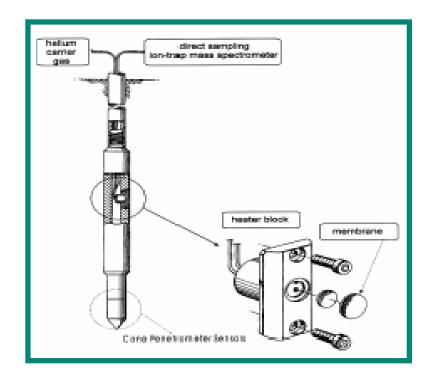
ESTCP Cost and Performance Report

(CU-9603)



Tri-Service Site Characterization and Analysis Penetrometer System (SCAPS) Membrane Interface Probe

January 2002



ENVIRONMENTAL SECURITY TECHNOLOGY CERTIFICATION PROGRAM

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LIST OF ACRONYMS

ASTM	American Society for Testing and Materials
BGS	Below ground surface
BTEX	Benzene, ethyl benzene, toluene, and xylenes
СРТ	Cone penetrometer test
DNAPL	Dense nonaqueous phase liquid
DoD	Department of Defense
ERDC	U.S. Army Engineer Research and Development Center
IDW	Investigation-derived waste
ITMS	Ion trap mass spectrometer
LNAPL	Light nonaqueous phase liquid
LOD	Limit of detection
MIP	Membrane Interface Probe
m/z	Mass to charge ratio of an ion
n	Number of replicate analyses
NAS	Naval Air Station
PCE	Tetrachloroethane
PEEK	Polyether ether ketone
R ²	Correlation coefficient
S	Estimate of standard deviation
SCAPS	Site Characterization and Analysis Penetrometer System
t $t_{n-1, \alpha/s}$	Student's t-value for <i>n</i> replicates at the 95 percent confidence level
TCE	Trichloroethene or trichloroethylene
TPH	Total petroleum hydrocarbons
USEPA	U.S. Environmental Protection Agency
VOC	Volatile organic compound

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At the time of publication of this report, Dr. James R. Houston was Director of ERDC, and COL John W. Morris III, EN, was Commander and Executive Director.

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1.0 EXECUTIVE SUMMARY

Several demonstrations of the ion trap mass spectrometer-Membrane Interface Probe (ITMS-MIP) system for volatile organic compounds (VOCs) were completed between August of 1998 and May of 2000. The purpose of each demonstration was to show the ability of the ITMS-MIP vapor sampling system to characterize the extent of subsurface contamination during a single field deployment. Previous Site Characterization and Analysis Penetrometer System (SCAPS) ITMS-MIP field investigations include a demonstration at Alameda Naval Air Station (NAS), Alameda, CA, completed in August 1998; Long Horn Army Ammunition Plant, Karnack, TX, in September 1998; and Lake City Army Ammunition Plant, Independence, MO, in March 1999. Validation demonstrations for the SCAPS ITMS-MIP system took place at the NAS North Island, Coronado, CA, in July 1999 and April-May 2000 and at the Department of Energy Savannah River Site, Aiken, SC, August-September 1999. Results of the demonstration at the Savannah River Site are discussed briefly; however, the major emphasis of this report is the demonstration at NAS North Island in April-May 2000, which was specifically carried out as a production deployment.

The ITMS-MIP system uses the commercially available MIP to collect vapor samples from the subsurface. The MIP collects VOC samples from the subsurface through a permeable membrane into a helium carrier gas that transports the sample above the ground surface for analysis. The analysis is performed in real-time by a direct sampling ITMS in accordance with U.S. Environmental Protection Agency (USEPA) draft Method 8265 (USEPA 1994). Approximately 4 minutes elapse from the time the MIP reaches the sample depth of interest until the analysis results are available.

The production deployment at NAS North Island in April-May 2000 yielded 493 depth-discrete samples collected and analyzed from 28 different investigation locations. The complete characterization screening of the trichloroethene (TCE) plume required 15 days. The overall cost was \$112,556 for the collection and analysis of subsurface samples, cone penetrometer testing (CPT) soil classification, and the disposal of investigation-derived waste (IDW).

