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ABSTRACT

DEVELOPMENT AND FIELD TESTING OF PULSE INTRODUCTION MEMBRANE EXTRACTION (PIME) FOR MEASUREMENT OF GROUND WATER CONTAMINATION

by
Anthony San Juan

VOCs are a class of aromatic and aliphatic compounds with a variety of functional groups, and are in general detrimental to human health even at trace levels. Conventional analysis of VOCs in groundwater usually involves sampling at site followed by laboratory analysis. This results in long turn around times, high cost and also errors associated with sample preservation during transportation and storage. In order to address these problems, a field portable instrument referred to as Pulse Introduction Membrane Extraction (PIME) has been developed for monitoring trace level halogenated organic contaminants in ground water. A membrane extraction approach has been used, to selectively extract and concentrate the organics from a complex aqueous matrix with no additional sample preparation, thereby attaining high sensitivity and low detection limits. Using a field portable gas chromatography, analysis of individual discrete as well as continuous on-line monitoring of VOCs in groundwater was performed at a Superfund site. The results of the field test demonstrated that the field-PIME could provide real-time, cost-effective data for site assessment and rapid decision-making. The results from field-PIME analysis were in good agreement with that from a certified reference laboratory. Statistical analysis of this comparative data is also presented.

DEVELOPMENT AND FIELD TESTING OF PULSE INTRODUCTION MEMBRANE EXTRACTION (PIME) FOR MEASUREMENT OF GROUND WATER CONTAMINATION

by
Anthony San Juan

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DEVELOPMENT AND FIELD TESTING OF PULSED INSTRODUCTION MEMBRANE EXTRACTION (PIME) FOR MEASUREMENT OF GROUND WATER CONTAMINATION

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CHAPTER 1

INTRODUCTION/BACKGROUND

Volatile organic compounds (or VOCs), which include a variety of alkyl substituted aromatic hydrocarbons, as well as organic molecules containing different functional groups, have been found in ground water in the parts per billion (ppb) to parts per million (ppm) levels. Since many of these compounds are toxic, carcinogenic and mutagenic, even at trace levels they are a threat to public health. Contamination in groundwater can be traced to leaking underground fuel/solvent storage tanks, landfills, and wastewater from industrial operations. Another source of groundwater contamination can be ascribed to the use of agricultural chemicals and pesticides. Large quantities of these chemicals are used to control insects, weeds, and diseases on plants. For example, pesticides have been found to be detrimental to the health of human beings and animals. The extensive application of pesticides in the past has created an enduring environmental problem; these compounds are the most abundant of the chlorinated aromatic pollutants in the global ecosystem [1].

The site assessment program was initially enacted by the EPA in section 105 of CERCLA, and under the National Oil and Hazardous Substances Pollution Contingency Plan (NCP), to specifically evaluate criteria for determining priorities among releases or threatened releases of hazardous substances for the purpose of taking appropriate response actions. These criteria and priorities are based upon relative risk or danger to human health and the environment presented by the site [2].

A Hazardous Materials Site Assessment (HMSA) is a type of environmental audit or investigation, and is generally separated into three distinct components: Phase I, Phase II and Phase III assessments. Whereas Phase I involves historical site review and Phase III involves remedial action, Phase II is where the collection, analysis, validation and evaluation of samples occur. A Phase II Hazardous Material Site Assessment (HSMA) is part of the general site assessment program and is defined as a structured process utilized "to provide the information necessary to characterize site, define site dynamics, define risks, and develop a program to mitigate or eliminate potential adverse human health and environmental impacts" [2]. Phase II assessment for volatile organic compounds contamination is usually carried out by commercial contractor laboratories (under the national Contract Laboratory Program (CLP)) to provide Superfund analytical support. Remediation of contaminated sites worldwide has been estimated to cost half a billion to more than a trillion dollars. Almost one-half this cleanup cost can be accounted to off-site laboratory analysis for all samples collected during site screening and characterization [3].

In general, extensive handling during sample collection, transportation, and storage can affect the integrity of the sample and thus the analytical results. Even though CLPs carry out chemical analytical services using state-of-the-art technology, the turnaround periods are fairly long. Lag time between sampling and analysis is an important factor since many analytes tend to be fairly unstable and require preservation steps to decelerate chemical degradation and volatilization [4]. It may

also be necessary to reduce the analytes' adsorption effects onto the storage containers, which lead to low concentration values [5]. One simple preservation technique that is widely used is refrigeration to 4 degrees Celsius. Note that the CLP laboratory-based (or reference lab) gas chromatography analysis still frequently provides reliable and accurate results. However, as previously mentioned, due to its multiple, labor-intensive handling steps, laboratory-based testing is often associated with exorbitant costs and lengthy turnaround periods, during which no remediation action may be undertaken. This limits the sample throughput and, therefore decreases the efficiency of site remediation [6].

Recent developments in portable instrumentation have made field investigation of contaminated sites feasible. Many new analytical techniques are currently being developed, and compact versions of existing instruments are becoming commercially available. Gas chromatography, due to its high sensitivity and separation capability, has emerged as a leading technique for the analysis of VOCs. Since portable GCs have produced data that closely match laboratory instruments, the US EPA has begun to encourage their use for on-site analysis to reduce the high cost of site assessments [7].

The main goal of field analytical chemistry is to generate high quality analytical data in the field so that real-time information can be made available. More specifically, the intent of field VOC analysis is to analyze pollutants with fieldable analytical instruments, fieldable analytical methods, and techniques to enhance the

information content of analytical results for immediate reporting. New real-time analytical information can be produced to facilitate effective chemical hazard assessments and undertake mitigative actions during chemical spills. It also facilitates remedial investigations and feasibility studies of hazardous waste sites during site assessment/characterization [8].

Field instruments and methods should have adequate selectivity, resolution, peak capacity, analyte range, sensitivity, precision and accuracy. In addition, it also should have high speed of analysis, portability, low power consumption, ease of operation, ruggedness, and low cost. With these figures of merit in mind, we investigated on-line membrane extraction/microtrap in conjunction with a portable GC as a feasible method for on-site measurement of trace level halogenated VOCs in groundwater.

The present instrument separates organics continuously or non-continuously from the aqueous matrix by membrane extraction. The organics are then concentrated into a microsorbent trap and injected into a gas chromatograph. This membrane extraction approach is used to selectively concentrate the VOCs with no additional sample preparation. The development of this novel instrument design in our group, referred to as Pulse Introduction Membrane Extraction (PIME) [9], fills an important niche in on-site testing, since there are currently no field analytical instruments in the market that are capable of analyzing discrete individual samples and continuous monitoring of VOCs in groundwater. With respect to the latter, there is a need for the continuous measurement of wastewater discharges and process streams in various industrial operations as well. This type of monitoring can provide

consistent data quality, and provide information about concentration fluctuations as a function of time. In addition to the faster turnaround times for obtaining results using this automated instrument, the analytical cost per sample is significantly lower when compared to using traditional laboratory-based analysis.

CHAPTER 2

OBJECTIVE

The goal of this study was to demonstrate the applicability of the PIME technique in real-world ground water measurements. The tasks to be performed were:

- Fabricate a field portable instrument
- Perform the field test at a Superfund site
- Demonstrate continuous monitoring capability of the PIME
- Evaluate the instrument performance
- Compare the results with standard EPA approved methodology.

The following performance evaluation goals were developed to evaluate the capabilities of the field PIME instrument:

Methodology: develop method to specifically identify halogenated VOCs

Deployment: instrument can be set up in less than 30 minutes

Completeness: 90% match of target VOC compounds with reference lab

Throughput: analysis per sample in less than 30 minutes (related to methodology)

Reported Data: results can be reported out as soon as sample run is complete

Precision: instrument RSD% less than or equal to 15%

Accuracy: instrument median results fall within +/- 50% difference of reference lab, >90% correlation coefficient, and meet the Wilcoxon Signed Rank equivalency test.

The rationale behind using the above performance goals, such as accuracy and precision, were roughly based on EPA methods 502.2 and 8260 for halogenated VOC analysis in water. Minor modifications to the performance goals were made since more allowance for error is usually given when utilizing field instruments.

CHAPTER 3

LITERATURE REVIEW/THEORY

3.1 Conventional Groundwater Analysis

The conventional methods for analysis of VOCs in aqueous matrix are purge and trap, headspace analysis, and solid-phase microextraction (SPME). Purge and trap (Figure 1A) involves bubbling an inert gas (usually nitrogen) through a water sample that is contained in a purging chamber. This in effect strips the volatile organics from the aqueous phase and delivers it into a sorbent trap. The trap is subsequently heated and backflushed into the gas chromatograph. Headspace (Figure 1B) analysis involves equilibrating an aqueous sample in a sealed container, then withdrawing a

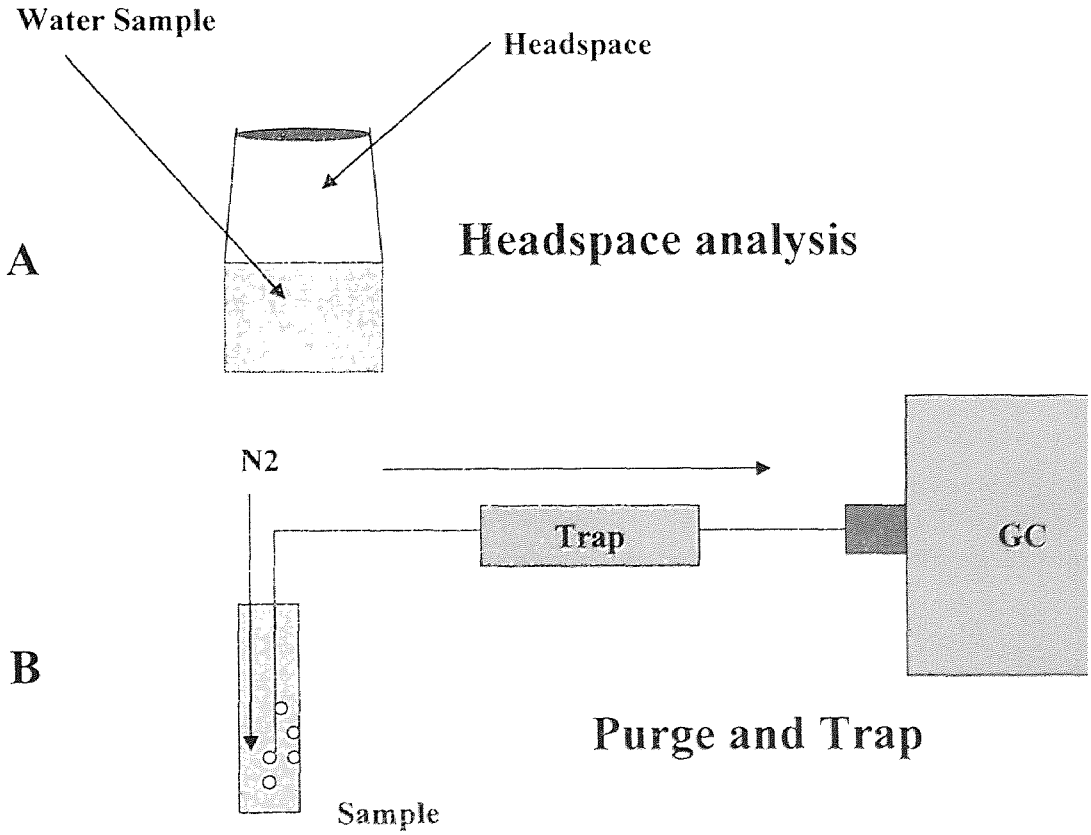

Figure 1 Conventional methods for VOC analysis

headspace sample from the container and injecting it into a GC or GC-MS. Finally, SPME involves dipping a microfiber coated with an adsorbent into an aqueous sample (or its headspace) where the organics equilibrate on the fiber surface. The fiber is then inserted into a GC injection port and desorbed for GC analysis. While these techniques have their merits, they also have many limitations. These include poor accuracy and precision for headspace analysis and SPME, as well as memory effects and incomplete desorption for purge and trap [10]. Therefore, none of these techniques can be used for continuous on-line analysis.

In PIME, separation of organics from the aqueous matrix is initially carried out by membrane extraction, which are then selectively concentrated with no additional sample preparation. The development of PIME also offers the advantage of having the capability to analyze discrete samples and continuously monitor VOCs in groundwater in the field. Callis [11] reviewed the necessity for on-line analysis in process analytical chemistry, and the need to eliminate the delay between sampling and analysis. In general, on-line analysis involves the measurement of the process parameters and the subsequent conversion of these data into process information. This information is then used to document, correct, and refine the overall performance of the unit. The continuous monitoring capability of the PIME allows it to be used as a process-monitoring device.

3.2 Theory of Membrane Extraction of VOCs

The use of membranes to separate volatile organic compounds is an emerging technology in analytical chemistry. Membrane separation is well established and has been utilized in numerous industries as unit processes for microfiltration, ultrafiltration, reverse osmosis, electrodialysis, etc. [12]. Membranes offer the advantage of on-line extraction of target compounds since the sample is continuously introduced into the feed side, while the analytes that have permeated to the other side are stripped off. It has also been reported that membrane separation processes can be inexpensive and energy efficient in comparison with conventional separation processes [13].

