Viton E60-C	none	none	1190 ± 130	69.7 ± 4.7
	PDCB	0.36	1140 ± 60	66.0 ± 0.6
	PDCB	1.0	1328 ± 26	69.7 ± 0.6
	PDCB	2.8	1230 ± 60	67.3 ± 0.6

Phase 2: Effect of Soil Interactions and Atmospheric Transport on PFT Vapor Detection

This phase is concerned with (1) determining what physical impediments the overburden of soil would provide to a PFT emitted from tagged HPFF cable fluid, and (2) the spatial and temporal behavior of the PFT vapor once it has been transported to the surface and subject to urban atmospheric transport and dispersion.

Task 2.1 PFT Adsorption and Transport in Sand

As a leak develops in a PFT-tagged HPFF cable, the tagged fluid will emit PFT to the surrounding sand-filled environment. Two factors will influence the rate of transport of the PFT through the sand to the surface:

(a) Physical adsorption of the PFT onto the sand. If the PFT is partially or totally adsorbed or retained by the sand, then this could manifest itself by total “loss” of the emitted PFT by the sand or by delayed transport of PFT through sand, i.e., if the PFT is partially retained, this will only produces a delay in transport through the sand; and

(b) Fickian diffusion will govern the transport rate of PFT to the surface (neglecting the above mentioned partial physical adsorption effects). The PFT will diffuse through the void spaces of the overburden sand by molecular diffusion. If there is any net flow of soil gas, upward to the surface, this will only serve to increase the rate of PFT transport to the surface. However, this is an unknown factor, consequently we will only consider molecular diffusion, which is the slowest transport process and should provide a realistic lower limit to the rate of transport.

Experiments which determined the important parameters governing the above mentioned processes will be detailed as follows:

(1) PFT adsorption on soil. In order to ascertain this potential delaying effect, an 8′ x 1/4″ O.D. column of sand, used as fill over the HPFF cable, was prepared. Humidified helium was flowed through the thermostated sand column (placed in the thermostated oven of the HP-5890 gas chromatograph) at a flow of 20 cc/min. The helium was humidified by flowing it through a column of Nafion membrane, contained in a thermostated beaker of water. Nafion membrane has the selective property of transporting water vapor across itself and provides an effective, reliable method of humidifying gas streams. The temperature of the beaker with the Nafion was varied independently of the sand to provide a range of relative humidities. The reason for humidifying the helium gas stream was to emulate subsurface humidity conditions which are almost always near 100% relative humidity. Experiments were performed at lower humidities and the resulting effects of this will be discussed as follows. The humidified helium requires at least 2 to 3 hours to equilibrate the sand column, i.e., to reach an equilibrium level of relative humidity within the sand column. Once equilibrated, a small injection of air was inserted at the head of the column by a microliter syringe. Its arrival at the outlet of the column was detected by the thermal conductivity detector of the HP-5890A gas chromatograph. The time delay between the air injection at the head of the column and its detection at the outlet represents the transport deadtime, i.e., air is inert and its transport time is not effected by any physical adsorption effects for sand at these studied temperatures. Subsequent syringe injections of small amounts of PFT vapors were made and their transit times were similarly measured and compared to that for air. If there is any physical or chemical, i.e., reactions, adsorption occurring, then the PFT transit time should be greater than that for inert air. Any possible delay due to physical adsorption in the humidified column is caused by reversible adsorption and desorption of PFT on the wetted sand surfaces.

Five sets of relative humidities and temperatures were examined and the results are given in Table 2.13. Note that (1) when the relative humidity is high the delay due to adsorption becomes negligible. This is due to the negligible solubility of PFTs in water, i.e., PFTs are not reversibly adsorbed and desorbed into wetted surfaces since they do not dissolve into these wetted surfaces; and (2) as the relative humidity drops, to unrealistic subsurface conditions, the amount of delay starts to increase. This is because the wetted surface area of the sand particles is being decreased, exposing an increased amount of dry sand particle surface which can reversibly adsorb and desorb PFT. As the helium carrier gas becomes bone dry, there remains no wetted surface area on the sand particles; just bare surface which, due to the large surface area of sand, delays the transport of PFT. However, this bone dry scenario is a totally nonrealistic subsurface scenario.

Table 2-13
PFT Delay Times in Sand Due to Physical Adsorption

		Δt, Delay Time, sec			
Sand Column t,°C	**Relative Humidity, %**	**PMCP**	**PMCH**	**PDCH**	**Air Transit Dead-Time, sec**
30	63	0.60	1.20	3.24	38.8
30	15.6	1.68	4.8	14.82	39.0
30	0, bone dry	18.5	60.1	—	38.8
45	100	0.12	0.24	1.20	34.8
60	19	2.2	4.1	10.1	35.8

Due to the high relative humidity of subsurface sand and soil environments, we can expect none or negligible delay in the transport of the PFTs to the surface due to PFT adsorption.

(2) PFT diffusion through sand. As a leak springs in the HPFF cable, the emitted PFT will diffuse through the sand, eventually to the surface, to be detected by the PFT sampling systems. Consequently, a necessary physical parameter needed to model this transport is the Fickian Diffusion constants for various PFTs in air and in sand void spaces.

A convenient method for measuring diffusion constants is the arrested flow gas chromatographic technique (AFGC), which shall be detailed as follows (6). Consider a gas chromatographic column without any column packing, i.e., an empty column. Now if we inject a small amount of PFT, at the injector, the detector should see a peak which has been broadened by diffusion only. A convenient measure of this broadening is the variance which is

$$\sigma^2 = \frac{W^2 1/2}{5.545} \qquad \text{(eq. 15)}$$

where W1/2 is the width of the peak at half-height. From the variance we can calculate the height equivalent theoretical plate (HETP) by

$$\mathrm{HETP} = \frac{L\sigma^2}{t^2} \qquad \text{(eq. 16)}$$

where L = column length, and t = retention time. Standard chromatographic theory relates the HETP to the molecular diffusion constant by

$$\mathrm{HETP} = \frac{2D}{v} + \frac{r^2 v}{24D} \qquad \text{(eq. 17)}$$

in which D is the diffusion constant, v is the carrier gas velocity and r is the column radius. Now at low velocities, v, which is experimentally achievable,

$$\mathrm{HETP} \approx \frac{2D}{v} \qquad \text{(eq. 18)}$$

i.e., the first term predominates. This, however, is not a convenient experimental method. Instead, flow the tracer injected carrier gas, until the injected slug is in the middle of the column, and arrest the flow, thus letting the tracer diffuse further, and further broadening the peak. After a certain “arrest” time, restart the flow and measure the variance. Theory states that a plot of the variance versus the arrest time, t, should be a straight line with a slope of 2D/v, i.e.,

$$\frac{d}{dt}\sigma^2 = 2\frac{D}{v^2} \qquad \text{(eq. 19)}$$

hence, a convenient method for the determination of the PFT diffusion coefficients in various carrier gases.

However, the above analysis is for determining diffusion constants of PFT in air, or any other carrier gas. Park et al. (7) have extended the AFGC technique to the determination of diffusion constants of gas in the void spaces of packed system, such as sand. This was accomplished by noting that this void space diffusion constant, De, satisfies the modified diffusion equation,

$$e\frac{\partial C}{\partial t} = De\,\nabla^2 C \qquad \text{(eq. 20)}$$

However, this is equivalent to the standard diffusion equation

$$\frac{\partial C}{\partial t} = D\,\nabla^2 C \qquad \text{(eq. 21)}$$

if we call De/e, an effective void space diffusion constant. Consequently, the above AFGC methodology can be used, and for packed system in which its De/e is determined by

$$\frac{d}{dt}\sigma^2 = 2\frac{(D/e)}{v^2} \qquad \text{(eq. 22)}$$

In this equation, e is the total porosity of the packed column which is related to, the void fraction and, the particle porosity by

$$e = \alpha + \beta(1 - \alpha) \qquad \text{(eq. 23)}$$

Typical values for three parameters are given in Table 2.14, as taken from reference 7.

Table 2-14
Typical Values for Three Parameters

Material (packed columns)	α, void fraction	β, particle porosity	total porosity
Varian Firebrick	0.4	.65	.78
99% Al_2O_3	0.38	.75	.84
Common Firebrick	0.45	.24	.58
γ -alumina	0.38	.54	.72

As a consequence of this equivalence between D and (De/e), the same AFGC technique can be used to measure both the free-air and packed sand system. The sand was the same used in the PFT adsorption experiment, i.e., a 7′ x 1/4″ column of construction sand. Delay times up to 20 minutes were needed in some instance for a reliable measurement of De/e. An example is shown in Figure 2.2 for the PFT PMCH in 100% humidified sand at 45°C. The abscissa is the arrest time and the ordinate is the squared half-width of the broadened peak. The slope is then proportional to (De/e). Note the AFGC technique generates relatively precise values of (De/e) when compared to other more classical methods of determining (De/e). The experimental conditions and results are as given in Table 2.15. The last column is an empirical estimation of the gas-phase diffusion constant; these values are high as expected for the large disparity in the molecular weights of PMCH and Nitrogen or Helium. In one instance, the flow rate was halved to verify that turbulent flow was not affecting the experimental conditions and indeed turbulent flow is negligible as shown by the equal values of the determined

De/e in the first two rows in Table 2.15. As can be seen in rows 5 and 6, there is a negligible effect of relative humidity on the measured effective (De/e) diffusion rate, which is reasonable since 100% relative humidity is equivalent to a 3% water content at 25°C.

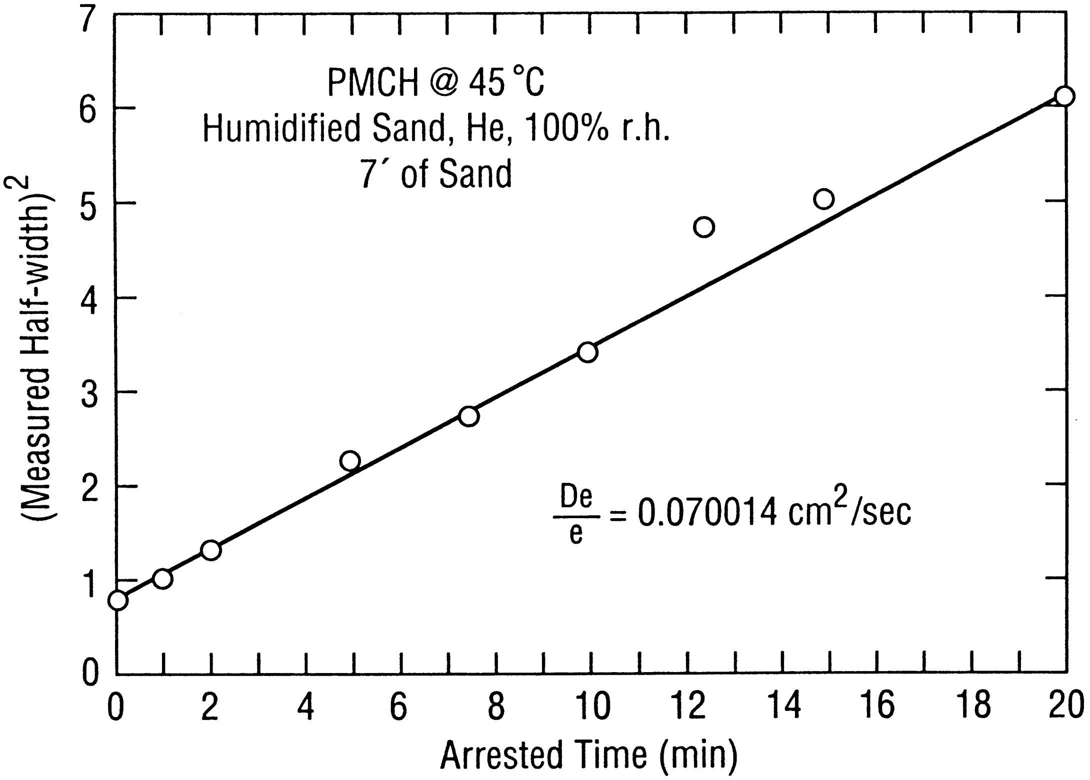


Figure 2-2
Determination of the gaseous diffusion constant by the AFGC (Arrested Flow Gas Chromatographic) technique. The least squares fitted slope is the diffusion constant.

Table 2-15
Results of AFGC Effective Diffusion Constant Determinations

Column	Tracer	T (°C)	Gas Flow (cc/min)	Carrier Gas, Humidity	De/e (cm^2/sec)	Dg Empirical
7' sand	PMCH	30	25	He, 60% r.h.	0.074 ± .003	—
7' sand	PMCH	30	12	He, 60% r.h.	0.075 ± .0010	—
7' sand	PMCH	45	25	He, 100% r.h.	0.0700 ± .0032	—
7' sand	PDCH	30	25	He, 60% r.h.	0.0750 ± .0026	—
empty	PMCH	30	25	He, 0% r.h.	0.172 ± .011[a]	0.29
empty	PMCH	30	24	He, 60% r.h.	0.172 ± .005	—
empty	PMCH	45	24	He, 100% r.h.	0.172 ± .0023	—
empty	PMCH	30	25	N_2, 0% r.h.	0.0499 ± .0025	0.066

[a] For the empty tube, this is then Dg, the gas-phase diffusion constant.

Due to experimental difficulties with the insensitivity of the thermal conductivity detector to Nitrogen, it was impossible to measure (De/e) for the PFT with Nitrogen (or equivalently air) but rather only with Helium. Consequently, we must calculate the (De/e) for PFT in Nitrogen from the results taken with Helium. This can be conveniently calculated by scaling (8), i.e.,

$$\frac{D_{PFT}\ \text{in}\ N_2}{D_{PFT}\ \text{in He}} = \frac{(De/e)_{PFT}\ \text{in}\ N_2}{(De/e)_{PFT}\ \text{in He}} \qquad \text{(eq. 24)}$$

and the ratio of the left hand side was measured by the AFGC technique, its value is (.0499/.172). Consequently, one can calculate (De/e)PFT in Nitrogen as 0.022 cm/sec, independent of tracer type and humidity level.

Task 2.2 Soil Diffusion Modeling

The goal of this task is to develop models for the diffusion of emitted PFT from subsurface HPFF fluid leaks to the surface. The resulting models will then be used in interpreting the results of Task 2.3, Field Test of Models. Depending on the results, the models will be adjusted and then used in developing PFT detection scenarios in later tasks of this program. Two simple geometries will be considered: (1) diffusion from an infinite plane held at one PFT concentration to a second infinite plane held at a second

PFT concentration and (2) diffusion from the surface of one sphere to the surface of a second concentric sphere.

1. Diffusion from one plane sheet to another plane sheet.

In this simple diffusion model we assume that the pool of leaked PFT-tagged fluid forms a sheet of infinite size emitting PFT at concentration C . The PFT diffuses through the soil overburden of depth L, at a rate controlled with diffusion constant De/e. The surface has PFT concentration of CL. This modeling scenario is displayed in Figure 2.3a. The steady-state solution for this model as given by Crank (9), for the PFT concentration profile through the soil is

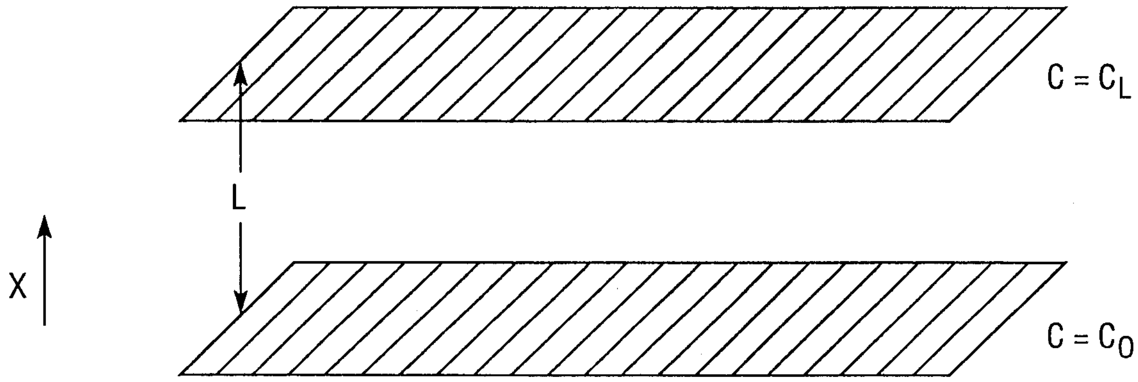
$$C = \frac{(C_L - C_o)}{L} + C_o \qquad \text{(eq. 25)}$$

in which x is the positive distance upward from the leak to the surface at x=L. The steady-state flux, J, is

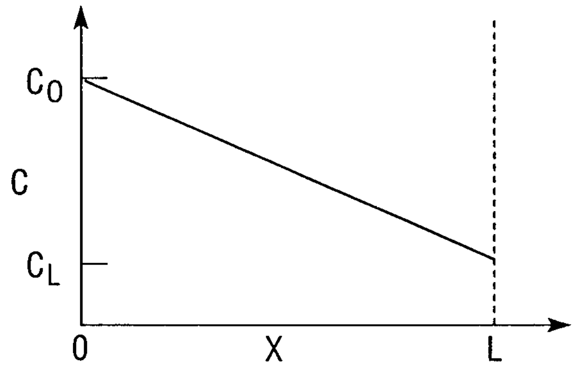
$$J = D\frac{dC}{dx} = \frac{D(C_o - C_L)}{L} \qquad \text{(eq. 26)}$$

Notice that the concentration profile is linear and that the flux is constant, as shown in Figures 2.3b and 2.3c. This solution makes sense from the standpoint of mass conservation. For example, let L = 100 cm and consider two planes, one drawn at 20 cm and the second at 30 cm. At steady-state, the flux (= mass/time) in at 20 cm must equal the flux out at 30 cm. Clearly, this is true since F = constant, and since F = -D(dC/dx) in one dimension, C must have a linear profile.

(a) One dimensional plate sheet model



(b) Concentration profile through soil overburden



(c) Flux profile through soil overburden

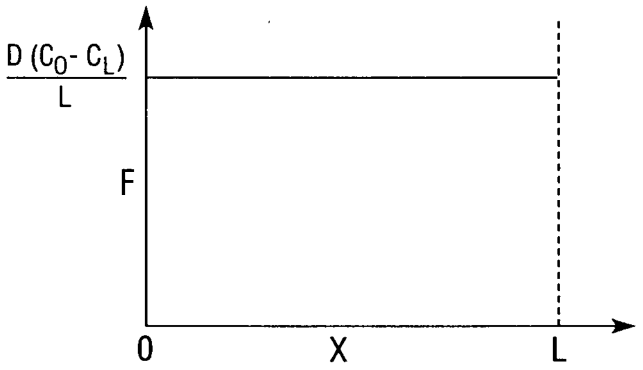


Figure 2-3
a) One dimensional plate sheet modeling scenario; b) Resulting concentration profile through the soil overburden; c) Resulting tracer flux through the soil overburden

Now it is intuitive that CL, the concentration at the surface, is not exactly zero because of the finite distance necessary to mix the PFT into the atmosphere. To be conservative, let us assume that for all practical purposes, the tracer concentration is zero at 10 cm above the surface, i.e., it has been fully removed by turbulent mixing of the atmosphere above the surface. According to conservation of mass, the mass leaving the surface at x = L must equal the mass or flux leaving a surface at x = L + 10 cm or 10 cm above the surface. Let D_s be the diffusion coefficient in the soil and D_{eddy} be the eddy diffusion coefficient in the air at the surface, then the flux at the surface is equal to the flux at 10 cm above surface or

$$-D_s \left.\frac{dc}{dx}\right|_{x+L} = -D_{eddy} \left.\frac{dc}{dx}\right|_{x=L+10} \qquad \text{(eq. 27)}$$

or equivalently,

$$\frac{D_s(C_o - C_L)}{L} = \frac{D_{eddy} C_L}{10} \qquad \text{(eq. 28)}$$

Now typically, Deddy /Ds is the order of 10,000 then we can calculate C /Cl as the order of 1,000,000. Therefore, the concentration at the ground surface is 10^6 times smaller than the concentration at the source, i.e., essentially zero.

The above discussion is for the steady-state solution, i.e., everything is equilibrated, the emission rates are equilibrated, constant. The initial solution, i.e., from the start of the fluid leak at t=0, as given by Crank(9) is

$$C(t) = C_o\left(1 - \frac{X}{L}\right) - \frac{2}{\pi}\sum_{n=1}^{\infty} \frac{C_o}{n} \sin\left(\frac{n\pi x}{L}\right) \exp\left(\frac{-Dn^2\pi^2 t}{L^2}\right) \qquad \text{(eq. 29)}$$

which as t becomes larger yields the steady-state solution, Eq. (25). The corresponding non-steady state flux is

$$J = -D\frac{dc}{dx} = \frac{DC_o}{L}\left(1 + 2\sum_{n=1}^{\infty} \cos\left(\frac{n\pi x}{L}\right) \exp\left(\frac{-Dn^2\pi^2 t}{L^2}\right)\right) \qquad \text{(eq. 30)}$$

which also reduces to the steady-state flux as t becomes larger. The buildup of PFT flux at surface (x=L) is then

$$J = \frac{DC_o}{L}\left(1 + 2\sum_{n=1}^{\infty}(-1)^n \exp\left(\frac{-Dn^2\pi^2 t}{L^2}\right)\right) \qquad \text{(eq. 31)}$$

2. Diffusion from one sphere to a larger sphere.

Here consider the case where the tracer is diffusing from one sphere with radius = r into another concentric sphere with radius = L, as shown in Figure 2.4a. The steady-state solution, as given by Crank for this modeling scenario for the concentration profile is

$$C = \frac{C_o r_o}{l - r_o}\left(\frac{L}{r} - 1\right) \qquad \text{(eq. 32)}$$

and for the concentration flux profile is

$$J = -D\frac{dc}{dr} = \frac{FDC_o r_o L}{(L - r_o)r^2} \qquad \text{(eq. 33)}$$

For the case where r << L, these equations reduce to:

$$C = C_o r_o\left(\frac{1}{r} - \frac{1}{L}\right) \qquad \text{(32a)}$$

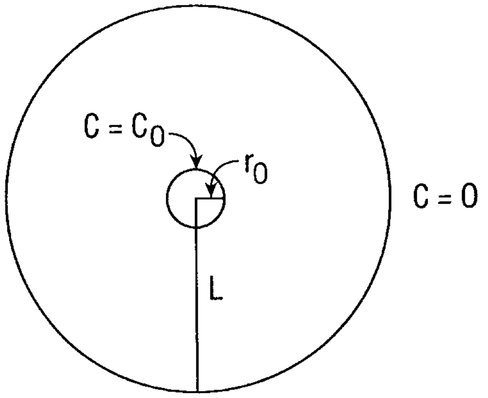
$$J = \frac{DC_o r_o}{r^2} \qquad \text{(33a)}$$

The concentration and flux profiles are shown in Figures 2.4b and 2.4c, respectively, in comparison to the infinite sheet modeling scenario.

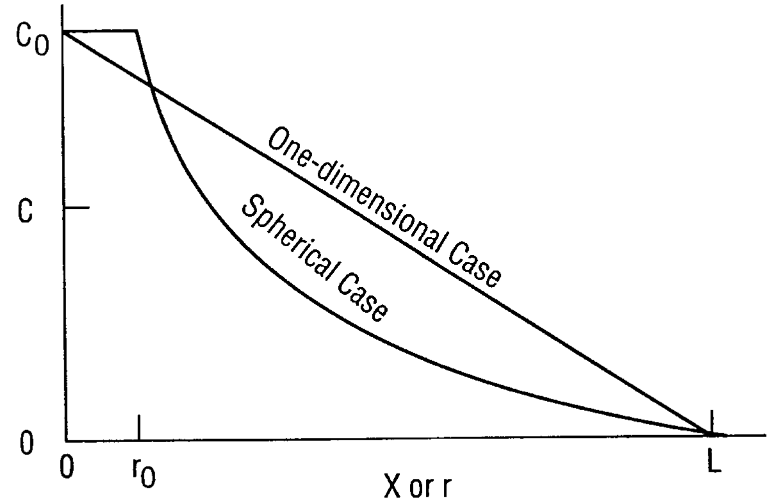
Notice that the flux for the spherical case is not constant. However, if we consider the flux through concentric spheres, we do get the same flux since the surface area of a sphere is proportional to r^2. These terms cancel and we are left with the flux equal to a constant. Thus, mass balance is satisfied.

Based on these two geometries, it can be expected that the PFT concentration and PFT flux profiles on the surface of the trench to look like that in Figure 2.5, with the concentration profile just below the surface falling off as 1/x and the flux falling off as $1/x^2$.

(a) Spherical geometry



(b) Concentration profile from release to surface



(c) Flux profile

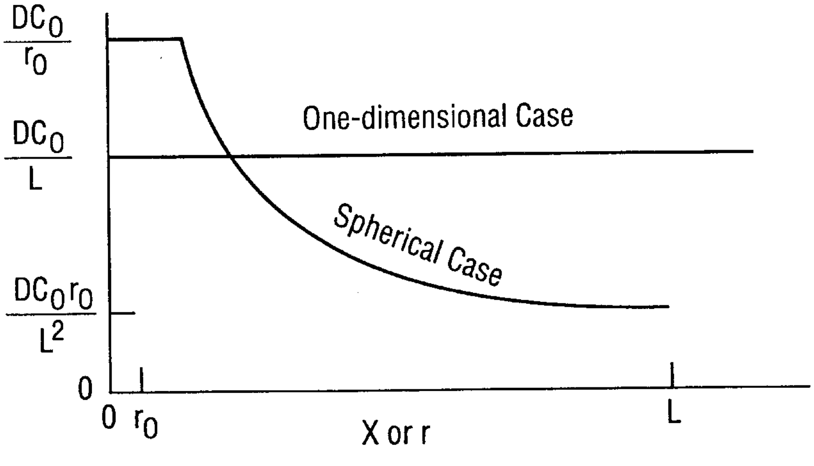


Figure 2-4
a) Spherical geometry used in the model; b) Concentration profile from the release point to the surface for both the spherical model and the one dimensional model; c) Flux profiles for the spherical and one dimensional models

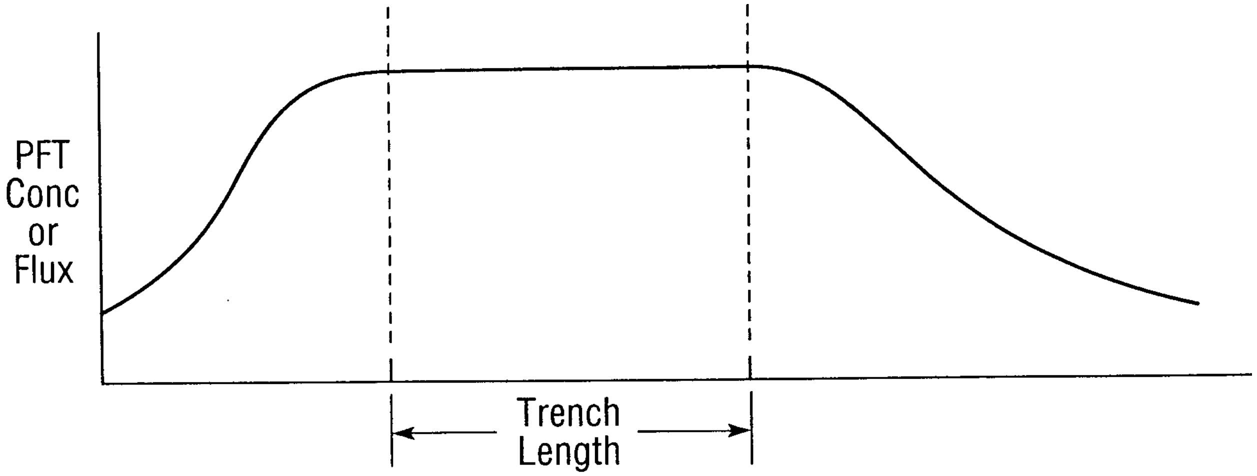


Figure 2-5
Expected concentration and flux profile for the trench experiment

Finally, the non-steady state spherical solution is given by Crank(9) for the concentration as

$$C = \frac{C_o r_o}{L - r_o}\left(\frac{L}{r} - 1\right) - \frac{2}{rp}\sum_{n=1}^{\infty}\frac{r_o C_o}{n}\sin\left(\frac{np(r - r_o)}{L - r_o}\right)\exp\left(\frac{-Dn^2\pi^2 t}{L - r_o}\right) \qquad \text{(eq. 34)}$$

and the flux at the surface (r=L) as

$$J = -D\frac{dc}{dr} = \frac{DC_o r_o}{(L - r_o)L}\left(1 + 2\sum_{n=1}^{\infty}(-1)^n \exp\left(\frac{-Dn^2\pi^2 t}{(L - r_o)^2}\right)\right) \qquad \text{(eq. 35)}$$

Now according to Crank, in both the one-dimensional and spherical cases, the steady-state is reached when

$$\frac{Dt}{L^2} \approx 0.4 \qquad \text{(eq. 36)}$$

In the scenario of a trench of depth, L = 100 cm, and a PFT soil diffusion constant of 0.02 cm/sec as measured in Task 2.2, we arrive at a time of 2.5 days for steady-state to have been reached. Notice that the time dependence for the flux to reach steady-state at the surface is identical for spherical (r << L) and infinite plane models, implying that this time dependence is probably accurate for most geometries. Consequently, the buildup of the PFT surface flux is plotted in Figure 2.6. As shown, the PFT flux builds up to 75% of its stead-state value in one day.

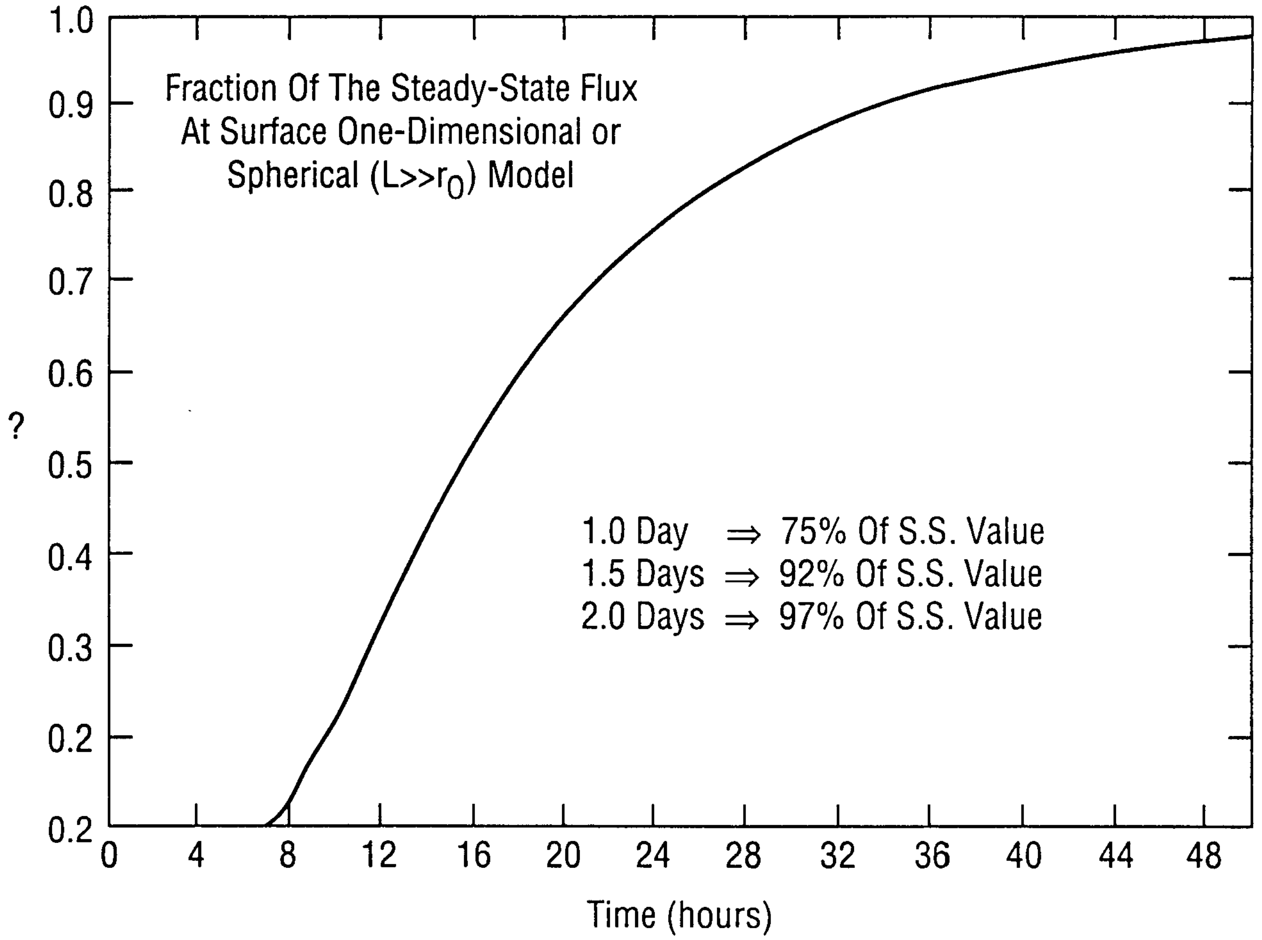


Figure 2-6
Fraction of the steady state flux at the surface as a function of time after release. The rate of buildup is identical for the spherical and one dimensional models

3. Effect of surface pavement.

In the above modeling discussion, it appears that the time dependence of PFT flux at the surface which results from a subsurface HPFF leak is more or less independent of geometry. However, a factor which will change this is the presence of a pavement on the surface. Landman(10) derived a model which is applicable to this modeling scenario. Consider that there is a concrete slab on top of soil with a regular series of cracks in it, as is shown in Figure 2.7. Landman calculated the flux through this cracked system and compared it to the flux through uncovered soil. It turns out that this ratio is given by

$$F = \frac{\text{flux through cracked cement}}{\text{Foux through uncovered soil}} = K\frac{L}{a}\left(\frac{Da}{Ds}\right)^{1/2} \qquad \text{(eq. 37)}$$

in which Da is the diffusion coefficient in air, Ds is the diffusion coefficient through soil, and K is the constant (actually this number varies slightly with the geometric configuration but has a limited range; K =11.5+ 2). Notice that L/a is just the fraction of the concrete surface that is cracked. Plugging in Da = .05 cm/sec, Ds = .02 cm/sec, the following Table is generated.