A comparison between the actual costs from the April 2000 effort and the estimated cost of completing a similar effort with monitoring wells showed that using the ITMS-MIP system potentially saved \$38,000, a 25 percent cost savings. The ITMS-MIP produced 493 samples versus the 28 samples that would have been sampled and analyzed by installing and sampling conventional monitoring wells. However, the timesaving may be the greatest value added. The Chapter 1 Introduction 1 site managers are now at a decision point that they may not have reached for another 2 years if they had completed the characterization using conventional methods.

The timesaving would not have been possible if the characterization had not been completed in one field deployment. This was made possible by the ability of the ITMS-MIP system to collect and analyze approximately 38 samples each day.

The ITMS-MIP system is a quick, efficient, and effective tool for gaining insight into the nature and extent of subsurface contamination. Groundwater monitoring wells are sensitive verification and long-term monitoring tools. Both are integral to site remediation.

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2.0 TECHNOLOGY DESCRIPTION

This chapter describes the ITMS-MIP system technology. This system collects and analyzes vapor samples from beneath the ground surface. The system is deployed by the Tri-Service SCAPS shown in Figure 1.

2.1 TECHNOLOGY BACKGROUND

This technology was developed to address the need to characterize chlorinated hydrocarbon contamination in the subsurface at Department of Defense (DoD) sites rapidly in a cost-effective manner. The objective was to have a system capable of making 50 or more depthdiscrete subsurface measurements per day. The ITMS-MIP system performs rapid field screening to determine the presence of VOC contaminants within the subsurface of a site. In addition, the ITMS-MIP system identifies specific analytes based on their mass spectra and estimates contaminant concentrations.



Figure 1. SCAPS Truck.

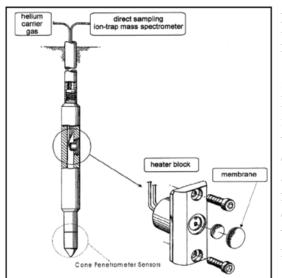


Figure 2. Combined Probe. (Courtesy of Geoprobe Systems, Salina, KS, from Christy 1997)

A combined probe was created by incorporating the heater block and membrane from a permeable membrane soil probe (Christy 1997) into a standard SCAPS cone penetrometer probe. Figure 2 shows the schematic of the combined probe, referred to as the MIP. The MIP can be driven or pushed to the depth of interest and operated to extract and collect a VOC vapor sample. This sample is then transported via a carrier gas within a transfer line to the surface for analysis. The MIP can then be driven or pushed to the next depth of interest, and the sample extraction and collection process repeated. Unless the membrane fails, there is no need to retrieve the device between measurements.

The membrane is located approximately 0.53 m(21 in.) above the CPT sensor tip. This means that the soil type is determined prior to the arrival of the MIP membrane at that depth. This delay allows the operator to stop at

unique geologic features as measured by the preceding CPT sensor and collect a VOC sample for analysis. This unique ability enables investigators to address doubts or questions while in the field so that the contaminant characterization can be completed during one field deployment.

2.1.1 Site Characterization and Analysis Penetrometer System

Cone penetrometry has long been used to characterize soil for geotechnical parameters such as soil strength and liquefaction potential. This is accomplished by advancing (pushing) a standard cone penetrometer probe into the ground. The SCAPS was developed as a Tri-Service program to use the capabilities of cone penetrometer technology for characterizing subsurface contamination.

The SCAPS truck is a standard 18.2-metric-ton (20-ton) cone penetrometer platform used to drive chemical and geotechnical sensor and hybrid sensor/sampler probes into the ground. The forward portion of the SCAPS truck houses the hydraulic rams used to translate the weight of the truck (reaction mass) into pushing force. The combination of reaction mass and hydraulics can advance a 1-m-long by 3.57-cm-diam steel rod into the ground at a rate of 1 m/min in accordance with American Society for Testing and Materials (ASTM) Method D3441 (ASTM 1995), the standard for geophysical sensing CPT. The rods, various sensing probes, or sampling tools can be advanced to depths in excess of 50 m (164 ft) in naturally occurring soils. As the rods are withdrawn, grout can be injected through 0.63-cm- (0.25-in.-) diam tubing within the interior of the SCAPS umbilical cable, thereby hydraulically sealing the push hole. While the rods are being withdrawn, they are cleaned within a pressure manifold housed outside and beneath the truck. The rinse water is contained for proper handling and disposal. The rear portion of the SCAPS truck houses the data collection components of SCAPS sensor technologies and onboard data acquisition/ processing computers.