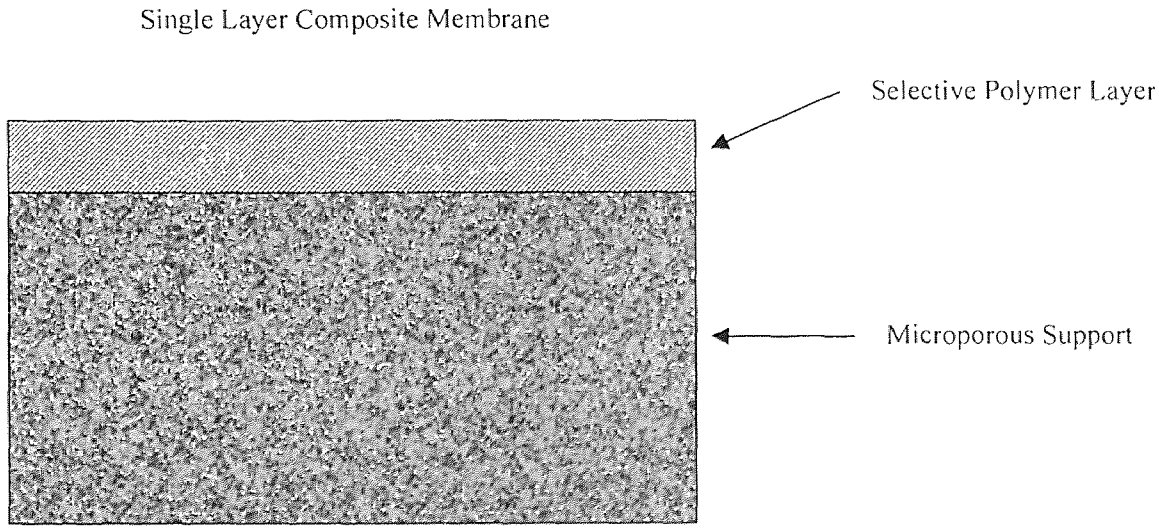

Figure 2 Composite Membrane: Porous layer provides mechanical support while the nonporous offers high selectivity.

One of the more common analytical applications of membrane separation has been its use as an interface with mass spectrometers (MIMS), wherein sample is continuously fed into the membrane, and the vacuum pulls the permeated analytes

directly into the ion source for analysis [9,14]. However, for multi-component mixtures, the spectrum obtained from MIMS is complex and often difficult to interpret.

The mechanisms of membrane permeation for VOCs depend upon the type of membrane used. In a porous membrane layer, convective flow occurs through the large pores, but selectivity with respect to water is low, while in gases, Knudsen diffusion processes occurs where the lighter molecules preferentially diffuse through pores which have diameters less than the mean free path of the molecules. A third mechanism for separation is molecular sieving in which huge molecules are excluded from the pores due to their size. Finally, in polymeric membranes, the permeation occurs via activated diffusion where the analyte dissolves into the membrane material prior to diffusing across it.

The membrane utilized in our experiments is a composite membrane (Figure 2) which incorporates two or more distinct layers. This membrane has a nonporous selective layer and a silicone layer deposited onto a porous support. Unlike the porous layer, which simply provides mechanical strength for the membrane, the nonporous layer offers high selectivity for organic molecules, which dissolve in the membrane matrix and diffuse under the concentration gradient. The combination of these layers into one composite membrane has the advantage of low-mass transfer resistance of the porous layer and the high selectivity of the nonporous layer [12, 15].

3.3 Theory of Instrument Operation

Analytes are loaded into a ten-port valve and through a sample loop (Figure 3). The sample can then be injected into the membrane module where it is carried by pumped Milli-Q deionized water. In the membrane module, organics begin to pervaporate through the membrane's inner wall and into the permeate side, where they are stripped off by nitrogen gas moving countercurrent to the flow of the eluent. Pervaporation is a unique phenomenon characterized by the imposition of a membrane layer between a liquid and a gaseous phase with mass transfer of solutes from the aqueous solution occurring selectively across the barrier to the gas side [16]. The permeated organics that come from the membrane module are then

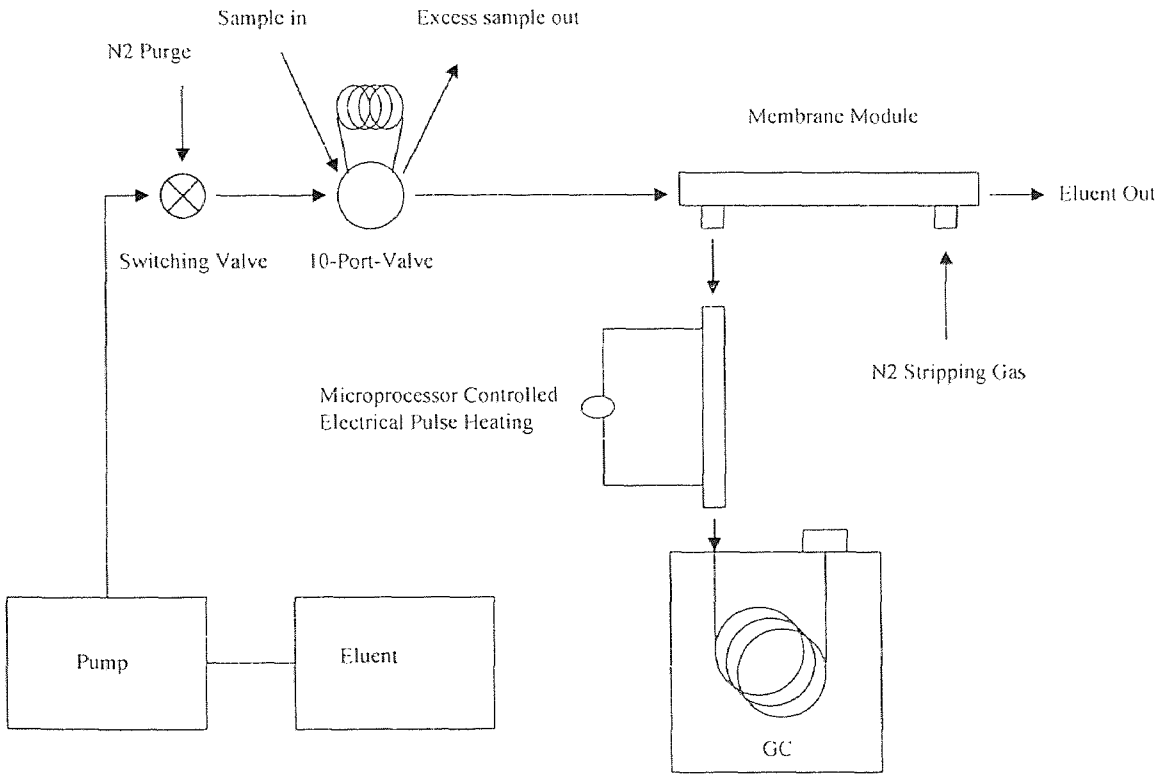

Figure 3 Pulse Introduction Membrane Extraction (PIME) setup

preconcentrated into a small sorbent cartridge referred to as the microtrap. After a sufficient time has elapsed (2-7 minutes), a pulse of electric current is applied to the microtrap. This results in desorption of the trapped organics as a concentration pulse, which serves as the injection into the GC where separation occurs.

3.4 OLMEM and PIME

In traditional analytical applications of membrane extraction, the sample is usually introduced continuously into the membrane, such as MIMS, where measurements are only made after permeation of the analyte through the membrane reaches a steady state. Previous developments in our group referred to OLMEM-GC [17-19], which also utilizes this same working concept, where a water (or air) sample is flowed through the membrane module, while a countercurrent stripping gas (N2) is passed on the outside of the membrane. The N2 transports the permeated analytes into a microtrap (small silica-lined tubing packed with adsorbent), which is then pulsed and the sample is subsequently injected into the GC. The OLMEM-GC configuration precludes it from having the capability to inject discrete samples since it flows continuously, and thus is only applicable for on-line analysis. Furthermore, it is necessary to wait until equilibrium is reached, a disadvantage since pulse injection prior to steady-state will result in a concentration value somewhere between the preceding and the current concentration value. Each chromatogram is an average response proportional to the permeation over that injection interval, since

the permeation flux is still not constant during this time. Measurements in this non-equilibrium region will provide a result that deviates from the true concentration value.

Permeation through polymers, is described by Fick's first law:

$$J=-D^*(\delta c/\delta x) \quad (1)$$

where J is the gas flux, D is the diffusion coefficient and $\delta c/\delta x$ is the concentration gradient.

Fick's second law describes the analyte concentration as a function of membrane thickness and time:

$$\partial C/\partial t=-D(\partial^2 C/\partial^2 x^2) \quad (2)$$

Measurement for OLMEM-GC is taken when the permeation rate reaches steady state. The left side of the equation 2 becomes zero and assuming that permeate side of the membrane is zero concentration, integration of equation 2 results in a steady state permeation flux Jss:

$$Jss=D(C/L) \quad (3)$$

where L is membrane thickness. The steady state permeation flux is constant for a certain sample concentration C.

The development of PIME, on the other hand, can be used for discrete sampling and non-continuous monitoring of organics in water. PIME differs from OLMEM-GC in that it can analyze samples by direct injection into a ten-port valve; in addition, the valve can simultaneously be connected to a process or waste discharge stream. In both cases, a sample pulse injection is made to the membrane module where the extraction of organics occurs. Compared to OLMEM-GC, PIME

does not require a steady-state permeation flux for analysis since the membrane receives a sample pulse of certain duration Δt. Thus the errors associated with steady state requirement are eliminated. Response time for PIME-GC is defined as the required time for complete permeation of analytes across the membrane. An important factor that reduces the permeation flux and increases the response time is mass transfer resistance due to poor mixing of the water and membrane. Nitrogen purge, as will be discussed later, eliminates the boundary and reduces response time, and thus the frequency of analysis [9].

For a pulse sample input, the boundary conditions are as follows:

At the feed side, at time t=0, C=0, changes to C=kC*

At $0<t<\Delta t$, C=kC*

At $t=\Delta t$, C=kC*, change to C=0

At $t>\Delta t$, C=0

where C is the analyte concentration at the membrane surface, C* is the concentration in water and k is the distribution coefficient of the organics between water and membrane.

Using the boundary conditions and solving for equation 1 and 2 gives us a mathematical solution.

$$Jns = Jss(1+2 \Sigma (-1)^n \exp. \{-n^2 (\Pi)^2 (D(t)/l^2)\}) \text{ when } t < \Delta t \quad (4)$$

$$Jns = Jss(2 \Sigma (-1)^n \exp.\{-n^2 (\Pi)^2 (D(t)/l^2)\} - 2\Sigma(-1)^n \exp.\{-n^2 (\Pi)^2 (D(t)/l^2)\}) \text{ when } t < \Delta t \quad (5)$$

Δt is a function of both sample size and flow rate. If Δt is small, then analysis time is limited by the response time needed for complete permeation.

Response time in this case is defined as the time required for all analytes to permeate through the membrane, and it determines the frequency at which samples can be analyzed. If Δt is large, then analysis time approaches steady state. PIME does not have a steady-state diffusion requirement, so the need to wait for equilibration after each sample injection is not necessary, and rapid sample analysis is feasible; moreover, each injection represents the true concentration value of the sample. The only consideration is removing any memory effect and sample carryover from the previous run, and this can easily be achieved by purging the membrane with N2 gas [9].

3.5 Optimization of the PIME

3.5.1 N2 Purging to Decrease Response Time

The analyte initially partitions into the membrane surface according to the partition coefficient $C=kC^*$, and equilibrium is established between the aqueous phase and membrane phase. The dissolved analyte rotates and translates the polymer segment utilizing diffusion activation energy, and then creates a suitable size vacancy for the analyte to move into, which is in the direction of the concentration gradient [9].

The boundary layer, which has been studied extensively [20-23], is a stagnant film formed at the membrane's surface, which prevents analyte diffusion and mass transfer. Specifically, its contribution to mass transfer resistance is a function of the chemical nature of the analyte, the hydrodynamic condition, and the membrane thickness. The Reynolds number represents the hydrodynamic condition:

$$Re=(vdp)/u \quad (6)$$

where v is the velocity of the water, d is the diameter of the tubing, p is the sample density and u is the viscosity of the sample. A Reynolds number of 20,000 and over usually eliminates the formation of any boundary layer. In our previous studies, our Reynolds value was calculated to be less than 300 with a membrane thickness as thin as 0.025 mm, which would indicate the presence of a well-formed boundary layer and thus a significant resistance to mass transfer.

The field portable GC uses the PIME setup in conjunction with an N2 purge. The nitrogen purge is used to break up the boundary layer formed on the surface of the membrane, thereby reducing the tailing and response time that would normally affect an OLMEM-GC system. The considerable tailing of the analyte's response is due to the axial mixing of the sample with the eluent water. Ideally, the sample should enter the membrane as a slug or block profile, but this is not the case. Instead, a skewed Gaussian curve is the resulting profile with a long tailing time. Use of an N2 purge after the maximum response is reached reduces the analysis time. However, a slight reduction in the overall sensitivity is the trade-off. For example, if the purge interval (interval between sample injection and nitrogen purge) is only 1 minute, the tailing response lasts for only 5 minutes. However, detection limit goes up since the extraction efficiency of the membrane goes down. If no purge is employed, then tailing response can last up to 25 minutes [9]. In the PIME portable field setup, the purge interval was set at 4 minutes to clear out the membrane for the next sample. Since the GC temperature programming was set to ramp up to 150 C, the microtrap was pulsed toward the end of the run to clear out

any remaining trace VOC contaminants that were stripped by the nitrogen from the membrane module; thus, the membrane and trap were clean upon equilibration of the GC system.