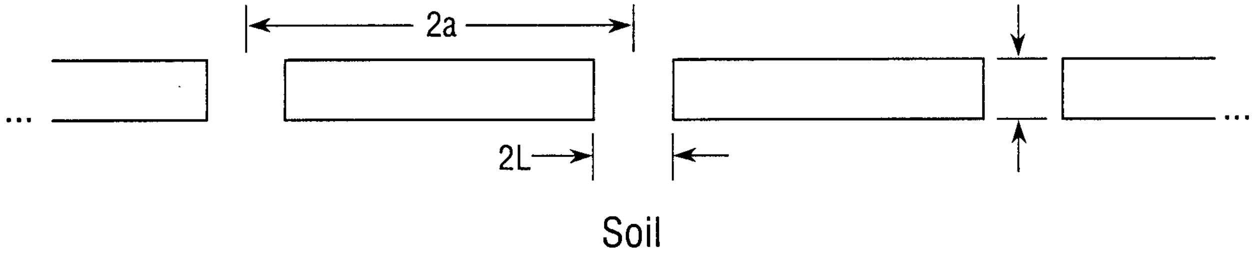


Figure 2-7
Geometry assumed for the effect of surface pavement on tracer flux and concentration

Table 2-16
Reduction Factor (R) Due to Presence of Pavement With Cracks

(L/a x 100) = % of surface area as cracks	Reduction Factor for Surface Flux, (R)
0.1	.018
0.5	.092
1	.182
2	.364
5	.909

Therefore, if 1% of the concrete surface exists as cracks, 18.2% of the tracer will be emitted from the surface compared with the case for an uncovered surface. Notice that when the crack area gets to 5%, the surface flux is virtually the same as if there was no concrete at all. Obviously, this equation cannot be linear for all values of L/a since R must be <1. It was derived under the assumption that L << a and should only be used that way.

A second interesting point of this work is to estimate the tracer concentration just below the concrete surface. [One of the sampling scenarios involves making boreholes in the concrete and sampling just below the surface.] To make this estimate we will let F = flux through uncovered sand and F = flux through covered sand. Then R = F/F or equivalently

$$\frac{C_L}{C_o} = 1 - R \qquad \text{(eq. 38)}$$

i.e., the ratio of the PFT concentration just below the surface to the PFT concentration at the surface of the pooled fluid leak is simply 1 - R. This is tabulated in Table 2.17.

Table 2-17
Ratio of PFT Concentration Beneath Concrete Pavement to that at Surface of Oil Pool

L/a x 100, (%)	R	$C_L/C_o = 1 - R$
0.1	.018.	982
0.5	.091.	909
1	.182.	818
2	.364.	636
5	.909	.091

So if 1% of the concrete exists as cracks, the PFT concentration just below the concrete will be 82% of its value at the surface of leaked fluid.

This analysis leads to additional questions which are to be explored in the urban field experiment in development of the sampling protocol:

1. In an urban setting where the cracks will not be homogeneous, will we be able to locate a leak by measuring the tracer concentration just below the surface? Suppose, for example, that the surface above the leak has a lot of cracks, but the surface around it is relatively intact. Is it possible that the subpavement concentration could actually be lower than at a further distance from the leak?

2. Is there any way of estimating what percentage of the paved surface area is cracks? It appears that this would be a useful estimate to have.

Task 2.3 Field Demonstration Experiment at BNL

The first two tasks of the preliminary laboratory experiments, involved the determination of the physical constants, i.e., the diffusion constant and adsorption coefficient which sets the rate of the PFT transport from the subsurface leak to the surface and the development of an appropriate model to analyze the results of the field test. A verification of these determined constants and the chosen diffusion modeling was achieved by a field test performed at BNL. Figure 2.8, gives a pictorial description of the field test, which will be described as follows: A site was chosen on the grounds of BNL in the meteorological field. At the center a trench, 10 meters long by 1/2 meter wide and 1 meter deep, was dug in order to simulate a buried HPFF cable trench with a leak. This trench was lined to half its depth with polyethylene lining to allow full recovery of the subsequent release of PFT-tagged fluid into the trench. A length of stainless steel tubing was laid lengthwise along the bottom of the trench from the center to the end and out of the trench to provide the source of the simulated leak. The trench was filled with sand, similar to that used by Con Edison and tamped into place according to Con Edison specifications.

A sampling ring with a radius of 100 feet was constructed about the trench with the trench at the center. This consisted of 1/2″ I.D. polyethylene tubing suspended on stakes every 3 degrees, or six feet apart. The 628 foot polyethylene tubing ring had been drilled with 120 equally spaced holes, specially sized so as to sample uniformly around the ring, i.e., when the ring was pumped at the chosen pumping port at 7.2 liters per minute, each hole in the ring would sample at 60 mL/min, thus providing uniform sampling around the ring. The purpose of the sampling ring was to sample the air that might contain PFT emitted from the tagged fluid released at the bottom of the trench irrespective of wind direction transporting the PFT away from the trench.

On the 120 stakes holding the sampling ring, a holder was placed for the BNL PFT CATS adsorbent sampler (11). These samplers would provide the directionality of the PFT emitted from the trench. These CATS samplers consist of a 1/4″ O.D. glass tube containing ~50 milligrams of Ambersorb, a carbonaceous adsorbent which has adsorptive affinity for the PFTs. When one end of the sampler is opened to the air, these sample passively, by Fickian diffusion, at ~0.2 liters per day. The CATS when placed in the holders on the stakes are slightly recessed within the holder to prevent the surrounding air turbulence, e.g., from the wind, from increasing the sampling rate of the CATS sampler. The CATS samplers and the sampling ring are both placed at 18″ above the ground.

Located within the sampling ring was a small portable surface meteorological station which recorded the air temperature, wind speed and direction at 18″ above the ground.

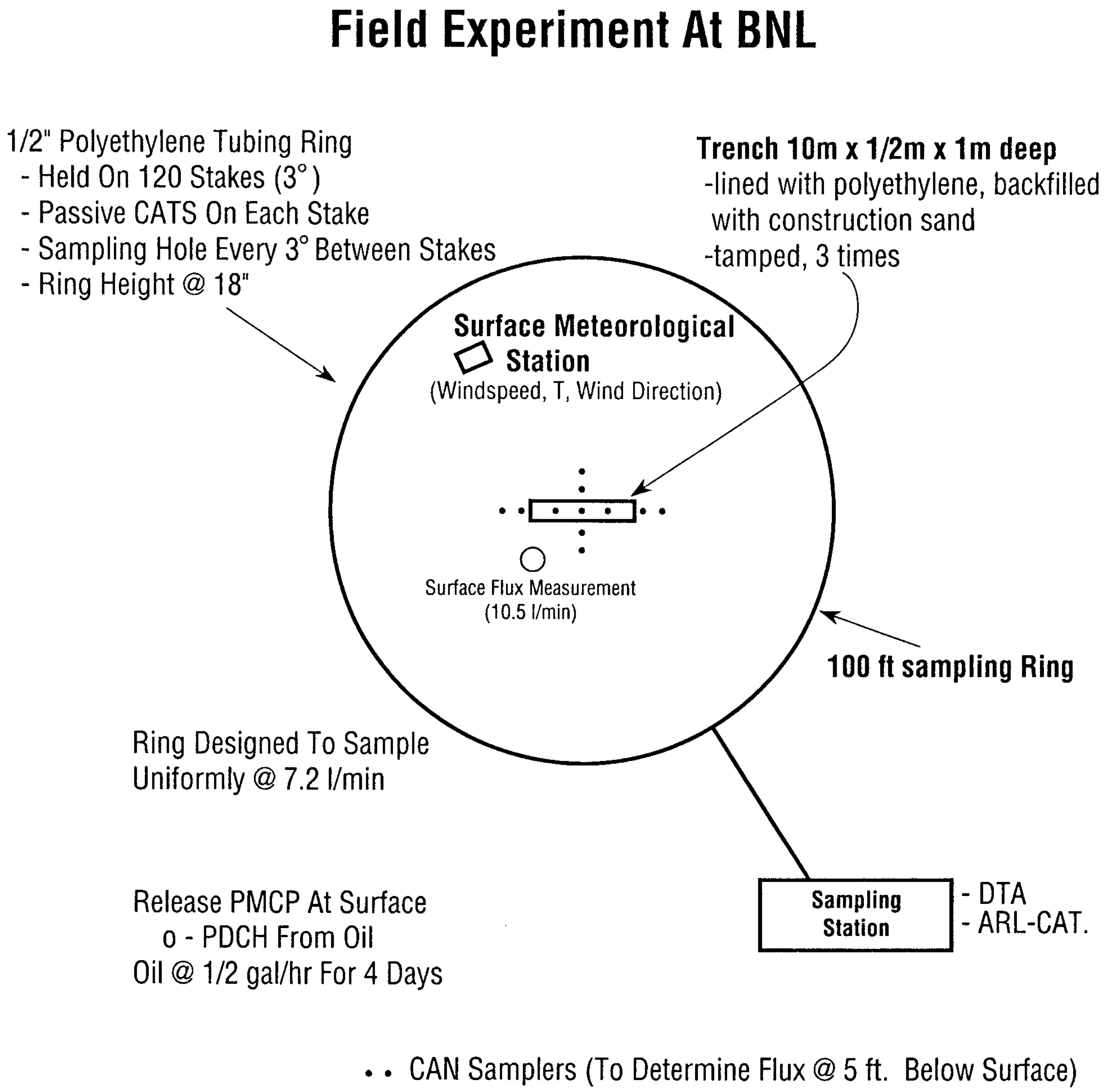


Figure 2-8
Pictorial description of the BNL field site

After the initial construction of the trench and sampling ring with the CATS holders, discussion arose within the tracer technology group as to the effectiveness of the various PFT sampling scenarios we had initially chosen for the Field Modeling test experiment. Since the experiment was a "one-shot" experiment, i.e., once the PFT-tagged fluid was released at the bottom of the trench, one could not repeat the experiment unless a new trench and ring, etc., were constructed at another site, it was decided to separate the experiment into two different experiments, one to test and evaluate the choice of sampling methods and the other to sample the PFT-tagged fluid release with the verified sampling methods.

The reasoning and concern for our initial choice of PFT sampling was as follows:

1. We had chosen four modes of sampling: a) CATS samplers on the stakes, which had been extensively field tested in past experiments; b) The sampling ring output was directed to two samplers, a real-time "two- trap" PFT analyzer (12) and a non-passive high volume CATS sampler. The ring had not been field tested but was based on similar field tested sampling lines. Still its performance needed verification; c) A surface PFT flux measurement system which was newly designed for this experiment, consisted of a modified 1 gallon can the size of a paint can. Its open end was placed on the surface of the trench. Along the side was a series of specially sized holes, allowing air to enter the can, to dilute the PFT emitted into the open end of the can. The can was pumped at 10 liters per minute with a 10 mL/min portion of the output directed to a BATS (Brookhaven Atmospheric Tracer Sampler) unit, which would collect air samples. Again, this was an untested system; d) A subsurface PFT flux measuring system consisting of a buried inverted coffee can, with the can bottom at the surface. In the middle of the end surface, a CATS sampler was placed with a flux restrictor, a 4" length of capillary tubing to reduce the sampling rate. This was a newly devised system, not having been previously field tested.

2. A worst case atmospheric transport and dispersion model was calculated for the trench and the sampling ring. Based on the earlier experiments performed in this phase and models it was expected that a steady state PFT flux of 0.04 milliliters of PFT vapor per m^2-h would be present at the top of the trench based on a 0.1% PFT in cable fluid concentration. The total PFT flux emitted from the entire trench would then be 17 x10^9 liters/sec. A worst case dispersion would dilute this to 0.32 x10^{-9} l/m at 100 feet, at the sampling ring. It thus appeared under the worst case dispersion scenario that, a) the CATS samplers on the stakes would only be marginal, i.e., the PFT collected by these samplers as emitted from the trench, would only be approximately twice the limit of detection (LOD) for PMCP, one of the PFTs to be used in this experiment, and b) the sampling ring output to the "two-trap" and the high volume CATS sampler would be adequate.

Consequently, an initial surface release experiment was performed to answer these above-mentioned concerns. The experiment was set up as follows:

1. PMCP, a PFT, was released at the surface and center of the trench at a rate of 20 Ml/min from a previously prepared cylinder of 0.0303% PMCP in air. This PFT release rate was consequently 6 x 10^{-6} l/min which would be equivalent to approximately six times the PFT release rate from the PFT emitted from the fluid beneath the trench.

2. A total of 120 CATS was utilized in the sampling ring stakes covering 360 for 24 hours during the surface PFT release.

3. Continuous sampling was done from the sampling ring. The output of the sampling ring was fed to two samplers located in a mobile van, located ~50 feet away from the sampling ring. The two PFT samplers were, a) the real-time "two-trap" PFT analyzer. This mobile instrument collected a PFT sample for 32 minutes (adjustable) and then analyzed the sample with the resulting output directed to an IBM-PC for data storage and computation, and b) the high volume CATS sampler accumulated PFT onto CATS samplers at an 0.5 l/min rate for 2 hours per sample with a total of ~60 liters of air sampled. The CATS are subsequently analyzed in the laboratory PFT analysis system.

4. The surface PFT flux measurement device was placed in the worst case position, i.e., directly downwind from the surface PFT release cylinder. This was done to test the degree of interference of a PFT released on the surface with that released beneath the trench. The surface PFT enters the surface flux measurement device through the side holes used to supply diluent air to the system.

The surface release experiment was performed on January 28 and 29, 1988, a period of highly directional winds during the day and dead stillness at night, a good example of worst case meteorology. The results will be discussed according to the respective sampling device.

1. CATS samplers on sampling ring stakes. A total of 120 samples were taken at 3 intervals about the release site. A resulting chromatograph obtained from the laboratory analysis of the CATS sampler is shown in Figure 2.9. This example is position No. 22, 66 from north and indicates a PMCP, the surface release PFT, concentration of 566 x 10^{-15} l/l. No other PFTs are evident, since no others were released. The resulting PMCP for all 120 positions are given in Table 2.18; the resulting concentrations are the total integrated 24-hr concentrations. Figure 2.10 gives a radial distribution plot. Note the maxima to the southeast (around 120), this corresponds to the prevalent northwest wind that occurred during the afternoon portion of the twenty-four hour experiments. There is also a minor maximum to the NNE (around 10) which corresponds to the southerly winds that occurred near the end of the experiment during the next morning. The lowest concentrations observed were approximately 60x 10^{-15} l/l which are approximately ten times the background PMCP concentration, clearly the CATS samplers on the ring stakes are not as marginal as indicated by the worst case calculation.

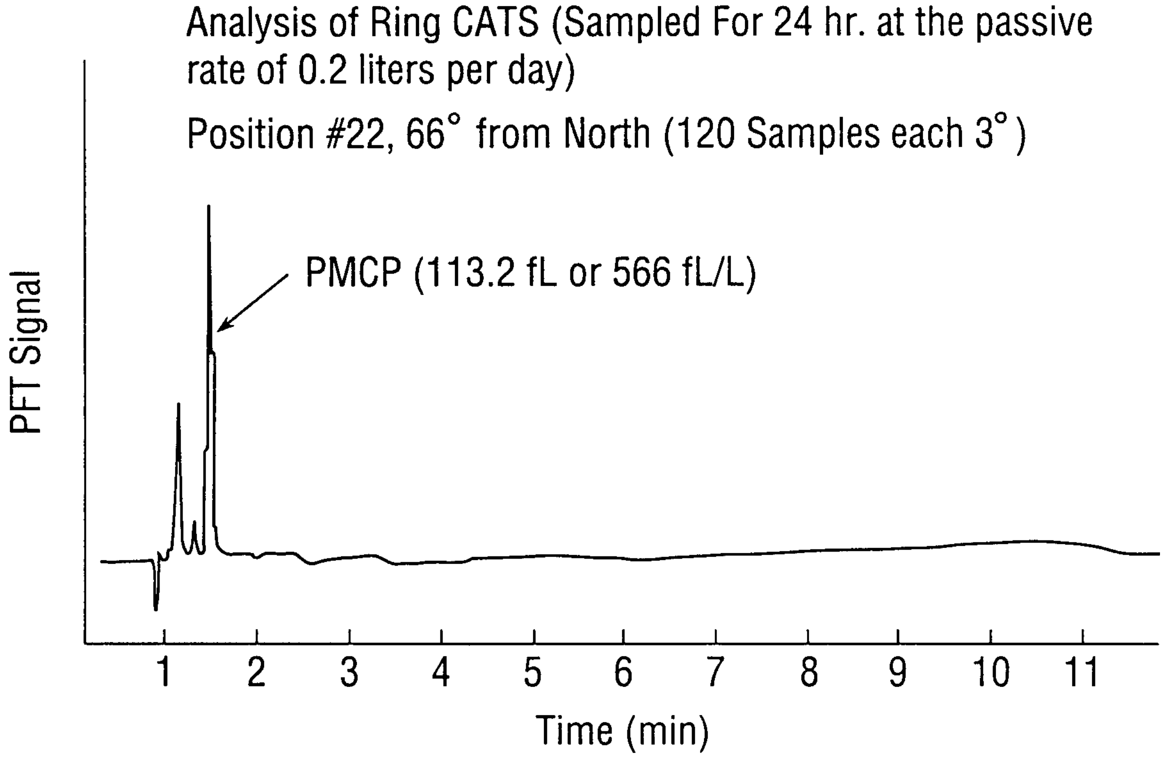


Figure 2-9
Chromatogram of the CATS sampler at position 22 (66 degrees from North). The resulting PMCP peak indicates a concentration 566 femtoliter per liter at a 100 feet from the release site

2. The high volume PFT sampler. The output of the 628 foot sampling ring was fed to the high volume PFT sampler and the "two-trap" PFT real-time analyzer. The CATS from the high volume sampler (referred to as the ARL sampler) were subsequently analyzed in the laboratory PFT analysis system. The resulting PMCP concentrations for each two-hour interval are given in Table 2.19, along with the averaged meteorological condition for that period as obtained from the portable meteorological unit located in the ring. The results are also given in Figure 2.11.

Table 2-18
PMCP Concentrations as Measured by the CATS on the Ring Sampling Stakes during the Surface Release Experiment

Angle (°)	PMCP*, fl/l	Angle (°)	PMCP, fl/l	Angle (°)	PMCP, fl/l
0	776	120	1291	240	140
3	718	123	1053	243	90
6	767	126	1251	246	161
9	974	129	1232	249	157
12	831	132	1303	252	160
15	669	135	1410	255	150
18	899	138	1330	258	163
21	497	141	1158	261	76
24	384	144	874	264	124
27	394	147	1022	267	163
30	403	150	897	270	145
33	360	153	833	273	216
36	289	156	811	276	219
39	324	159	852	279	165
42	296	162	746	282	107
45	309	165	725	285	199
51	321	171	778	291	193
54	428	174	501	294	198
57	393	177	822	297	115
60	473	180	240	300	175
63	566	183	182	303	185
66	446	186	122	306	196
69	381	189	200	309	179
72	368	192	81	312	231
75	447	195	59	315	197
78	399	198	68	318	203
81	383	201	77	321	286
84	457	204	58	324	241
87	576	207	43	327	170
90	981	210	63	330	270
93	742	213	73	333	312
96	838	216	67	336	232
99	986	219	61	339	328
102	920	222	65	342	308
105	777	225	155	345	266
108	1196	228	155	348	266
111	1265	231	141	351	357
114	1328	234	149	354	356
117	1406	237	138	357	391

Average = 465 fl/l
* fl denotes femtoliter (= 10^{-15} l)

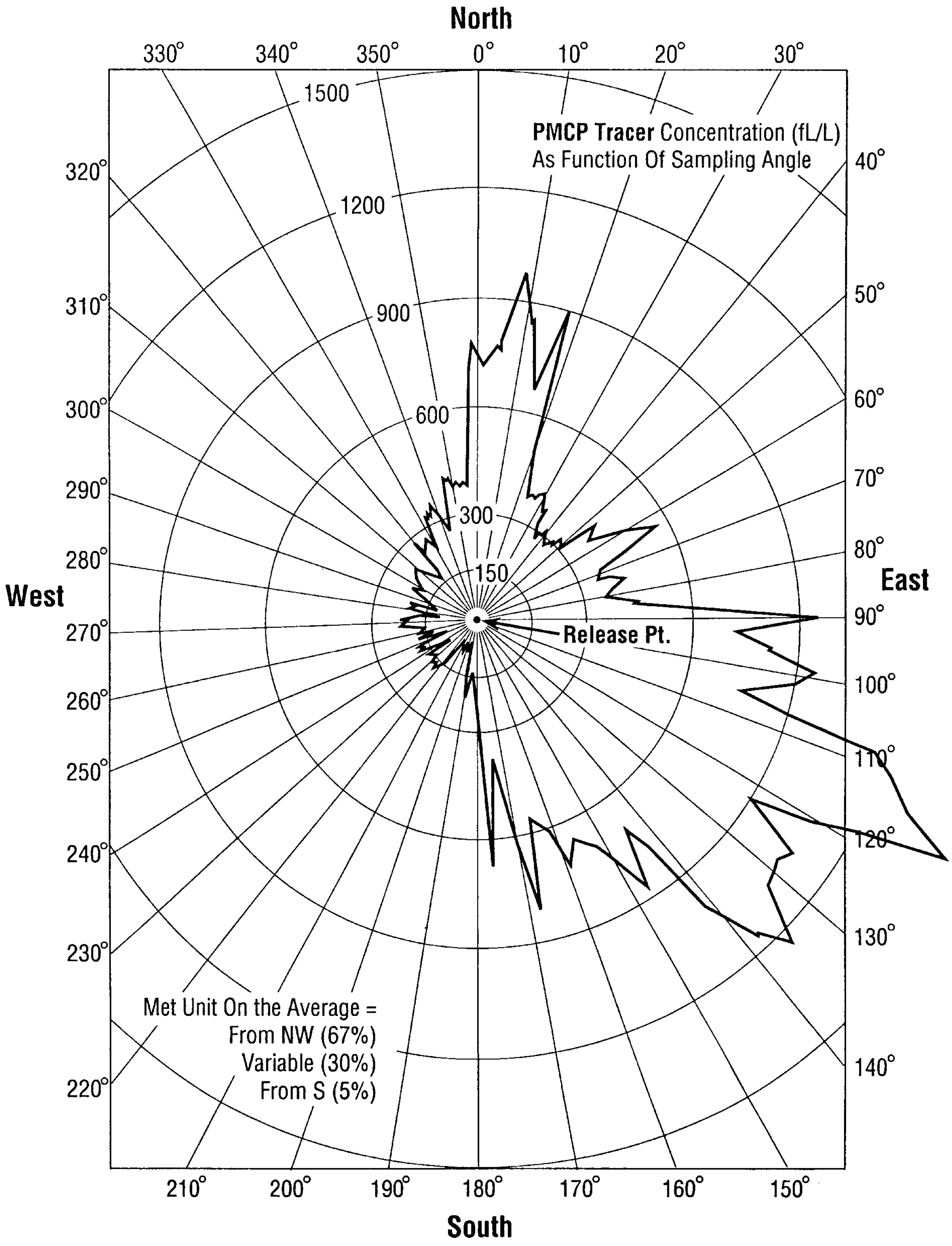


Figure 2-10
Radial distribution plot of the PMCP tracer concentrations (fLIL) as function of sampler radial position

Table 2-19
ARL-CATS PMCP Concentrations

			Weather Conditions	
File No.	**Sampling Period**	**PMCP Concentration, fl/l**	**Wind Speed**	**Direction**
1	02:35–04:35 PM	750	4–6 mph	NW
2	04:35–06:35 PM	125	5->2 mph	NW
3	06:35–08:35 PM	22.2	2->4 mph	NW
4	08:35–10:35 PM	214	3–4 mph	NW
5	10:35–12:25 AM	917	~0	highly variable
6	12:35–02:35 AM	20.8	~0	NW
7	02:35–04:35 AM	375	~0	NW
8	04:35–06:35 AM	167	~0	NW
9	06:35–08:35 AM	416	~0	highly variable
10	08:35–10:35 AM	6.9	0–3 mph	NW→N
11	10:35–12:35 PM	42.4	0–5 mph	variable
12	12:35–02:35 PM	85.6	2–4 mph	variable→S
13	02:35–04:35 PM	7.6	no PFT released	

Release rate 20 ml/min x 0.0303% = .00606 ml/min of PMCP
Time Average = 261.8 fl/l

Note that the PMCP concentration rose to high levels during very stagnant midnight conditions, i.e., 10–12 PM, 2–4 AM. This corresponds to “pooling” of the PFT and movement of this pool to the sampling ring. Windier conditions tended to disperse the PFT by upward dilution which does not get sampled at the 18” high sampling ring. The high volume CATS sampler takes a large volume sample, 60 liters, which allows the backgrounds of the other PFTs to be measured. These PFTs were not used in this experiment and are present in the ambient air due to limited industrial use over the previous forty years. The values calculated during this experiment are comparable to those measured earlier and at other locations, as is given in Table 2.20, thus providing additional verification of the effectiveness of this sampling mode. The PFT concentrations obtained from the CATS on the ring sampling stake are averaged over the 24 hours of the experiment but are sampling angle dependent. Consequently, if the high volume CATS are averaged over time and the ring stake CATS are averaged over angle, we should get the same PFT concentration. The results are:

High volume CATS - time average = 262 fl/l PMCP (over 24 hr)
Ring stake CATS - angle average = 465 fl/l PMCP (over 360)

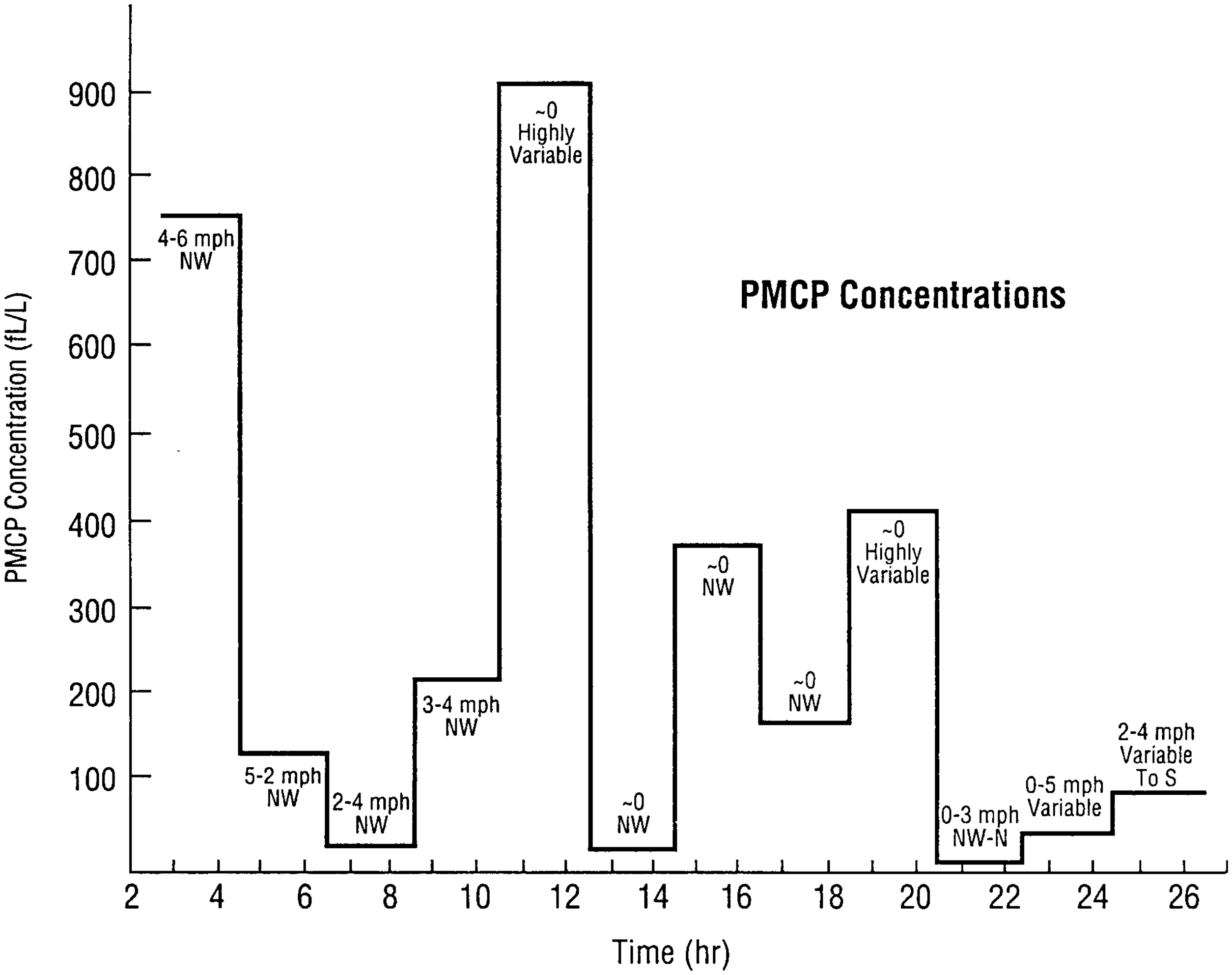


Figure 2-11
PMCP concentrations for each two hour interval and sampler by the ARL high volume sampler. The averaged meteorological conditions are given for each two hour interval.

Table 2-20
ARL-CATS PFT Backgrounds
[for other PFTs not used in the surface release experiment]

	Background		
Tracer	**Measured (fl/l)**	**(11/4/82 data)**	**(5/31/85) data**
PMCH	5.41 ± .83	3.34 ± 0.10	4.46 ± 0.05
oc PDCH	0.382 ± .104	0.15 ± 0.03	—
(mp + pc) PDCH	11.54 ± 1.43	11.1 ± 1.2	—
(mc + ot) PDCH	8.07 ± .88	6.82 ± 0.3	—
pt PDCH	4.42 ± .62	4.7 ± 0.4	—

Note the discrepancy by a factor of two between the two averages which should theoretically be equal. Several potential reasons have been identified which might cause this discrepancy. They are as follows:

a) The high volume CATS and the ring stake CATS were analyzed on two separate laboratory PFT analysis systems. There could possibly have been a factor of two difference in the PFT calibration curves;

b) The high volume CATS sampler was sampled at a relatively high rate of 0.5 liters/min for 2 hours. The CATS absorbent samplers are not limitless in their absorptive capability for PFTs, but rather have a defined “breakthrough volume” which cannot be exceeded. If exceeded, the PFT is not fully absorbed and not quantitatively collected(13). This breakthrough volume is PFT dependent, the more volatile PMCP having a smaller breakthrough volume. Consequently, the appropriate background concentrations for the other PFTs as measured by the high volume CATS sampler, given in Table 2.20, do not apparently indicate a breakthrough problem. However, PMCP, the surface release PFT, is the most volatile and has approximately a factor of three smaller breakthrough volume than PMCH. It is quite conceivable that breakthrough occurred with PMCP and not with PMCH, PDCH, etc. If this is so, then the measured high volume PMCP concentrations would be on the low side.

c) The ring stake CATS samplers are recessed to minimize the turbulence effects at the sampler entrance. If the degree of shielding was insufficient, the sampling rate of the passive CATS is increased, thus yielding PMCP concentrations on the high side for the ring stake CATS.

d) Conceptually, the sampling ring is designed to sample uniformly about the ring. However, some holes could have been clogged, improperly drilled, etc., which would bias the uniformity of the ring sampling which was used to provide samples for the high-volume CATS sampler. Overall, based on the collective experience of the Tracer Technology Center, we believe the most probable reason for the discrepancy is (b), the breakthrough of PMCP on the high volume sampler. This, and the other potential reasons will be investigated and resolved before the second part of the trench experiment, the subsurface fluid release.

3. The real-time two trap PFT analyzer. This instrument was also collecting and analyzing air samples taken by the sampling ring. Figure 2.12 gives a typical chromatogram taken at 9 PM on the evening of the release. Note the large “hump” at the end of this, which indicates the presence of water vapor in the sampler. Figure 2.13 gives the observed PMCP area counts as a function of time. The PMCP concentrations are not yet available, but will be when the calibration of the instrument has been performed. Note the time response, i.e., the peaks in PMCP area counts, correlates well with those in Figure 2.11, a similar graph for the PMCP concentrations observed by the high-volume CATS sampler. However, several problems were encountered with the real-time “two trap”instrument, namely:

a) Unequal sampling between the two traps. The instrument has two collection traps. While one trap is collecting, the other is being analyzed, alternating between these two modes. It was noted that one trap was producing area counts 60% of the other for comparable air samples, possibly indicating a flow imbalance problem.

b) There appeared to be a water vapor problem, i.e., breakthrough of water vapor from the driers. This interfered with resulting chromatographs.

c) The experiment was performed in January and the temperature dropped to -20°C at night. The real-time two trap was located in the mobile van which had poor temperature regulation. This caused an extreme baseline drifting on the instrument since the instrument is temperature sensitive.

d) There might also be a PMCP breakthrough problem with this instrument since the PFT traps are essentially CATS samplers.