2.1.2 Geophysical Cone Sensor

The standard cone penetrometer probes are instrumented with strain gauges to measure cone tip force and sleeve friction force in accordance with ASTM Standard D3441. The soil type is then determined from a ratio of cone tip force and sleeve friction force using one of the empirically derived classification schemes (Lee et al. 1994).

2.1.3 Membrane Interface Probe

The membrane interface portion of the MIP consists of a small polymer port that is permeable to gas but impermeable to liquid. The permeable port is a stainless steel screen with an area of 37.42 sq mm and a thickness of approximately 0.76 mm impregnated with a thin film of Teflon® (TFE). The permeable port is brazed onto a steel housing that also contains a resistive heater coil and a thermocouple allowing the temperature of the membrane to be controlled and monitored. Increasing the heater temperature increases the rate of adsorption into the membrane (Kotiaho et al. 1991), diffusion through the membrane, and evaporation from the membrane surface into ultrapure grade helium carrier gas. This carrier gas is circulated over the back of the membrane through a 61-m transfer line (3.17 mm OD by 1.57 mm ID, polyether ether ketone (PEEK), Alltech, Inc., Part 35717) to a surface-mounted ITMS.

Engineers at the U.S. Army Engineer Research and Development Center (ERDC) made several modifications to the MIP as received from Geoprobe Systems, Inc., Salina, KS. Through-the-tip grouting was added so that once the measurement is complete, grout can be injected as the MIP is retracted. This minimizes the potential for vertical transport of chemical contamination through less

permeable soil materials. Standard CPT soil classification sensors were installed to identify soil types in advance of the membrane sampling port.

2.1.4 Direct-Sampling Ion Trap Mass Spectrometer

A variety of detectors could be used to analyze the contents of the returning helium carrier gas. For this effort the detector of choice was the direct-sampling ITMS developed by the U.S. Department of Energy Oak Ridge National Laboratory, Oak Ridge, TN. It comprises a quadrupole ITMS, a capillary restrictor interface, and a variety of sample inlets for use with gas (air and soil gas), soil, and water. The system employed was one of three ITMS models: (a) a Teledyne 3DQ ITMS, (b) a Finnigan ITMS 40, or (c) a Varian Saturn. Each ITMS is fitted with a 20-cm-long, 100-µm-ID capillary (J&W Part 160-2635) and restrictor-heated interface (Scientific Information Service, Inc., Part 912000) operated at 105 °C. The capillary-interface limits flow into the ITMS to 0.1 to 1.0 mL/min, which is compatible with both electron impact and chemical ionization sources. Chlorinated solvents such as TCE are analyzed using electron impact, and benzene, ethyl benzene, toluene, and xylenes (BETX) are analyzed using water chemical ionization.

The ITMS is operated in a full scan mode (40 to 250 daltons) during calibration and in situ sample analysis. Since no separation technique is used before vapor samples are introduced into the ITMS, the resulting mass spectral data (Figure 3) consist of a series of scans containing ions indicating the presence of VOC analytes (Wise et al. 1997). Individual compounds are identified and quantified based on ions of selected masses indicative of the individual compound (i.e., 130/132 m/z for TCE by electron impact and 79 m/z for benzene by water chemical ionization where m/z is the mass to charge ratio of an ion).

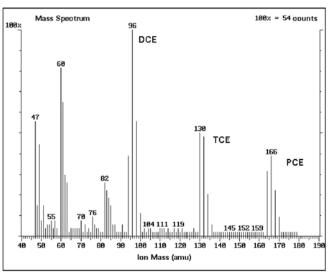


Figure 3. Typical ITMS Analysis Results for Dichloroethane (DCE), TCE, and Tetrachloroethane (PCE).