3.5.2 Using a Spiral Membrane Module

The portable PIME system's sensitivity was further enhanced using a spiral module membrane. The spiral module was constructed by inserting 3 hollow membrane fibers through the length of a straight tube (40 cm). The tube was then circularized 3 times so that the diameter of each spiral was about 11 cm. The spiral module allows more perturbation in the membrane matrix because of the sample flow path, hence minimizing the boundary layer and allowing an increase in mass transfer of analyte to membrane.

From previous studies, it had been shown that system response increases with increasing membrane length, since extraction efficiency also increases. For example, a 40cm membrane fiber quantitatively extracts more from the sample than a 10cm membrane's fiber simply because of the increase in membrane active surface area. It follows that multiple fibers of membrane will also increase system response as sample residence time is increased. In the portable PIME setup, the use of 3 membrane fibers was sufficient to extract most of the analytes in the low ppb levels.

In the following paper, the field application of PIME-GC for continuous and non-continuous analysis of halogenated volatile organics is presented. A sample valve is used for injecting the samples into the membrane module for both discrete and on-line monitoring. For on-line analysis, the sample is injected into the

membrane at set interval times. For each sample loading, an injection is made for GC analysis. A comparison of field data and a certified commercial laboratory's data will also be presented, which will be used to evaluate the performance of the field PIME instrument.

CHAPTER 4

EXPERIMENTAL

To minimize the cost of deployment, our site selection criteria was based on the following factors: easy accessibility with a normal two-wheel drive vehicle, contaminated media of interest (groundwater) containing the target analytes, an appropriate facility location and presence of support personnel. The Naval and Engineering Station (NAES) is located in Lakehurst, NJ (Figure 4) and was therefore readily accessible by car from NJIT. The NAES was designated as an NPL (National Priority List) site in 1987, and the contaminated areas were identified through review of facility records, aerial photographs, interviews with past and present base personnel, and visual observation. Areas of concern varied in size from

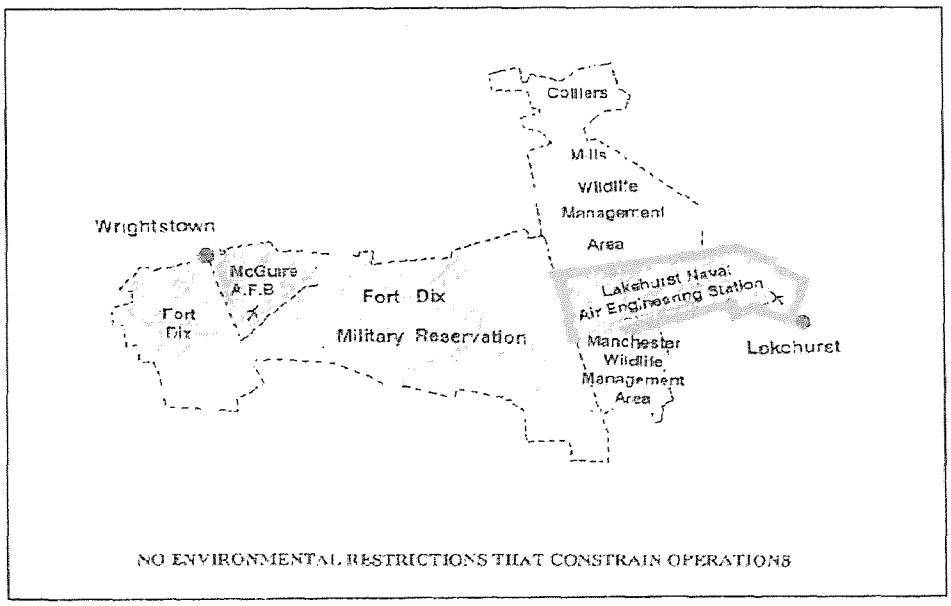

Figure 4 Naval and Engineering Station (NAES), Lakehurst, NJ

a few square feet to several acres. The most common substances released at these sites were aviation fuel, gasoline, lubricating and hydraulic oils and other solvents. Thus halogenated VOCs were known to be present in groundwater in the low ppb levels. Support personnel in the base proved to be helpful in collecting well samples from the groundwater, and were very accommodating in our gaining access to several locations within the site to set up our instrumental apparatus.

4.1 Instrumental Apparatus

Our injection volume was selected to be one milliliter. This provided adequate sensitivity for ppb level analysis. The injection was made using a one-milliliter sample loop constructed of 1/8 inch stainless tubing and mounted on an automatic ten port valve. The membrane (0.290 mm OD x 0.240 mm ID, Applied Membrane Technology) was composed of a 1 um thick film of homogeneous siloxane as the active layer supported with a layer of microporous polypropylene. The membrane module was constructed by inserting 3 composite membrane strands through the stainless steel tubing (0.5 mm ID, Restek Corp.) and sealed at both ends with "T" units (Small Parts Co.). Epoxy was then applied to both ends of the "T" units thereby separating the gas inlet/outlet from the aqueous phase.

Approximately 15 cm length of fused silcosteel tube was packed with 0.035g of Carbotrap C adsorbent (Supelco, PA). The microtrap was placed between the membrane module and the capillary column. Approximately ten amperes of electric current was supplied by a variac to rapidly heat the microtrap. The microtrap was pulsed for a period of 1.2 seconds at 30 Volts and the interval between pulses were

set such that the analytes permeated through the membrane and column separation was completed. The microtrap operation was controlled using a microprocessor-based controller developed in-house.

A portable pump (FMI Lab Pump QG150) was used to pump the water eluent through the 10-port valve and membrane module. The capillary column used was a J&W Scientific DB-624 0.53 ID 30-meter column that was suitable for halogenated organics and was as per specification of related EPA methods. Countercurrent nitrogen flow was used as the stripping gas and the flow rate was set to 7 ml/min. The temperature programming was as follows: 45 C hold 6 min, 15 C/min ramp to 150C.

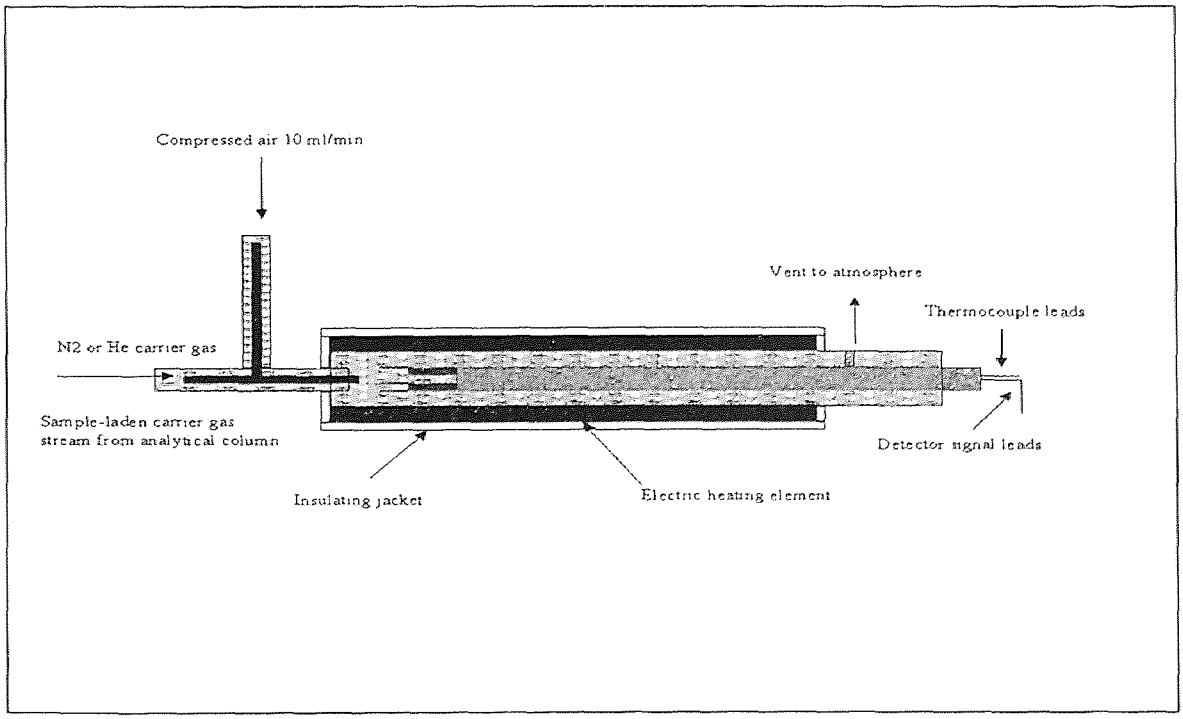

Figure 5 Simplified Diagram of Basic Dry Electrolytic Conductivity Detector

A SRI Instrument model 8600/9300 portable GC equipped with a photoionization (PID) and dry-ELCD (DELCD) detector was used for analysis (SRI specifications are shown in Table 1). Because of its selectivity and sensitivity to halogenated compounds, ELCD is widely used in environmental analysis, and is specified in many EPA methods for detecting organic pollutants in drinking water [24]. The PID detector was in series with the DELCD but was not used for quantitation since the target analytes were halogenated VOCs and more amenable to DELCD quantitation.

The conventional electrolytic conductivity detector contains reference and analytical electrodes, a gas-liquid contractor, and a gas-liquid separator. The conductivity solvent enters the cell and flows by the reference electrode. It combines with the gaseous reaction products in the gas-liquid contactor. This heterogeneous mixture is separated into gas and liquid phases in a separator, with the liquid phase flowing past the analytical electrode. The electrometer monitors the difference in conductivity at the reference electrode (solvent) and the analytical electrode (solvent + carrier + reaction products). [25]

The DELCD, in contrast to the conventional ELCDs, operates slightly in a different manner. The halogenated compounds exiting from the analytical column are immediately reacted in an air-rich reactor heated to 1000 C, where it is oxidized and quantitated by the detector's platinum collector electrode element. Since the DELCD operates in an oxidative mode, it requires a constant flow of air to maintain the reaction. Compressed air from a gas tank was redundant for this GC operation since there was a built-in air pump in the GC unit that supplants this need [26]. Thus,

the only gas tank necessary to operate this GC/DELCD configuration is the carrier gas, which is N2. Performance-wise, the DELCD is similar to that of the conventional ELCD described above. The significant advantage of the DELCD is that it does not use any solvents since all the reaction products are detected in the gas phase.

The computer used was an IBM PC110, which is at the moment the smallest Windows 95 "notebook", and most powerful high-end palmtop available. It is about the size of a VHS-video cassette (about 1/6 smaller in width). At this small size, the analyst could have the power of a 486 CPU and the expandability through PCMCIA-II/III ports and a small docking station. The serial connection in the docking station was used to connect to the SRI portable GC.

Software used for data collection was the Peaksimple Data System supplied by SRI Instruments. It provided precise temperature controls for the GC oven and its detector. Calibration, real-time qualitative/quantitative analysis, documentation of analytical results, and report output were also controlled and handled by this data system. Thus, on-site analysis was greatly simplified and reliability of the tests was also greatly improved.

Appendix A shows the field PIME configuration used for discrete sample testing and continuous monitoring of groundwater.

Table 1 SRI SPECIFICATIONS 9300 GC

Oven Size	10" x 4.75" x 3"	
TEMPERATURE	Ambient to 400 degrees Centigrade. 0 to 400 degrees Centigrade with subambient option.	
TEMPERATURE PROGRAMMING	Oven temperature program computer-controlled by software supplied with the chromatograph or isothermal. Unlimited temperature ramps.	
TEMPERATURE/PRESSURE DISPLAY	Multifunctional display (LCD) – indicates set and actual temperature for heated zones, detector voltages and currents. Temperature displayed to 0.1 degrees, pressure to 0.1 psi.	
CARRIER GAS FLOW CONTROL	High precision pressure regulator with thermostated flow controller, calibrated in ml. per minute, regulating the flow of carrier gas through the column.	
DETECTORS	**AVERAGE DETECTION LIMIT**	**DESCRIPTION**
PID	100 ppb	Mounts accepts HNU-type lamps – supplied with 10.2 Electron volt lamp. 40 ul cell volume, 0 to 2 mA. Adjustable lamp current with LCD readout.
ELCD	1 ppm	Selective to halogenated compounds.
FID	1 ppm	Provides universal response to most organics.
WEIGHT	30 to 60 pounds	
DIMENSIONS	11.25" x 13"d x 13"h	
POWER REQUIREMENTS	110 VAC, 60 Hz / Consumption approximately 750 watts. May be operated with 12VCD for isothermal operation	

4.2 Overview of Field Test

A groundwater sampling program generally includes investigating the presence or absence of contamination in a given study area and defining the extent of contamination. This is confirmed by drilling monitoring wells around the site.

For the discrete sampling study, groundwater collection from 5 pre-drilled monitoring wells was completed in one day. Collected samples were split into two sub-samples, one for PIME on-site analysis on the day of sampling, and the other was shipped to a certified analytical laboratory for analysis. The samples were collected, labeled, stored, and shipped in accordance to the EPA Guidelines for sample collection [27].

For the continuous monitoring study, the samples were previously analyzed and reported out by the reference lab for one of the pump and treat locations prior to the field test, so no split sub-samples were necessary. Thus for this part of the study, accurate comparison of the field and reference data could be compromised.