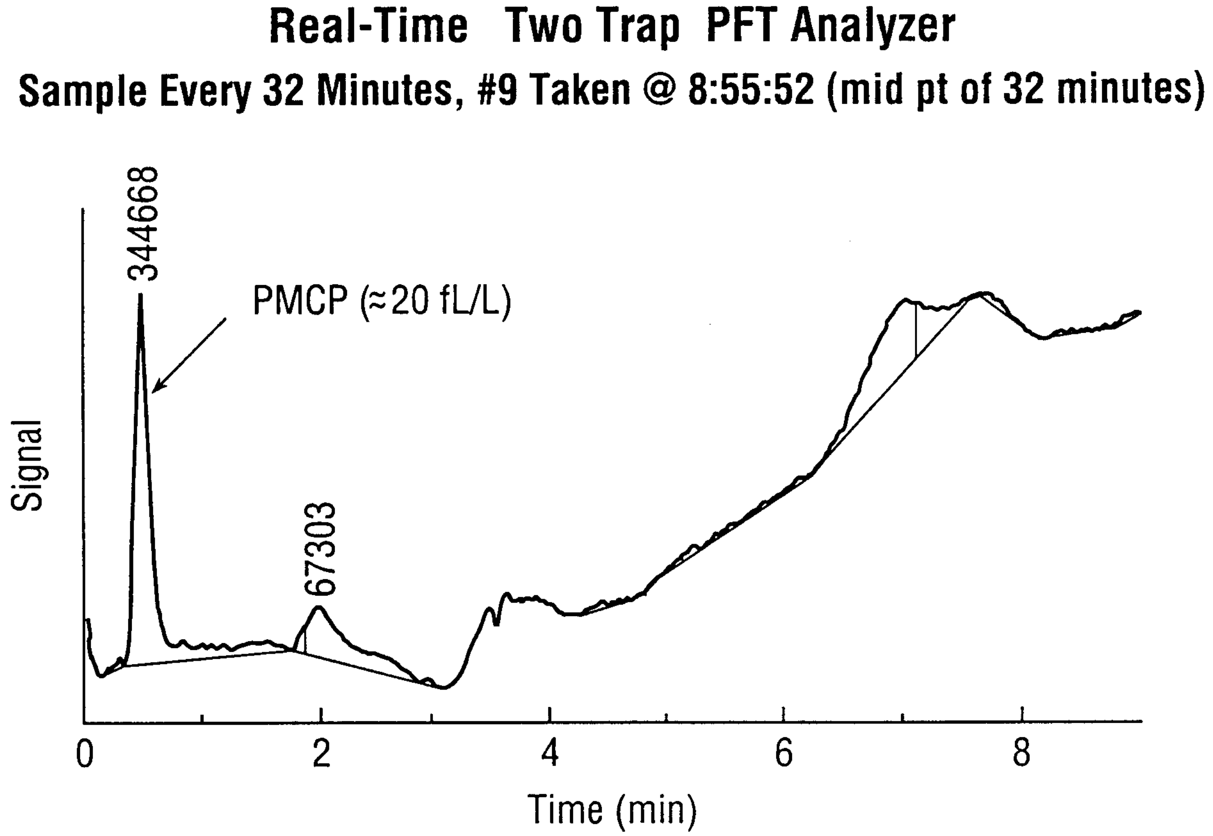


Figure 2-12
Chromatogram of a Two-Trap (DTA) sampler. Large "hump" near seven minutes indicates the presence of water in the sample

4. Surface PFT flux measurement instrument. The air sampled by this device was collected by a BATS unit and subsequently analyzed. The device had been positioned in the worst case position, however, the results indicated no interference from PMCP, even though, it was present in large quantities.

Overall, the surface PFT release experiment was successful and indicated several minor problems which have to be resolved before the subsurface PFT-fluid release experiment.

The remaining experiment in this Task 2.3, is the intentional subsurface fluid release experiment which was performed after the cut off for data in this interim report.

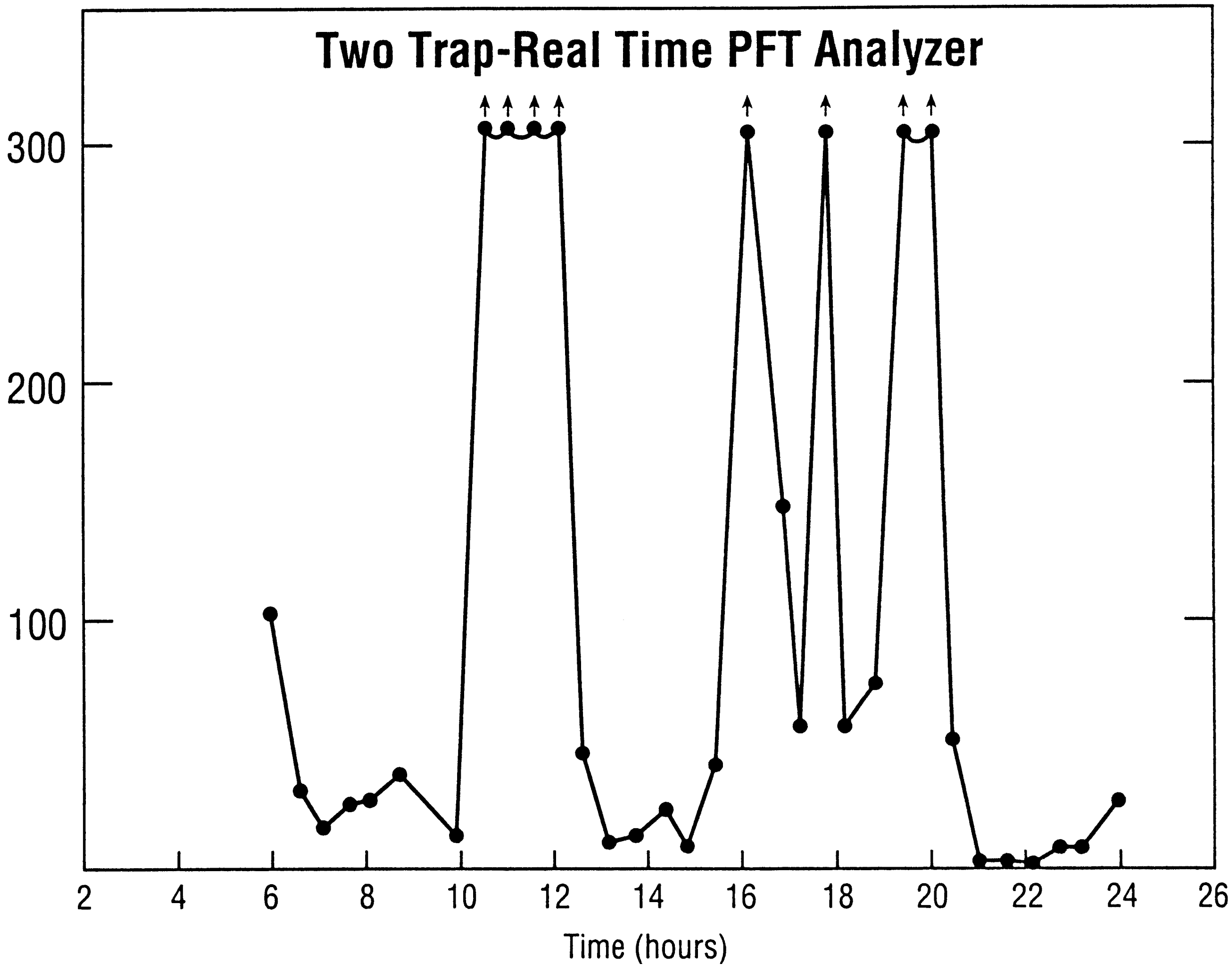


Figure 2-13
PMCP concentration obtained by the two trap (DTA) instrument Figure 4.1 Flow diagram for apparatus used for tagging dielectric fluids. Figure 4.2 Flow diagram for apparatus used to introduce and mix tracer into 55 gallon drums. Figure 4.3 Setup used to deoxygenate the dielectric fluid

Task 2.4 Intentional Subsurface Fluid Release Experiment

This was the continuation of the experiment in the BNL meteorological field where the surface release experiment was performed.

On April 6, 1988, 25 gallons of fluid tagged with 0.1% o-PDCH was injected in the bottom of the trench. The fluid release rate was approximately 1/3 gal/h, resulting in a four-day injection period.

Four types of PFT sampling were performed at the trench in order to evaluate their potential for inclusion in the sampling protocol. The results will be discussed according to each type of sampling.

(1) Subsurface "Can" sampling

Approximately ten inverted coffee cans had been placed in the ground in and around the trench area. The can was placed with the opening downward in a similarly sized hole, so that the sealed bottom of the can was level with the ground. A hole was placed in this bottom so as to permit a CATS sampler to sample the air inside the can which should be in equilibrium with the soil air, and the consequent PFT vapors emanating from the tagged fluid. CATs samples were taken after the start of fluid injection, and the measured PFT concentrations were extremely high, so much as to render this form of PFT sampling useless, because of the overly high PFT concentration. Based on these results, an alternate sampling strategy was devised which will be discussed later.

Conclusions

The results to date have indicated the potential for tagging the dielectric fluid used in urban HPFF transmission lines with PFTs for subsequent detection for leaks. The conclusions from each task are enumerated according to task.

Task 1.1 PFT Solubility

The PFTs are soluble up to 5% by weight in the four samples of dielectric fluid examined. The PFTs have an adequate partial pressure above the PFT tagged fluid solutions so as to emit PFT vapor into the surrounding soil air spaces when leaked from an HPFF line.

Task 1.2 Literature Review of PFT Compatibility

A review of the PFT manufacturers literature indicates that PFTs are compatible with all materials used in HPFF lines with the possible exception of Viton and Teflon seals and seats. However, the rate of PFT diffusion into these materials is negligible, so in practical terms, these Viton and Teflon materials are compatible.

Task 2.1 PFT Adsorption on Soil

PFTs were found to have a negligible adsorption onto soil under typical subterranean conditions, i.e., high humidity. The diffusion constants of PFTs in soil were measured for the sand used in the HPFF trench overburden and found to be 0.022 cm/sec for both PFTs examined. The PFT diffusion coefficient in air was measured as 0.05 cm/sec, indicating only a factor two hindrance in diffusional transport of PFT through the sand overburden.

Task 2.2 Soil Diffusion Modeling

The two models examined, plane sheet and concentric spheres, dictated very slight geometric dependence of the rise of PFT surface flux from a field trench experiment. It was calculated that surface flux should reach its equilibrium value 2 1/2 days after the start of the fluid leak, based on one meter deep HPFF trench. The presence of a cracked pavement attenuated the surface flux, but increased the immediate subsurface PFT concentration, indicated a promising PFT sampling scenario, which will be field tested in a latter phase of this program.

Task 2.3 Field Test of Model

A initial surface PFT release experiment was performed to test the PFT sampling equipment. Minor problems were found, but are correctable before the actual field test experiment.

3

FIELD DEMONSTRATION EXPERIMENT

This section involved two tasks: A. Development and Urban Field Test of the Leak Detection Protocol with a known leak site; and, B. Demonstrated Detection of an actual Buried HPFF cable fluid leak

Development And Urban Field Test Of The Leak Detection Protocol With A Known Leak Rate

The urban field experiment reported on here took place at a moderately busy commercial street in Queens, an eastern borough of New York City. A 138 Kv transmission line runs directly under the street. The tagged fluid was released over a two and a half day period starting on July 27, 1988 with tracer sampling continuing through the end of September 1988.

Tracer Release Equipment

The PFT-tagged fluid was released into the ground by pumping the fluid mixture through a nominal 3/4 inch OD by 25 foot long pipe drilled through a manhole and into the ground adjacent to the high voltage cable (see Figure 1). This was an attempt to simulate a fluid leak without actually disturbing the high voltage cable, which was operational during the course of the experiment. The tracer tagged fluid was released at a rate of 0.5 gal/h for 2.5 days for a total release of about 30 gallons of fluid. This release rate required a pressure of 100 psig. The pressure and flow were recorded every hour around the clock by a Con Edison crew, which was needed to divert traffic around the release equipment. The released fluid contained 0.03% by weight of 1,2 cis-perfluorodimethylcyclohexane (ocPDCH), a PFT chosen for its low ambient background concentration (0.3×10^{-15}) L/L, high sensitivity for detection, and lack of interferences. A second tracer, perfluoromethylcyclohexane (PMCH), was present at 0.003% by weight and was used in the data analysis when the ocpdch concentrations overloaded the analytical instrumentation. A third PFT, perfluoromethylcyclopentane (PMCP), was released directly into the atmosphere at a known emission rate from a pressurized gas cylinder located in the manhole. The purpose of this tracer was to factor out meteorological conditions in estimating the emission rate of the ocpdch. In other words, by measuring the ratio of PMCP to ocPDCH in downwind tracer samples and by knowing the emission rate of the PMCP, one could calculate the total emission rate of the ocpdch through the ground surface and into the air.

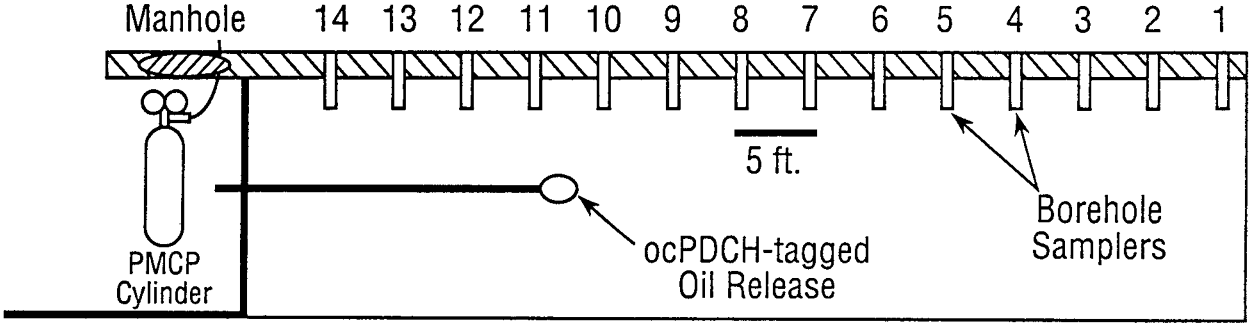


Figure 3-1
The tracer release and borehole sampling systems. Cable fluid tagged with ocPDCH, a perfluorocarbon tracer (PFT), was released from a 25 foot pipe drilled under the road surface while a second PFT was released from a gas cylinder located in the manhole. A network of 14 borehole samplers was used to measure the ocPDCH concentration in the interstitial soil air about one foot below the surface.

Sampling Equipment

Passive sampling tubes known as CATS (Capillary Adsorption Tube Sampler) were used to measure the tracer concentrations in the surrounding neighborhood. CATS are about the size of a cigarette and sample by diffusion of the PFTs onto an adsorbent material contained in the tube. Analysis of the CATS occurred at an analytical laboratory located at BNL. The CATS were taped to light poles over approximately a five block radius around the release site and collected time-integrated samples over a 2–7 day period. The network of these samplers, subsequently referred to as Pole CATS, is shown in Figure 3.2.

As shown in Figure 3.1, 14 boreholes were drilled along the length of the high voltage cable above the release site. The depth of the drilled holes matched the depth of the asphalt plus concrete surface - about one to one and a half feet. The boreholes were two inches in diameter, placed five feet apart. Sampling devices, shown in Figure 3.3, were inserted into boreholes 3–14. The borehole samplers are made of two inch diameter PVC pipe with a recessed top plate. A specially designed fitting containing a silicone rubber septum is contained within the top plate permitting sampling of the subsurface air using a syringe. For this experiment, samples were withdrawn from the borehole sampler using a 100 µL, gas-tight syringe and injected onto CATS tubes. Two inch, styrofoam inserts were placed in the top of the borehole samplers when they were not being used.

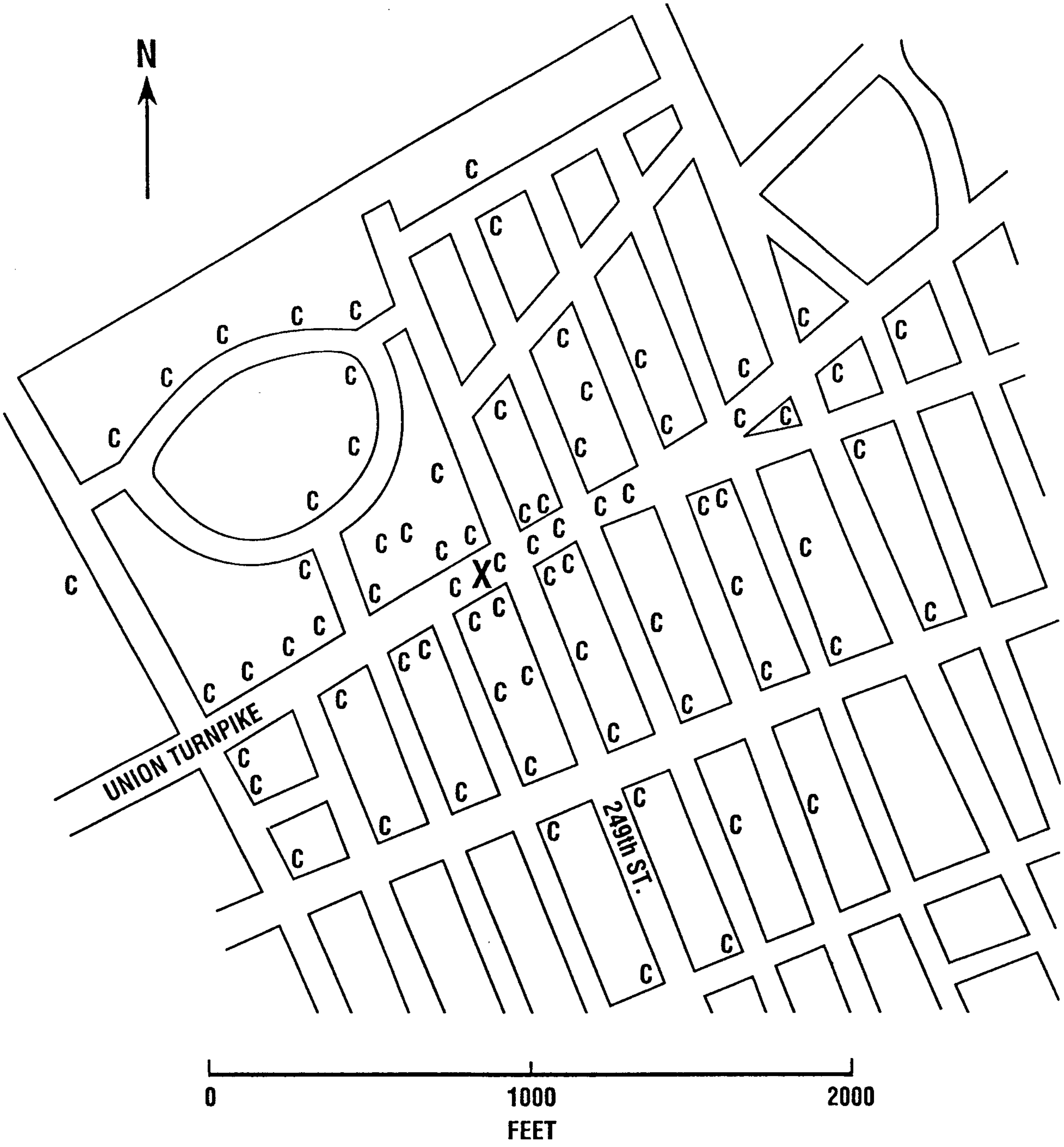


Figure 3-2
The network of passive air samplers (CATS) that was used to measure the ambient air concentrations of the released tracers at the Queens, New York experimental site. CATS locations are indicated by a "C". The release site is indicated by an "X". A total of 77 CATS were deployed during each of five measurement periods.

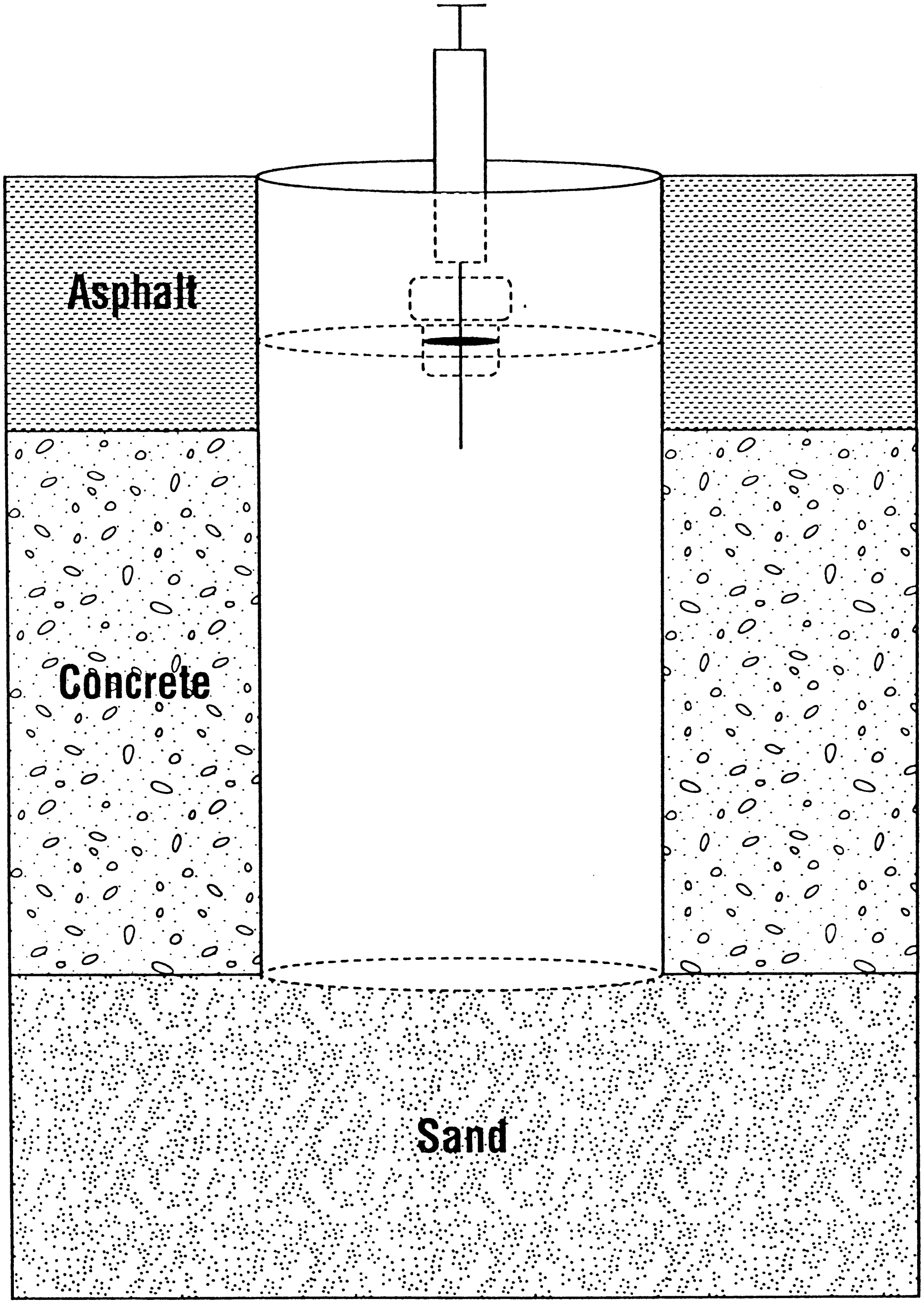


Figure 3-3
The borehole sleeve insert pictured here was constructed of nominal 1.5 inch diameter, schedule 40, PVC pipe cut to approximately 18 inch sections. A recessed top plate contains a mounted septum permitting sampling of the subsurface air with a 100 µL syringe.

A second type of sampler, known as the BATS (Brookhaven Atmospheric Tracer Sampler), was deployed at approximately 30 foot heights on eight telephone poles surrounding the release site. The BATS is a programmable, PFT sampling system containing 23 adsorbent tubes similar to the CATS. A valve steps between the tubes at user-defined intervals with an internal pump drawing ambient air through the tubes. The BATS is a totally self-contained system about one cubic foot in volume and draws its power from internal rechargeable batteries. For the Queens experiment, the BATS were set to collect four hour integrated samples beginning at the start of the fluid release and ending eight days later with the goal of measuring the initial rise in the PFT concentrations. Like the CATS, the BATS are returned to the laboratory for tracer analysis. A full description of the CATS, BATS, and the laboratory analytical system can be found elsewhere [17].

Two real-time instruments were also used in this experiment. The first type, known as the COPS (Continuously Operating Perfluorocarbon Sniffer), is a small (about 20 lb.), battery operated, portable instrument capable of measuring changes in PFT concentrations in as little as 10 seconds [18]. This instrument does not have the capability of separating tracers before detection. It measures the sum of the PFT concentrations as well as other stable halogenated compounds (such as SF_6) that are not destroyed by the internal catalytic combustion system contained within the COPS. The detection limit of the COPS is about 50 picoliters of tracer per liter of air (pL/L), making it useful for measuring PFT concentrations at major ground level leak points and in sewers and manholes, where estimated PFT concentrations were in the nanoliters per liter (nL/L = 1000 pL/L) range.

A second real-time instrument called the DTA (Dual-Trap Analyzer) is a scaled-down, portable version of the BNL laboratory analytical system (12). The DTA contains two CATS samplers, one of which is collecting an air sample while the other is being analyzed. The two traps cycle with a user-selectable frequency of between 2 and 60 minutes, which determines how quickly each new PFT concentration is obtained. For a cycle time of five minutes, the DTA can measure PFT concentration down to 10 femtoliters per liter (fL/L = 0.001 pL/L). The DTA provides separate measurements of each of the perfluorocarbon tracers. Physically, the DTA is 20″x10″x20″, about twice the size of the COPS, and weighs 50 pounds. The DTA runs on 120 VAC but can be converted to DC power if desired. For the Queens experiment, the DTA was used to measure PFT concentrations in the ambient air around the release site. In addition, syringe samples taken from the boreholes were directly injected into the instrument for on-the-spot analysis and pre-screening for the laboratory analytical system.

Finally, a special system was developed to measure tracer flux, i.e., the amount of ocPDCH emitted from particular areas of the ground surface. These flux measurements were used to measure the emission rate from suspected hot spot areas such as sewers and manholes and also from high emission areas located with the COPS. The flux measuring apparatus consists of a cover which can be placed over the suspected area, a pumping system which draws air through the cover, and an automated CATS sampling system for collecting tracer samples.

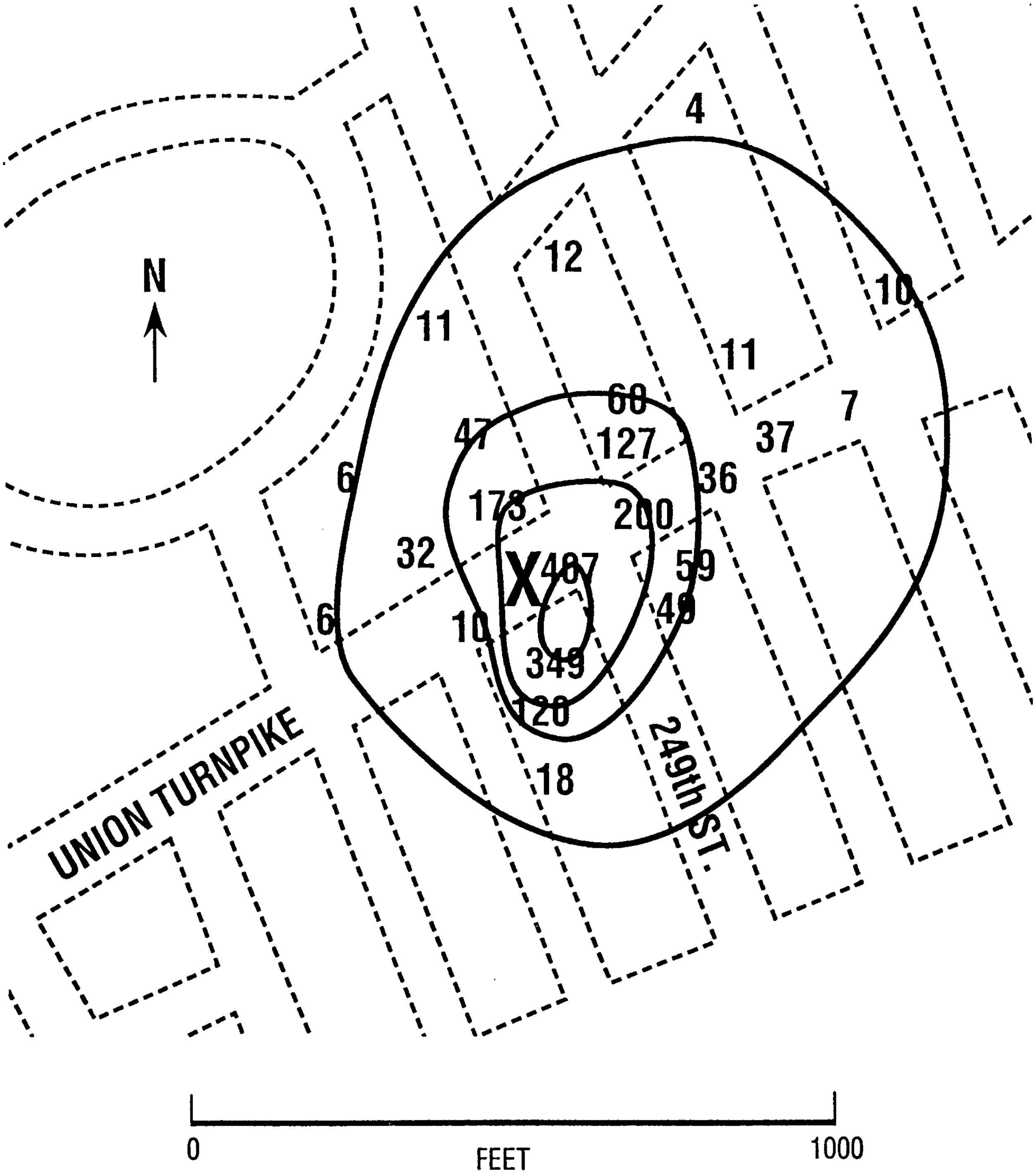
Results and Discussion of the Urban Field Test

The goal of the current leak detection research at BNL is to locate fluid leaks as small as one gal/h to within ~10 feet at a time not to exceed three days. Prior theoretical, laboratory and field work at BNL indicated that this goal is reachable using a two-part, leak detection strategy. The first part of the protocol, Leak Locale Estimation, makes use of aerial sampling and surface penetrations sampling to isolate the leak to within a city block (approximately 200 feet), Aerial Sampling, involves detection of the PFT vapors in the ambient air above the leak site using CATS samplers on poles and/or real-time instrumentation at street corners. In addition, PFT concentrations can be measured at or below the street surface using real-time PFT instrumentation in sewers, manholes, street cracks, etc., which will also approximately indicate the leak location to within 100 feet. The second part of the strategy (Leak Pinpointing), designed to locate the leak to within ~10 feet or less by below-surface borehole sampling equipment. Experimental results obtained by applying these strategies and methods to the Queens leak site are reported here.