2.1.5 Dynamic Range

Figure 4 shows that the ITMS-MIP system can respond to analytes in concentrations ranging over five orders of magnitude. All of the in situ analysis samples shown were collected in real-time and without sample dilution. Further, the system can quickly recover from exposure to large concentrations of analyte.

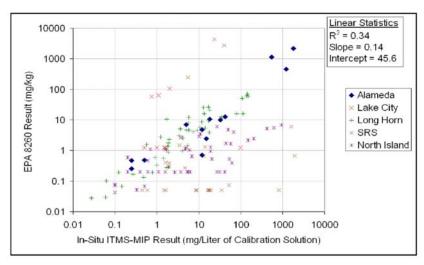


Figure 4. Comparison of Co-Located Soil Samples Collected in the Saturated Zone and Analyzed by In Situ ITMS-MIP and EPA Method 8260 for TCE. (USEPA 1993)

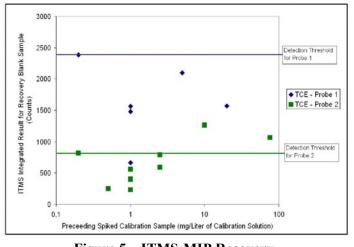


Figure 5. ITMS-MIP Recovery.

Figure 5 illustrates the ITMS-MIP recovery after analysis of calibration samples with concentrations up to 100 mg/L. Note that in all cases for Probe 1 and all but two cases for Probe 2, the blank response immediately after calibration analysis is below the detection threshold for the ITMS-MIP.

The ability to analyze samples without dilution is possible because of the ion trap and automatic gain control of the ITMS. The ion trap is scanned to deter-mine the load of molecules present in the system. Once the load is determined, a portion of

the analyte is allowed into the mass spectrometer. Once mass analysis is complete, the results are corrected based on the portion of the molecules analyzed. This entire process is automated and occurs in approximately one second. The ability to acquire data in near real-time over a dynamic range of 105 makes the ITMS an ideal detector for the MIP since sample dilution is not an option with the current system design.

2.1.6 System Limit of Detection

Three quantities are needed to determine the detection limits of the ITMS-MIP system: electronic noise, background, and sensitivity. These quantities are determined using the calibration samples prepared during the investigation using standard analytical techniques.

Limit of detection (LOD) calculations are conducted using the method prescribed in SW-846 (USEPA 1993). This method involves n replicate measurements of a low but detectable analyte concentration, estimation of analytical system noise as the variance of the *n* replicate measurements, and calculating the LOD using the following equation:

$$LOD = t_{n-l, \alpha \prime s} S \tag{1}$$

where $t_{n-I, \alpha/s}$ is the Student's t-value for n replicates at the 95 percent confidence level and S is the estimate of the standard deviation. For n values between 5 and 9, $t_{n-I, \alpha/s}$ ranges between 2.78 and 2.23. Measurements for LOD calculations are obtained using the entire ITMS-MIP system to determine overall system performance for in situ applications. The ITMS-MIP system detection limits will vary with analyte, but are in the range of 100 to 500 µg/L for the 34 VOC analytes listed on the USEPA Target Compound List.

2.1.7 Calibration and Quality Control

The ITMS was initially set up and calibrated in a stand-alone mode. Once the ITMS operation was verified, it was coupled to the MIP via the PEEK polymer transfer lines. The carrier gas flow rate was set to a nominal value (80-120 mL/min), which was monitored and adjusted to remain constant throughout operation. This flow rate was determined through experiment, and was a compromise between analyte dispersion and analyte adsorption loss.

Once the flow rate was set, the coupled ITMS-MIP system was ready to be calibrated. The procedure began by filling a calibration jig (Figure 6) simultaneously with spiked deionized water and sand (No. 2 bast sand). Once the calibration jig was filled, the membrane heater and ITMS were simultaneously initiated. Figure 7 illustrates that this method, though a crude approximation of the wide variety of subsurface soil conditions, allows calibration of the ITMS-MIP system. It should be noted that mixing the sand and spiked water, particularly at low analyte concentrations, can lead to wide variation in the calibration data and that caution must be taken when developing the calibration curve.



Figure 6. ITMS-MIP Calibration.