4.2.1 Standard Preparation

Certified Stock Standards were purchased from NSI Environmental Solutions, and were used to make up working standards as follows:

- 1.25 ml each of 5000 ug/ml stock standards of 1,1-Dichloroethane, cis-1,2-Dichloroethylene, Tetrachloroethylene, 1,1,1-Trichloroethane, and Trichloroethylene were pipetted into a 25 ml volumetric flask containing

deionized water and then diluted to volume to make a 250 ppm secondary dilution standard (solution a). 1.25 ml each of 1000 ug/ml stock standards of trans-1,2-Dichloroethylene and 1,1-Dichloroethylene were pipetted into a 5 ml volumetric flask containing deionized water and then diluted to volume to make a 250 ppm secondary dilution standard (solution b).

- Pipetted 0.1 ml of solutions (a) and (b) into a 50 volumetric flask containing deionized water and diluted to volume to make a 500-ppb working standard solution.

- Pipetted into separate 50-ml volumetric flasks 0.1, 0.2, 0.5, 1, 2, 3, and 4 ml of solution (c) and diluted each to volume with deionized water to make a 1, 2, 5, 10, 20, 30, and 40 ppb, respectively of calibration standard solutions.

- Diluted the 1 ppb calibration standard solution 1:1 v:v to make a 0.5 ppb standard.

A quality control (QC) standard was injected before the field samples. The QC standard was a 20-ppb working solution prepared similarly as the calibration standards. Only method blanks, which consisted of HPLC-grade water, were used to safeguard against chronic laboratory contamination.

4.2.2 Discrete Analysis of Field Samples

For the discrete configuration, a 5-ml gas-tight stainless-steel syringe was used to withdraw a 5-ml sample from the 25-ml sample vial containing the well sample. The needle was removed and a filter cartridge was placed in between the syringe and

the needle. The sample was then loaded into the injection valve. Since the sample loop capacity was only 1 ml, excess sample from the syringe was deposited into a waste bottle. The sample in the loop was then injected into the eluent stream, which carried it into the membrane module. After a 7-minute wait, the microtrap was pulsed using a controller and a variac, and the data acquisition software was started. Four minutes into the GC run, the eluent pump was switched off, and the two-way valve was switched from the water eluent to the nitrogen gas to purge the membrane.

4.2.3 Continuous Monitoring of Pump and Treat Facility

The PIME was also configured to do on-line monitoring of a groundwater pump and treat facility. The setup was analogous to the discrete configuration except that the PIME's ten-port valve was directly connected (using approximately 20 foot tubing) to the influent inlet of the pump and treat facility, thereby bypassing the syringe injection port of the valve. Opening the inlet valve at the bottom of the pretreatment tank released a constant stream of untreated groundwater into the PIME's ten-port valve and into its 1-ml sample loop. The valve was left open for a sufficient enough time (7 min) to allow a "fresh" sample to enter the sample loop from the length of the tubing. The sample was then injected into the eluent stream upon switching the valve. Table 2 summarizes the configuration and programming parameters used in the discrete and continuous field tests.

Table 2 PIME Gas Chromatograph Operating Conditions

GC	SRI Instruments 8600/9300 Series/ Peak Simple Win95	
Injector	Microtrap-based, 0.0035 mg Carbotrap C (Supelco)	
Column	J&W Scientific DB-624 0.53 ID 30-meter	
Protocol/ Temperature Programming	**Non-Continous Sampling**	0 min: Sample loaded and injected 7 min: Microtrap pulsed for 1.2 sec GC temp. programming initiated: 45C hold 7 minutes 15C/min ramp to 150C 11 min: N2 purging initiated 14 min: N2 purging terminated
	Continuous Sampling	0 min: Microtrap pulsed for 1.2 sec 4 min: Inlet valve open to load sample 11 min: Inlet valve shut/ Inject sample 15 min: N2 purging initiated 18 min: Microtrap pulsed for 1.2 sec GC temp. programming initiated: 45C hold for 6 minutes, 15C/min ramp to 120C 45C hold for 7 minutes (equilibration) Note: 18 min = 0 min
Data Acquisition	IBM PC110 Palmtop/ Peaksimple 32-bit operating on Win95	
Sample Valve	10-port Valve / Accepts Discrete/Continuous Samples Sample loop: 1 ml	
Detector	PID / Dry ELCD in Series → Gain set at high/ Attenuation: 1	
Carrier Gas	Nitrogen at 7 ml/min	
HPLC Water Flow	0.85 ml/min	

4.2.4 Analytical Method/Instrumentation of Reference Laboratory

For the discrete analysis, the Naval and Engineering Station sent their part of the split sample for analysis to VAL Associates Laboratory, Inc., a contract laboratory that specialized in water, air and soil analysis. The samples were received on the same day of collection, but were not analyzed until the following week. For continuous monitoring part of the study, however, samples were previously analyzed by Aguilar Associates, also a contract lab. The methods employed for testing were EPA Methods 502.2 and 524.2. Quantitation of the organics was made with the former method while the latter was used for verification since it utilized mass spectrometry. Results were reported out almost one month after sample collection.

Method 502.2 [10] was used for identification and measurement of purgeable volatile organic compounds in raw source water, or drinking water at any treatment stage. The highly volatile organics are extracted from the sample matrix by bubbling an inert gas (N2) into the 5-ml sample. The purged organics are carried and trapped into a tube containing sorbent material. The sorbent material is then heated after complete purging and the organics are desorbed into the GC. The column is temperature programmed to separate the analytes, which are then detected with a photoionization detector (PID), and a halogen specific detector placed in series. Identifications are confirmed by analyzing standards under the same conditions based on matching retention times. Quantitation is then done based on a calibration curve.

An O.I. Model 4430 photoionization detector mounted together with the model 4420 electrolytic conductivity detector (ELCD) as a dual detector was used to

develop the single laboratory method performance data for Column 2. The system and the operating conditions used to collect these data are listed in Table 3.

Table 3 Commercial Laboratory Purge and Trap Specifications (Method 502.2)

Gas Chromatograph	GC not specified
Column:	105 m long x 0.53 mm ID, J&B DB-624 capillary column
Temperature Programming	35C hold 10 minutes 4C/min ramp to 200C, held until all compounds elute out
The purge-and-trap unit:	O.I. 4460A
Detector	PID/ELCD
Reactor tube:	Nickel 1/16 in. OD & .02in.ID
Reactor temperature:	950°C
Reactor base temperature:	250°C
Electrolyte:	100 % n-propyl alcohol
Electrolyte flow rate:	0.050 mL/min.
Reaction gas	Hydrogen at 100 mL/min
Carrier gas plus make-up gas:	Helium at 30 mL/min.

CHAPTER 5

RESULTS/DISCUSSION

5.1 Groundwater Areas of Contamination

5.1.1 Site Description and Observed Contamination

Results for the discrete field-testing are summarized in Table 4. A brief description of each well site (Figure 6) will be discussed below along with the observed VOC levels. Five well areas were tested: Area F, H, J, K, and I. These areas were specifically selected for field-testing since the presence of the target halogenated VOCs and their approximate concentrations were relatively well known.

Area H is where the Recovery System Track sites were located. This site was used for the operation of experimental machinery during the late '60s and early 70's. The chemicals used in the operation and maintenance of sled-mounted aircraft and simulated aircraft landings at this location were assumed to be responsible for all the groundwater contamination. In addition, it was reported that jet fuel, hydraulic fluid and ethylene glycol were used and stored at this site. This site had been

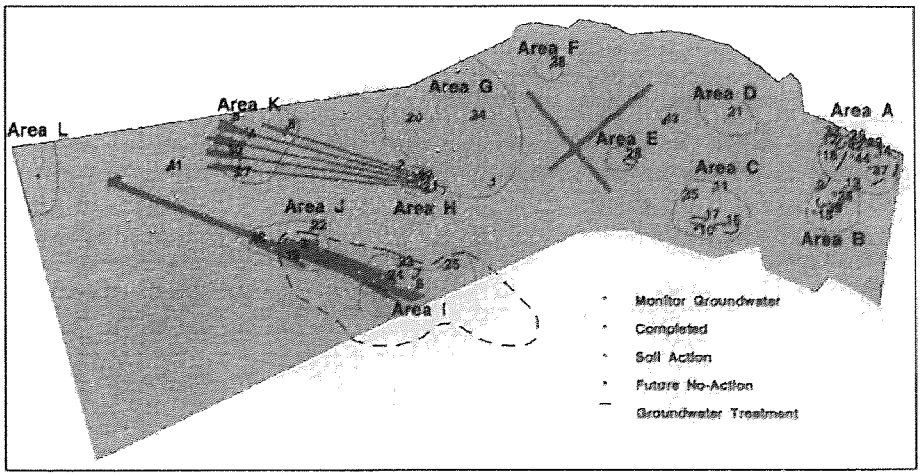

Figure 6 NAES well testing sites used in the field study: Area F, H, I, J and K

Table 4. Comparison of PIME and P&T for Halogenated VOCs in Groundwater
concentration in ppb

SAMPLE	1,1 Dichloroethylene		trans 1,2 Dichloroethylene		1,1 Dichloroethane		cis 1,2 Dichloroethylene		1,1,1 Trichloroethane		Trichloroethylene		Tetrachloroethylene	
Technique	PIME	P&T	PIME	P&T	PIME	P&T	PIME	P&T	PIME	P&T	PIME	P&T	PIME	P&T
Well NAES LH	1.05	<0.5	ND	<0.5	ND	0.67	11.92	12.51	ND	<0.5	37.42	22.89	ND	1.15
Well NAES LI	0.83	<0.5	ND	<0.5	ND	<0.5	28.53	21.55	ND	<0.5	8.58	6.45	ND	0.82
Well NAES LK	1.5*	<5	3*	<5	0.5*	<5	303.80	191.60	ND	<5	155.49	158.50	157.50	100.00
Well NAEK LJ	ND	<0.5	ND	<0.5	ND	<0.5	ND	<0.5	ND	<0.5	ND	<0.5	ND	<0.5
Well NAEK LF	7.46	5.60	0.2*	<0.5	6.19	6.03	48.62	50.71	6.35	<0.5	15.24	13.17	8.00	9.00

ND = not detected
* = Single point calibration

successfully treated by the cleanup facility, but a proactive approach is still being taken in decontaminating the area. From the field test results, it was shown that 1,1 Dichloroethylene, cis 1,2 dichloroethylene and trichloroethylene were present, but in fairly low ppb levels.

Area I/J is located in the west central portion of the naval base. It had been documented in previous studies between 1985-1992 that the main contaminations in the site occurred in groundwater, and were due to halogenated volatile organic compounds. Contamination levels in Area I were present but at low concentrations, and were likely the result of contaminated wastewater releases into the drainage swale at Site 3. Field analytical measurements in Area J showed that very low, if any contamination, existed at this site. On the other hand, Area I showed relatively higher levels of chlorinated organic contamination. Area I is situated south of the Catapult runaway. The contamination could be traced to areas where steam cleaning of a number of equipment had occurred. Other sources cited were from catapult testing, and unregulated disposal of liquid wastes in the vicinity. From 1958-78, industrial wastewater (hydraulic fluid, ethylene glycol, trichloroethylene and lubricating oil) was generated from the surrounding buildings (catapult facility, power plant, photography lab, etc.) and dumped into holding ponds. It had been determined that volatile organics and inorganics still persist to contaminate the area, and thus remedial action is still ongoing. Again, our field testing of the area verified that levels of trichloroethylene and cis-1,2 dichloroethylene were significantly higher in this location than Area J

Area F contained the most types of halogenated species. Six out of the seven targeted compounds were detected in the well sample. Only trans-1,2 dichloroethylene was not detected. However, of the six halogenated VOCs in this well, 1,1,1-Trichloroethane was the only compound that was characterized by the field PIME but not detected by the reference lab (Appendix B1 shows well LF sample chromatogram).

In comparison to all other areas tested, Area K proved to contain the most substantial levels of contamination. Site 4 (Deadload Maintenance Shop, Bldg. 372), between the late 50's and early 80's, was used to store drums of dry cleaning solvent, trichloroethylene and lubricating oil for equipment maintenance purposes. Unfortunately, barrels were reported to have leaked and contaminated the ground soil with tetrachloroethylene and trichloroethylene. Thus, NAES initiated an extensive program to carefully monitor this area by adding several more monitoring wells in order to better determine the extent of the contamination. The primary contaminants found in Area K were trichloroethylene and tetrachloroethylene. Field-tests in that area showed both tetrachloroethylene and trichloroethylene levels at about 150 ppb, cis-1,2 Dichloroethylene also was present in high levels at 300 ppb (PEL in water is 0.07 mg/L), while trace levels of 1,1 dichloroethylene, 1,1 dichloroethane and trans-1,2 dichloroethylene were detected. Site remediation for Area K is still ongoing [28].

5.2 Field Test Limitations

During the discrete (non-continuous) portion of the field test, time was an important factor since all 5 groundwater well samples had to be analyzed at least in duplicate in one day in addition to the calibration curve, QC standard check, and blank. Due to the time constraints, a fairly small number of samples were collected, which significantly reduced our ability to draw up any conclusions about the target analytes to be compared with the reference lab. For example, 1,1 dichloroethane occurred only once in the entire study, so the assumption that the PIME data was equivalent to reference lab data really could not be made with any confidence. One way of dealing with our small amount of sample pairs was to pool all our samples into one group so that most of the uncertainty measurement factors would average out. In doing so, we assumed that the accuracy and precision data for the various target compounds were not too different from each other. This was a fair assumption to make for this study, since all our target compounds were halogenated VOCs with similar chromatograph and detection properties. Consequently, in pooling our samples, we would be able to gain an understanding of the overall performance of the field PIME system compared to the reference lab [29].