Leak Locale Estimation

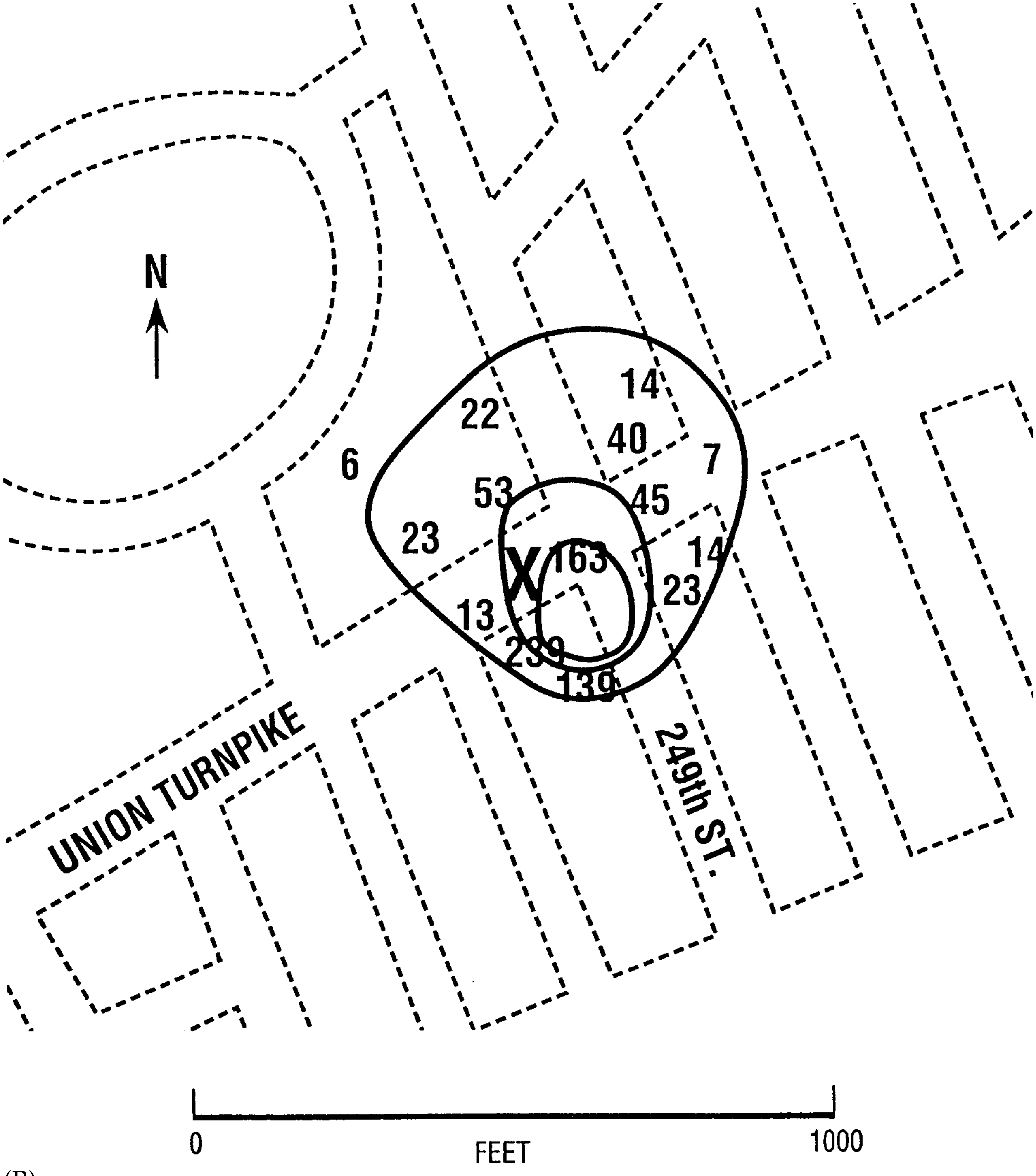
Aerial sampling ambient air samples were taken using CATS in 77 separate locations spanning a radius of about 1000 feet around the release site. The network of Pole CATS is shown in Figure 3.2. Five sets of time-integrated samples were taken consecutively starting on July 26, one day before the fluid release, and ending on August 11, two weeks after the end of the release. The results from these five measurement sets are shown in Figures 3.4A-3.4E. Plotted on these figures are the concentrations of ocPDCH and isopleth contour lines, i.e., estimated lines of constant tracer concentration. The fluid release site is indicated by an "X".

While connecting the fluid pumping equipment to the underground release pipe, a small amount of the tracer-tagged fluid was spilled in the working manhole. Attempts were made to clear as much of this spillage as possible but, inevitably, some remained, allowing PFT to evaporate from the fluid into the atmosphere. The effects of this spillage can be seen very clearly from the decrease, rather than increase, in the PFT concentration seen by the sequential Pole CATS samplers until about five days after the beginning of the fluid release. Due to the spillage, information from both the Pole CATS and the BATS about the buildup of PFT concentration in the atmosphere from the underground fluid release was lost. Fortunately, we were able to retrieve this information from the borehole samplers, which were not affected by the spillage.



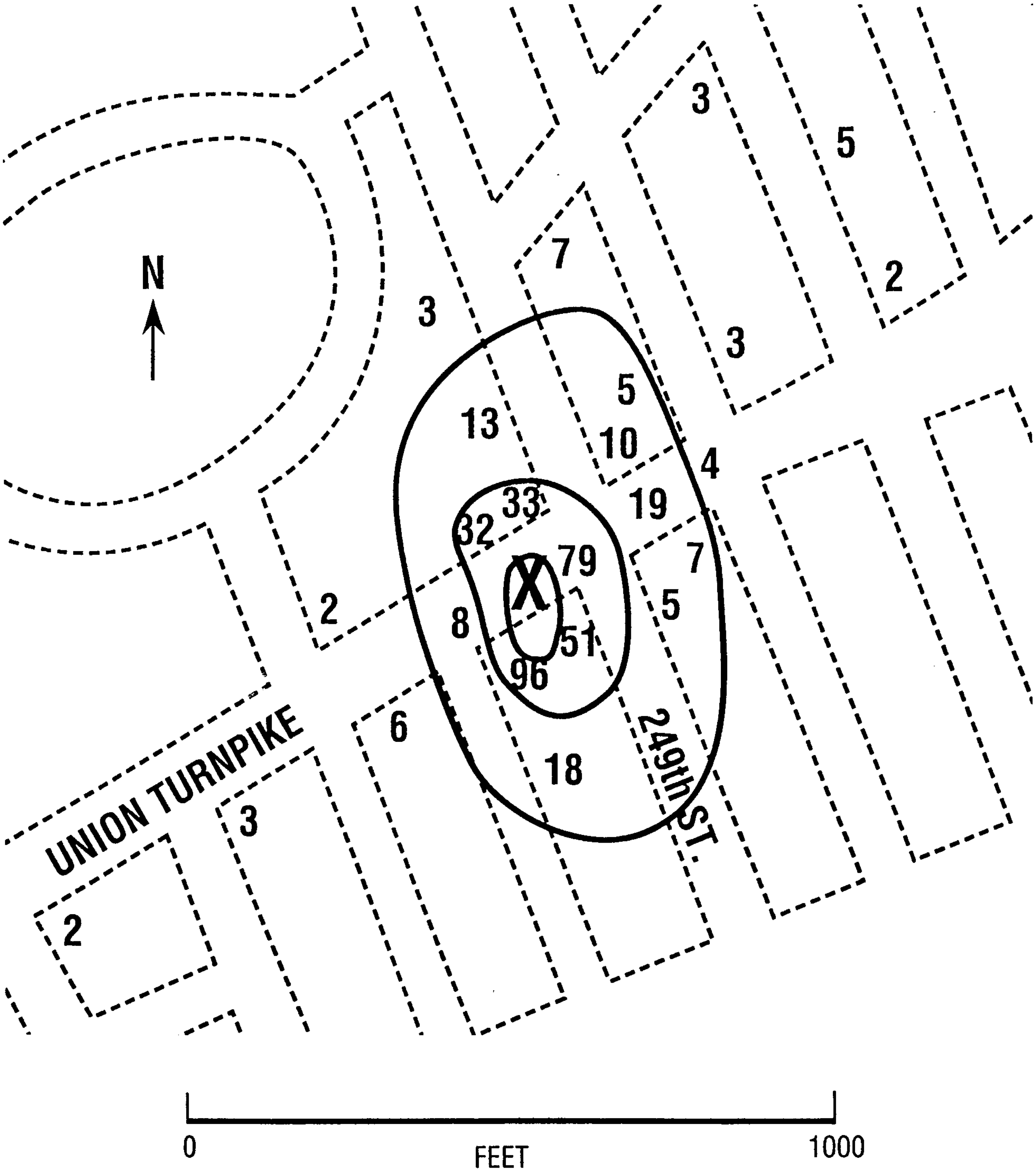
(A)

Figure 3-4
Five measurement sets showing the concentrations of ocPDCH measured in the ambient air around the release site using CATS. All concentrations are in fL/L (fL = 10^{-15} L). The solid lines represent contours of constant tracer concentration (isopleths). Measurement dates for these figures are as follows: 7/26 - 7/28/88 (4A), 7/28 - 7/29/88 (4B), 7/29 - 8/1/88 (4C), 8/1 - 8/3/88 (4D), 8/3 - 8/11/88 (4E).



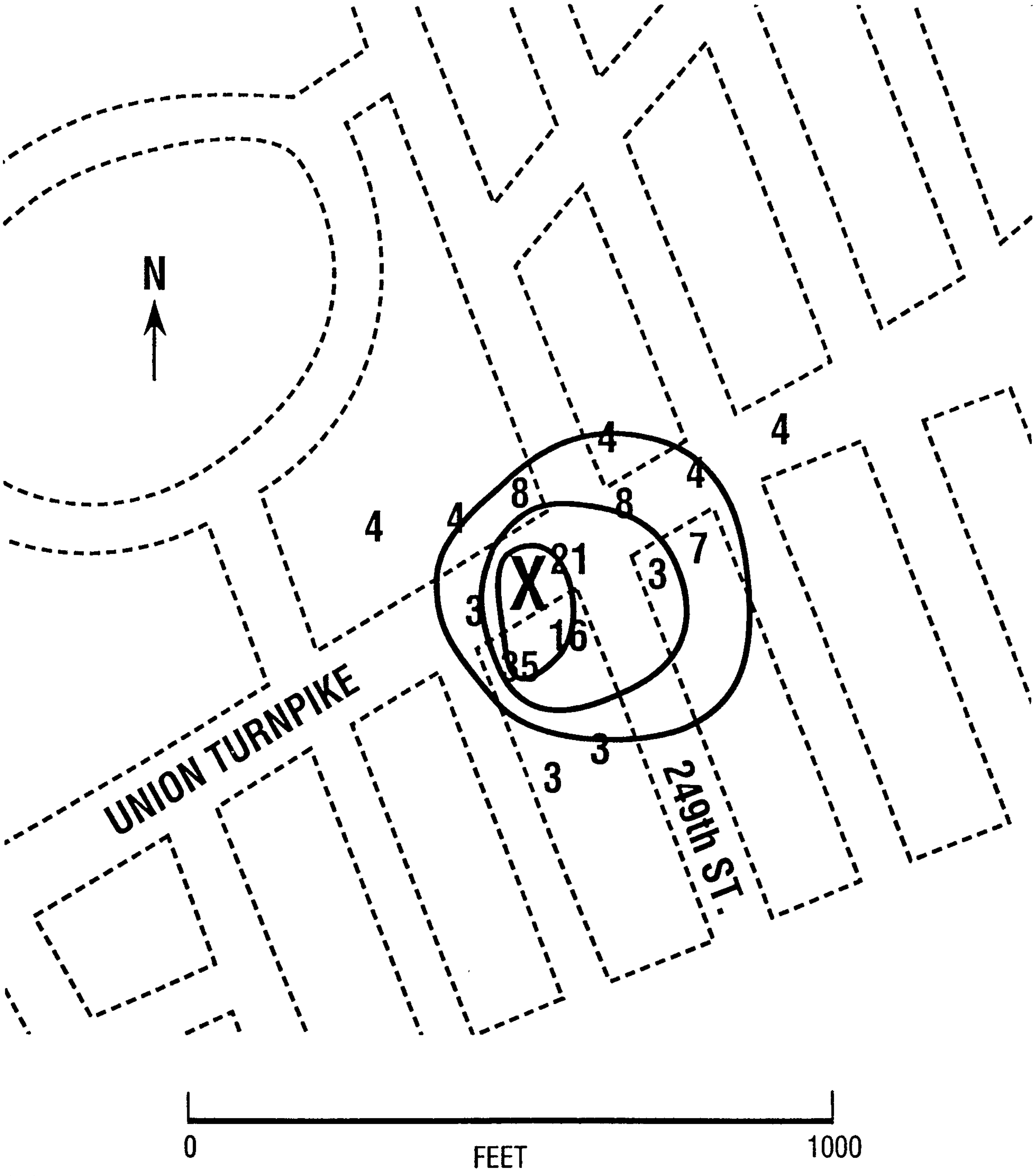
(B)

Figure 3-4
(Continued)



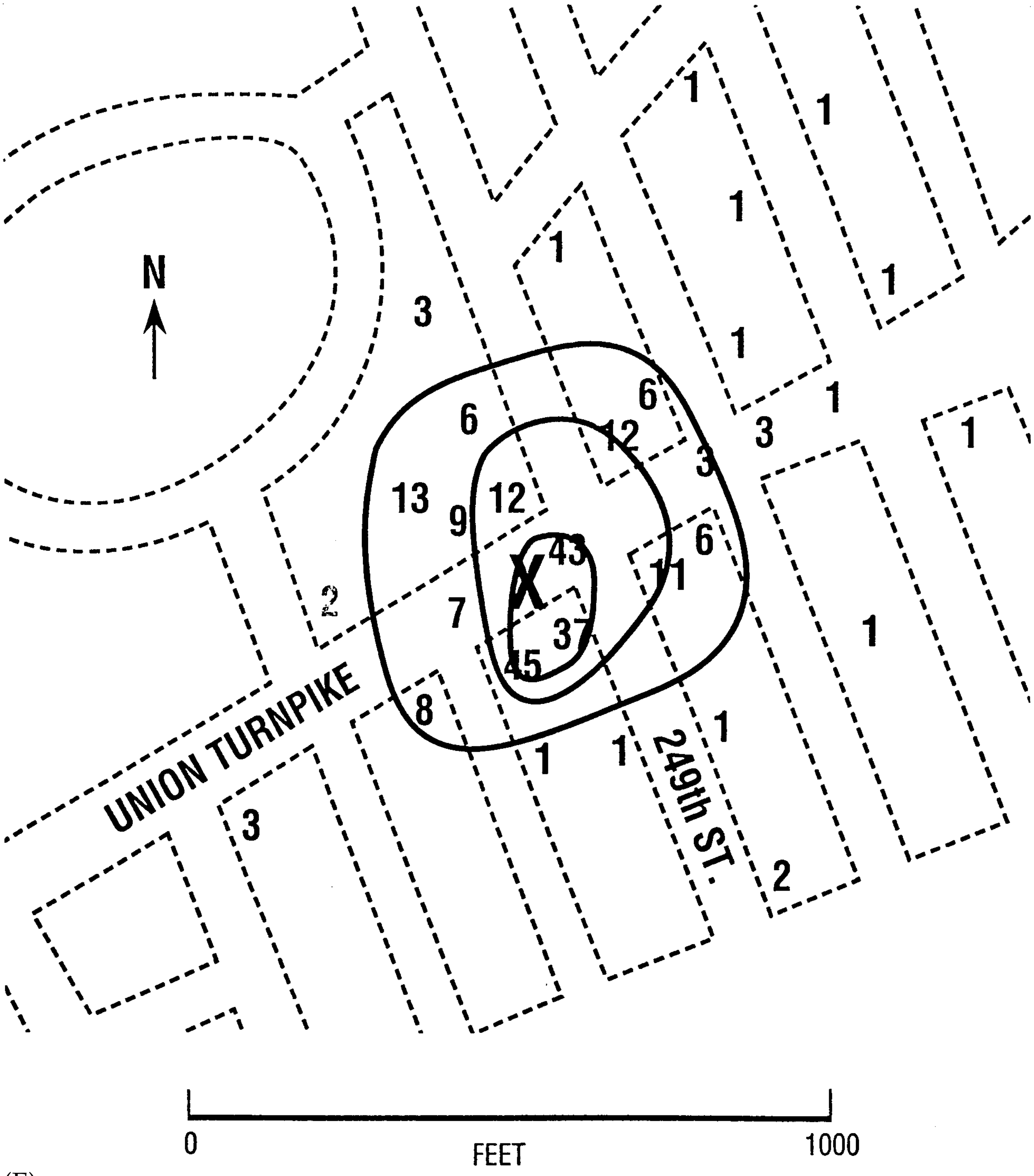
(C)

Figure 3-4
(Continued)



(D)

Figure 3-4
(Continued)



(E)

Figure 3-4
(Continued)

In addition to the buildup information, the Pole CATS were also to be used as a means of estimating how well a leak could be localized using aerial sampling. Since the spillage and the underground fluid release were essentially located at the same spot, the spillage had no effect on this information. As can be seen from the isopleths in Figures 3.4A-3.4E, aerial sampling has the ability to locate underground fluid leaks to within at least 100 feet. The release site location indicated by the isopleths is clearly influenced by winds and traffic flow which, in this experiment, were both from the southwest. Winds were fairly steady and light over the entire experiment.

Ambient air measurements made around the release site with the Dual Trap Analyzer were mostly unsuccessful primarily because the tracer concentrations were generally at or slightly above the limit of detection of this instrument as it is currently designed. This is unfortunate since the DTA, which avoids bringing samples back to an analytical laboratory, would be a more desirable method of executing the first part of the leak locating protocol. One possible solution is to increase the amount of PFT dissolved in the cable fluid. At current costs, however, this remedy would appear to be economically untenable. (A 0.03% solution of PFT in cable fluid, the concentration used in this experiment, raises the cost of the fluid about 3%). A second remedy is to improve the detection capabilities of the DTA. Currently available methods indicate that the sensitivity of the DTA could be improved by about a factor of 100 using a more rapid sampling rate and a more sensitive detector system.

Surface Penetration Sampling

Two types of local sampling for general localization of the leak site were pursued during this experiment: sniffing street cracks and openings with the COPS, and surface-level flux measurements. The COPS was able to locate the two major emission sites, the utility manholes and a nearby sewer manhole, as well as a few smaller hot spots including a tuft of grass growing at the intersection of the road surface and the street’s center island, and leaks from some of the more poorly sealed borehole samplers. The COPS sampling indicated that no perceptible amount of tracer was being emitted through other small street cracks around the release site. This was confirmed by the flux measurements, the results of the tracer flux measurements are shown in Figure 3.5. The total measured flux of ocPDCH on August 11 was found to be 0.75 µL/min, with about two-thirds of this amount coming directly out of the two utility manholes and most of the remaining amount being emitted from a nearby sewer manhole. The large amount of material being emitted from the manhole may be due to tracer vapors diffusing along the fluid release pipe back into the manhole. A small amount of tracer was also found to be emitting from several of the borehole samplers as well as from a tuft of grass growing from a seam between the road surface and the center island.

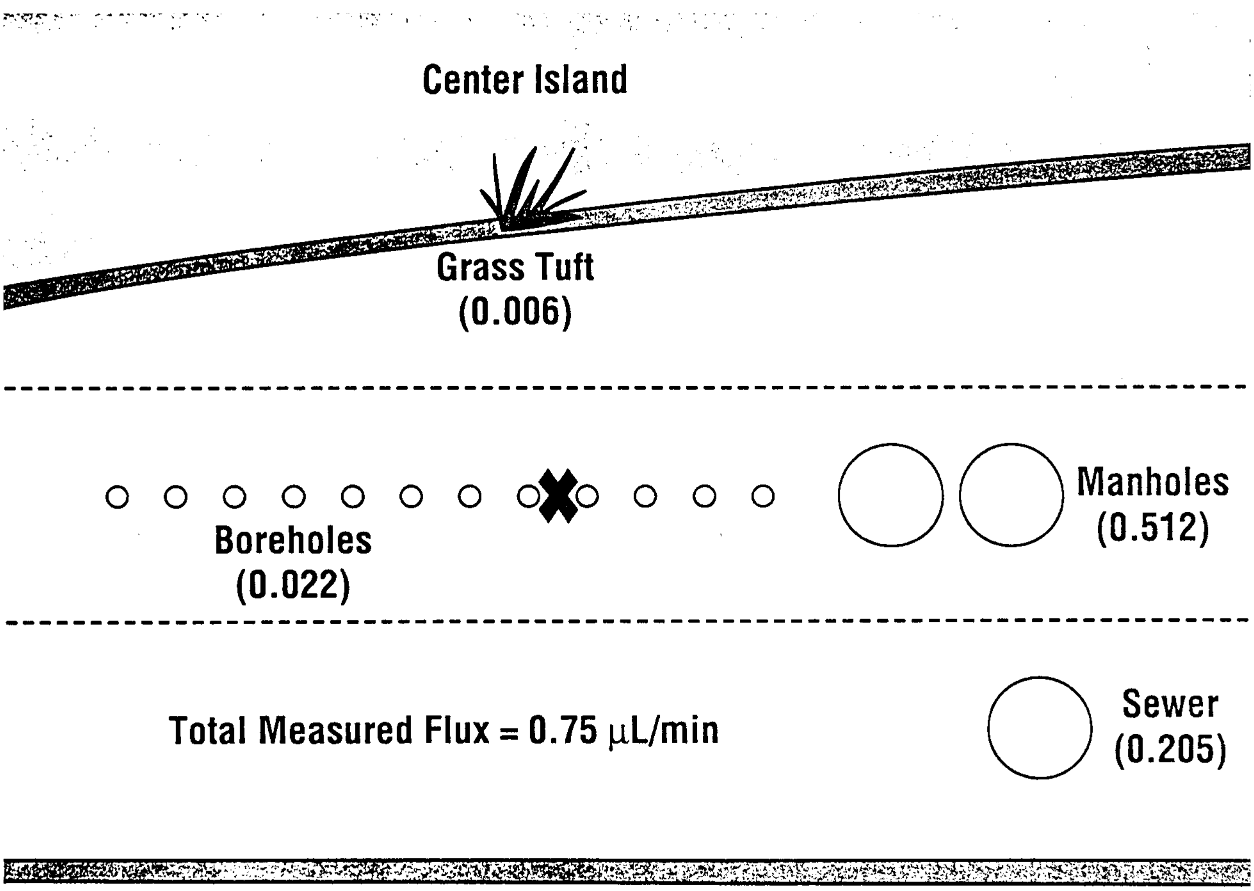


Figure 3-5
Flux measurements made around the release site (shown as an "X") indicate that most of the tracer was emitting from the two utility manholes and the sewer manhole. All measurements are in µL/min of ocPDCH.

In addition to these measurements, a special high sensitivity test was made to see if any measurable amount of tracer was being emitted through visible as well as invisible cracks in the street surface. To perform this test, 15 small cans were sealed to the street surface around the release site. Passive samplers in the cans then measured any tracer emitted through the street surface under the cans. The results from this test showed no measurable amount of tracer coming through small cracks in the street surface. In addition to the direct flux measurements described above, the total flux of ocPDCH was measured in a second way by ratioing the concentration of ocPDCH found on Pole CATS to that found for PMCP, the tracer being emitted at a known rate from a gas cylinder located in the utility manhole. From the known flow of PMCP from the gas cylinder (12.6 cc/min) and the known PMCP concentration in the cylinder (300 ppm), we can calculate an emission rate for PMCP of 3.8 µL/min. The ratio of PMCP to ocPDCH on the Pole CATS was 4.7 leading to a calculated emission rate for ocPDCH of

0.81 µL/min. This compares very well to the emission rate of 0.75 µL/min measured with the flux apparatus and indicates that most if not all of the major emission hot spots were located at this site.

Based on these results, it appears that the COPS may prove to be most valuable in preliminary leak location surveys. Current leak location procedures start by visually inspecting sewers and manholes along the feeder for fluid. The probability of locating a leak in this way can be vastly improved using PFT-tagged fluid and a COPS sniffer.

Leak Pinpointing

Borehole sampling along the street above the release site proved to be an efficient and reliable way of locating the underground fluid release to within ~10 feet or less. Thirteen sets of borehole measurements were taken over a 29 day period following the start of the fluid release. Figure 3.6 shows the results from three of these sets which show both the increase in the PFT concentration with time just below the surface and the pinpointing capability. Maximum values reached about 7 parts PFT per million parts air (ppm) which is consistent with a 0.03% PFT solution in fluid at a ground temperature of 65°F. Figure 3.6 indicates that, in this case, borehole sampling was able to locate the fluid release point which was between boreholes 11 and 10 and about two feet from borehole 11, to better than five feet. In addition, borehole sampling performed within 24 hours of the start of the oil leak showed the technique to be immediately effective. BNL is continuing to use the borehole samplers as a means of monitoring the spread of the PFT vapors underground.

The borehole samplers were also able to provide information about the time necessary for the PFT vapors at the surface to buildup to its steady state value. A time plot indicating the increase in tracer concentration at four of the boreholes is shown in Figure 3.7. This plot shows a general increase in tracer concentration up to 15 days and then a decrease. The increase is attributable to the time to reach the steady state concentration, which is a function of the ground temperature since that effects the tracer partial pressure above the leaked oil. The air temperature during the first 15 days was in the mid 90's and much lower during the following 15 days. The cooler weather also reduced demand for air conditioning power which also probably reduced ground temperatures.

Assuming during the first ten day period that the steady state concentration at constant temperature would have been 6 + 1 ppm, for borehole 11, 20% of that level (1.2 + 0.2 ppm) was reached in three to four days. A model, based on gaseous diffusion theory, was used to calculate the concentration rise to steady state and is displayed in Figure 3.8 for various pipe depths, which is the distance between the fluid release point and the ground surface. Reaching the 20% level in three to four days corresponds on Figure 3.8, to a depth of about 7.5 to 8.5 feet. However, the model was for an unpaved surface, whereas the measurements were performed under a street pavement. The latter would tend to prolong the time to reach steady state and, hence, the depth should be less than 7.5 to 8.5 feet. The actual pipe depth was estimated to be about 7 feet in excellent agreement with the model.

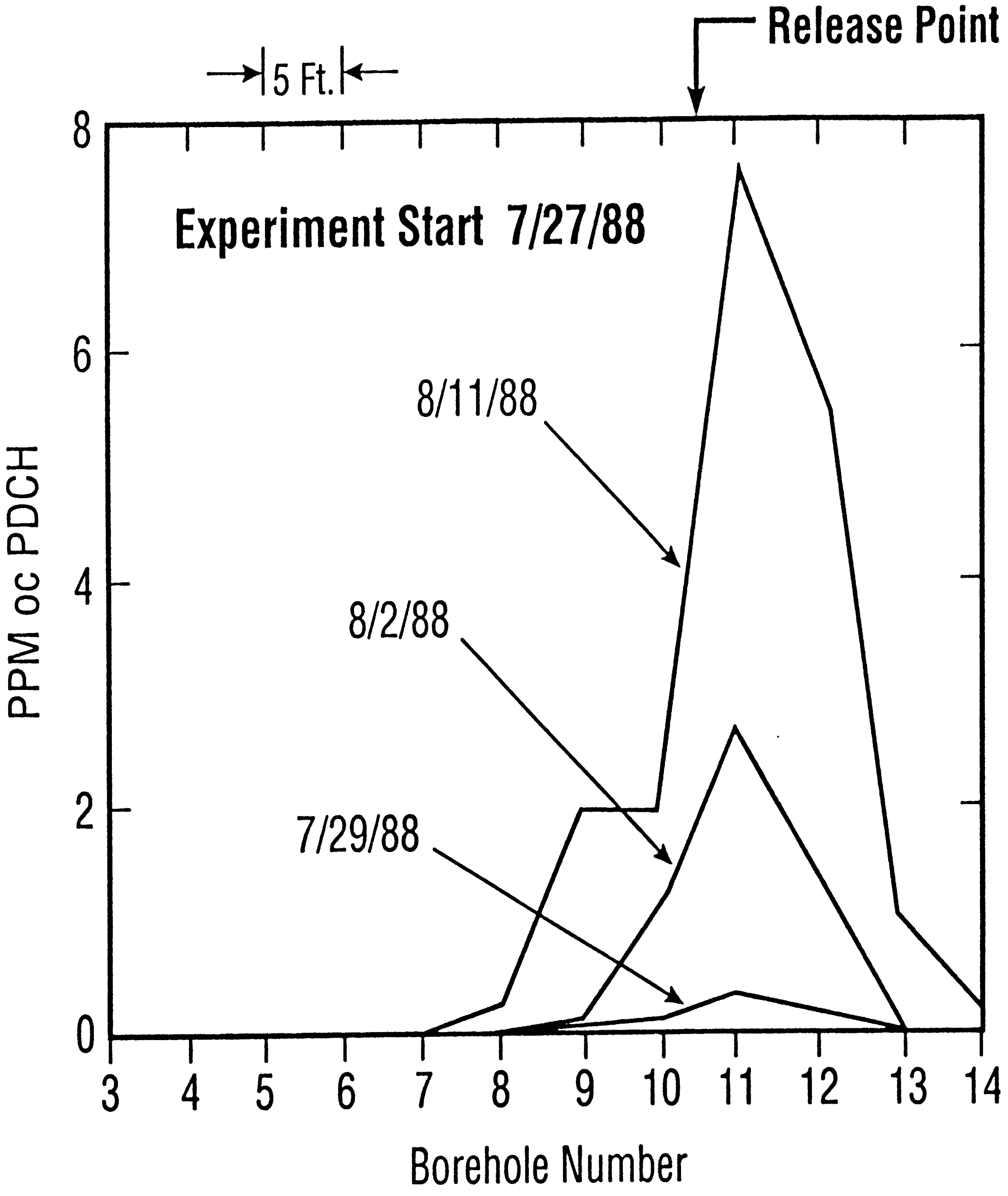


Figure 3-6
Results from three sets of borehole analyses showing both the buildup and spread of the released PFT just below the street surface.

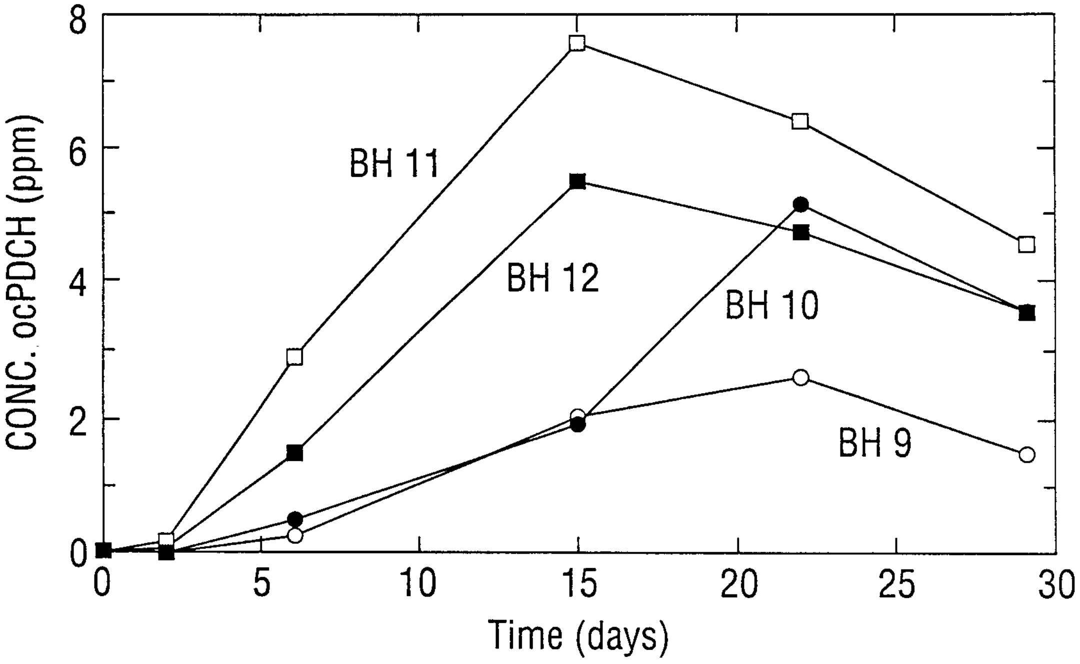


Figure 3-7
The concentration of ocPDCH as a function of time as measured by four of the borehole samplers just above the release site.

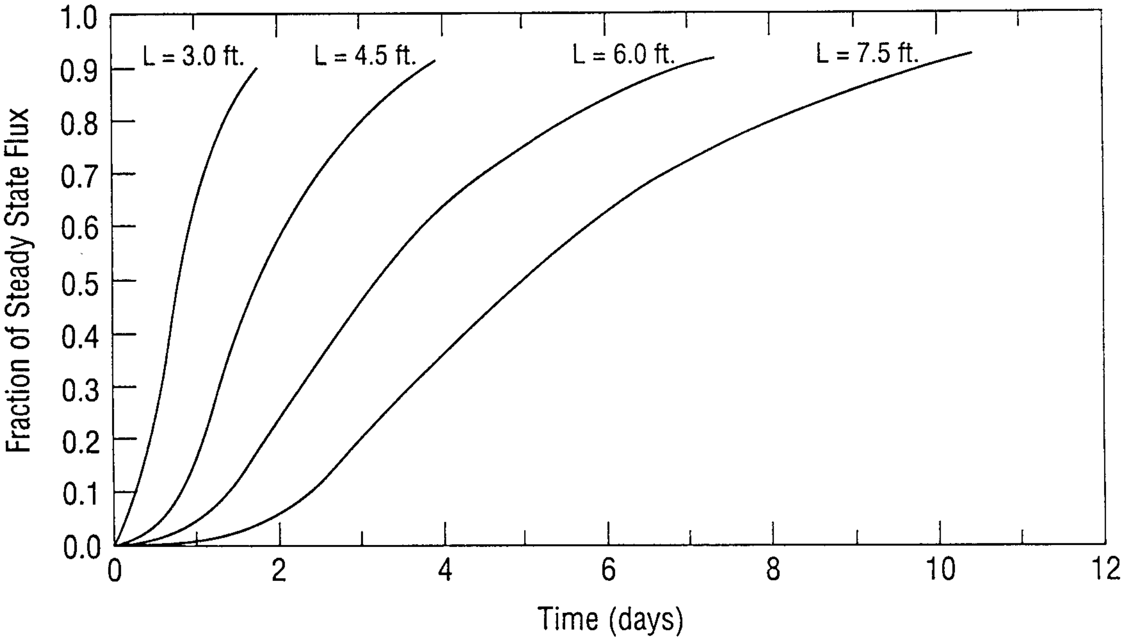


Figure 3-8
Theoretical calculations showing the rise to steady state of the tracer emission from the surface just above the leak location. L is the distance between the leak site and the surface. Transport is assumed to be caused solely by gaseous diffusion.

Conclusions

The detection of tracer vapors from PFT-tagged fluid appears to be a viable method for both detecting the locale of an oil leak from any underground HPFF electric feeder and subsequently pinpointing the exact location of the leak. The measurements reported in this paper involving a simulated fluid leak in Queens, New York, lead to the following major conclusions:

1) Sampling the ambient air around a leak site can successfully locate a fluid leak to within less than 200 feet (~ one block). For the 30 gallons of 0.03% PFT in cable fluid solution released in this experiment, measurable tracer concentrations existed over about a 500 foot radius around the release site indicating that one tracer sample per block taken along the path of a leaking fluid feeder would be sufficient to detect the presence of a leak. Once detected, closer spaced aerial sampling should indicate the leak location to within 100 to 200 feet.