The spiked water was prepared by injecting an amount of

stock standard solution into 250 mL of deionized water. The standard solution, containing the analytes of interest, was prepared by injecting neat (99 percent) VOC analytes into a 10-mL volumetric flask containing approximately 7 to 8 mL of methanol. Care was taken to ensure that the neat analyte was dropped directly into the methanol and did not touch the unwetted glass surface of the volumetric flask. The stock solution was prepared in the concentration ranges of 1 to 5 mg/mL. Multiple analyte mixtures in a single stock solution were used as long as no analytes yielding identical m/z ratios were mixed. Details of VOC stock solution preparation can be found in EPA Method 8260 (USEPA 1993).

The ITMS was operated in the full scan mode performing an analysis every second over a period of 3 min for both the calibration and in situ sample measurements. Data acquired during calibration

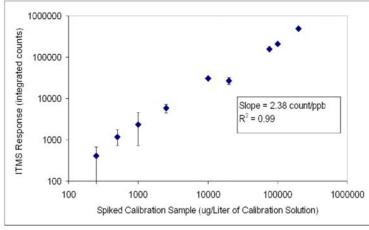


Figure 7. ITMS-MIP Calibration for PCE.

and in situ measurements were reduced by integrating a fixed number of mass spectra scans (typically 80 to 100 scans) of the specific ions for a given analyte (USEPA 1994). Typical calibration curves for analytes of interest extended over three to four orders of magnitude (Figure 7). Data acquired during each in situ measurement were quantified based on the calibration curves.

A system blank check was performed before and after each set of in situ measurements. Daily calibration check

standards and performance evaluation check standards were analyzed to ensure data quality.

2.2 PERSONNEL TRAINING REQUIREMENTS

Personnel operating the SCAPS CPT platform are trained in methods to install groundwater monitoring wells and other traditional drilling methods. Operators of the ITMS should have training in mass spectrometry and volatiles analysis. All personnel should have the capability to operate computer software and should be familiar with procedures for working with heavy equipment. Other than health and safety training requirements, there is no mandated training required to operate the CPT or the ITMS.

2.3 ADVANTAGES OF THE TECHNOLOGY

The ITMS-MIP vapor sampling system uses a CPT platform to provide near real-time field screening of the distribution of VOC contamination at hazardous waste sites. The current configuration is designed to distinguish VOC-contaminated areas from uncontaminated areas and provide semiquantitative estimates of groundwater and soil VOC contaminant concentrations quickly and cost-effectively. This capability allows further investigation and remediation decisions to be made more efficiently and reduces the number of samples that must be submitted to laboratories for costly analysis. In addition, the SCAPS CPT platform facilitates the characterization of contaminanted sites with minimal exposure of site personnel and the community to toxic contaminants, and minimizes the volume of IDW generated during typical site characterization activities.

The ITMS-MIP vapor sampling system is an in situ field screening technique for characterizing the subsurface distribution of VOC contamination before installing soil borings or groundwater monitoring wells. The method is not intended to be a complete replacement for traditional soil boring and/or monitoring wells, but is a means of placing a reduced number of borings and monitoring wells more accurately to achieve a valid site characterization.

2.4 LIMITS OF THE TECHNOLOGY

This section discusses the limits of the ITMS-MIP detection system, as they are currently understood.

2.4.1 Truck-Mounted Cone Penetrometer Access Limits

The SCAPS CPT support platform is an 18.2-metric-ton (20-ton), all-wheel-drive, diesel-powered truck. The dimensions of the truck require a minimum access width of 3 m (10 ft) and a height clearance of 4.6 m (15 ft). It is conceivable that some sites, or certain areas of sites, might not be accessible to a vehicle the size of the SCAPS CPT truck. The access limits for the SCAPS CPT vehicle are similar to those for conventional drill rigs and heavy excavation equipment. However, the ITMS can operated from the back of a van and a smaller direct-push rig used to advance the MIP.

2.4.2 Cone Penetrometer Advancement Limits

The CPT sensors and sampling tools may be difficult to advance in subsurface lithologies containing cemented sands and clays, buried debris, gravel units, cobbles, boulders, and shallow bedrock. As with all intrusive site characterization methods, it is extremely important that all underground utilities and structures are located using reliable geophysical equipment operated by trained professionals before undertaking activities at a site. This should be done even if subsurface utility plans for the site are available for reference.