In addition to the somewhat small population of samples analyzed, another limitation was encountered in dealing with the PIME accuracy criteria--whether we could really assume the reference laboratory data to be the "true" concentration of the sample, with no inaccuracies or deviation. The performance criteria of +/- 20% percent difference (used in EPA 502.2 and 8260) was therefore increased to 50% to account for any unexpected variations found in the reference measurements.

5.3 Laboratory Performance of Instrument

To demonstrate the efficacy of the field PIME instrument before the field test, its performance was initially investigated in terms of linearity, precision, and detection limits. Calibration curves of all 7 halogenated VOCs are presented in Figure 7. From the data, it was observed that a linear relationship between system response and VOCs concentration existed in approximately the interval concentration range (0.24-16 ppb) of the field samples of interest. Precision values from the same

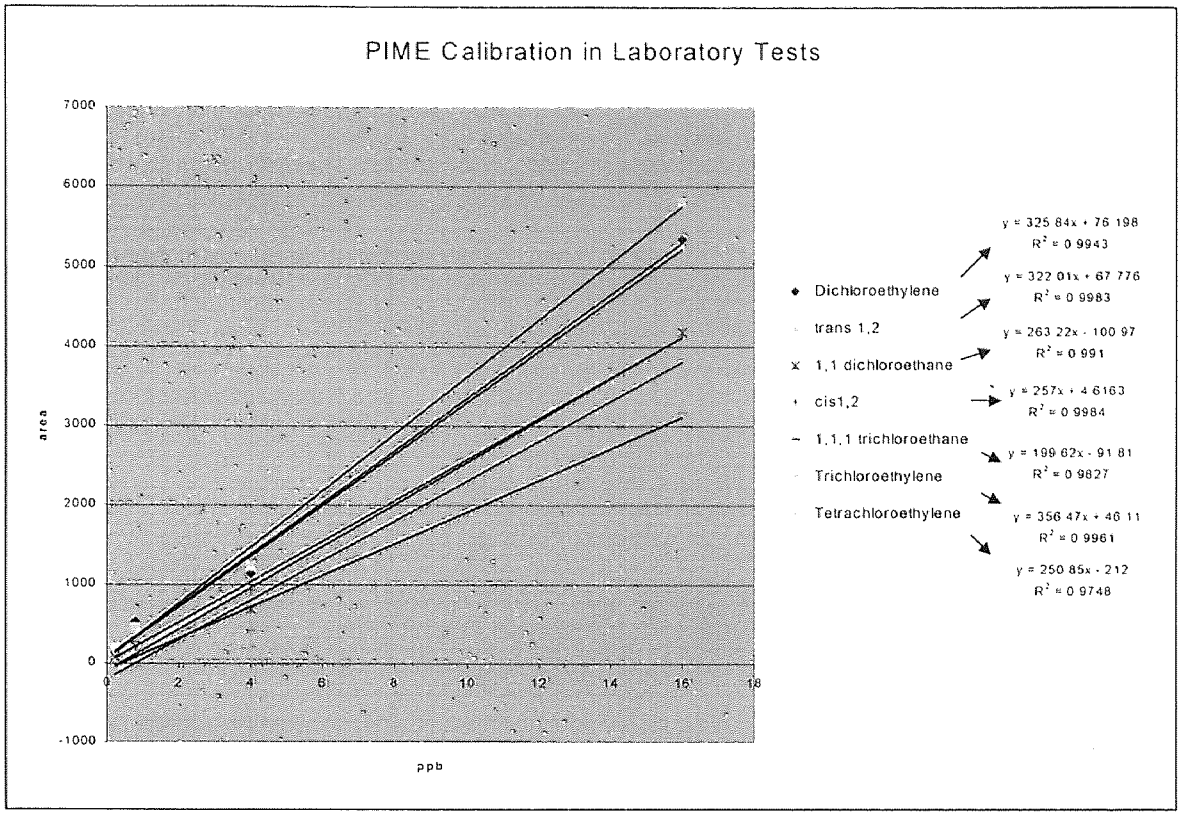

Figure 7. Calibration curve of the 7 halogenated VOCs prior to field-testing

calibration curve (Table 5) showed acceptable RSD%, although the lowest concentration exhibited relatively higher variation (about 21% for trichloroethylene at the 0.24 ppb level). Detection limit is roughly equal to 3 times the std dev of the

blank over the slope of the calibration curve. However, the most generally accepted qualitative definition of detection limit is that it is the minimum concentration or weight of the analyte that can be detected at a known confidence level. Method detection limits (MDL) are shown in the Table 6 and were determined using 7 replicates of the 7-standard concentration.

Table 5 Precision analysis using RSD% of each calibration standard point prior to field testing

	ppb/RSD% using standard concentrations				
Analyte	**0.24**	**0.8**	**4**	**8**	**16**
Dichloroethylene	10.31	3.69	3.84	10.73	1.59
trans 1,2 Dichloroethylene	10.02	3.25	3.02	3.76	2.06
1,1 Dichloroethane	15.39	7.63	8.16	15.75	5.51
cis 1,2 Dichloroethylene	13.88	2.07	2.73	8.00	2.38
1,1,1 Trichloroethane	1.53	7.96	3.66	2.81	3.55
Trichloroethylene	21.05	3.47	3.99	5.40	1.28
Tetrachloroethylene	5.71	5.40	17.12	8.39	5.58

Table 6 Method detection limits (in ppb) for the field PIME setup

Analyte MDL	**PIME**	**EPA 601**	**EPA 502.2**
1_1 Dichloroethylene	0.06	0.13	0.07
trans 1_2 Dichloroethylene	0.15	0.10	0.06
1_1 Dichloroethane	0.08	0.07	0.07
cis-1_2-Dichloroethylene	0.16	NA	0.01
1_1_1-Trichloroethane	0.39	0.03	0.03
Trichloroethylene	0.04	0.12	0.01
No MDL for Tetrachloroethylene			

5.4 Field Instrument Performance

Calibration performance of the field instrument can be seen in Figure 8. It was observed that a linear relationship existed from the 0.5-40 ppb range in some of the standards, where at least a 4-point calibration curve for each analyte was used (except 1,1,1 trichloroethane, which used a 3-point range). From these curves, VOC concentrations were extrapolated from the area responses of each analyte and then calculated (Appendix B2 shows a chromatogram of a 30 ppb standard mixture). The following sections below will discuss the field instrument's performance in more detail, such as accuracy, precision, etc., and whether the PIME had met each criterion set in our objectives.

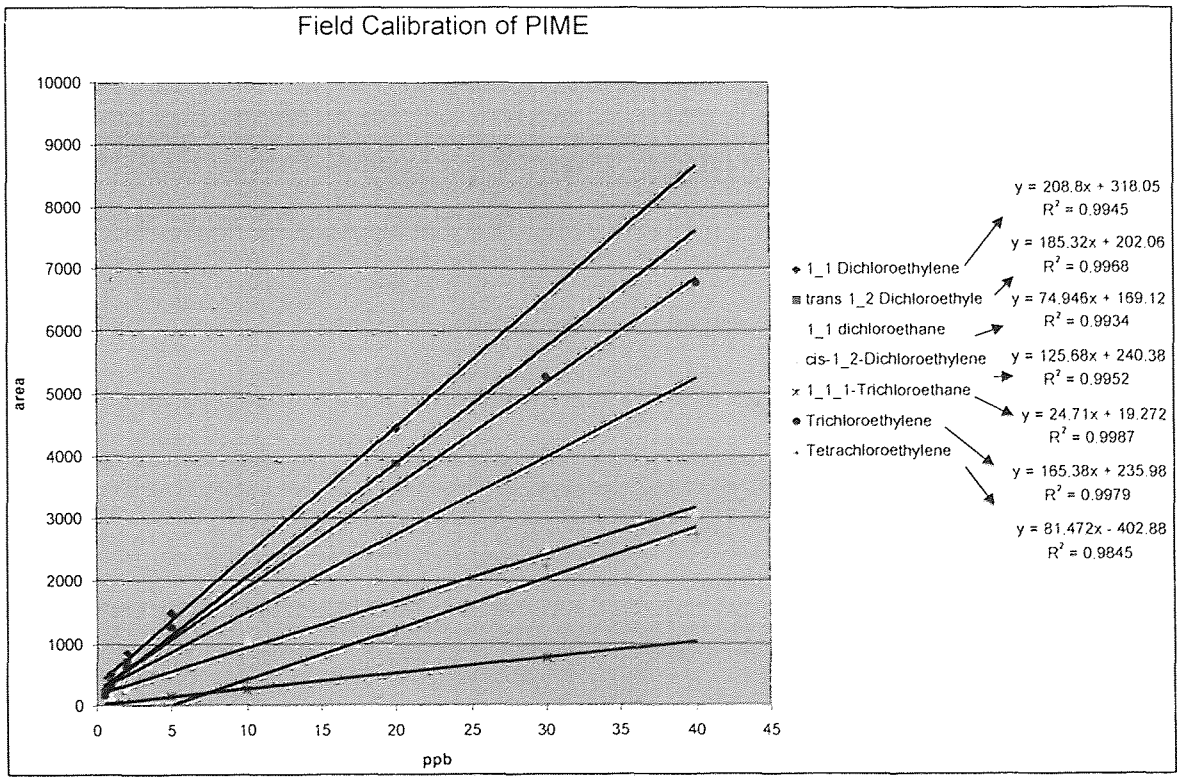

Figure 8 PIME calibration curve of the 7 halogenated VOCs during field-testing

5.4.1 Methodology

The Naval and Engineering Station specified the target analytes for the field study. Seven target halogenated VOCs were designated as the analytes of interest. We encountered some difficulties in the development of the GC analytical method due to interfering contaminants in our deionized water supply. Consequently, identification of the standard peaks was complicated in both the PID and ELCD due to interfering peaks and other ghost peaks. The use of ultra-pure HPLC-grade water (EM Science) eventually resolved most of the problems.

5.4.2 Deployment

The field PIME system was set up and running in less than 40 minutes starting from the vehicle unloading. Although our performance goal was set to have a deployment time of 30 minutes or less, a few minutes over the setup time could be considered to have met the criterion.

5.4.3 Throughput

Discrete: Analysis of each sample using discrete sampling showed that trapping took up to 7 minutes to complete, while GC analysis accounted for another 11 minutes. Finally, equilibration of the column oven took 4 minutes for a total of 22 minutes sample and analysis frequency. Thus, since analysis time was less than 30 minutes, the performance goal for throughput was achieved.

Online: Analysis time for the first sample was the same as for discrete analysis, but thereafter was reduced to 18 minutes, since sample trapping of the halogenated VOCs could be started after the microtrap pulsing. Thus, the performance goal was also met for online analysis.

5.4.4 Results Output

The Peaksimple data collection system was configured to output concentration values as soon as a calibration curve was input. However, during the actual field test, data calculations were made using Microsoft Excel 7.0 and preliminary results were reported at the end of the day. Thus, the ability to immediately report results met our performance goal for the fast output of data.

5.4.5 Accuracy

In evaluating the performance criteria for accuracy in detecting the presence/absence of the target VOCs, a stringent condition was made. Analyte concentrations listed below the detection limit were assumed to be not present in the sample, and vice versa. The field study contained 35 pairs of target VOCs for comparison. Of the 35 pairs, using the condition mentioned above, 29 pairs matched with the reference lab, a number corresponding to 82% of the total. This is below the set goal (90% hit) we established before the field test. However, most problematic matching occurred in the very low ppb to ppt levels. For example, a sample pair that had <5 ppb for the

reference lab and 3 ppb for the PIME was excluded from our statistical analysis, primarily because the reference lab concentration was below their detection limit and could not be assumed to be the same value as the PIME's 3 ppb.

A commonly used absolute percent-difference criterion for an instrument relative to a performance evaluation standard is around +/- 20% [10,29], thus we used this limit for our evaluations (Note: our quality control standard of 20 ppb showed all standards (except TCE) to be within the 20% diff. limit). However, as previously explained, due to the fact that the reference laboratory data may actually have some intrinsic accuracy problems (due to transport, storage, improper instrument calibrations, operator error, etc.), the absolute percent difference criterion for the field PIME value to the reference lab was increased to +/- 50%. If the median-absolute percent-difference value of our field results fell out of this range, then we can conclude that there is a significant difference between the PIME and reference laboratory instrument. Cornell [26,30] examined the error associated with field and reference methods and concluded that maximum overall uncertainties of 200-500% in field analytical data were still acceptable in most site characterizations. However, in our pursuit to supplant reference laboratory instrumentation, this range is unfortunately not acceptable to us, so we insisted on the 50% difference limit. Our results showed that even though 3 out of 12 single values fell out of this range, the median absolute percent difference was still below the 50% limit we set, so no additional bias significance testing was deemed necessary.

A linear regression analysis (Figure 9) of the same field PIME and reference lab (P&T-Purge and Trap) data pairs showed a correlation coefficient at 0.9326. In

general, a qualitative comparison of the field-PIME and the P&T showed paired results that implied similarity.