2) Borehole sampling can further isolate a leak location to within ~10 feet. Borehole samples at the Queens site, spaced at five foot intervals above the leak site, were able to locate a simulated fluid leak to within a few feet.

3) For some leaks, a survey of the manholes and sewers along the effected feeder line with real-time PFT instrumentation may be an effective way to quickly isolate leak locations and eliminate the need for ambient air sampling.

4) PFT vapors (at this site) are emitted primarily from obvious ground openings such as sewers and manholes. Therefore, real-time instrumentation, which was able to locate these major emission points, may not be able to isolate leak locations to ~10 feet. A great deal of future work needs to be performed before this method of locating underground fluid leaks can be implemented on a routine basis. First, this experiment needs to be repeated in a way which more closely simulates an actual fluid leak scenario. For example, an actual fluid leak is seldom detected until several days after the start of the leak. Assuming a leak rate of 1 to 10 gal/h for three days, this means that 72 to 720 gallons of fluid will have been released when the leak locating procedure is initiated and the leak will continue while its location is being isolated, perhaps for another three days. In this sense, the 30 gallon release for the Queens experiment actually represented a worst case detection scenario. On the other hand, a great deal of the tracer vapor emitted during this experiment may have been caused by channeling of PFT vapors along the fluid release pipe. Both of these issues need to be addressed in a future experiment.

Future work in this area also needs to concentrate on meeting the goal of locating these fluid leaks in no more than three days. Current PFT technology has shown that it is possible to make the tracer measurements necessary to find underground fluid leaks. However, when time is important, real-time instrumentation is invaluable. Existing

PFT real-time instrumentation was designed over ten years ago for atmospheric transport experiments and needs to be adapted to a scenario of rapidly locating fluid leaks in mobile vans. This will require improvements to both the sample collection and the sample detection capabilities of these instruments.

4

DEMONSTRATED DETECTION OF AN ACTUAL BURIED HPFF CABLE FLUID LEAK

Introduction to the Demonstration Detection of an Actual Leak

Transmission of high voltage electrical power in cables requires a dielectric medium for electrical insulation and heat dissipation. Traditionally, dielectric fluids, gas and plastic materials have been used to accomplish this double task. The fluid surrounds the cable and is itself contained in a pipe, an arrangement known in the industry as HPFF cable (high pressure, fluid-filled cable). Occasionally, leaks occur in these pipes, and the location of these leaks can be a costly, time-consuming procedure.

Leak detection with a liquid tracer such as perfluorocarbon tracers (PFT) constitutes a different solution to the leak detection problem. The PFT is mixed into a certain amount of "primary" fluid which then is added to the pipe fluid. At the leak site the PFT molecules migrate to the fluid/soil interface where they volatize into the soil pores. Subsequently the PFT is then transported to the street surface and is dispersed into the ambient air. Here they can be detected to within 70 feet by simply patrolling the street surface with a van equipped with PFT detection instrumentation. The advantages of the PFT technology over other tracers are outlined in Section 3.

To actually demonstrate the superiority of this PFT technology several simulated fluid leaks were created in 1988 and 1990. The location of these simulated leaks was known only to the utility, and not revealed to the leak search team. Procedures were then developed to find a leak in a cable under actual, real life circumstances. The experiments with the simulated, known leak location are described in Section 5, and those with the simulated, unknown leak location successfully demonstrated in 1990 in Section 6.

Review of Conventional Leak Locating Systems

Conventionally there are two primary types of leak location systems:

1. Locating systems which rapidly locate the leak to a manhole section length (2000 to 4000 feet) in a circuit that may be 15 miles long.

2. Pinpointing systems to find the exact location of the leak.

Table 4.1 and Table 4.2 (reprinted from Ref. 1) are overviews of the most commonly encountered methods of leak locating and pinpointing. The existence of a sufficiently large leak is detected through lowered reservoir levels or too-frequent operation of a pressurizing pump. The feeder then has to be de-energized and utilities usually “freeze” the fluid up to the mid point of a circuit, then to the quarter points, etc.

Table 4-1
Determination of General Location

Method	Resolution	Lowest Flow	Dielectric Compatibility	Physical Interference	Cost of Use	Environmental Effects	Suitable for Self-Contained GITL
FLOW DIRECTION INDICATORS							
1. Thermal Probe	Section[1]	20 liter/hr.	OK	Maybe[2]	Low	None	No
2. Dyes	Section[1]	7	Test	Maybe[2]	Low	None	No
3. Radioactive isotopes	Section[1]	7[3]	OK?	Maybe[2]	Med	Yes	Maybe
4. Hot or Cold Injection	Section	7	OK	No	Med	No	No
5. Totalizing Flowmeter	SSJT[4]	Varies[5]	OK	Maybe[6]	Med	None	No
6. Differential Pressure	Stop Joint	Low	OK	No	Med	No	Self-Contained Only

NOTES:

[1] Section length between two manholes. Adding weldolets and access pits on half and quarter points, etc. can increase resolution on new lines.

[2] Concern of damage to cable if the occupied pipe is pressure-tapped.

[3] Increased resolution could be obtained by placing probes at opposite ends of a joint casing.

[4] Semi-stop joint sections (usually 4–10 km); oil stop in the cable is needed, plus bypass piping.

[5] A function of time installed in system. Typically 2 days for a 40 liter/hr leak.

[6] Concern about large numbers of stop joints if added only for leak location.

Table 4-2
Determination of Specific Location

Method	Resolution	Lowest Flow	Dielectric Compatibility	Physical Interference	Cost of Use	Environmental Effects	Suitable for Self-Contained GITL
PINPOINT							
1. Tracer gases	Pinpoint[1]	Low[2]	Test	Remove?	Low-Med	Maybe	Yes
2. Odorants	Pinpoint[1]	Low[2]	Test	Remove?	Low	Maybe	Yes
3. Radioactive isotopes	Pinpoint	Low[3]	Test	Remove?	Med-High	Yes	Yes
4. Subsurface Radar	Pinpoint	Low	OK	OK	Med	Maybe	Maybe4
5. Trained Dogs	Pinpoint	Low	OK	No	Low	No	Yes
6. Acoustic Emission	Pinpoint	Test	OK[5]	Maybe	Med-High	No	Maybe
7. Dissolvable Insulation Wire[6]	50 meters	Low	OK	No	Med	No	S.C.
8. Microphonics	Pinpoint	Med	OK	No	Low	No	No

NOTES:

[1] Bar-holing may be necessary. Resolution affected by other underground services - ducts, etc.

[2] Assuming gases are pre-mixed in oil. Transit time to a leak is too long for introduction at time of leak. Addition at time of leak may be suitable if rapid circulation is possible.

[3] Suitable only if it can be put in place by rapid circulation.

[4] Possibly suitable for self-contained, not for GITL.

[5] May need to add a gas to give hissing sound.

[6] Suitable only for non-urban, new installations.

The leak introduces a flow in one of the frozen sections which should be detectable by one of the methods described in Table 4.1; however, the fluid velocities due to leaks are extremely small, a 10 gal/h leak resulting in a velocity of only 0.022 feet/minute.

The most widely used instrument to find such small flow rates is the Thermal Probe, developed by Con Edison in the mid-1960's. Unfortunately, for newer cable systems with low viscosity fluids (Sun #4 and low viscosity polybutene) the Thermal Probe frequently gives false readings. More details on this technique are given in Reference 16.

Welch Chemical Company of Schenectady has developed an Enhanced Conductivity Oil (ECO) probe which is now used on low viscosity systems. The probe is inserted into a valve in a manner similar to the thermal probe. A very small quantity of enhanced-conductivity oil, less than 1 ml, is injected inside the electrode array using a high-pressure syringe and needle. When the fluid bridges a pair of electrodes and causes a pair of LED's to light, indicating flow direction, a bleed valve is opened and several liters of the filling fluid are flushed to remove all of the contaminated fluid.

Unfortunately, a major problem was uncovered in the use of any probe that is installed in a cable pipe. By the injection of low streams of dyes into a full size clear acrylic joint casing, it could be shown that often natural convection currents are far larger than the downstream migration of the fluid due to a leak (16).

If the leak search is successful and the leaks are isolated to sections of about 2000 to 5000 feet, pinpointing is usually attempted with tracer gases. HPFF cables typically have a blanket of dry nitrogen at 1/2 atmospheres over the fluid in the pumping plant storage tank to prevent moisture and oxygen from diffusing the fluid. Replacing the nitrogen with a tracer gas has the advantage that the tracer will begin diffusing into the earth as soon as the leak begins. However, several weeks are necessary for the tracer gas to saturate the fluid. The second possibility, once the general location of a leak is known, is to add the tracer to the fluid by injection at an adjacent manhole.

Based on results of electrical compatibility tests with oil/paper insulation, sulfur hexafluoride (SF_6) and a Freon (c-C_4F_8, perfluorocyclobutane) seemed promising but would have to be present in large quantities in order to be detected at the earth surface due to the rather insensitive detection technology for these tracers and the comparably high background concentration of SF_6, about 1 ppt (part per trillion).

It was calculated that about 2.2 pounds of the SF_6 tracer had to escape the HPFF cable before leak location could begin. This corresponds to 375 gallons of fluid saturated at 10 psi if the pumping plant is blanketed with SF_6, or 150 gallons saturated at 60 psi if bulk SF_6 is added to the pipe near the leak during leak location operation. It was assumed that at a leak rate of 10 gal/h the SF_6 tracer would appear at the surface after about 40 hours (16).

Since it was generally not feasible to patrol the street surface with a leak detection instrument, placing traffic cones over the route of the feeder, at 10 feet maximum spacing, and sniffing the air inside the cones after they had been in place for a half-hour or more was a viable substitute. Small boreholes, approximately 3/4 inches in diameter, 6 inches deep and spaced 10 feet apart were recommended for final pinpointing.

Theory of PFT Leak Detection

General PFT Theory and Instrumentation

The perfluorocarbon tracer technology has been described in detail elsewhere (17). The types of tracers available are shown in Appendix A along with their relevant physical properties. The instrumentation used to detect PFT vapors is listed in Appendix B.

The Dual Trap Analyzer (DTA) with its strip chart recorder read-outs is an almost "instantaneous" or real time leak locating instrument. "Real time" in this case implies a delay of only 6 minutes, the time necessary to desorb and analyze the adsorbed PFT tracers. The DTA in its present configuration can detect concentrations above 10^{-15} L/L (>11 fL/L, where fL is femtoliter or 10^{-15} liter), which is near the ambient PFT background concentration. By contrast, the ambient concentration of sulfur hexafluoride, SF_6 is in the range of 10^{-12} L/L.

The programmable sampler or BATS (Brookhaven Atmospheric Tracer Sampler) can detect concentrations as low as 10^{-16} liters of tracer per liter of air (i.e., 0.1 fL/L). It is more sensitive than the DTA, but lacks the real-time detection capability of the DTA, because the internal adsorption tubes of BATS have to be brought back to the laboratory for subsequent PFT analysis.

Thus, for any leak search, simulated or real, two types of instruments are available:

a) Real time (or almost real time) instruments:

The DTA with Nelson Data acquisition system with an electrical power source such as a generator for mobile locating (or traversing, the terms are explained in Section 6), ten-block localizing, and intra-block localizing, and, the COPS (Continuously Operating Perfluorocarbon Sniffer) for 50-feet pinpointing;

b) Instruments, dependent on subsequent laboratory analysis:

The BATS or NSS (NOAA Sequential Sampler) which can provide a duplicate PFT sampling technology and verify the results of the real-time instrumentation. However, these samplers require a laboratory-based PFT analysis for mobile locating (traversing), ten-block localizing, and intra-block localizing, and the CATS (Capillary Adsorbent Tracer Sampler), also a laboratory-based analysis technology for stationary i.e., preliminary localizing.

Mixing Equations for the Preparation of PFT-Tagged HPFF Fluids

Although the perfluorocarbon tracers are available at ambient temperatures as liquids (specific gravity ranging from 1.7 to 1.85 g/ml) they cannot be added directly to the fluids, i.e., direct addition of PFT to the fluid would result in a layer of tracer at the bottom of the fluid container or conduit due to the density difference. Pumps might additionally cause the formation of small PFT droplets in the fluid, which, over time, would eventually dissolve; however, due to time limitations this process has to be accelerated and the tracer has to be mixed or stirred into the fluid by mechanical means.

A second problem arises because of the large quantities of fluid encountered in these feeders (2 gallons per foot). For practical reasons these large quantities, about 10,000 gallons for a 1 mile feeder, cannot be taken out of the cable and mixed with the perfluorocarbon.

Hence, the following approach was developed by the Tracer Technology Center. First, a primary solution was created which contained the maximum possible amount of PFT in the fluid (about 1% to 2% by weight). Only a limited quantity of this solution has to be prepared as will be shown:

The mass of PFT to be used for any experiment (MPFT) is equal to:

$$\text{MPFT} = \text{Moil,f} * \text{Coil,f} \qquad \text{(eq. 1)}$$

where

Moil,f = Mass of fluid in the final application (which can be the feeder cable, a cable model or any other application)
$C_{\text{oil,f}}$ = Concentration of PFT in that final application, gm PFT per gm of oil

Now, the mass of the PFT in the primary solution is the same as the one in the final solution (Eq. 2):

$$M_{\text{PFT}} = M_{\text{oil,f}} * C^{\text{pft}}_{\text{oil,f}} = M_{\text{oil,p}} * C^{\text{pft}}_{\text{oil,p}} \qquad \text{(eq. 2)}$$

From Eq. 2 one can create the ratio $M_{\text{oil,f}}$ / $M_{\text{oil,p}}$,

which is equal to

$$\frac{M_{\text{oil,f}}}{M_{\text{oil,p}}} = \frac{C^{\text{pft}}_{\text{oil,p}}}{C^{\text{pft}}_{\text{oil,f}}} \qquad \text{(eq. 3)}$$

and, therefore,

$$M_{oil,p} = \frac{C_{oil,f}^{pft}}{C_{oil,p}^{pft}} * M_{oil,f} \qquad \text{(eq. 4)}$$

By dividing through the density, one obtains an equivalent expression in terms of volumes rather than mass:

$$V_{oil,p} = \frac{C_{oil,f}^{pft}}{C_{oil,p}^{pft}} * V_{oil,f} \qquad \text{(eq. 5)}$$

According to these equations the quantity required for the primary solution is a function of the dilution ratio, Coil,f / Coil,p, that is, the concentration of the final solution to that of the primary solution.

For instance, if the final solution was to contain 0.01% PFT and the primary solution was prepared at 1% PFT, only 1/100 of the volume of the fluid in the cable had to be tagged initially as primary solution (e.g., 0.01% / 1% = 1/100). Thus, if the feeder contained 10,000 gallons, the primary solution had to consist of 100 gallons (or two 55 gallon drums). This quantity of primary PFT-tagged fluid can be conveniently injected into the cable and allowed to mix with the main stream in the cable. The required final solution of 0.01% would be established after a time t_{circ} (see Eq. 7 below).

From Eq. 5, the volumes per unit time (or flow rates) and the circulation and tagging times can be derived by applying the quantities per unit time:

$$V_{oil,p} = \frac{C_{oil,f}^{pft}}{C_{oil,p}^{pft}} * V_{oil,f} \qquad \text{(eq. 6)}$$

The circulation time is the total volume divided by the flow rate:

$$V_{oil,p} = \frac{V_{oil,f}^{pft}}{\dot{V}_{oil,f}^{t}} = t_{circ} \qquad \text{(eq. 7)}$$

The tagging time equals the volume of the primary solution divided by the injection rate. Thus, it can be seen that the circulation time equals the tagging time by dividing Eq. 5 by Eq. 6.

$$\frac{V_{oil,f}^{pft}}{\dot{V}_{oil,f}^{t}} = t_{tag}\frac{V_{oil,f}}{\dot{V}_{oil,f}^{t}} = t_{circ} \qquad \text{(eq. 8)}$$

Preparations

Compatibility Testing of PFT-Tagged Fluid With Cable Insulation

Prior to the field demonstration the impact of perfluorocarbons on the quality i.e., dielectrical property, of the cable fluid had to be determined. To this purpose a dissipation or power factor test was undertaken in accordance with ASTM Standard D924. The dissipation factor may be useful as a means of quality control, and as an indication of changes in quality resulting from contamination and deterioration in service or as a result of handling. A power factor test consists of samples in special cells which are subjected to alternating electrical fields. The dielectric losses and the heat energy dissipation then measured may be due to added components such as the PFTs.

The power factor tests were conducted with various types of cable fluid, such as Chevron DF 100, a mixture of alkylbenzene/polybutene and with a mineral oil based fluid (Sun #6) from actual Con Edison cables. These fluids were subjected to 100% stress (318 V/mil), to 150% stress (477 V/mil) and to temperatures of 90°C, the tests lasting from a few days up to six months.

The tests were conducted with filtered and unfiltered fluid. The procedure started by degassing 2 liters of the filtered and unfiltered fluid and by tagging the samples with 0.05%, 0.3% and 1% of PFT. A special tagging apparatus was developed which is shown in Figure 4.1. The tagging procedure itself consisted of first creating a 1% PFT stock solution of a few 100 ml of fluid and then adding and dissolving this solution in larger quantities (e.g., 2 liters) to attain the desired concentration.

The results of these tests generally indicated that the PFT had no measurable influence on the quality of fluids as expressed by the power factor.

Table 4.3 shows the test results for a mixture of polybutene and alkylbenzene at 150% stress (477 V/mil) and 90°C. The addition of 0.05% of PDCH actually decreased the power factor for filtered fluid from 0.775 to 0.69 and for unfiltered fluid from 1.028 to 0.633. The results for the other fluid types were in the same range. Further details are given in Appendix C.

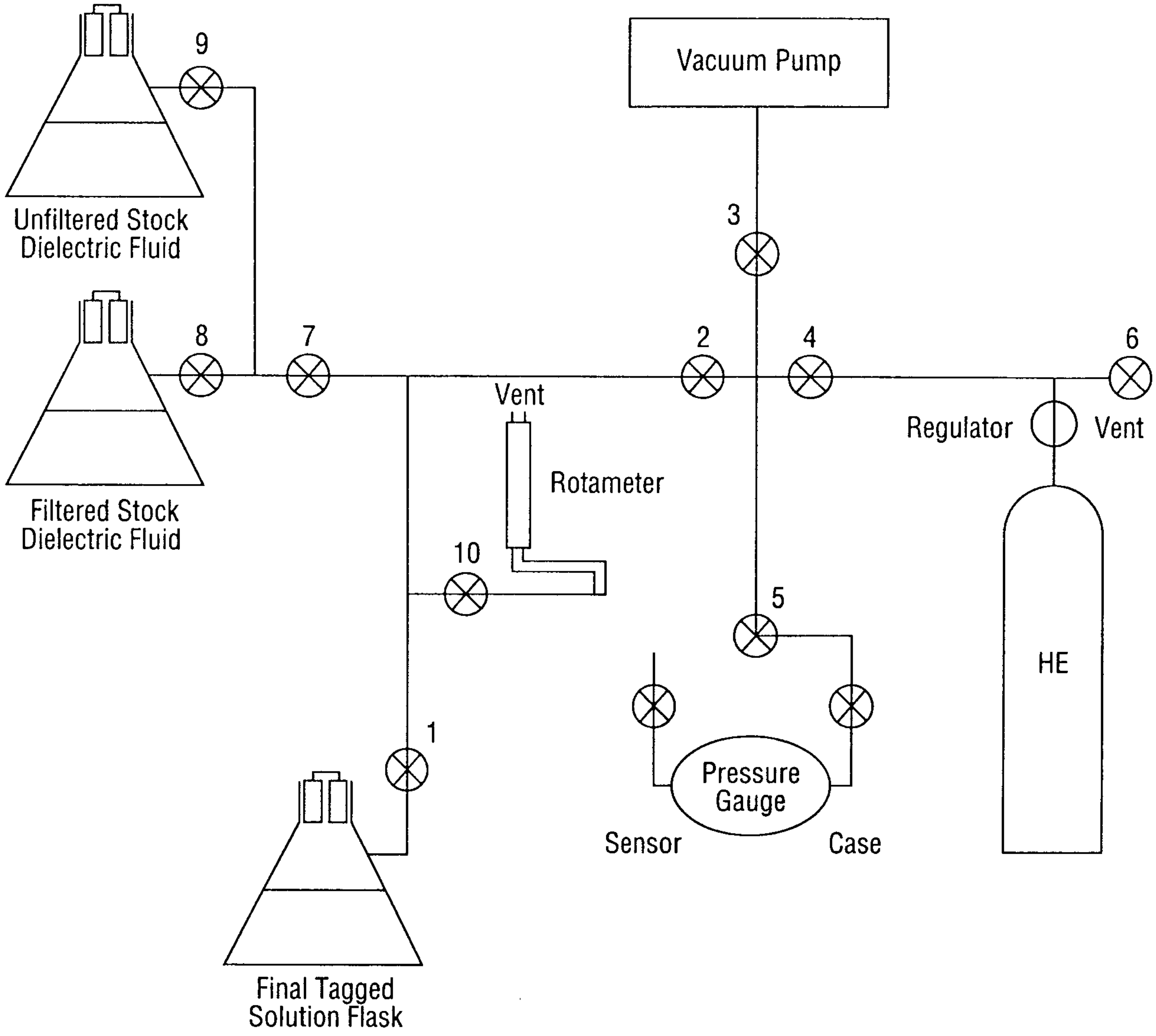

9
Unfiltered Stock
Dielectric Fluid
8
Filtered Stock
Dielectric Fluid
7
Vacuum Pump
3
2
4
6
Vent
Regulator
Vent
Rotameter
10
5
HE
1
Pressure
Gauge
Sensor
Case
Final Tagged
Solution Flask

Figure 4-1

Table 4-3
Power Factors for Alkylbenzene/Polybutene Dielectric Fluid

At 1.5 Rated max. Stress (477 V/m) - 10.7 Kv			
0% PFT		0.05% PFT	
Filtered Oil	Unfiltered Oil	Filtered Oil	Unfiltered Oil
#1	#3	#5	#7
0.661	0.407	0.499	0.375
0.893	0.781	0.724	0.491
0.781	0.866	0.683	0.490
0.775	1.028	0.690	0.633

Tagging and Mixing of Fluid

For the simulation experiments a primary solution of 2% tagged ortho-PDCH fluid was prepared. The final solution was targeted to be 0.1% by weight of o-PDCH in fluid with a dilution ratio of 1/20 (0.1%/2%). The volume of final solution for the simulations was planned so as to fill a 55-gallon drum, portions of which were to be injected into the subsurface for the purpose of a later leak search.

For the simulation experiments the above mentioned dilution ratio of 1/20 required that a quantity of about 2.5 gallons of primary solution be prepared. This was done by transferring an appropriate amount of PFT into a flask containing the fluid and mechanically stirring the mixture overnight with a magnetic stirring to obtain the primary solution.

That primary solution was then mixed with the fluid from the 55 gallon drum yielding the required 0.1% final solution. The injection of the primary solution into the drum was accomplished by using a dual head metering pump, the flow rates of the two heads adjusted such that a dilution ratio of 1:20 was achieved (see Figure 4.2 for pumping and mixing arrangement).

De-oxygenation and tagging of the actual feeder fluids were accomplished with a drum mixer as shown in Figure 4.3. The primary solution needed de-oxygenation before PFT tagging. This was generally accomplished by either vacuum desorption or helium sparging.

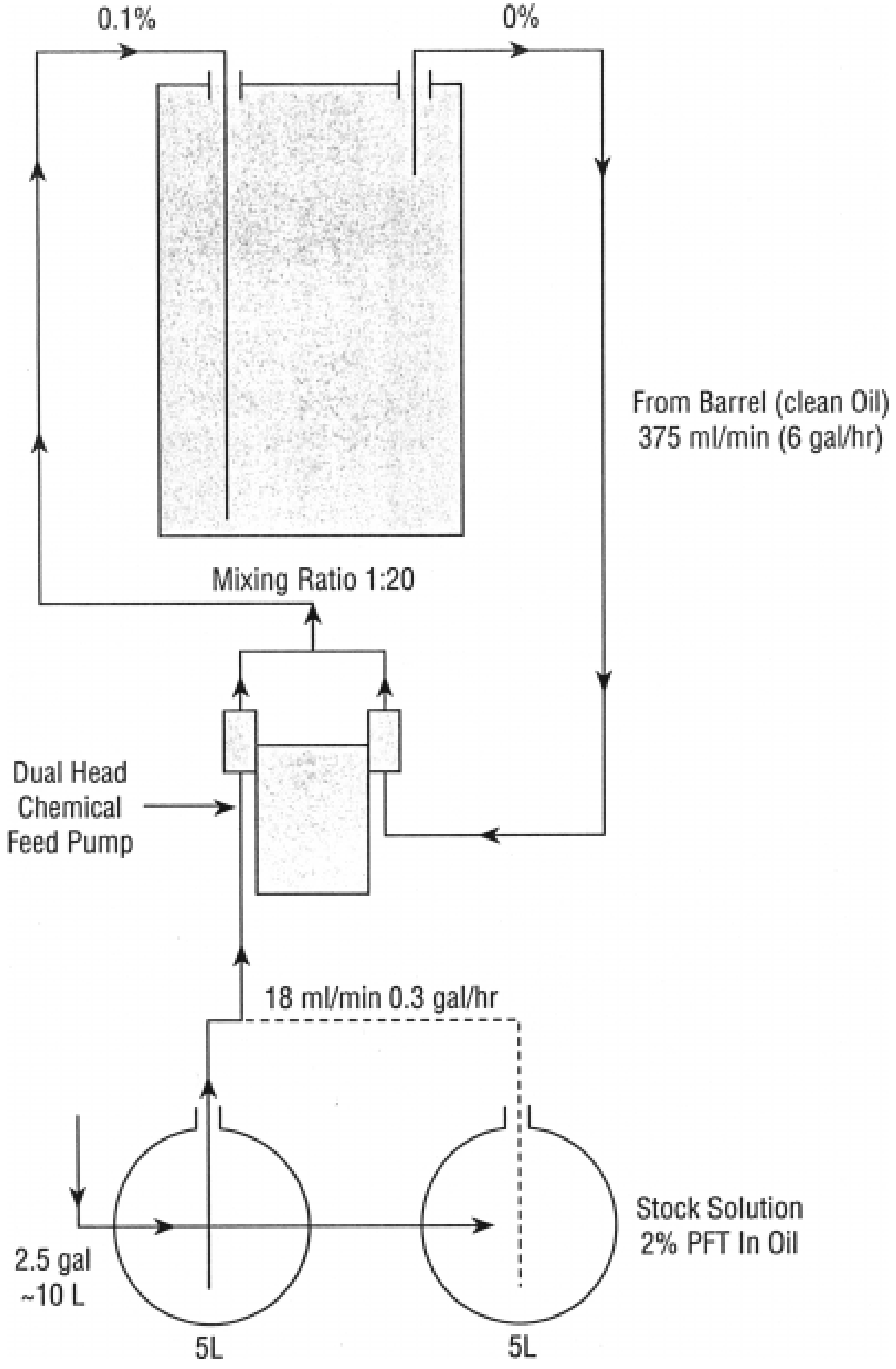

0.1%
0%
From Barrel (clean Oil)
375 ml/min (6 gal/hr)
Mixing Ratio 1:20
Dual Head
Chemical
Feed Pump
18 ml/min 0.3 gal/hr
Stock Solution
2% PFT In Oil
2.5 gal
~10 L
5L
5L

Figure 4-2

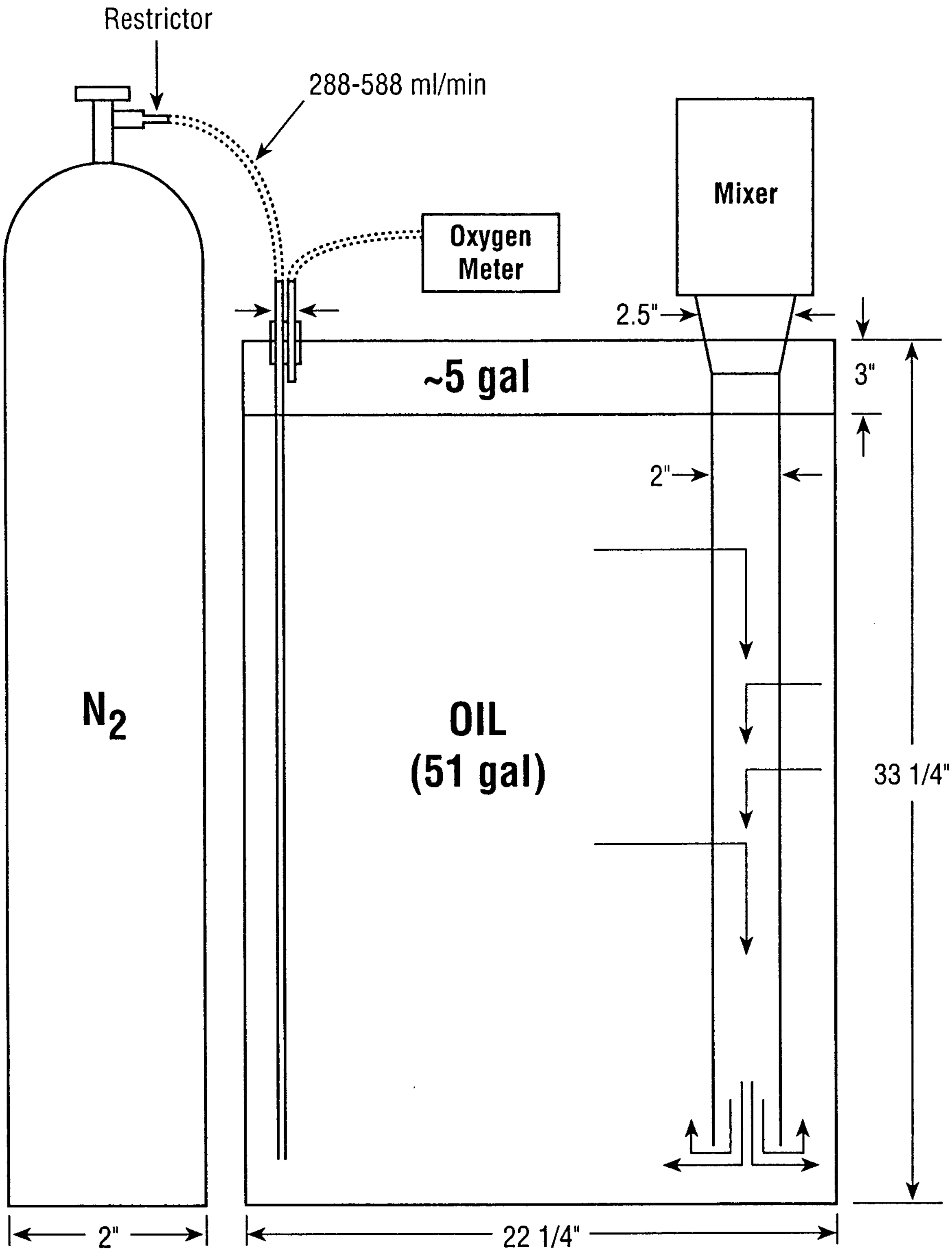

Restrictor
288-588 ml/min
Oxygen Meter
Mixer
2.5"
~5 gal
3"
2"
N_2
OIL (51 gal)
33 1/4"
2"
22 1/4"

Figure 4-3

Confirmational Analysis

In order to quantify the amount of PFT in the primary and final solutions the following method was used. A small amount of the primary solution (with 2% tracer) would contain too high a concentration of PFT, about 1 to 2 x 10^{-6} liters, to be conventionally detected by a gas chromatography/ electron capture detection (GC/ECD). Dilution was accomplished by microwave-evaporation of droplets of the primary solution placed on a filter paper enclosed in a container of about 2.7 liters. The resulting vapors contained only a few microliters of PFT so that 5 to 10 microliters of these vapors could be injected into the PFT analysis system, i.e., the resulting injection was in the 10^{-12} level, in the range of the GC/ECD.

A second approach consisted of taking 10 microliters of head space vapor above the fluid samples, diluting them into a 2.6 milliliter container and then injecting a few microliters of this diluted vapors into the CG/ECD. Both approaches gave varied results and further refinement of the analysis procedure is needed.

Simulated Leak Search With A Known Location

Reason For the Simulations

The reason for the two simulations (with known and with unknown leak location) was to test and refine the actual leak search procedure and determine if the amount of PFT added to the cable fluid was sufficient to be detected above ground.

By the performance of various steps of the leak search procedure it was hoped that any possible flaws in the procedure could be corrected and that unforeseen eventualities would be uncovered and eliminated before a real feeder demonstration.

The initial tests were also designed to measure the total PFT flux and the flux intensity at various points of tracer surface emission. It was also planned to determine if the sum of local PFT emission flux intensities would equal the total estimated flux, based on the quantity of released PFT tagged fluid.

The 1988 Simulation Experiment With Known Location

The first simulation experiment took place in 1988. A 25 foot pipe was drilled horizontally into the subsurface, from a manhole about 5 feet below the street surface. About 30 gallons of PFT tagged fluid was released through this pipe at a rate of 0.5 gallons per hour over 2.5 days. The fluid contained 0.034% by weight of the tracer ocPDCH (ortho-cis-perfluorodimethylcyclohexane). Unfortunately, during the connection of the pumping equipment to the underground release pipe, a small amount of the tracer-tagged fluid was spilled in the manhole; thus, the determination of the buildup of PFT concentration in the atmosphere was not feasible.