2.4.3 Extremely High Level Contamination Carryover

The effective dynamic range for the ITMS-MIP detection system is determined by two factors: the dynamic range of the ITMS and the potential for carryover or cross contamination of the MIP membrane and helium transfer line by a highly concentrated sample (greater than 500 mg/L). The lower LOD of the ITMS-MIP system during the 1999 NAS North Island demonstration was occasionally affected by carryover contamination of the transfer line. Residues remaining in the lines caused carryover of VOC analytes between successive analyses. The effect was less analytical sensitivity and an increase in the system LOD. The problem was identified through the analysis of a system blank between each in situ measurement. Carryover from the transfer line was eliminated by replacing the Teflon lines with nonsorbing PEEK polymer transfer lines.

Another source of carryover for the ITMS-MIP system was VOC or petroleum hydrocarbon residuals in the MIP Teflon membrane. In situ MIP operation was conducted in one of two ways: initiating the membrane heater once the depth of interest was reached or continuously heating the membrane during the entire push. Keeping the membrane hot at locations where high concentra-tions of contaminant were expected prevented the MIP membrane from being saturated by VOC analytes and thereby biasing future measurements from carryover contamination. Controlled, intermittent membrane heating was desired when contaminant concentrations were expected to be near the lower LOD.

2.4.4 ITMS Limitations

The ITMS was operated as the detector for the ITMS-MIP detection system as detailed in USEPA Method 8265 (USEPA 1994) and as described by Costanza and Davis (2000). This method is

intended for field screening applications of direct-sampling ion trap mass spectrometry. One of the limitations of the ITMS is that it cannot distinguish between particular pairs of analytes that yield identical mass fragments. For example, 1,1,2,2-tetrachloroethane and chloroform (trichloromethane) yield ions primarily at masses 83 and 85. The current ITMS technology cannot differentiate between these two analytes; therefore, they are reported as a sum of the two analytes. It should be noted that the current method, USEPA Method 8260 (USEPA 1993), using gas chromatography/mass spectrometry is still not able to differentiate between some analyte pairs (i.e., meta- and para-xylene). Nevertheless, even when samples are contaminated with complex mixtures of analytes, the ITMS can usually provide some level of useful qualitative and quantitative information.

2.4.5 Membrane Interface Probe Limitations

The MIP samples VOCs in direct contact with its heated membrane (approximately 37 mm2). The sample size or area influenced by the heated membrane has not been studied; but is affected by temperature of the membrane, the type of subsurface media (vadose zone soil or saturated soil), and contact time between membrane and soil. Because the sample mass and volume are not known, the ITMS-MIP data are considered to be estimates that are a function of depth and lateral distribution.

The ITMS-MIP data appear to be biased toward detection of VOCs in the saturated zone. Correlations between ITMS-MIP data and validation data yielded an R2 of 0.95 for saturated soils and R2 of 0.60 and 0.01 for vadose zone soils. This may be a direct result of the method of calibrating the ITMS-MIP using spiked, saturated sand and since the sampling volume of the MIP is not known.

The thin Teflon membrane coating on the MIP port is subject to damage through repeated use in sandy or gravely strata. In the configuration used for this demonstration, the stainless steel screen membrane support was brazed onto the steel housing. To replace the membrane, the MIP block was removed from the probe housing and sent back to the manufacturer for repair or replacement. For the MIP used in this demonstration, membrane failure occurred only once in six field trips after hundreds of pushes. A new port with a field-replaceable membrane is now available from the manufacturer.

3.0 DEMONSTRATION DESIGN

This chapter discusses the technology claims, demonstration objectives, sampling design, and data analysis protocols that were used to evaluate the results of the demonstration.

3.1 PERFORMANCE OBJECTIVES

This technology was developed to address the need to characterize chlorinated hydrocarbon contamination in the subsurface rapidly in a cost-effective manner. Therefore the ITMS-MIP detection system should not only be as accurate as traditional sample collection and analysis techniques, but should also be able to complete contaminant characterization in less time at a significantly lower cost. With these objectives in mind, the SCAPS ITMS-MIP detection system performance was compared to conventional sampling and analytical methods for the following.