Another more robust statistical comparison was needed to ascertain whether the range of differences encountered between the two methods could be explained by random variability, or alternatively, whether a significant or true bias existed between the two techniques. Statistical analysis using a paired T-Test was not

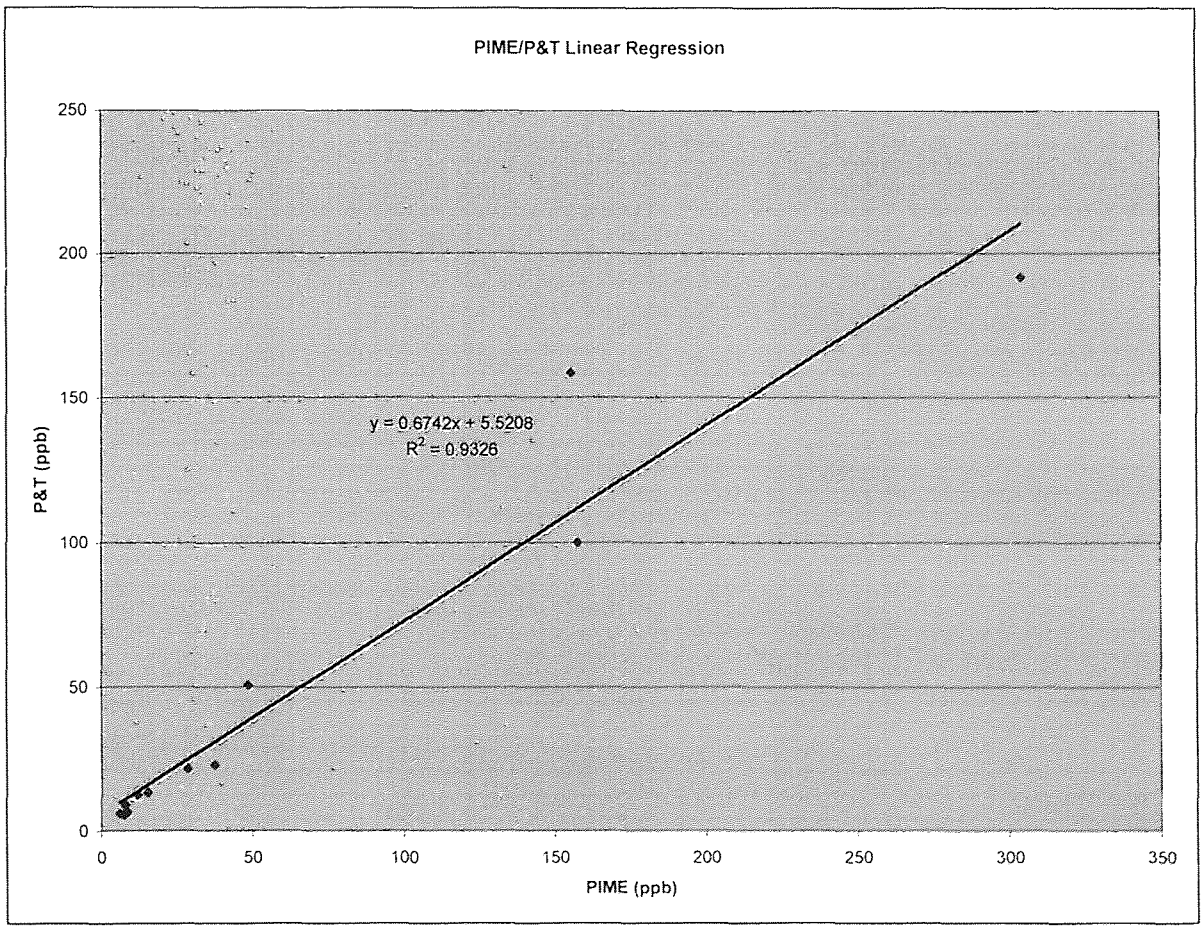

Figure 9 PIME and P&T linear regression plot to determine correlation between the two paired techniques.

possible, since the reference lab analyzed the well samples only once so no standard deviations for each analyte were provided. Thus, raw data from both the PIME and

P&T tests were subjected to the Wilcoxon Signed Rank Test (Table 7) in order to determine whether or not the two methods are equivalent [31]. This particular test, which is useful for comparing two data sets for which there are paired observations, involves separating and ranking the negative and positive differences between the paired values, summing the observed differences, then equating the T statistic with the lower summed value. The computed T statistic is then compared to the critical points of T and the null hypothesis is rejected or accepted. The Wilcoxon test is influenced somewhat by the larger value data pairs of the populations set, and thus normalization of each data pair using percent difference was used to eliminate this unwanted effect.

A p-value of 0.05 is traditionally used as the decision point as to whether or not there is a statistically significant difference between two different methods. A p-value greater than 0.05 indicates that the two methods are equivalent and any

Table 7 Wilcoxon Signed Rank Test: used to determine equivalency of the 2 methods

Well	PIME	P&T	D%	Rank	Rank -	Rank +
LH	11.92	12.51	-4.72	4	4	
LH	37.42	22.89	63.48	12		12
LI	28.53	21.55	32.39	7		7
LI	8.58	6.45	33.02	8		8
LF	7.46	5.6	33.21	9		9
LF	6.19	6.03	2.65	2		2
LF	48.62	50.71	-4.12	3	3	
LF	15.24	13.17	15.72	6		6
LF	8	9	-11.11	5	5	
LK	157.5	100	57.50	10		10
LK	303.8	191.6	58.56	11		11
LK	155.49	158.5	-1.90	1	1	
					13	65
					Two tailed p=0.05 n=11	11

differences between the measurement can be explained by random variation alone. *More specifically, a p-value of 0.05 indicates that there is a 5% probability that two equivalent methods would produce by chance alone, as great a difference as the one observed in the experiment.*

In this case, the null hypothesis is that the PIME field measurements made are comparable to reference laboratory measurements using the P&T tests. A T-statistic of 13 was calculated from data gathered using the two different methods, and the critical value for a two-tailed test was determined to be 11 at the p=0.05 level for n=11 measurements. *Since the computed value of T is greater than the critical value at the p=0.05 level, the null hypothesis is not rejected and the PIME field measurements are considered to be comparable to measurements using the P&T tests in the reference laboratory.*

5.4.6 Precision

The field PIME precision was calculated by determining the relative standard deviation or RSD:

$$RSD\% = \text{Std. Dev.} / \text{Mean Conc.} \times 100 \quad (7)$$

where triplicate measurements were required. Our field-data of the well samples had at least 2-3 replicate concentration values so precision analysis was feasible. Table 8 shows the precision data with standard deviation and RSD% for data sets with 3

replicates. With the exception of 1,1,1 trichloroethane, which showed a 28% RSD, most data points fell within the acceptable RSD% limits of less than or equal to 15%. Note that the 1,1,1 trichloroethane shown in Table 8 was detected only in one of the well samples using the field PIME, but was not detected in any reference-laboratory samples, so this peak may not actually be a real" VOC peak.

Table 8 Precision in the Field PIME based on sample triplicates

ppb/RSD%	1,1 Dichloroethylene	cis 1,2 Dichloroethylene	1,1,1 Trichloroethane	Tricholoroethylene
Well NAES LH	1.05	11.92	NA	37.42
RSD%	13.83	12.36		7.91
Well NAES LI	NA	28.53	NA	8.58
RSD%		3.01		4.95
Well NAES LK	NA	303.8	NA	155.49
RSD%		2.31		7.04
Well NAEK LJ	NA	NA	NA	NA
Well NAEK LF	NA	NA	6.35	15.24
RSD%			28.57	4.24

NA - Data not available due to analyte not present or insufficient replicates

Table 9 shows a comparison between a PIME laboratory and PIME field setup RSD% using actual well samples from the Lakehurst Naval Base. The PIME lab setup was used to analyze the well samples using a GC-FID configuration as opposed to the GC-DELCD used in the field. It is shown from two representative analytes in the table (DCE and TCE) that the field precision samples test conducted in the field were in general comparable to the in-house laboratory precision samples.

Table 9 Precision of laboratory PIME (GC-FID) compared to field PIME (GC-ELCD)

Well Sample	Dichloroethylene		Trichloroethylene	
	Field PIME	Lab PIME	Field PIME	Lab PIME
LH	13.83	5.4	7.91	5.2
LI	ND	ND	4.95	11.9
LK	ND	ND	7.04	4.6
LJ	ND	ND	ND	ND
LF	ND	ND	4.24	5.3
ND - Not Detected				

5.5 Groundwater Online Analysis

In addition to discrete sampling, continuous monitoring was performed in a ground water treatment facility (Figure 10). Normal operation of the pump and treat facility is as follows [28]: water is pumped from various well locations into a pretreatment tank, where separation of water, metals, and floating fuel products occurs. The fuel floats to the top of the tank and is skimmed off while the heavier metals sink to the bottom where they are removed. From the pretreatment tank, the water flows through sand filters and a filter press to remove the smaller metal particles. The water is then passed through two 22-foot tall Air Stripping Columns where air is blown from the bottom of the tower as the water trickles down. The VOCs are stripped out of the water by the airflow, which are then blown through activated carbon filters that adsorb the contaminants. Since no VOCs were expected in the effluent treatment part of the tank, on-line analysis was only done on the influent valve, just right before the pre-treatment tank (Appendix C shows a picture of the NAES pump and treat facility).

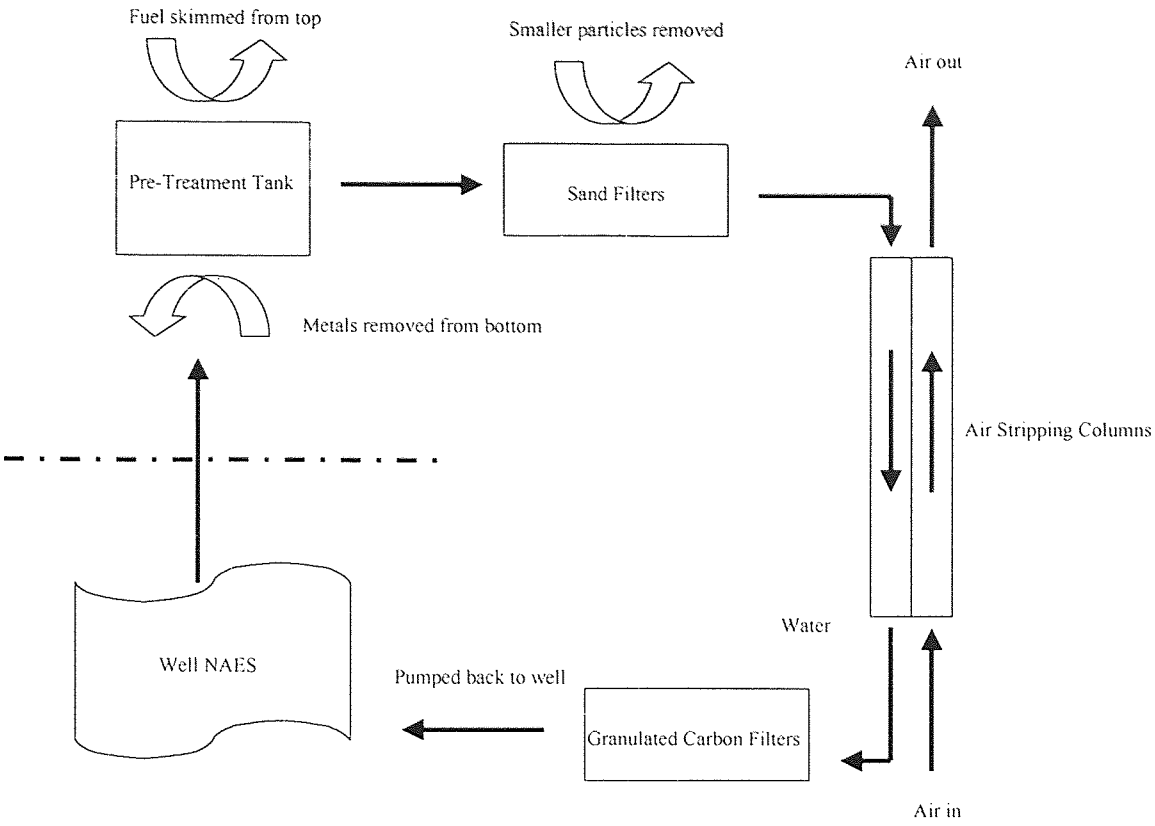

Figure 10 Operation of a pump and treat facility. Arrows (clockwise) show direction of water flow.

The sample of water entering the air strippers was analyzed by a reference-lab (Aguilar Associates & Consultants Inc., Matawan, NJ) for volatile organics using EPA Method 502.2. The commercial-lab analysis found that the influent water contained the following volatile organic compounds: cis-1,2 dichloroethene (3.4 ppb), 1,1,1-trichloroethane (0.41 ppb), trichloroethene (2.3 ppb), and tetrachloroethene (1.3 ppb). These results were based on grab sample methodology, in which a grab sample is a discrete aliquot that is representative of one specific sample site at a specific point in time. Since the entire sample is collected at one particular point and at one time, a grab sample is representative only of those static conditions.