The PFT tracer emission flux was measured by releasing a known flow rate of another PFT, PMCP, in the manhole. Measurement of the concentration ratios of the PMCP and ocPDCH could then be used to calculate the ocPDCH tracer flux. Another method for the determination of PFT flux emission was to measure the sampler flow rate and the PFT concentration from which a local emission flux rate could be calculated. Both techniques were used in this flux simulation experiment.

Results of the tracer flux measurements are shown in Figure 4.4. The total measured flux of ocPDCH was found to be 0.75 µl/min, with about two thirds of this amount coming directly out of the two utility manholes and most of the remainder being emitted from a nearby sewer manhole. The large amount of material emitted from the utility was probably due to tracer vapors diffusing along the external fluid injection pipe external surface into the manhole.

Nevertheless, by taking samples from boreholes (a procedure explained in the next section) the leak location could be isolated to within 10 feet. A detailed account of the 1988 experiment was described in section[feel in].

The 1990 Simulation Experiment With Known Location

The second simulation was designed to alter and improve the injection procedure so that the PFT would not egress from the injection hole itself. It was planned to drill vertical injection holes and observe every possible precaution to avoid releasing PFTs from these holes. The site for these boreholes was a property owned by Con Edison, Vernon Center, in Queens, New York.

After injection of PFT tagged fluid, the area was inspected with a leak search vehicle and the concentration levels of PFT in the air were determined. It was hoped that the highest concentrations would be found close but not right at the injection site (e.g., the simulated leak location). The PFT emission flux at the injection site was measured so that the efficiency of the vertical injection procedure could be evaluated.

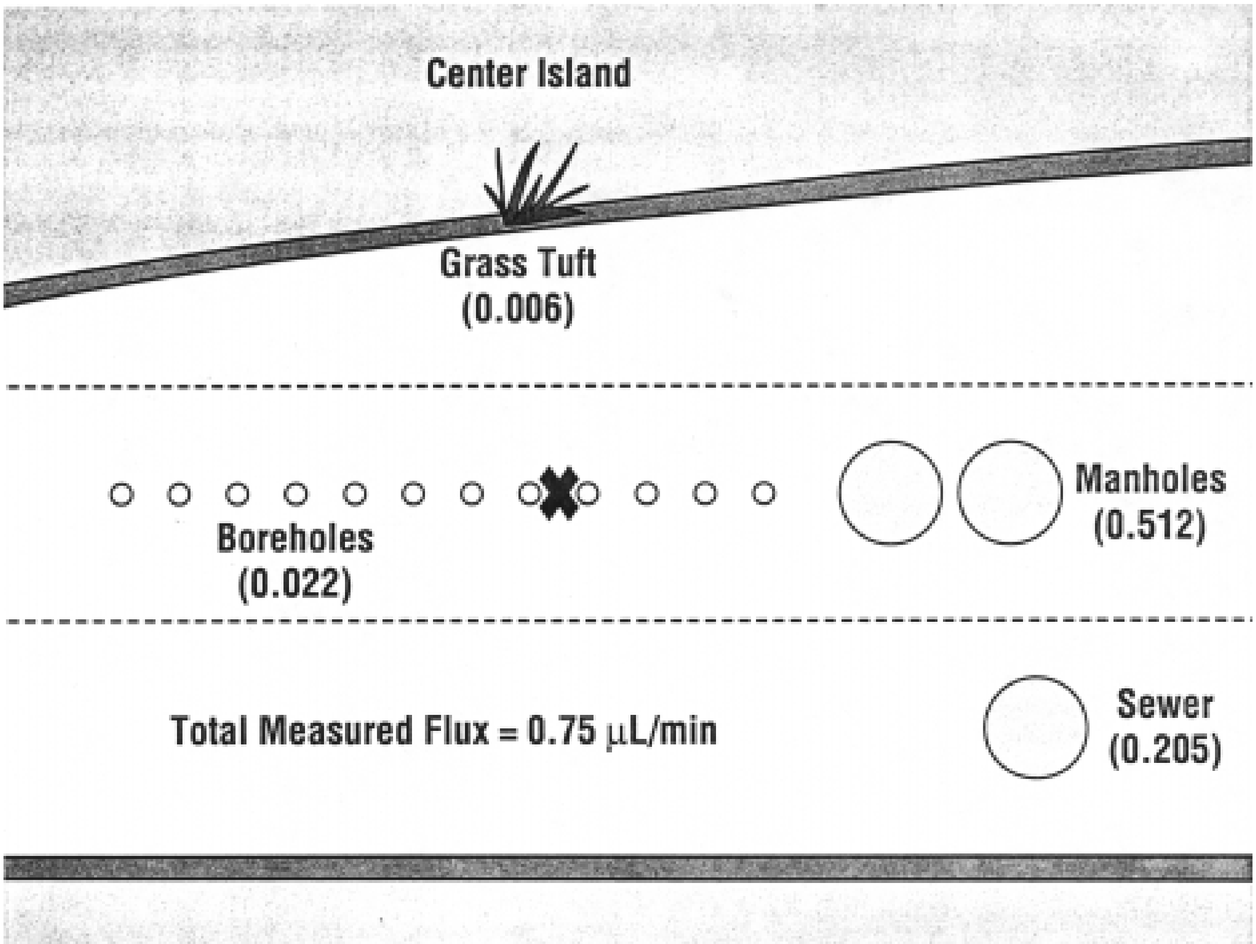


Figure 4-4
Results of the tracer flux measurements at the Queens Boulevard demonstration experiment

A leak search procedure was developed encompassing the following steps:

1. Mobile Locating (Traversing):

For the Vernon Center experiments this was not necessary, as the location of the underground fluid "spill" was known.

2. Mobile and Stationary Localizing of Candidate Street Blocks:
   2.1 Ten Block Localizing with DTA and BATS;
   2.2 Stationary Localizing with CATS.
3. Pinpointing
   3.1 Preliminary Pinpointing:
      50-feet-Pinpointing with COPS;

- 3.2 Borehole Pinpointing:
  - 3.2.1 Approximate Pinpointing (50 feet distances) with DTA;
  - 3.2.2 Final Pinpointing (5 feet distances) with DTA.

Creation of Simulated Underground Fluid Spill With Realistic PFT Emission Rates

Two boreholes were drilled by Con Edison in the northern section of their Vernon Center Facility in Queens. They were 4 feet deep and about 2.5 inches in diameter, and about 6 feet apart. Nominal 2 inch PVC pipes (2.375 inches OD) were inserted into the boreholes to prevent the holes from collapsing; the tops were capped off and Duxseal was used to prevent rainwater from entering the boreholes.

Into these boreholes brass injection pipes were placed to later accommodate the actual injection of tagged fluid. To permanently install the injection pipe, the PVC pipes were removed and gravel was poured into the hole to a level about 3 inches above bottom. Then a 1/4-inch brass pipe was inserted into the center of the hole such that it rested on the gravel (see Figure 4.5). Another 3 inches of gravel was then poured into the hole (total gravel ~1/2 liter). The purpose of the gravel was to provide a large surface area for fluid to penetrate into the soil. Sand was then poured on top of the gravel and periodically tamped with an iron bar. Finally, the top of the borehole was sealed with epoxy cement to about 2 inches below the asphalt surface. The thickness of the epoxy cement layer was about 3 inches. A quick-connect-coupling on the end of 1/4" brass pipe was allowed to protrude above the epoxy cement.

The surface of the brass injection tubing had been coated with an epoxy-sand mixture to ensure a tight and seamless connection to the sand in the borehole. Because of this treatment it was assumed that PFT vapors would not seek a preferential path along the external pipe surface directly up to the asphalt.

Injection of Tagged Fluid

In order to facilitate the injection of the tagged fluid into the ground an injection rack was designed which contained a user-friendly arrangement of injection pump, back-flush pump, rotameter and valves (Figures 4.6 and 4.7). This arrangement was first tested in the laboratory to insure its safe functioning later in the field. The first of a series of tests was a leak test conducted at 200 psi. Problems were encountered with O-ring seals in the rotameter and in the "Quick-Connect-Couplings". These brass O-ring seals began to swell after short exposure to the fluid and were replaced with Viton O-rings seals.

On May 30 and 31, tagged fluid (0.1% ortho-PDCH or 0.034% oc-PDCH) was injected into the first (southern) borehole. A 55 gallon drum with a drum pump and the injection rack had been transported by van from BNL to Vernon Center. Upon arrival, the hoses between the drum and rack and between rack and injection tubing were connected with the quick-connect- couplings (see Figure 4.6). The drum and the rack were left in the van throughout the injection procedure. This arrangement proved advantageous for several reasons. First, in case of a fluid spill, which indeed occurred, the van could be driven away after termination of the injection procedure and no split tracer would be left remaining at the site. Secondly, the van could be locked at night providing a protected space against unauthorized tampering.

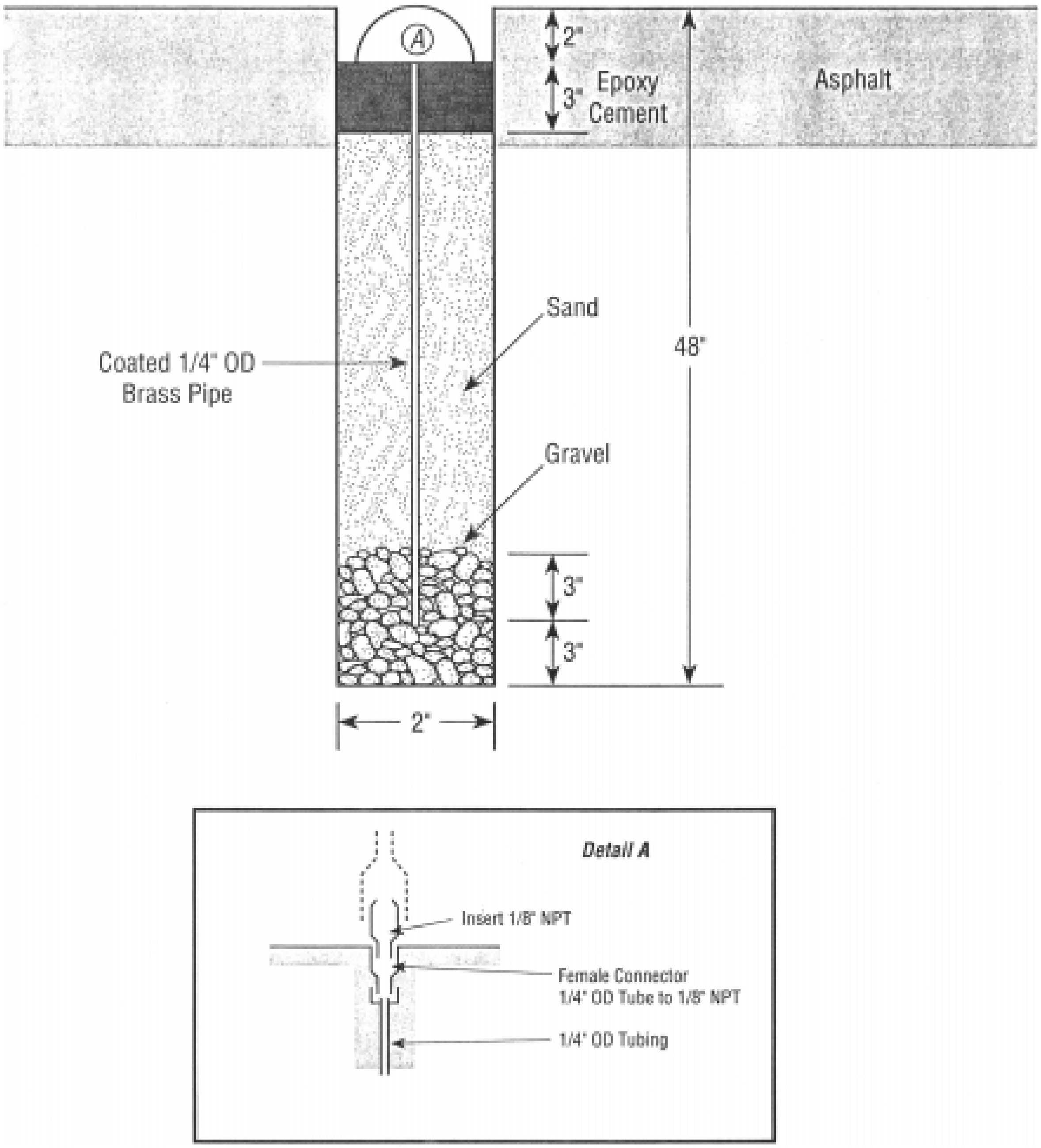


Figure 4-5
Cross sectional view of the injection pipe used to inject tagged dielectric fluid

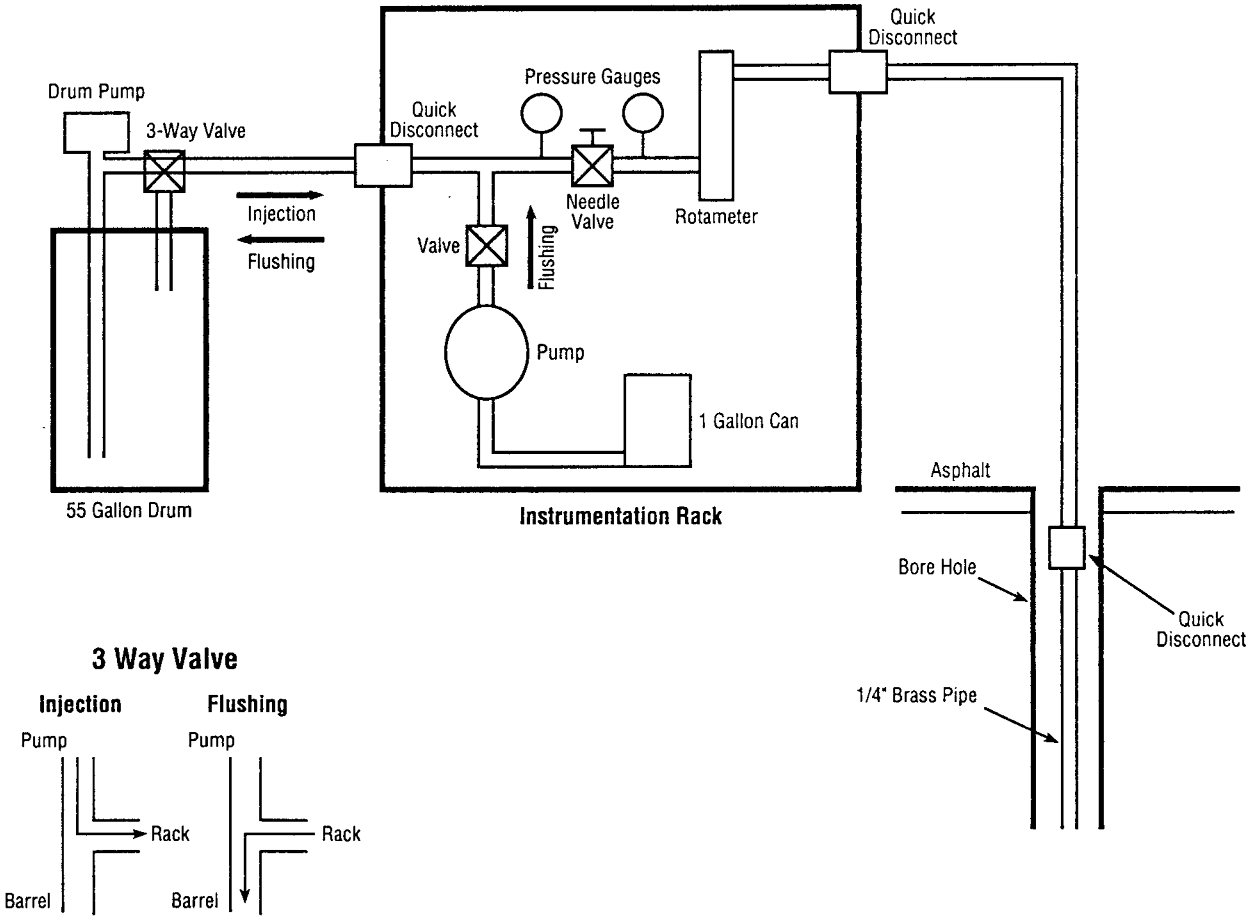


Figure 4-6
Apparatus used to inject tagged dielectric fluid into the injection site

Unfortunately, the line from the drum pump to the 3-way valve burst at the beginning of the experiment and a small amount of fluid was spilled into the interior of the van. The hose was replaced immediately and the fluid spill was cleaned up. No further mishap occurred throughout the remainder of the experiment.

Consequently, the injection pressure, originally set at 100 psi at the first gauge (upstream of needle valve) was later reduced to about 40 psi. The injection pressure measured by the second gauge (downstream of needle valve) decreased from 13 to 11 psi and stayed at about 11 psi during the afternoon of May 30. Flow rates during this first day fluctuated between 13 to 15 ml/min. On the next day at noon, an “upstream” pressure of about 22 psi, a “downstream” pressure of 6 psi and flow rate of 9 ml/min were recorded. No explanation has yet been determined for the lower pressures and flow rates that developed overnight.

Overall, the procedure proved successful and could be used at the future simulated leak search with unknown location.

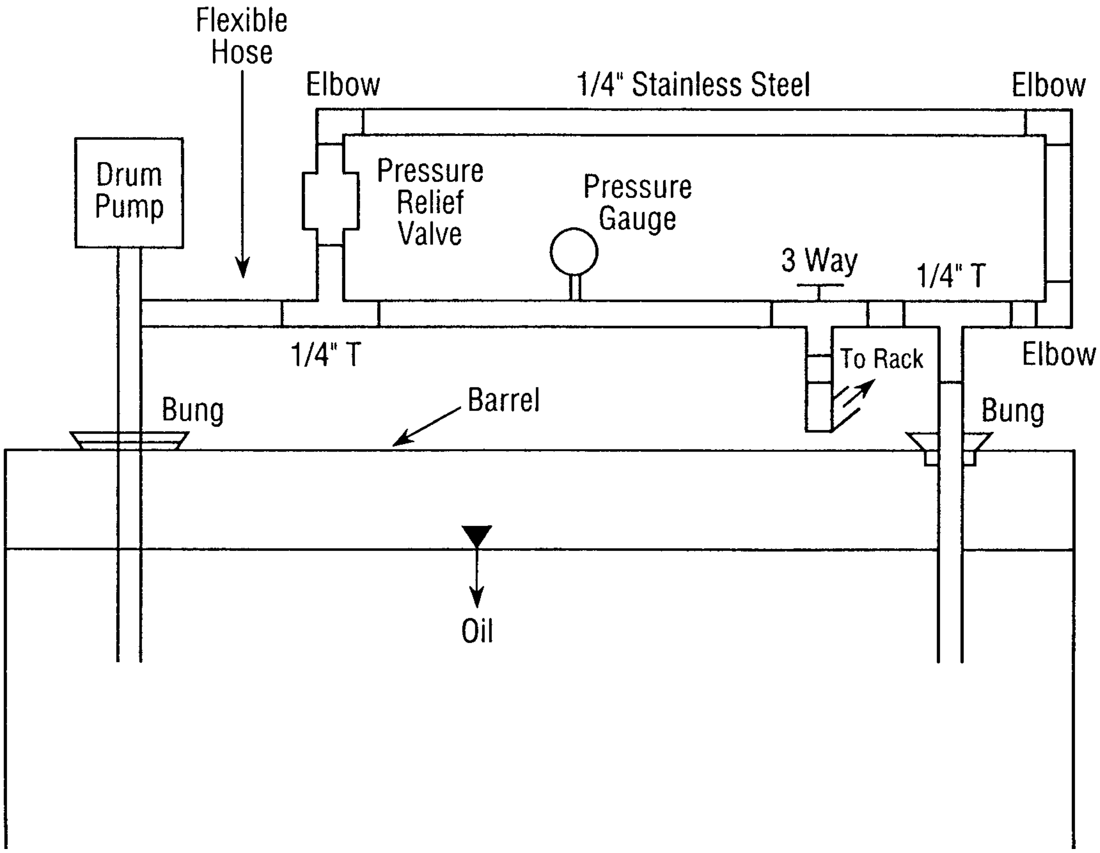


Figure 4-7
Close up of the flow diagram in Figure 4.6

Monitoring of Tracer Concentration During and Immediately After Injection

On the first day, capillary adsorption tube samplers (CATS) were deployed surrounding the equipment at the Vernon Center yard and programmable samplers (BATS) were deployed at locations as indicated in Figure 4.8. The gradual rise of the PFT concentration as measured by the BATS (set at a sampling rate of about 6 hours) can be seen in Figure 4.9. The first peak resulted from the fluid spill on that day and the second peak arose because the van doors were opened on the second day at about noon, thus releasing residual vapors remaining in the van overnight. After the van was driven away in the evening, PFT concentrations dropped to almost background levels.

The CATS concentrations after 4 days of exposure can be seen in Figure 4.10. Obviously, the northern CATS show higher concentrations due to predominantly southerly winds. The isopleths drawn in Figure 4.11 reveal that the injection point can be located with great accuracy (within 20 feet) just by determining the center of these lines of equal PFT concentration. Subsequently, CATS were also deployed on June 4 and June 8 for a period of 4 days and their results duplicated the findings of the first set of CATS samplers.

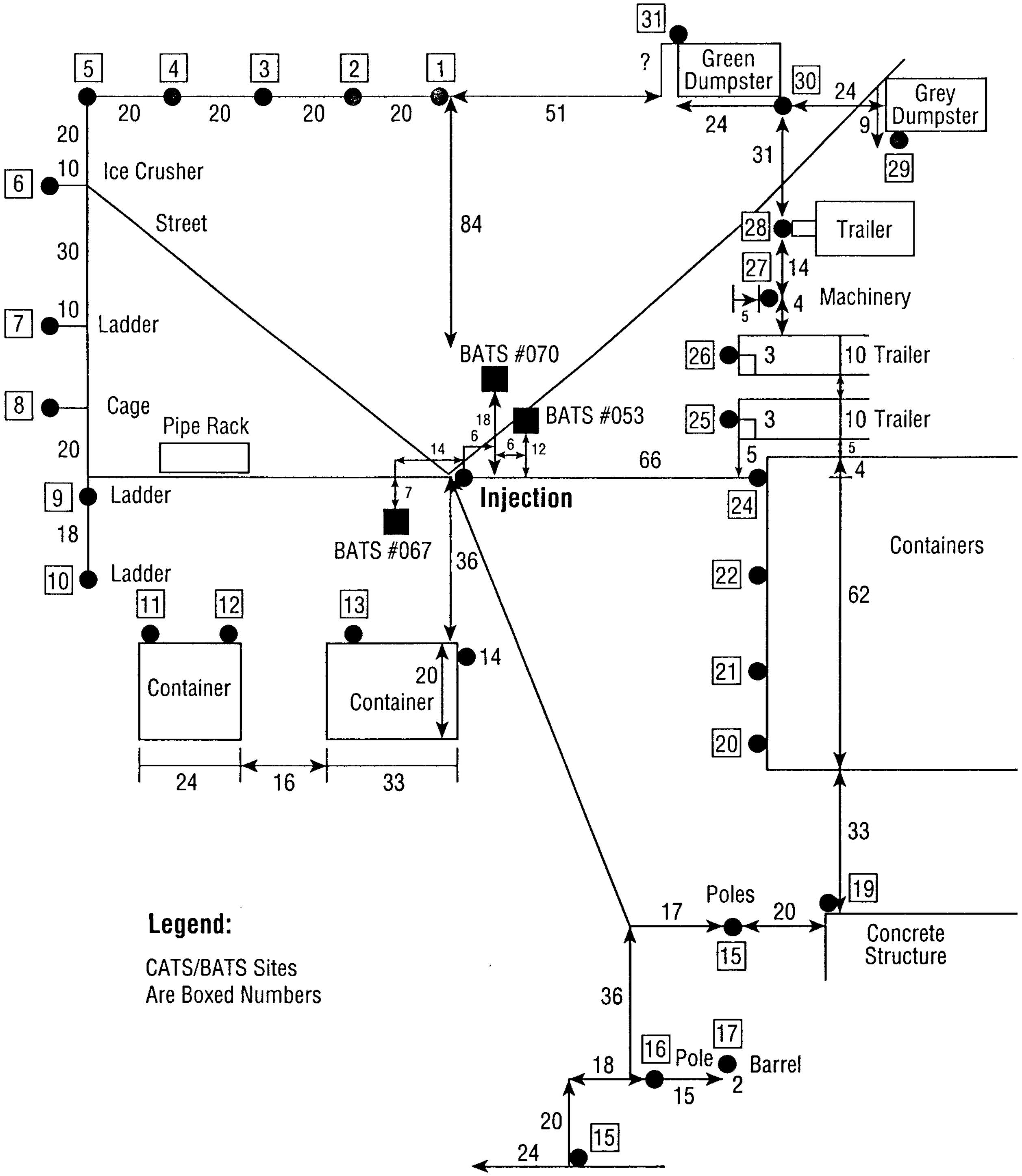


Figure 4-8
Map of the deployment sites for the CATS and BATS samplers at Vernon Center yard

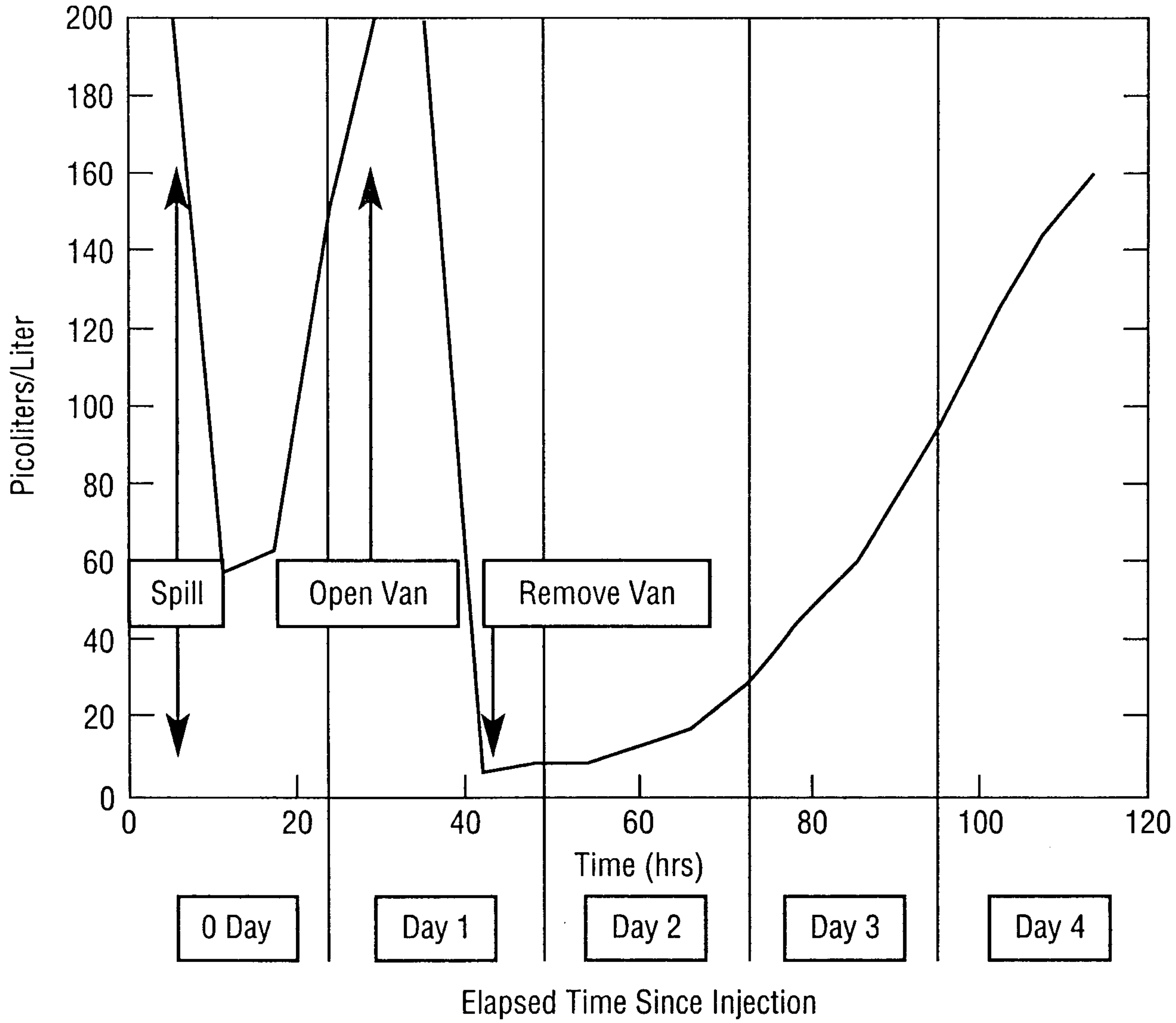


Figure 4-9
Observed rise in PFT concentration as a function of time after release. The first peaks are due a fluid spill from injection apparatus. The second peak is from the open van door containing residual tagged dielectric fluid.

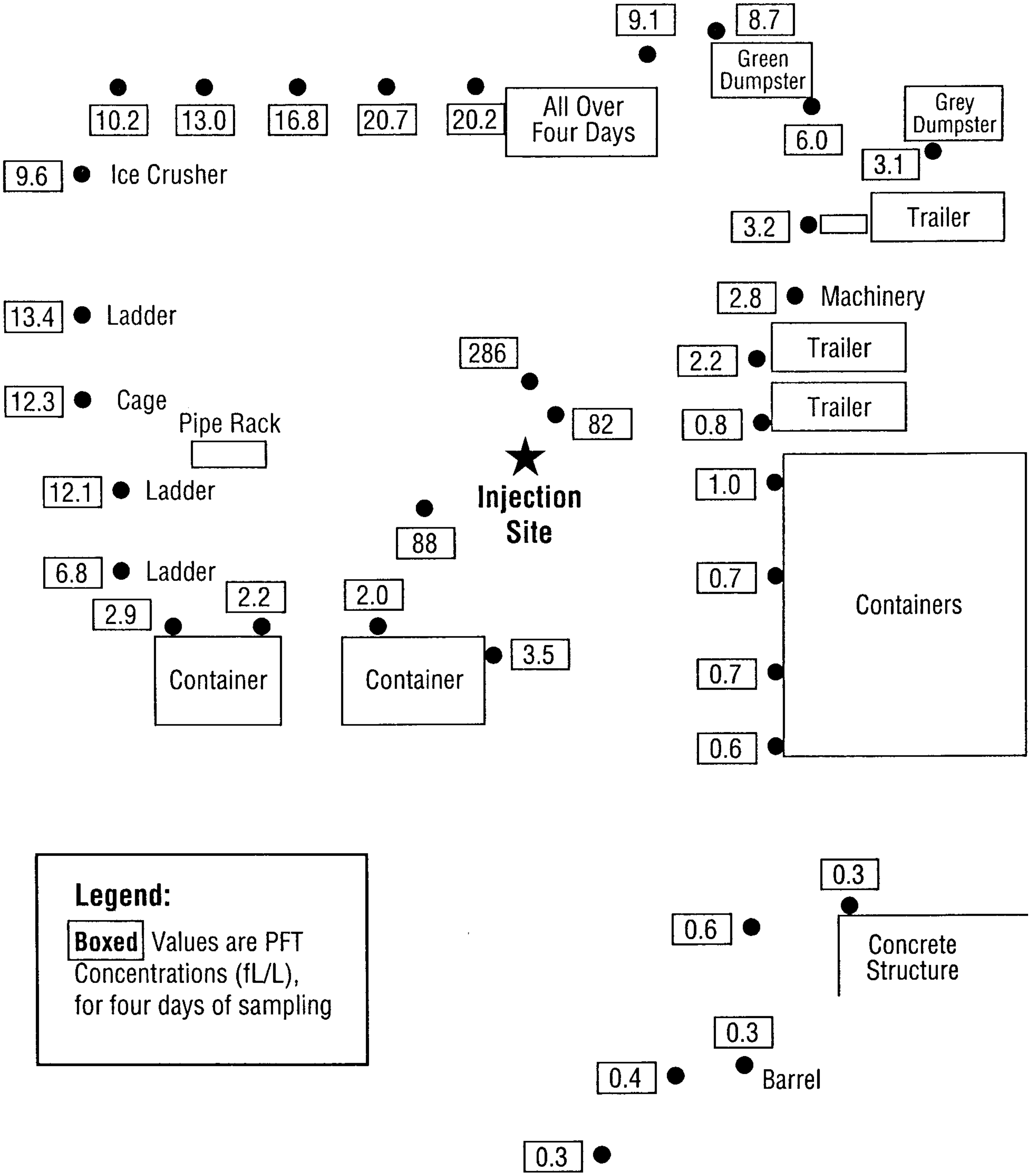


Figure 4-10
PFT concentrations in the Vernon Center yard four days after tracer release

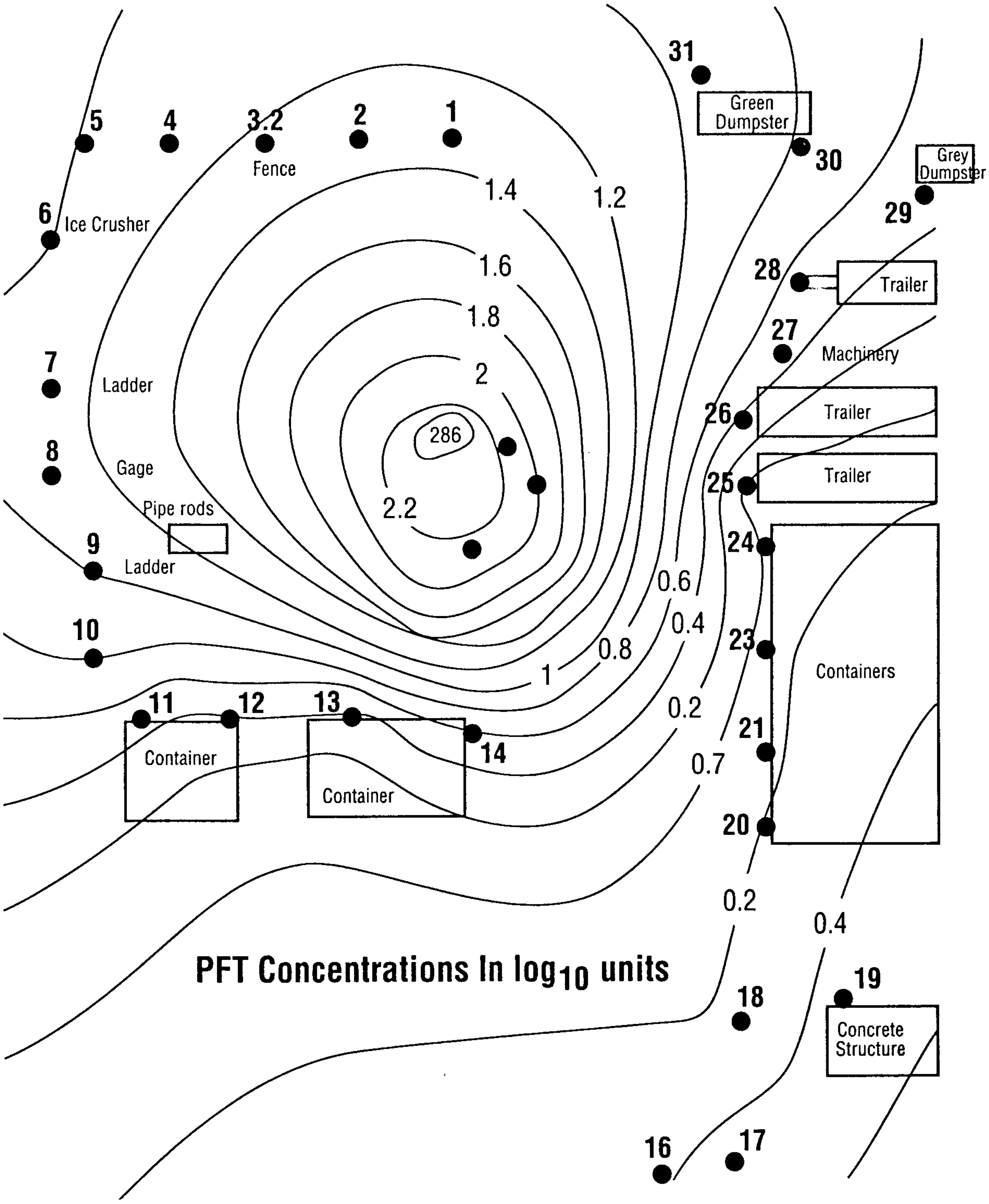


Figure 4-11
PFT concentration isopleths shows that the injection point can be located within 20 feet by CATS sampling

Mobile and Stationary Localizing of Candidate Street Blocks

Since the PFT from the underground site was detectable in the air, the simulated leak search could be started. Hypothetical street blocks were outlined at distances of 200 feet and designated blocks A through G. The injection point coincided with street block D (see Figure 4.12). At Vernon Center the surrogate street blocks were delineated with the help of a surveyors wheel.