- a. Accuracy of analytical results.
- b. Time required to characterize the extent of contamination.
- c. Reliability and ruggedness.

3.1.1 Accuracy

Accuracy was determined by collecting soil and groundwater samples from within 0.15 m (6 in.) of in situ measurements performed by the SCAPS ITMS-MIP system. These verification samples were sent to an independent laboratory for analysis by EPA Method 8260 (USEPA 1993). Soil samples were collected using a direct-push soil coring device that collects a soil sample within a tube approximately 46 cm by 5 cm (18 in. by 2 in.). Subsamples from the soil core were collected according to EPA Method 5035A (USEPA 1993) and preserved in methanol for transport to the offsite laboratory. Water samples were collected from direct-push, 5-cm- (2-in.-) diam microwells with 0.6 m (2 ft) of exposed inlet screen section. Accuracy was evaluated by determining the correlation between the ITMS-MIP data and the validation data.

3.1.2 Time Required to Characterize Extent of Contamination

Field implementation of conventional characterization technology is typically a deterministic process. Once the sample collection locations are chosen, they are not changed while the sampling crew is in the field. The lapse of time between collecting samples and receiving a report detailing the sample analysis results is normally 6 months to a year. Once the analysis results are available, they usually reveal that more samples are required before remediation decisions can be made. Additional time is required to complete sample collection plans and let contracts to implement the sampling plans. These time lapses can easily exceed one year.

The objective of this demonstration was to characterize the extent of chlorinated solvent contamination in one field deployment.

3.1.3 Reliability and Ruggedness

The reliability of the ITMS-MIP detection system is measured by the consistent days on which sample collection and analysis occurred. Ruggedness refers to the ability of the sensor to endure

physical, thermal, and chemical shocks without interfering with the repeatability of measurements and the operational availability of the system.

3.2 PHYSICAL SETUP AND OPERATION

Typically, a four-person crew is needed to conduct field operations including one field geologist, two push room personnel, and one ITMS-MIP system operator. SCAPS operation encompasses a large part of the field activities; the responsibilities and training are similar to those of a standard geotechnical CPT field crew. The ITMS-MIP system operator requires a background in science and ITMS theory in addition to detailed training with each of the system components to be able to maintain the system and to make field repairs.

The SCAPS truck-mounted CPT platform is a stand-alone operations unit requiring neither outside utilities nor special structures (either permanent or temporary). The CPT platform is capable of providing an 18.2-metric-ton (20-ton) pushing capability. An onboard generator and hydraulic pump driven by a power take-off unit from the truck diesel engine provide the necessary power to operate the electrical and hydraulic systems. During normal operation, the hydraulic system advances the rods and MIP probe while the electrical system provides power to run the data acquisition system. The SCAPS does not bring significant quantities of soil to the surface; however, IDW is generated during the pressure cleaning of the rods and probe during retraction. Water from an onboard tank is consumed by the pressure cleaning system and in preparing a grout mixture. A local source of water is required for refilling the onboard tank. Other consumables are bentonite and cement used to prepare the grout mixture and high-purity helium gas used as the carrier gas. After completion of subsurface interrogations, the MIP and penetrometer rods are retracted and the tremie grout method is used to seal the penetrometer hole(s).

Successful site characterization requires the close cooperation of a variety of organizations. Table 1 outlines the organizations involved in this demonstration along with their roles and responsibilities.

3.3 MONITORING PROCEDURES

Monitoring the ITMS-MIP detection system performance consisted of quality assurance checks and independent analysis of verification sample analysis.

Calibration samples of known analyte concentration were analyzed at the beginning of each working day as described in Chapter 2. In addition, a single calibration check sample of known concentration was analyzed immediately prior to in situ ITMS-MIP vapor sampling events. Once daily, an externally prepared calibration check standard was analyzed to evaluate the accuracy of the working calibration stock solution and continuing calibration.

Method blanks from reagent water were analyzed at the beginning of each workday and after each in situ measurement event to ensure that the background within the ITMS-MIP system remained constant.