Table 10 Continuous monitoring of groundwater at the pump and treat facility inlet

On-Line Groundwater analysis (ppb)

time	Dichloroethylene	time	cis 1,2 Dichloroethyhlene	time	Trichloroethylene
21.17	0.61	23.63	1.38	26.08	0.77
39.32	0.52	41.85	1.15	44.12	0.50
57.25	0.47	59 73	1.78	62.13	0.91
75.30	0.43	77.78	1.84	80.15	0.93
93.53	0.45	96.02	1.78	98.23	0.90
111.28	0.38	113.75	1.92	116.15	0.87
129.27	0.37	131.72	1.88	134.15	0.76
147.33	0.35	149.78	1.89	152.17	0.66
168.66	0.31	173.58	1.67	178.30	0.45
186.81	0.34	191.83	1.81	196.40	0.58
204.56	0.31	209.48	1.97	214.30	0.70
222.75	0.36	227.68	2.42	232.37	1.11
241.25	0.37	246.12	2.13	250.52	0.95
258.60	0.31	263.52	1.79	268.30	0.62
276.83	0.35	281.73	1.84	286.37	0.85
294.66	0.33	299.58	1.86	304.32	0.88
297.80	0.33	305.17	1.78	312.35	1.15
315.91	0.37	323.25	1.99	330.40	1.33
334.36	0.35	341.93	1.81	348.80	1.04
average ppb	0.38		1.83		0.84

* single-point calibration

Using a single-point calibration, the PIME configured for on-line analysis detected 1,1 dichloroethylene in the range of 0.31 to 0.61 ppb during a six-hour sampling plan (Table 10). It also detected cis-1,2 dichloroethylene in the 1.15 to 2.42 ppb, and 0.45 to 1.33 ppb of trichloroethylene during the same time stretch. The PIME, however, was not able to pick-up the trace levels of 1,1,1 trichloroethane and tetrachloroethylene. Note that the reference lab data was based on analysis performed a few weeks prior to our field test, and thus the VOC concentrations/presence in the well could very well have changed during this time.

The ability of the PIME to show varying concentrations of the analytes during a short time span (Figures 11-13) was indicative of the applicability of this

analytical tool in the continuous monitoring of process streams and wastewater discharges. Figure 14 shows about a 150-minute cross-section of the continuous monitoring analysis. The injection at I1 shows the blank with some interference near the 1,1 dichloroethylene peak. I2-I9 shows the subsequent pretreatment groundwater injections. Thus, the PIME was able to observe the temporal variations in concentrations of the analytes whereas the reference-lab produced a static and poor representation of the analytes present in the stream.

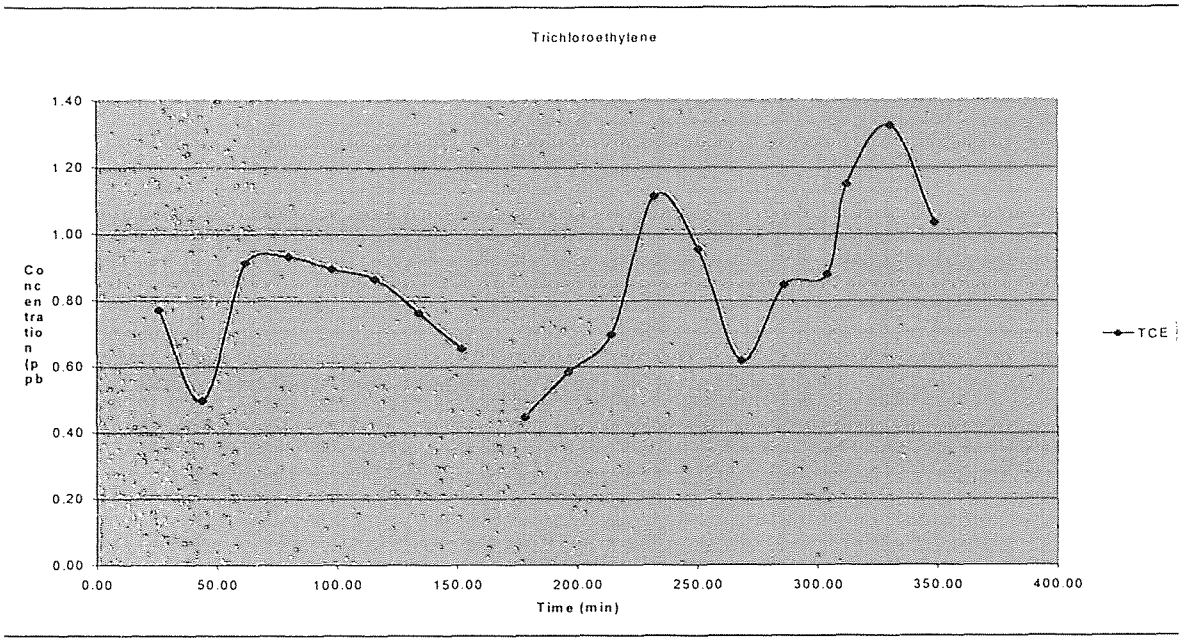

Figure 11 Trichloroethylene concentration detected in the pump and treat facility as a function of time

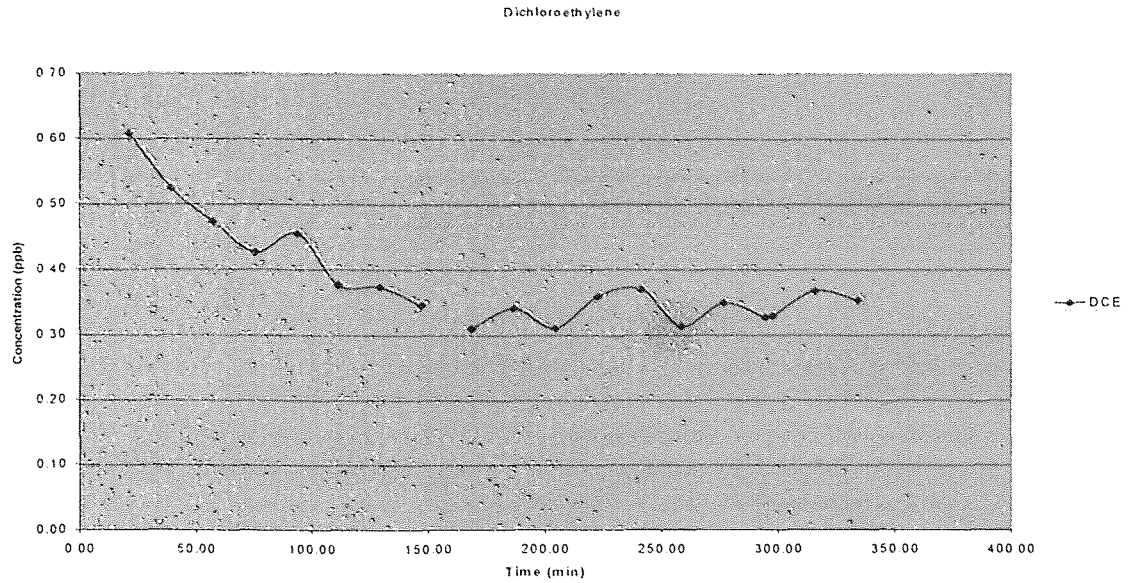

Figure 12. Dichloroethylene concentration detected in the pump and treat facility as a function of time

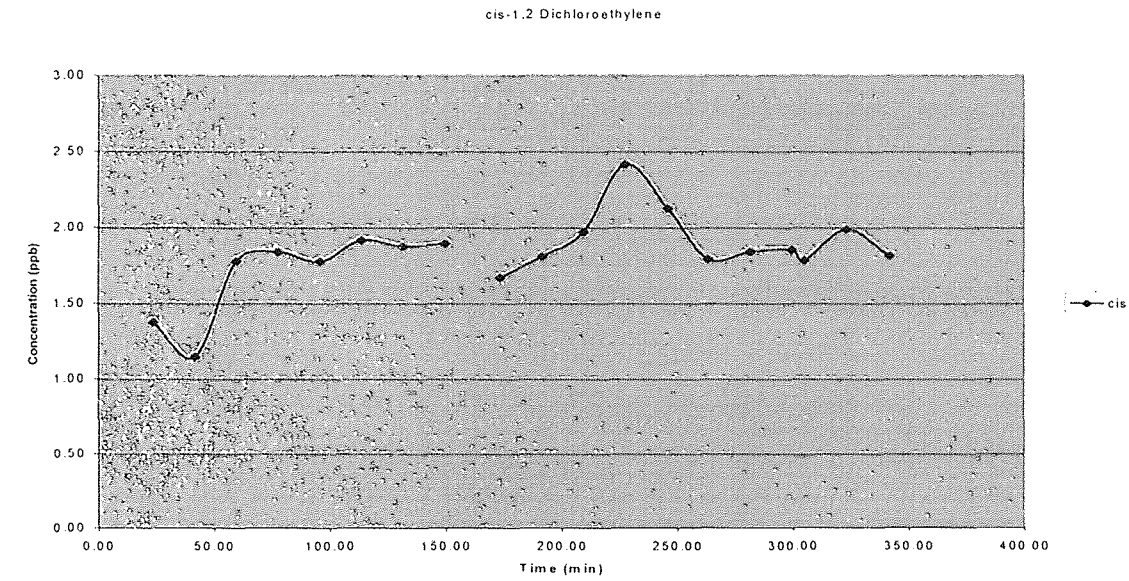

Figure 13 cis 1,2-Dichloroethylene conc. detected in the pump and treat facility as a function of time

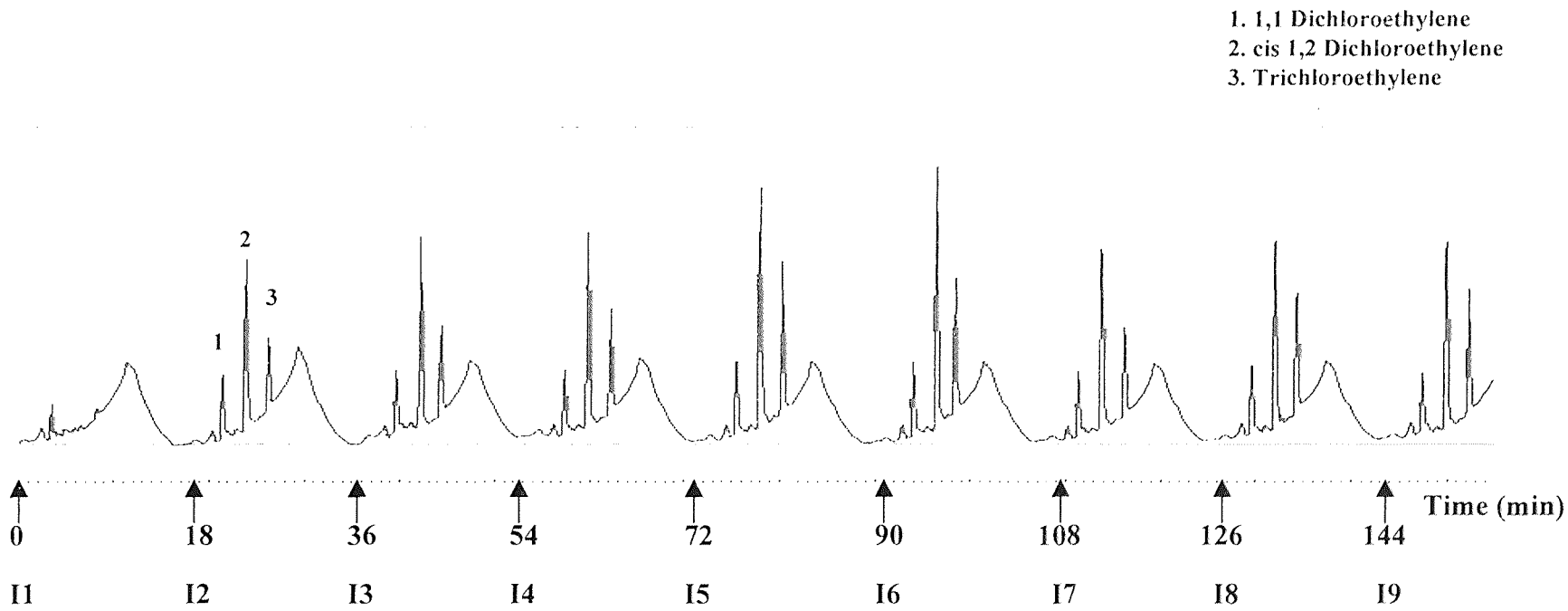

Figure 14. Cross-sectional time-frame of the Field PIME monitoring of the groundwater well for halogenated VOCs. In the chromatogram, I1 shows a blank injection while I2-I9 illustrates the VOC varying concentration over time

CHAPTER 6

CONCLUSION

The results of this demonstration (Table 11) provided us with an evaluation of how well the portable GC equipped with a microtrap unit compared with the reference-laboratory. Since the data collected from the portable setup and the reference-lab did not deviate significantly from each other, and most of the performance goals had been met, it is hoped that this technique could be used in future applications as a rapid, field-screening and field-characterization tool for environmental site assessments.