Ten Block Localizing With the DTA

Since the injection site was known, it was located by traversing with a detection instrument. The next objective of the leak search procedure, namely “Localizing”, which is finding higher than background PFT concentrations within ten street blocks (or seven blocks in this simulation), were started immediately.

At Vernon Center “Localizing” started at about 10 am at “street block A”. Air samples were collected on both traps (6 minutes each) of the DTA and on 2 tubes of the programmable sampler, the BATS (as backup for the DTA). The BATS has higher ultimate sensitivity, but the tubes have to be analyzed in the laboratory; since the BATS has no real time detection capability. In addition, adsorption tube samplers, or CATS, were deployed at the “street corners” on nearby locations, for example, for block A on the fence just a few feet south. No signal was detected at “street corner A” with the DTA.

Localizing continued in the same manner for street blocks B and C. The first signal with the DTA was detected at about 10:40, less than one hour after the start of the experiment at street corner D-East (Figure 4.10). The rather strong signal (48 fl/l, see Figure 4.13) indicated that the “street block” with the “leak” had been found. At this point one of the members of the crew started “sniffing” suspicious points with the continuously operating perfluorocarbon sniffer (COPS). The rest of the crew continued “localizing” to blocks E, F, G and back to D+50/East. Driving from D+50 East to D+50/West produced another strong peak of 61 fl/l (Figure 4.14).

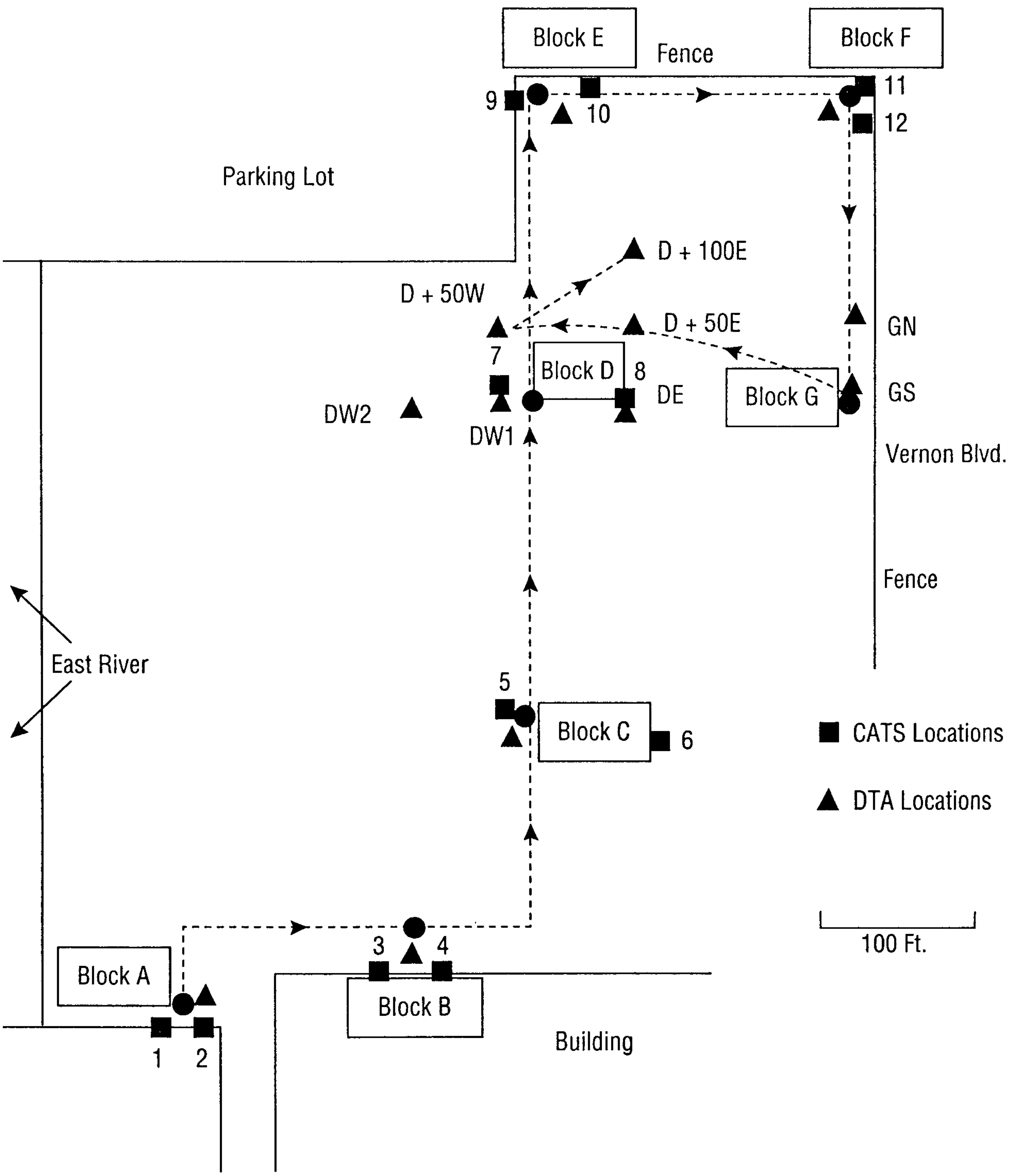


Figure 4-12
Mobile sampling path

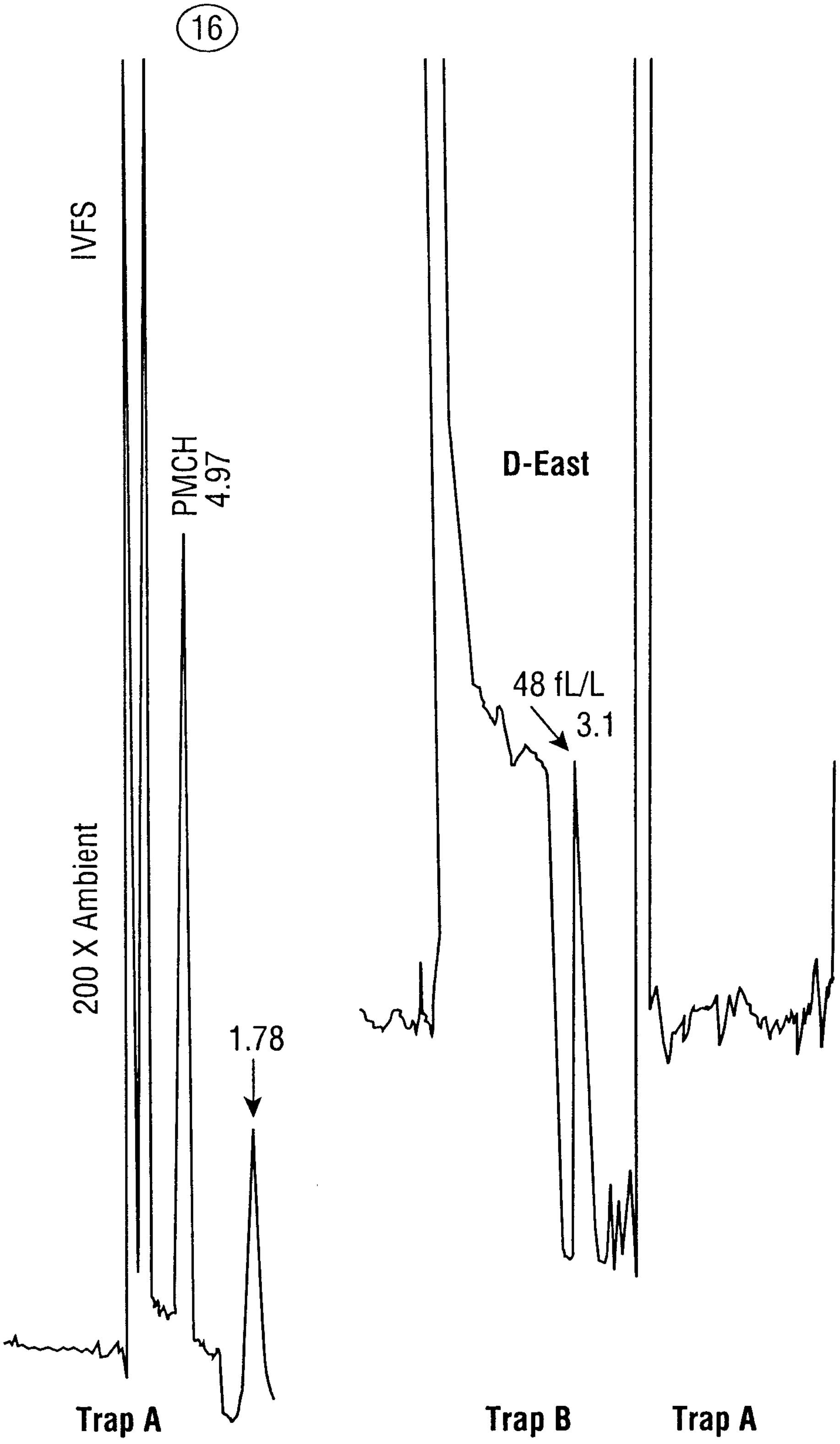


Figure 4-13
Chromatogram from PTA indicating a strong PFT signal at the "street block" nearest the leak

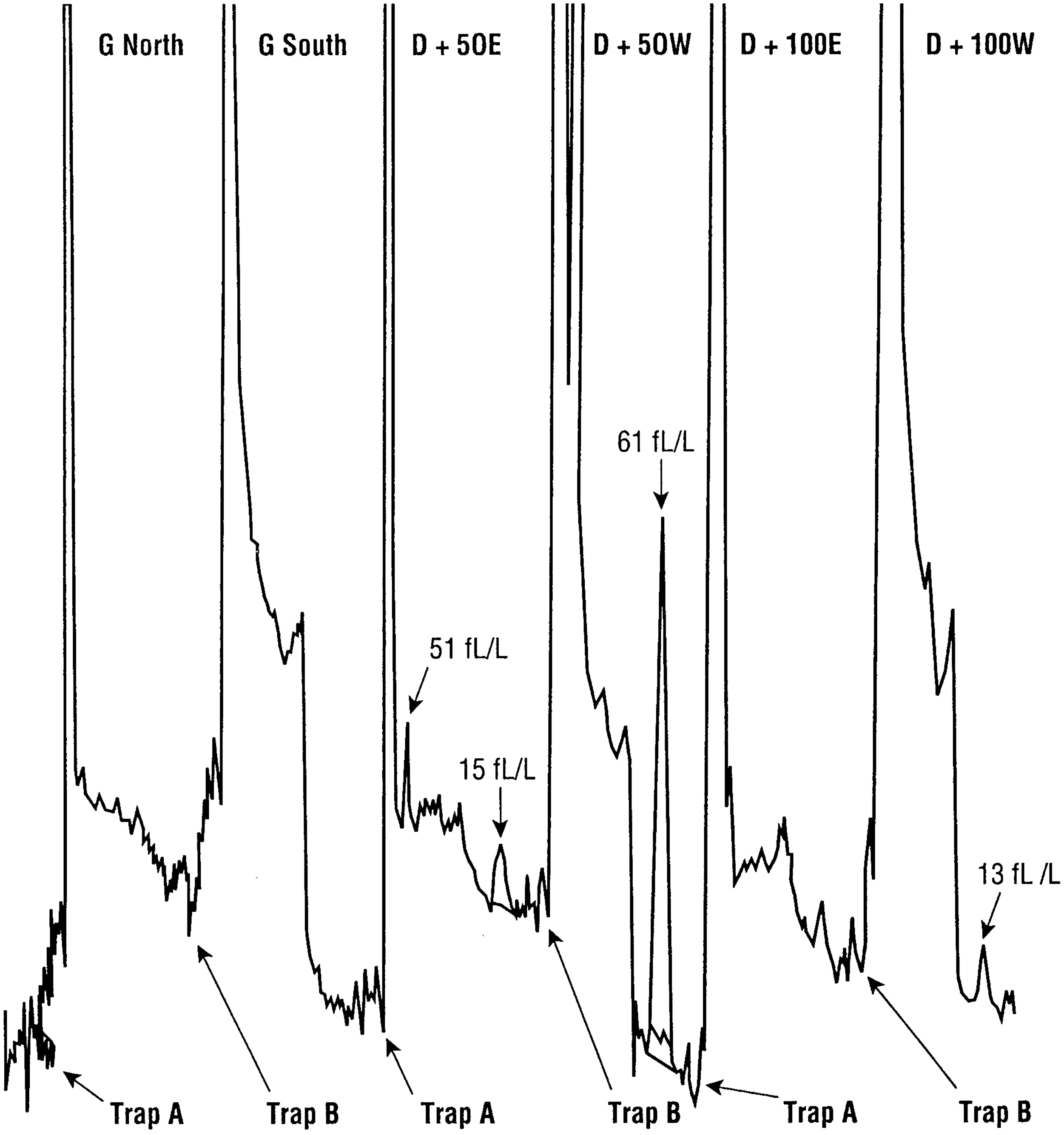


Figure 4-14
Chromatogram obtained by the PTA in driving from block G north to block D+ I 00W, indicating a high signal in block D+50W

As expected, "Localizing" had resulted in one candidate street block.

Stationary Localizing through CATS

The analysis of the "Street Corner CATS" a day later corroborated the DTA findings. Indeed, the highest readings were found at points 7 (= D/West,1) with 114.5 fl/l and east of the injection point at location 8, D/East, with 18.3 fl/l (Table 4.4).

Table 4-4
Stationary Localizing With CATS

File/Tube	Pos	CATS	PMCH	ocPDCH	ptPDCH	mPDCHT	PMCP	PTCH
7285C1	1	2700	9.4	2.1	10.6	37.5	9.3	2.3
7285C2	2	2692	12.3	1.6	12.5	41.5	10.5	0.0
7285C3	4	4102	11.1	2.9	10l.6	38.0	10.5	3.7
7285C4	5	2622	11.3	2.9	12.2	40.7	15.3	6.6
7285C5	6	9229	12.1	4.3	13.6	39.9	23.7	0.0
7285C6	7	6695	17.3	114.5	15.7	187.3	456.6	3.2
7285C7	8	2796	10.1	18.3	12.2	60.6	69.0	0.0
7285C8	9	4621	13.8	11.7	11.4	50.8	47.9	1.2
7285C9	10	8914	11.8	8.0	12.0	44.6	30.0	0.0
7285C10	11	6588	11.3	4.5	10l.4	34.8	13.0	0.0
7285C11	12	5360	10.4	4.5	14.1	37.7	13.5	2.6
7285C12	1	4702	11.7	47.2	13.4	99.8	188.2	0.0
7285C13	2	11072	12.2	50.2	10.65	99.8	213.0	0.0
7285C14	3	10959	10.4	37.1	8.5	80.5	139.1	0.0
7285C15	4	3803	12.2	28.1	9.5	73.6	86.3	0.0
7285C16	5	11042	10.4	16.6	13.1	58.4	52.2	1.2
7285C17	6	11573	11.1	16.6	9.0	53.5	53.9	0.0
7285C18	7	9021	10.6	20.7	10.4	60.3	66.1	0.0
7285C19	8	8321	10.4	18.0	11.7	57.6	34.6	0.0
7285C20	9	7254	9.1	20.7	8.5	58.4	30.5	0.0
7285C21	10	3889	11.9	16.4	12.8	55.4	27.4	3.3
7286C1	11	5094	9.4	11.2	10.1	48.8	18.1	0.0
7286C2	12	1559	9.1	11.2	9.8	47.5	21.2	0.0
7286C3	13	1012	11.1	24.5	9.3	61.6	53.0	0.0
7286C4	14	3296	14.2	52.9	12.3	104.7	218.3	0.0
7286C5	15	11339	9.1	15.0	10.4	51.8	90.6	0.0
7286C6	16	6540	9.6	4.6	8.2	38.2	27.0	0.0
7286C7	17	5017	9.4	4.1	10.4	39.8	18.8	0.0
7286C8	18	6712	12.9	5.5	11.2	42.3	33.6	0.0
7286C9	19	3923	9.6	6.3	11.2	44.5	28.9	0.0
7286C10	20	8336	11.4	10.6	12.5	48.0	51.5	0.0
7286C11	21	1182	10.4	11.7	12.5	53.7	58.0	0.0
7286C12	22	10357	9.6	12.8	7.6	46.4	55.6	0.0
7286C13	24	6053	7.6	15.8	8.7	50.2	65.6	0.0
7286C14	25	8135	10.1	17.5	8.5	54.6	70.1	0.0
7286C15	26	3858	8.9	23.2	8.5	62.7	80.1	2.7
7286C16	27	10437	12.4	27.0	8.87	66.8	83.0	0.0
7286C17	28	4961	9.1	21.8	10.4	60.3	61.3	0.0
7286C18	29	4630	10.1	15.3	11.7	53.5	46.3	1.8
7286C19	30	7939	9.6	17.5	8.5	54.3	61.3	0.0
7286C20	31	7311	9.4	18.0	9.5	54.8	64.4	0.0
7286C21	32	5759	10.1	14.5	11.2	50.2	51.0	0.0

Pinpointing

As already stated, once the candidate street block (block D, in this experiment) was located or "localized", "COPS Pinpointing" started by "sniffing" salient surface points in the area, such as seams in the asphalt, manhole covers, sewers, drains, and curbs with the COPS. Three PFT concentration readings were obtained above background, namely: a) 5 mV (~53 pl/l = 53 picoliters/liter) at the injection point; b) 1.6 mV (~17 pl/l) about 7 feet north of the injection point (see Figure 4.15); and, c) 0.6 mV (~6.5 pl/l) at a point 14.5 feet north of the injection point. Hence, the leak previously located with the DTA was confirmed with the COPS.

Approximate Borehole Pinpointing

Approximate borehole pinpointing consists of drilling boreholes every 30 to 50 feet within the candidate block. The boreholes are indicated in Figure 4.15 as boreholes "50", "100" and "150" (the numbers symbolize distances in feet from south-east corner of parking lot fence, see Figure 4.12). While these boreholes were drilled, COPS readings were taken as soon as the drill broke through the asphalt and reached the soil. The readings obtained were:

1. Borehole 50: 50 mV (~533 pl/l)

2. Borehole 100: 79 mV (~843 pl/l)

3. Borehole 150: 1 mV (~11 pl/l)

According to these readings, a leak was likely to exist between borehole 100 (with 843 pl/l) and borehole 50 (with 533 pl/l).

Final Borehole Pinpointing

With the likelihood of a leak occurring between borehole 100 and 50, the last phase could now commence by drilling pinpointing boreholes at 5 feet intervals between borehole 100 and 50.

These boreholes were drilled and immediately sealed with Duxseal. Implanted into the Duxseal was a 1/4 inch stainless steel tube with an inserted septum. This arrangement prevented the soil gas from escaping into the atmosphere and diluting the subsurface PFT concentration. A syringe needle was introduced through the septum; 50 and 100 microliter soil gas samples were collected and injected into adsorption tube samplers (CATS) and into the DTA. It was found that borehole 85 and 95 showed the highest peaks (see Table 4.5 and Figure 4.16). Surprisingly, borehole 90 indicated a low PFT concentration of only 305 nl/l (nanoliters/liter), though it was only 2.5 feet away from the leak. The reason for this anomaly is not known but it suspected that the drill might not have penetrated the asphalt entirely. Nevertheless, the leak site was now known within a 10 foot radius.

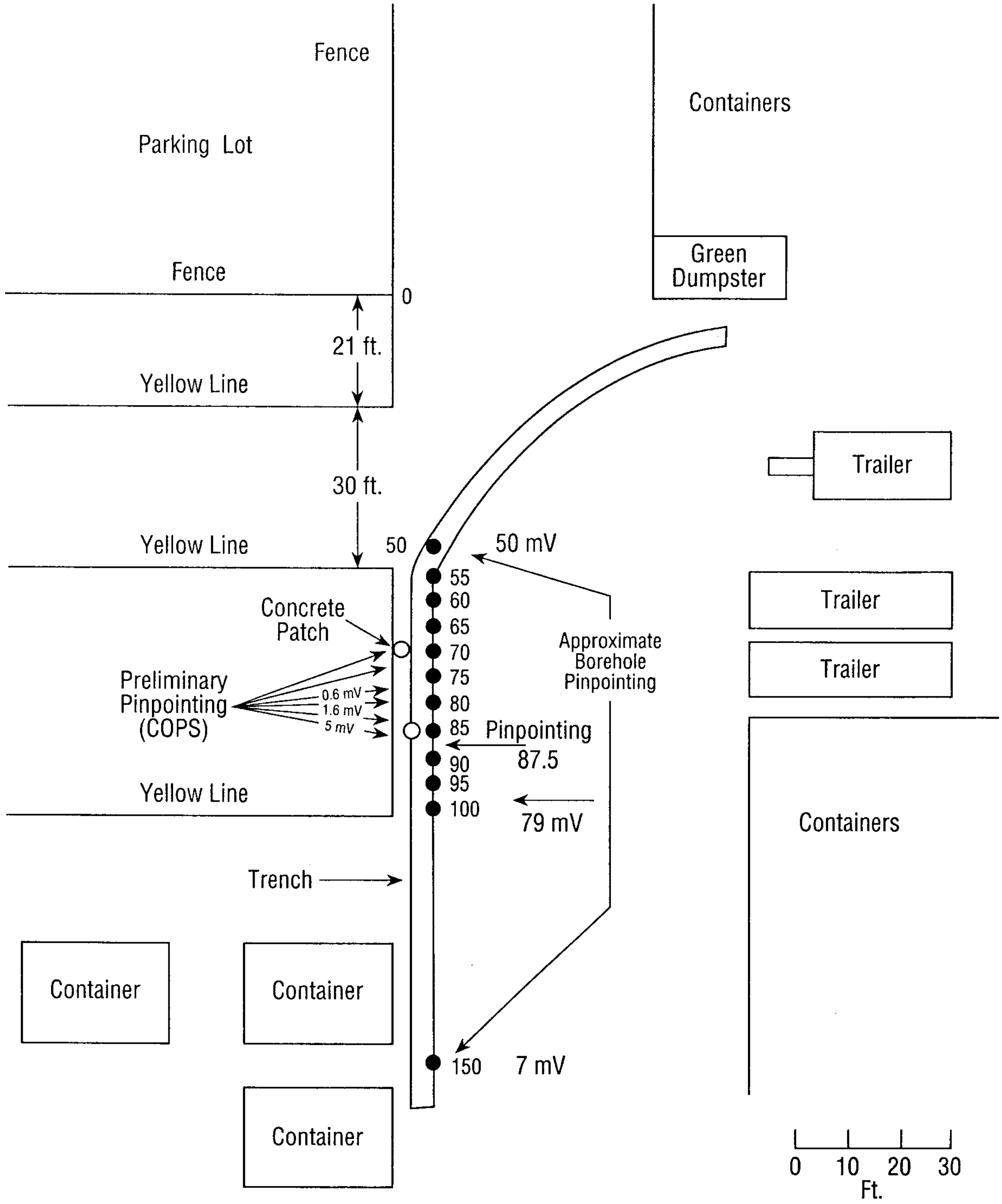


Figure 4-15
Pinpointing the leak location with the COPS

Table 4-5
Final Borehole Pinpointing

File/Tube	Site	CATS	Sample (µL)	PMCH	ocPDCH	ptPDCH	mPDCHT	µL/L
7282C2	0	5995	100	0.0000	0.0000	0.0000	0.0000	0.0000
7282C3	50	1262	10	0.0006	0.0168	0.0000	0.0313	0.0017
7283C4	50	6150	50	0.0048	0.1182	0.0000	0.2243	0.0024
7283C5	50	10949	100	0.0098	0.2186	0.0000	0.4048	0.0022
7282C13	55	1937	10	0.0245	0.7727	0.0000	1.4544	0.0773
7282C14	55	8120	50	0.1311	3.7871	0.0596	7.3498	0.0757
7282C12	60	10625	10	0.0000	0.0589	0.0000	0.1224	0.0059
7282C15	60	7813	50	0.0000	0.1426	0.0000	0.2816	0.0029
7282C11	65	3121	10	0.0630	1.6467	0.0000	3.0628	0.1647
7282C16	65	5212	50	0.3795	10.2630	0.1425	19.4887	0.2053
7282C10	70	4566	10	0.1271	3.2274	0.0000	5.8504	0.3227
7282C17	70	949	50	0.6222	17.4131	0.2054	31.4679	0.3403
7282C9	75	6425	10	0.1859	4.8097	0.0696	9.1190	0.4810
7282C18	75	4300	50	0.8546	23.0254	0.2870	43.5532	0.4605
7282C8	80	552	10	0.3063	8.0567	0.1324	16.1475	0.8057
7282C19	80	1531	50	1.2002	31.2863	0.4402	62.3875	0.6257
7282C7	85	9747	10	0.0000	10.9014	0.1669	21.1600	1.0901
7282C20	85	4997	50	3.1879	100.4941	1.5234	202.2251	2.0099
7282C6	90	5817	10	0.0000	2.4047	0.0000	4.7060	0.2405
7283C1	90	10520	50	0.6210	18.4219	0.2478	35.2264	0.3684
7282C5	95	3789	10	0.0000	27.4879	0.3649	53.5829	2.7488
7283C2	95	5153	50	4.5331	127.0000	1.6930	151.3269	2.5400
7282C4	100	6318	10	0.0000	13.5646	0.1410	24.4243	1.3565
7283C3	100	6872	50	2.1909	60.2300	0.6694	90.4699	1.2046
7282C1	150	6076	100	0.0000	0.0140	0.0000	0.0000	0.0001

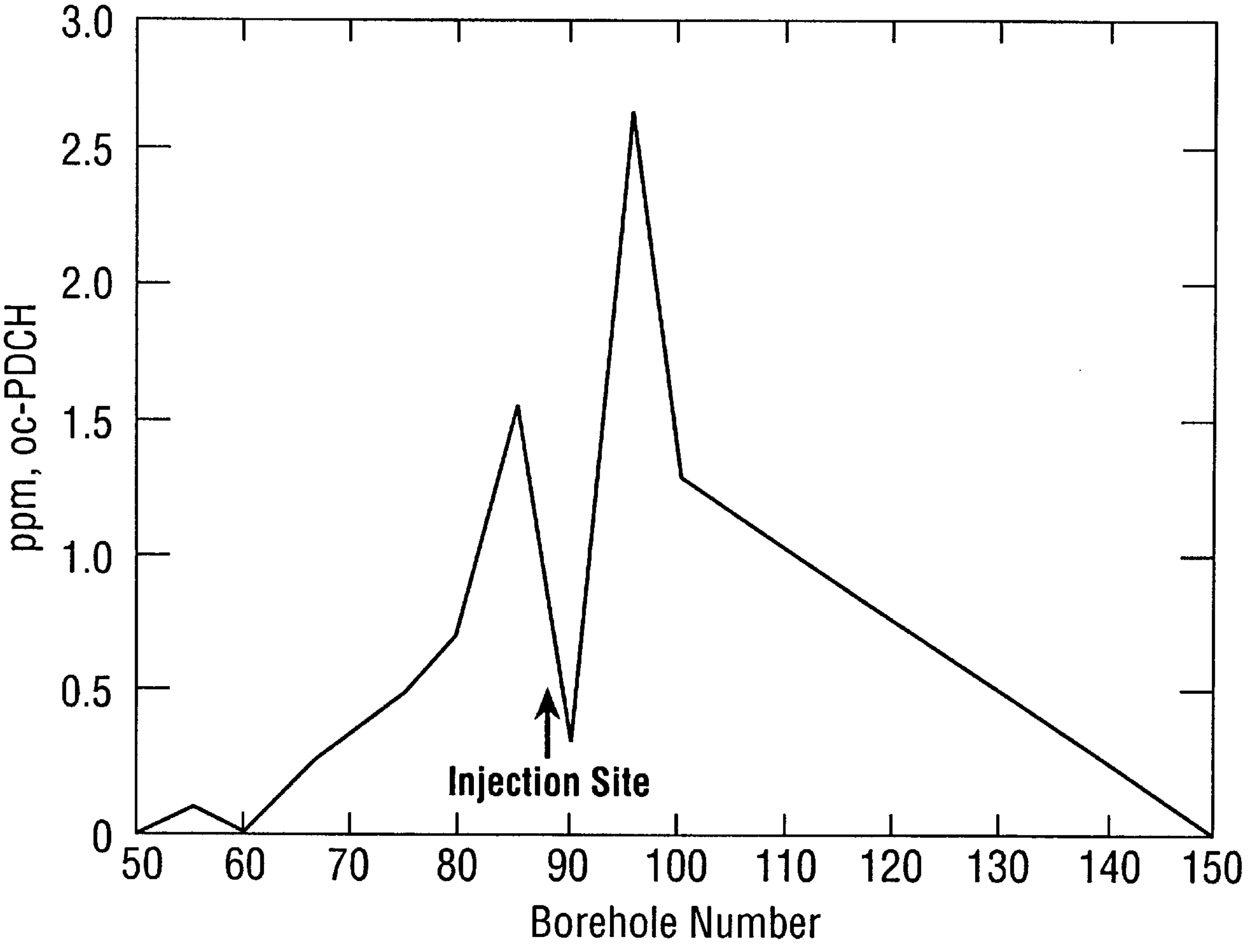


Figure 4-16
Borehole sampling locating the leak to within I0 feet

Flux Measurements

Flux measurements were determined using the same techniques as in the earlier simulation at the locations previously determined as PFT emission points with the COPS (7 and 14.5 feet north of the injection point). The most interesting result of this experiment was the fact that the PFT emission flux from the 7 ft point was about 15 times higher than the flux from the injection point itself (0.126 µl/min versus 0.0008 µl/min, see Table 4.6). In addition, the total PFT flux amounted to 0.75 µl/min, equivalent to the flux recorded two years ago during the first experiment on Union Turnpike in Queens. In 1988, the total flux was also 0.75 µl/min, but the emission from the injection manholes amounted to 0.5 µl/min. The vast improvement of the vertical injection technique can be evaluated from these numbers. It is in a large measure attributed to the epoxy cement sealing technique employed during the Vernon Center experiments.

Table 4-6
Flux Measurements

File/Tube	Site	CATS	Sample (µL)	Flow (L/min)	ocPDCH (pL/L)	Flux (µL/min)
7283C6	7FT N	796	100	14.84	799	0.0119
7283C7	7FT N	5682	100	14.84	849	0.0126
7283C8	7FT N DC	5123	20	9.91	0	0.0000
7283C9	7FT N DC	9367	20	9.91	95	0.0009
7283C10	7FT N DC	4706	100	9.91	424	0.0042
7283C11	7FT N DC	9385	100	9.91	512	0.0051
7283C12	12 FT N	10429	100	14.84	979	0.0145
7283C13	12 FT N	10522	100	14.84	648	0.0096
7283C14	INJECT.	5241	100	14.84	122	0.0018
7283C15	INJECT	4955	100	14.84	53	0.0008
7283C16	SEALED	1048	100	14.84	566	0.0084
7283C17	SEALED	5324	20	14.84	570	0.0085
7283C18	SEALED	11407	20	14.84	490	0.0073

Simulated Leak Search With Unknown Location

Introduction

On July 17 and July 18, 1990 the experiment with a simulated leak unknown to the search crew was conducted at Union Turnpike in Queens. The goal of the experiment was the detection of a simulated fluid leak within a 1.8 mile distance between Utopia Parkway and Francis Lewis Boulevard. The experiment served as the ultimate test to prove that the instruments and techniques developed at the Tracer Technology Center were able to locate and pinpoint potential leak locations.

Five days prior to the experiment a Consolidated Edison crew had pumped approximately 5 gallons of PFT-tagged fluid into the ground (Thursday 7/12 through Friday 7/13, 1990). Injection procedures followed the detailed plan demonstrated earlier at Vernon Center (see Section 5). The fluid was tagged with 0.1% ortho-PDCH (ortho-perfluorodimethylcyclohexane), equivalent to 0.034% oc-PDCH (ortho(cis)-PDCH), the isomer that was destined to serve as the prime detection taggent. It was anticipated that the vapors of the oc-PDCH would diffuse through the vadose subsurface to the street surface and then into the air where they could be detected.

At the outset of the experiment the only guide available to the BNL-TTC team was a map prepared by Con Edison showing the cable with its diffusion chambers and by-passes. A street map of the general location is shown in Figure 4.17. The length of the search distance was about 1.8 miles.

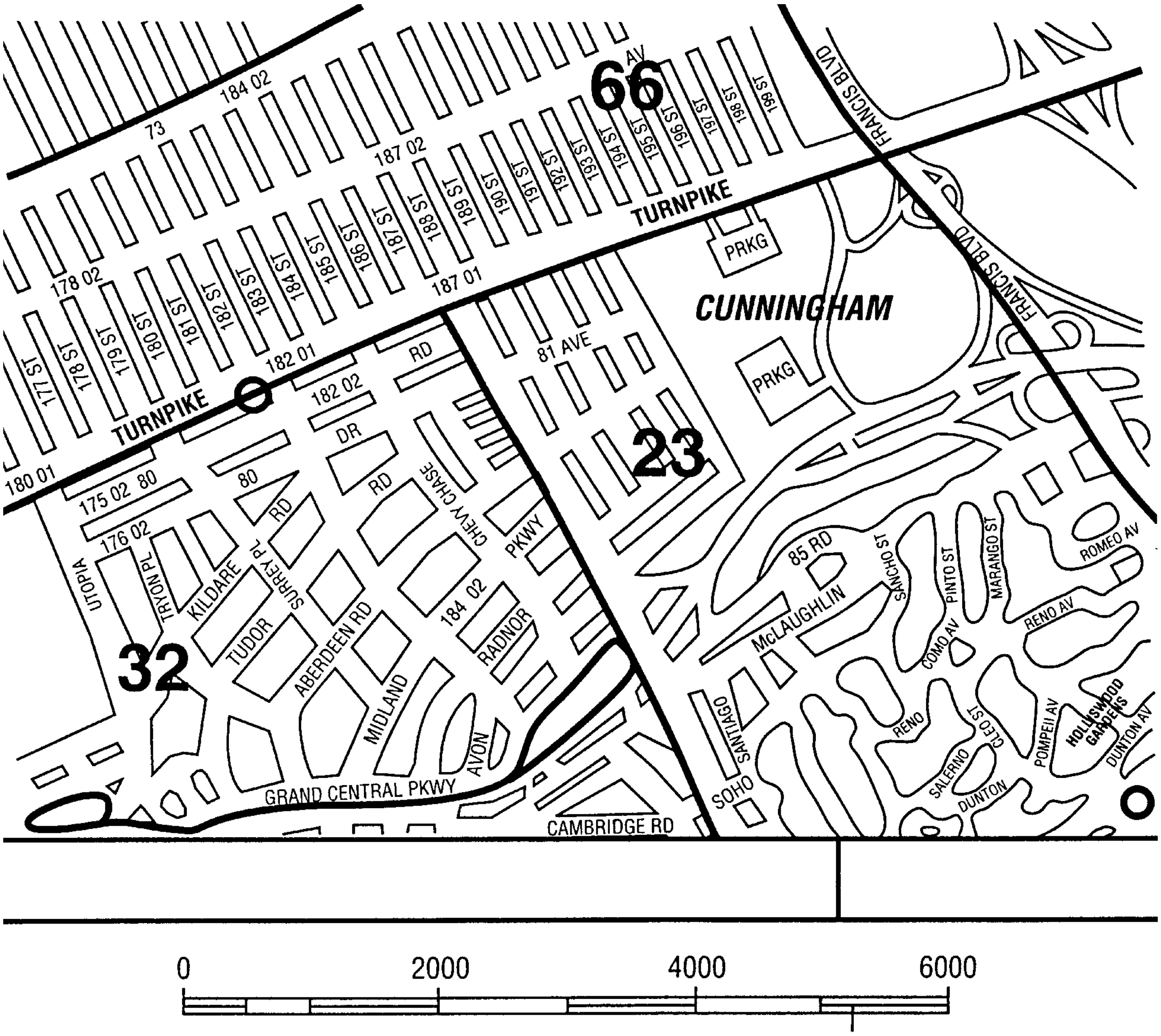


Figure 4-17
Street map of the area of the simulated leak search with unknown location experiment

The leak search was implemented with three instruments, two of them in the leak search van (the Dual Trap Analyzer or DTA and the BATS programmable sampler, see Appendix A). The continuous sampler or COPS was mounted on a separate cart and used for preliminary pinpointing. The passive samplers or CATS which were attached to trees and telephone poles served as additional tools to corroborate the findings obtained via the mobile approximate locating procedure (using the DTA and BATS). The CATS cannot be considered as actual instruments since they passively absorb the tracers in the air (see Appendix B) for subsequent analysis.

The previously developed leak search (see Section 5) was further refined to the following steps:

1. Mobile Locating (Traversing): Mobile Locating with DTA and NSS;

2. Mobile and Stationary Localizing of Candidate Street Blocks: 2.1 Ten-Block Localizing with DTA and NSS; 2.2 Intra-Block Localizing with DTA and NSS; 2.3 Stationary Localizing with CATS.

3. Preliminary Pinpointing: 50-feet-Pinpointing with COPS;

4. Borehole Pinpointing: 4.1 Approximate Pinpointing (30 feet distances) with DTA and COPS; 4.2 Narrow Range Pinpointing (10 feet distances) with DTA and COPS; 4.3 Final Pinpointing (2 feet distances) with DTA and COPS; 4.4 Approximate, Narrow Range and Final Pinpointing with CATS.

Mobile and Stationary Approximate Locating.

On July 17, 1990 at 8:40 am the mobile van started at Utopia Parkway and Kildare (see Figure 6.1). The experimental vehicle traversed the test distance in an easterly direction at about 5 miles/hr while air was continuously sampled with the Dual Trap Analyzer and the BATS. A Con Edison van with flashing yellow lights followed the BNL vehicle to divert traffic.

Within 20 minutes a PFT peak was observed by the DTA indicating a leak somewhere between 180th and 189th Street. Thus, within 20 minutes the potential leak location was narrowed down to an area of nine street blocks.

On the reverse trip, traveling west, also at about 5 miles/hr, a PFT peak was detected between street blocks 180 to 185, thereby confirming the findings of the first run.

Table 4.7 provides the quantified DTA and BATS results of the field observations as seen in the van during traversing of the 1.8-mile test region along Union Turnpike and Utopia Parkway. During the first traversing peaks of 20.2 and 17.6 fL/L respectively for the DTA and BATS were detected between 180th and 189th street. The other PFT concentrations were close to the oc-PDCH ambient background of 0.3 fL/L.

Table 4-7
Mobile Locating

	DTA		BATS		
Location	**Trap**	**ocPDCH (fL/L)**	**ocPDCH (fL/L)**	**PMCH (fL/L)**	**Direction**
Utopia at Kildare	A	<1	0.33	4.29	East Bound
180 to 189 St.	B	20.2	17.62	5.10	″
189 to 199 St.	A	3.1	0.52	4.29	″
199 to Clearview	B	<1	0.38	4.14	″
Clearview to 196 St.	A	<1	0.43	4.14	West Bound
196 to 185 St.	B	<1	2.14	4.10	″
185 to Utopia & 80 RD	A	27.7	57.14	6.19	″
Utopia at Kildare	B	<1	0.43	3.86	″

A larger PFT concentration was detected during the westbound mobile locating between 185th Street and Utopia Parkway (U.P.), because the southwesterly winds carried the emitted tracer vapors primarily to the north side of the streets.

Mobile and Stationary Localizing of Candidate Street Blocks

Next, a more thorough procedure was started at about 10 am. Now, only 189th to 180th street was tested by stopping the mobile van at each of the nine street corners in a westbound direction, with results that found the highest PFT concentration between 185th and 184th Streets (Table 4.8). Thus, only 2 hours after the start of the experiment the street block containing the leak was known.

Table 4-8
Ten Block Localizing

Location	DTA		BATS		Direction
	Trap	ocPDCH (fL/L)	ocPDCH (fL/L)	PMCH (fL/L)	
187 to 186 St.	A	2.9	6.57	5.38	West bound
186 to 185 St.	B	7.8			
185 to 184 St.	A	119.2	302.90	14.05	″
184 to 183 St.	B	36.1	36.57	5.57	″
183 to 182 St.	A	7.9	2.29	4.10	″
182 to 181 St.	B	1.6	0.38	4.05	″
181 to 180 St.	A	3.1	0.48	4.00	″
182 to 183 St.	B	<1	0.33	4.24	East bound
183 to 184 St.	A	<1	0.43	3.95	″
184 to 185 St.	B	4.2	5.67	4.29	″
185 to 186 St.	A	1.8	3.33	3.95	″
186 to 187 St.	B	3.3	5.14	4.24	″
187 to 188 St.	A	1.6	7.43	4.38	″
185 to 184 St.	B	77.7			
184 to 183 St.	A.	7.1	21.57	4.86	West bound
183 to 182 St.	B	4.0	0.71	4.14	Repeat
182 to 181 St.	A	<1	0.48	3.90	″

The findings were confirmed by east bound localizing. Since the DTA was upwind of the leak site when traveling east bound, the leak location is considered found when there is an abrupt increase in the tracer signal above background which occurred between 184th and 185th street.

Intra-Block Localizing With DTA and BATS

The 185th to 184th street block was then tested by stopping at 1/2 block and then 1/3 block distances. This procedure yielded high peaks at 185 and “184 2/3” (Table 4.9, see also Figure 4.18 for an overview of the area). Hence, in the early afternoon with winds from the south-south west it was clear that a leak had to exist somewhere around the center of the 184th/185th Street block.

Table 4-9
Intra-Block Localizing

Location	DTA		BATS		Direction
	Trap	ocPDCH (fL/L)	ocPDCH (fL/L)	PMCH (fL/L)	
185.5	B	47.8	50.00	5.86	
185 West Corner	A	39.7	153.19	9.43	West bound
184.5	B	38.3	41.95	5.29	1/2 block
184	A	7.6	17.10	4.33	″
183.5	B	3.8	5.48	4.24	″
183 to Exxon at 184	A	<1	0.33	3.67	″
185	B	189.7	239.71	11.90	
184.67	A	38.9	164.95	9.48	West Bound
184.67	B	266.0	295.43	14.24	1/3 block
184.33	A	20.7	113.48	7.86	″
184.33	B	105.6	123.81	8.38	″
184	A	2.1	4.24	4.05	
184	B	6.8	0.86	4.00	

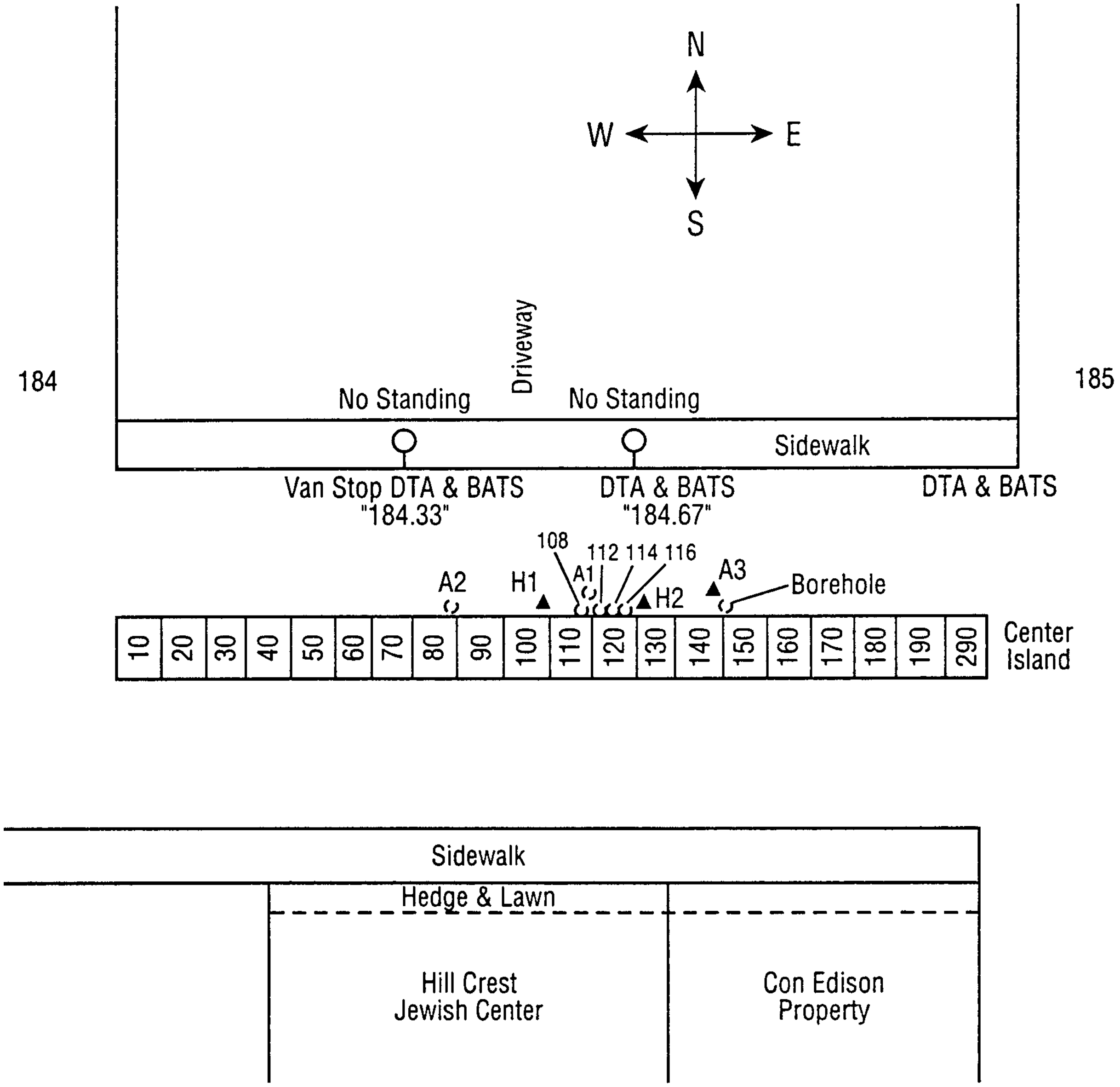


Figure 4-18
The 185th to 186th block section

Stationary Locating With CATS

The CATS had been attached to poles along the test route at about half-block intervals and the analysis results for 21 of the total of 68 deployed are shown in Table 4.10 for the region of interest. In column 3 (ocPDCH) the highest concentration clearly indicates the leak is between 184th and 185th Streets. That value of 343 fL/L is more than five times higher than the adjacent CATS reading at 185th Street and ten times higher than the one at the 184th street corner (which are 64 and 33 fL/L, respectively).

Table 4-10
Stationary Localizing with CATS

Site Location	Duration (hours)	PMCH (fL/L)	ocPDCH (fL/L)
NW POST @188	27.8	8	4
S MID @187-188	23.0	7	4
ISLAND POST @187	23.3	5	4
ISLAND POST MID 186-187	22.7	6	5
ISLAND POST @186	22.5	7	12
ISLAND POST @ CHEVY CHASE	22.5	6	21
ISLAND POST @185	22.5	10	64
ISLAND POST MID 184-185	23.8	19	343
ISLAND POST @184	23.8	8	33
S MID 184-183	26.5	6	3
ISLAND POST @183	26.8	5	1
N MID 183-182 (KENT)	23.8	8	<1
ISLAND POST @182	23.8	8	<1
ISLAND POST MID 182-181	23.8	6	<1
ISLAND POST @181	23.8	7	<1
ISLAND POST MID 189-181	23.7	7	<1
NW CORNER @180	26.6	7	<1
S MID 180-179	23.8	7	<1
NW CORNER @179	23.7	6	<1
S MID 179-178 (NEAR 178)	23.7	6	<1
ISLAND POST @178	23.5	6	<1
Limit-of-detection			
- in 24 hours (1 day)		1.20	0.80
- in 1 month (30 days)		0.04	0.03
Ambient Background		4.00	0.35

Consequently, by analysis of the CATS alone, the location of the leak could have been anticipated on the morning after the start of the test and the subsequent pinpointing could have started just with this information alone. Note that about one week sampling would be sufficient to quantify down to the ambient background of ocPDCH.

The corroboration, as demonstrated by the DTA, BATS and CATS results, is one of the great strengths of the PFT technology, and makes it a very powerful detection technology particularly in cases where one instrument alone might give misleading indications due to the small quantities of tracer encountered.

Preliminary Pinpointing

The finding of section 6.3.2 (Intra-Block Localizing) was confirmed by "sniffing" with the Continuously Operating Perfluorocarbon Sniffer" or COPS which yielded one point of tracer detection between 184th and 185th street in the center island around a tuft of grass.

The COPS was mounted on a separate cart and one member of the group "sniffed" air at various points along the center island. The results shown in Table 4.11 suggested a peak around the 113-foot mark. Hence, pinpointing could have resumed the next day around the 100- to 115-foot area, even without knowing the CATS results and the DTA readings (which, at this time, were only qualitative).

Table 4-11
Preliminary Pinpointing with COPS

Date Time	Site	Location	Sampling Time (sec)	Atten.	Peak Reading (mV)	Approx. pL Measured	Conc. * Normalized to 15 sec.
7/17/90	184-185	115 feet Clump of grass	10	16	10	53	80
1420		Dirt east of clump	15	16	38	202	202
		107 feet Tuft of grass	15	16	3	16	16
		113 feet Crack of Curb Seam	5	16	20	107	320

* Approx. concentration = mV * Atten./3 (3 mV/pL/L).

Borehole Pinpointing (Introduction)

The next step in the detection sequence was pinpointing. The pinpointing sites were shown in Figure 4.18. Pinpointing consisted of drilling 1 foot deep holes (boreholes) and capping off the holes with Duxseal. Inserted into the Duxseal was a 1/4" pipe which in turn was closed off with a Swagelok nut and septum. The septum allowed the insertion of a micro-syringe needle to sample the subsurface air. The holes were drilled initially at distances of 30 feet (at the 110, 140 and 80 foot marker), then at 10 feet based on sampling the 30 ft. space boreholes (100 and 120 foot markers) and finally at 2-foot intervals again, based on sampling the ten foot space boreholes (116, 114, 112, 110, 108 feet). Small amounts (20 µL) of air were drawn from the borehole with a micro-syringe and the air samples were injected into DTA and into CATS.

Approximate Pinpointing (30 feet distances) With the DTA

Three boreholes at distances 80, 110 and 140 feet away from 184th (between 184th and 185th) street were drilled. The center borehole (110 feet) showed the highest concentration (see Table 4.12). The readings were obtained by syringe injection of small amounts (20 µl) of borehole air into the Dual Trap Analyzer.

Narrow Range Pinpointing (10 feet distances) With the DTA

Subsequent boreholing at locations 100 ft and 120 ft (10 feet away from the center borehole) again confirmed the center borehole (110 feet) as the one with the highest emission (Table 4.12).

Final Pinpointing (2 feet Distances) With the DTA

Finally, boreholing at distances 2 feet apart (at 108, 110, 112 and 114 feet) indicated PFT concentration peaks on the DTA. These peaks indicated in a qualitative manner the strength of the subsurface PFT concentrations. Figure 4.19 shows a copy of one of the PFT analysis printouts which demonstrates the PFT analysis concentrations in various boreholes. Borehole 114 and 112 had the highest peaks, which led the TTC team to conclude that the leak had to exist around the 113-foot mark and it so informed Con Edison.

At this point the actual location of the injection point was revealed: it was situated at 112 1/2 feet. Thus, the locating procedure had succeeded to pinpoint the leak to within 0.5 feet.

Table 4-12
Pinpointing With DTA

Trap	Location	Inject. Vol. (m icro v/L)	Conc. (nL/L)	Action
B	100’ site	20	70	
A	140’ site	100	1	Approximate Pinpointing at 30-foot intervals
A	80’ site	80	0.4	
A	100’site	60	1	
B	100’site	20	2	Narrow Range Pinpointing at 10-foot intervals
A	120’ site	60	7	
B	120’ site	20	6	
A	166’ site	20	7981	
B	166’ site	20	8531	
A	114’ site	20	13,644	
B	114’ site	20	13,891	Final Pinpointing at 2-foot intervals
A	112’ site	20	9951	
B	112’ site	20	10,585	
A	110’ site	20	8829	
B	110’ site	20	7851	
A	108’ site	20	878	
B	108’ site	20	842	

At the time of the experiment no quantitative measure of actual PFT concentrations was known; therefore, the strip chart peaks had to be calculated into concentration values by means of the calibration procedure performed back in the laboratory. The results are shown in Table 4.12.

From Table 4.12 it becomes evident that the samples stemming from the 116 to 110 sites yielded very large voltage readings (above 5 Volts) for the ocPDCH tracer requiring the use of calibration equations (see Appendix B). The maximum reading of about 13900 nL/L (24.2 ppm) at the 114 foot site and about 10 000 nL/L at 112 ft.

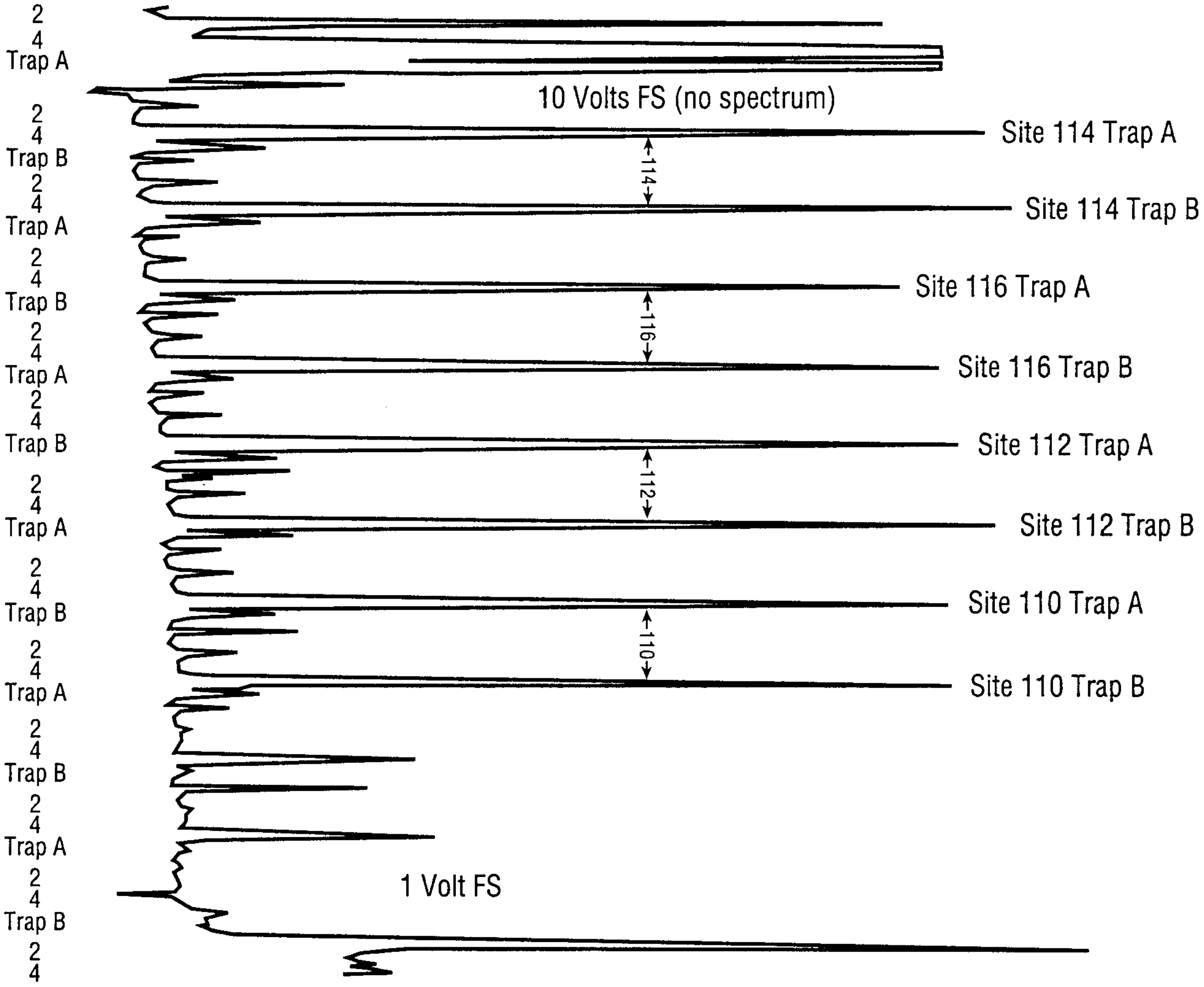


Figure 4-19
DTA PFT concentrations from two foot spaced boreholes

Approximate, Narrow Range and Final Pinpointing with the CATS

The concentration profile found through borehole CATS analysis is shown in Table 4.13. Here, clearly, the highest value resulted from the 114 foot borehole (23199 nl/l of ocPDCH), followed by the 116 and 112 foot holes (12149 and 10622 nl/l, respectively).

Analysis of the tracer PMCH (present is a minor impurity in o-PDCH) also showed a maximum at about the same location but with a larger uncertainty (about 112 ± 3 feet).

These findings were consistent with the similar maximum levels found in the borehole in the July 1988 Queens test of almost 8 ppm.

Since the PMCH levels were in the linear region and the ocPDCH-to-PMCH ratio was shown to be about 28.5 to one, the actual ocPDCH levels were 8.1, 15.3 and 8.3 ppm for the 112, 114 and 116 foot boreholes, respectively, close to the DTA values.

Table 4-13
Pinpointing with Borehole

		Tracer Quantities			Ratio	Tracer Conc.	
Loc	**Sample (micro/L)**	**PMCH (pL)**	**ocPDCH (pL)**	**ptPDCH (pL)**	**ocPDCH-to-PMCH**	**PMCH (nL/L)**	**ocPDCH (nL/L)**
80	20	0.00	0.02	0.00	-	0.0	0.8
80	100	0.00	0.01	0.00	-	0.0	0.1
100	20	0.00	0.02	0.00	-	0.0	0.8
100	100	0.00	0.01	0.00	-	0.0	0.1
108	20	0.63	19.06	0.25	30.19	31.6	953.2
110	20	0.18	5.79	0.05	32.98	8.8	289.5
110	100	0.92	21.99	0.25	24.02	9.2	219.9
112	20	5.71	212.44	2.04	37.18	285.7	10,622.1
114	20	10.76	463.98	3.56	43.11	538.2	23,199.1
116	20	5.80	242.99	2.61	41.93	289.8	12,149.3
120	20	0.00	0.11	0.00	43.83	0.1	5.3
120	100	0.01	0.36	0.00	33.35	0.1	3.6
140	20	0.00	0.01	0.00	-	0.0	0.5
140	100	0.00	0.02	0.00	-	0.0	0.2

Conclusions

Approximate locating, localizing, and pinpointing a subsurface "leak" of as little as 5 gallons of 0.1 wt percent PFT-tagged fluid was demonstrated to be viable in a period as short as 6 hours for a 2 mile section of feeder.

With the presently available DTA mounted in a van, localizing a PFT-tagged subsurface fluid leak to within about one-half block (about 100 feet) in less than 2 hour was demonstrated for a 2-mile test region. Further localizing with the real-time COPS clearly showed "hot spots" only in a 10-foot stretch about mid-way between 184th and 185th Street, consistent with the DTA results.

Detecting the presence of subsurface fluid leaks was demonstrated with the inexpensive passive sampling approach (CATS). In permanently tagged feeders, periodic monitoring of cable feeder runs with CATS holds the promise of detecting, localizing, and quantifying fluid leaks over the entire length of the cable.

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B

PERFLUOROCARBON TRACER DETECTION INSTRUMENTATION

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1. The Dual Trap Analyzer

In the late 1970s, James Lovelock, the developer of the ECD, under a contract to the National Oceanic and Atmospheric Administration, built a prototype two-trap instrument that was subsequently modified at BNL. The unit consisted of two adsorbent traps, packed with a charcoal-like adsorbent and an in situ gas chromatograph (GC) equipped with an electron capture detector (ECD).

While one trap is sampling at 1 L/min for 5 min, the other is heated to recover and analyze the collected PFTs. Once heated into the GC, the tracers are separated in a Carbopack packed GC column before being detected in the ECD. Since the traps reversed position every 5 min, no sampling time is lost.

A new version of this real-time analyzer was built in 1983 for atmospheric tracer experiments. Improvements allowed the separation of 4 to 5 PFTs in a 4-min chromatogram of a 4-min air sample collected at the rate of 1 L/min. The unit was able to detect to the ambient levels of PMCP and PMCH, indicative of the limit of detection of about 10 fL (D'Ottavio et al., 1986), i.e., 10×10^{-15} liters of PFT.

2. Programmable Sampler (BATS)

These samplers were developed at Brookhaven. The units measure 14 x 10 x 8 inches and weigh 7 kg. They contain 23 sampling tubes, each containing 150 mg of a charcoal-like material (Ambersorb) which can adsorb all the PFTs in more than 30 liters of air. The air is pumped sequentially through one tube after another. The contact time as well as the flow rate can be pre-programmed by an internal computer.

Batteries provide power for up to one month of unattended operation of all the automatic and recording functions. In the laboratory, sample recovery is accomplished by direct ohmic heating of the adsorption tubes to 400°C, with the PFTs being purged from the BATS tube through an automated ECD-GC system, analyzing all 23 tubes in about 4 hours.

3. Capillary Adsorption Tube Samplers

The passive samplers are made from 6 mm OD by 4 mm ID glass tubing exactly 2.5 inches long. They contain 64 mg of Ambersorb and in their non-sampling state are sealed with small rubber caps. Sampling occurs by the process of Fickian diffusion when one cap is removed. From empirically derived diffusion coefficients of PFTs in air, it was determined that the CATS sampled at a rate equivalent to about 200 ml of air per day, CATS are similarly desorbed as BATS for GC analysis.

4. Continuously Operating PFT Samplers (COPS)

This instrument continuously responds to ECD sensitive tracers by combusting inlet air with hydrogen in a catalyst bed. The PFTs remain uncombusted and are subsequently detected by an ECD. Its detection capability is limited to about 30 pL/L. Table A1 provides an overview of the current sampling and analysis methodologies.

5. DTA Calibration

The procedure is started by injecting a certain amount of tracer gas standard into the DTA inlet. The response, in volts, is then measured and recorded. The power of the DTA can be noted that the extremely low tracer volume of 5.1×10^{-12} L resulted in a peak that occupied more than half the strip chart paper height, definitely a clearly visible signal (total paper height represented 1 volt).

The process of injection and peak measurement was repeated for increasing amounts of tracer and also for various types of tracers. The resulting non-linear correlation of volts versus tracer volumes were plotted and regression analysis were performed. Figure A1 show the resulting straight regression line for the tracers ocPDCH and PMCH and for the two traps of the DTA. These figures only cover the response up to about 1 volt (about 10 pL of PFT). Since ocPDCH signals from the boreholes were more than 6 volts, the actual calibration equation used was:

H/V(volts/pL) = a - b x H(volts) where

	a	**b**
Trap A	0.1352	0.0173
B	0.1507	0.0191

which is applicable up to about 7.4 volts (about 1000 pL).

With the help of these correlations the voltage measured peaks of the field experiments could be calculated into tracer volumes and further into tracer concentrations (since the DTA air flow rate or volume injected was known).