Table 11 Summary of PIME Performance Goals

Performance Goal	Performance	Goal Met?
ACCURACY (Reference Lab Data Comparison: Median absolute percent difference within 50% of reference value Wilcoxon Signed Rank Test	Percent-difference values usually were higher in the lower concentration range. Wilcoxon Signed Rank Test shows data results from PIME and reference lab are equivalent.	Yes. Median APD (0.5) < 50% Yes. $p>0.05$
PRECISION: Relative standard deviation of standards and samples within 15%	RSD% for standards were acceptable. RSD% for samples were acceptable (except for Well LF – 1,1,1 Trichloroethane 28%)	Yes. RSD%<15%
DEPLOYMENT: Installation complete within 30 minutes	Setup took 40 minutes from vehicle unloading. Can be considered acceptable.	Yes.
THROUGHPUT: Depends on methodology used for discrete and online.	Discrete: 22 minutes Online: 18 minutes	Yes
RESULTS OUTPUT: Data reported at the end of day.	Data was collected, analyzed and reported out the same day.	Yes

APPENDIX A

CONTINUOUS AND NON-CONTINUOUS PIME

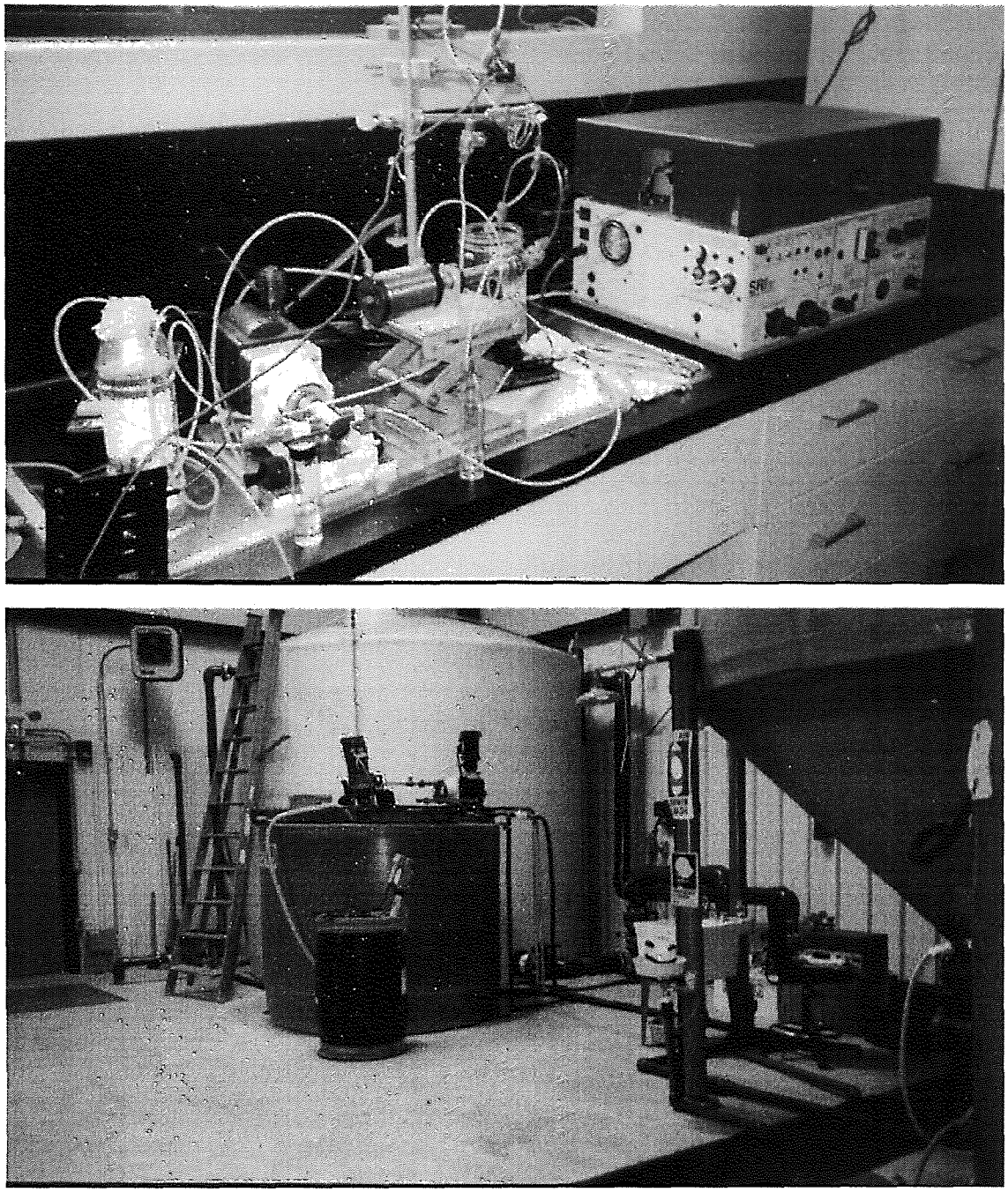

Figure 15 Field PIME configuration used for discrete (top) analysis and continuous (bottom) monitoring of groundwater for halogenated VOCs.

APPENDIX B1

FIELD CHROMATOGRAM OF WELL LF SAMPLE

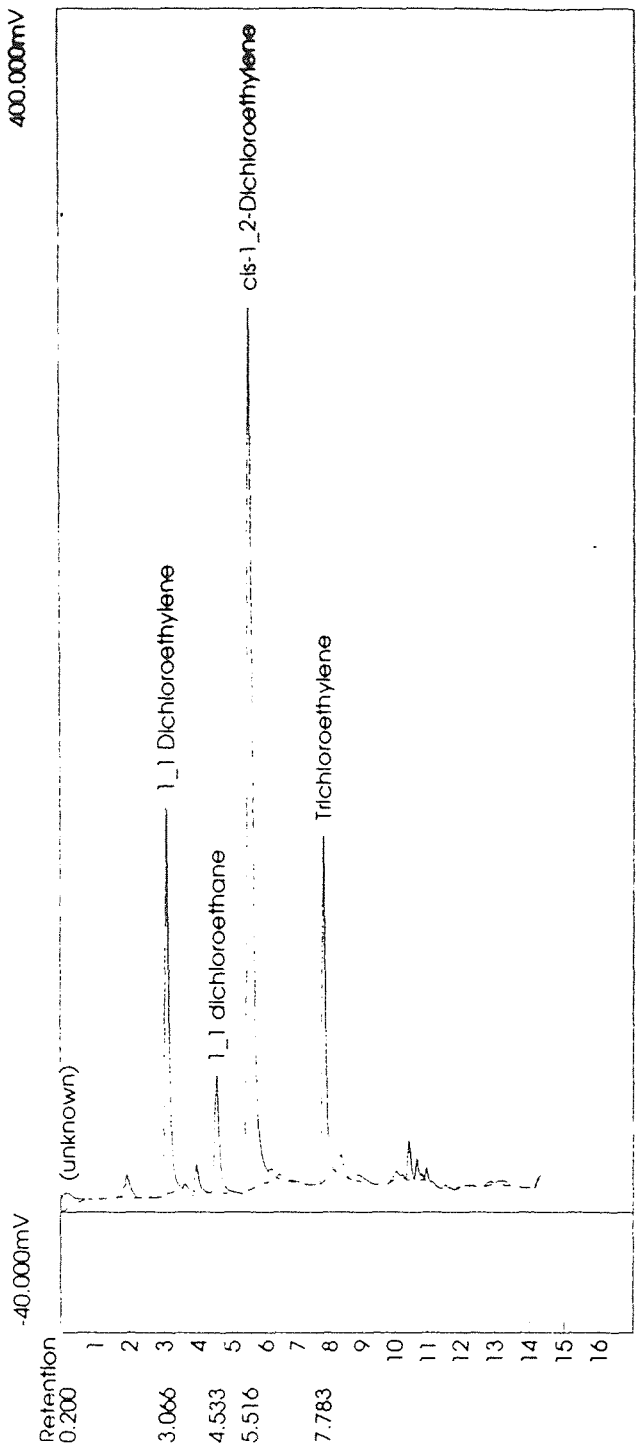

Figure 16 PIME chromatogram of well sample LF using discrete sampling. The volume of the sample loop was 1 ml. The detector used was a DELCD.

APPENDIX B2

FIELD CHROMATOGRAM OF 30 ppb STANDARD

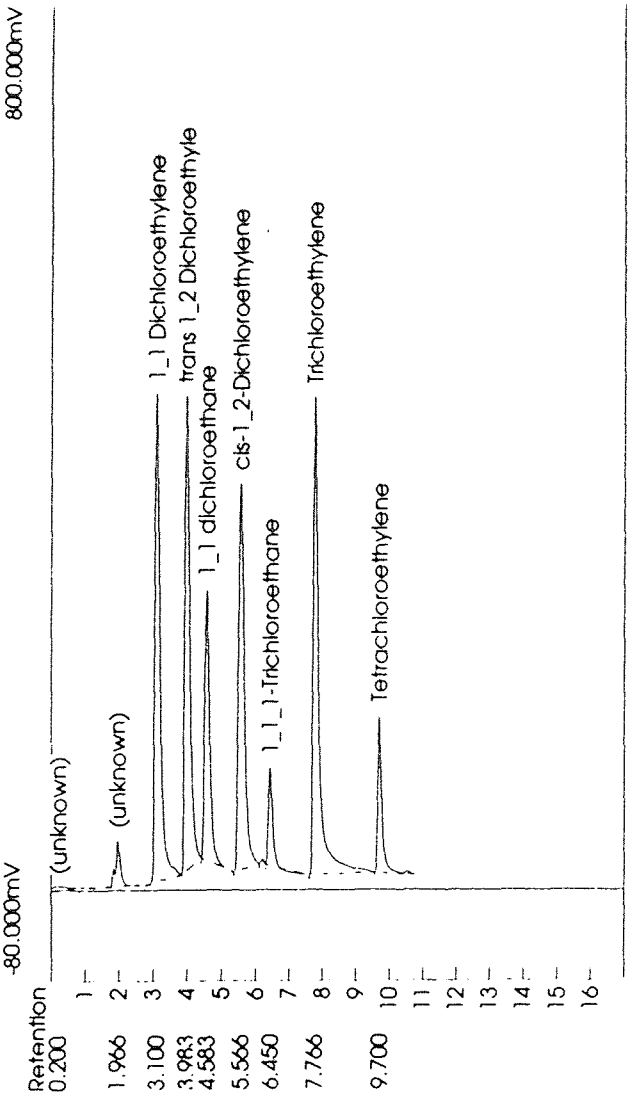

Figure 17 Non-continuous field PIME chromatogram of a 30-ppb standard set consisting of 7 halogenated volatile organic compounds. The volume of the sample loop was 1 ml. The detector used was a DELCD.

APPENDIX C

PHOTOGRAPH OF PUMP AND TREAT FACILITY

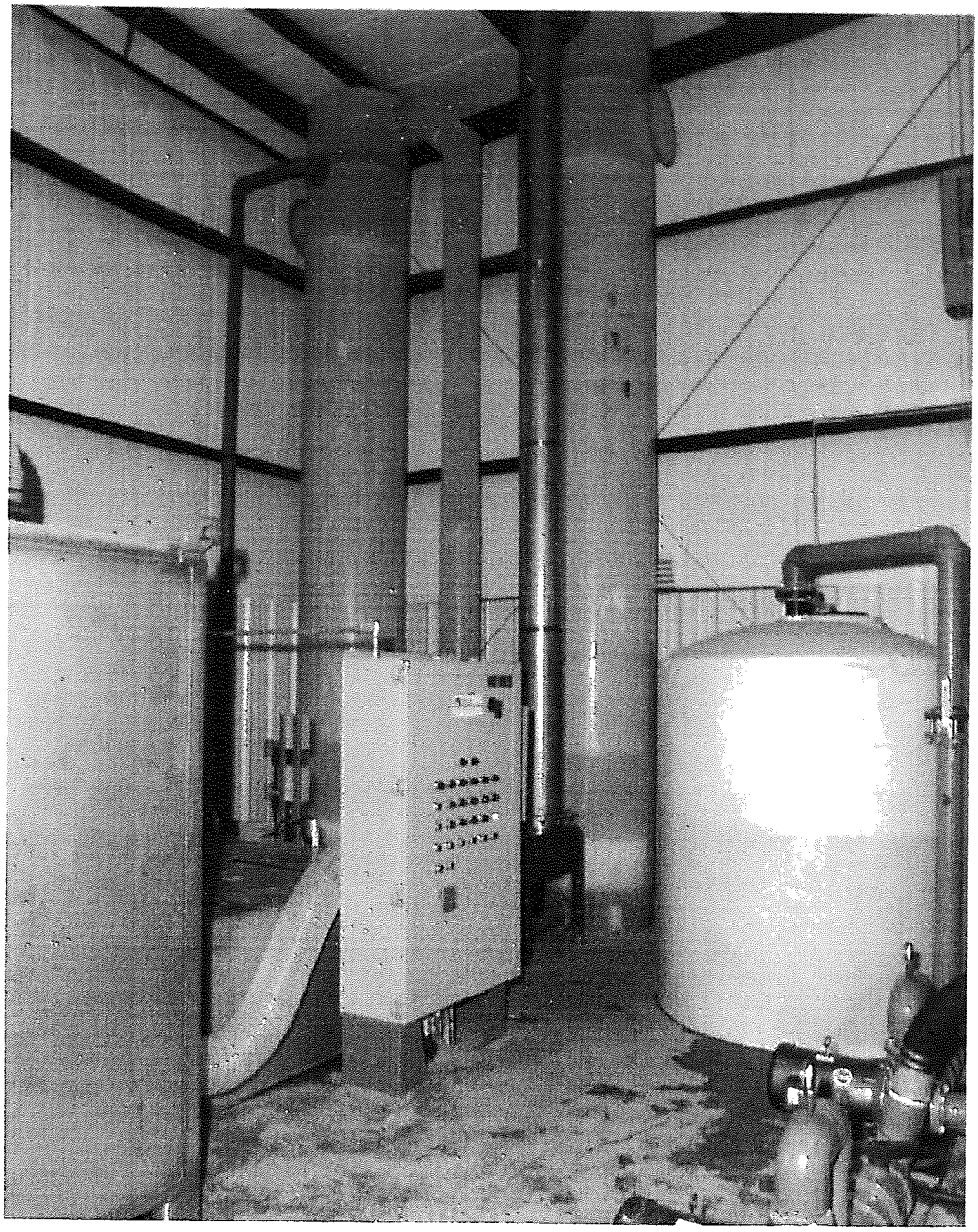

Figure 18 Groundwater treatment facility located in Lakehurst, New Jersey.

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