As discussed previously, soil and groundwater samples were collected for offsite independent laboratory analysis by USEPA Method 8260 (USEPA 1993).

Organization	Responsibility				
Environmental Security Technology Certification Program (ESTCP) Funded Activities					
U.S. Army Engineer Research and Development Center (ERDC)	Operate and maintain ITMS-MIP system. Communicate sample analysis results with OHM. Ensure verification samples are collected and sent to fixed laboratory. Generate Demonstration Plans and Final Reports for ESTCP.				
U.S. Naval Facilities Engineering Service Center	Provide real-time data model.				
Navy Fund	ed Activities				
U.S. Naval Facilities Engineering Command, Southwest Division (SWDIV)	Remedial Project Manager duties. Overall project direction.				
OHM Remediation Services Corporation (Now The IT Group)	Design and implement remediation system. Obtain permitting and utility clearance. Manage IDW. Understand and communicate previous day's sample analysis results. Recommend next sample collection locations.				
Public Works Center, San Diego	Operate SCAPS truck. Be responsible for logistics of each push hole. Prepare final report for SWDIV.				
California Environmental Protection Agency, Department of Toxic Substance Control	Review demonstration findings for accuracy and completeness.				

Table 1. Demonstration Participants.

3.4 DEMONSTRATION SITE/FACILITY BACKGROUND

3.4.1 Savannah River Site

While the data for the Savannah River Site were not used in this demonstration cost report, the site and its results will be discussed briefly.

The Savannah River Site is a 917-km² (354-square-mile) Department of Energy facility located near Aiken, SC. The site selected for the ITMS-MIP demonstration was in a reactor fuel and target assembly area called the A/M area. From the 1950's through the 1980's, approximately 1,587,575 kg (3.5 million pounds) of waste solvent, primarily TCE and PCE, were discharged to the A-14 outfall and the M area settling basin. Releases of large amounts of TCE and PCE lead to significant vadose and saturated zone contamination in both dissolved and free phase form (i.e., dense nonaqueous phase liquid (DNAPL)). Previous investigations of the site indicate that sufficient DNAPL was released to penetrate the vadose zone and capillary fringe.

During this demonstration the MIP made 5 penetrations to collect 154 discrete ITMS-MIP measurements to a maximum depth of 34.4 m (113 ft). Thirty-one verification samples were taken for analysis by USEPA Method 8260 (USEPA 1993). PCE was the primary contaminant detected

at the site with validation correlation results R^2 by soil type: clay $R^2 = 0.74$, slope 89.1; sand $R^2 = 0.97$, slope 0.0035; and sand mix $R^2 = 0.56$, slope 0.00023. Overall data correlation for the Savannah River Site was $R^2 = 0.010$, slope -0.02.

3.4.2 Naval Air Station North Island

NAS North Island is part of the largest aerospace-industrial complex in the Navy. It includes Naval Amphibious Base Coronado, Outlying Field Imperial Beach, and Naval Air Landing Facility, San Clemente Island. The complex's 2,024 ha (5,000 acres) in San Diego bracket the city of Coronado. North Island itself is host to 23 squadrons and 75 tenant commands and activities, one of which, the Naval Aviation Depot, is the largest aerospace employer in San Diego.

The site selected for the ITMS-MIP demonstration was near Buildings 379 and 397 at the Naval Aviation Depot (Figure 8). The site is located in the northeast quadrant of NAS North Island and is bounded by three buildings: Building 379 to the east, Building 397 to the west, and Building 391 to the south. Jet engine tests and maintenance are conducted in Building 379. Numerous former and existing underground storage tanks are located within, between, and around Buildings 379 and 397. Buildings 379 and 397 overlie the previously delineated light nonaqueous phase liquid (LNAPL) plume. Building 391 is down gradient from this plume (OHM Remediation Services Corporation 1997).

3.5 DEMONSTRATION SITE/FACILITY CHARACTERISTICS

In 1991, Jacobs Engineering Group, Inc. (1991), conducted an initial site assessment for potential leaking underground storage tanks. Seven soil borings and three monitoring wells indicated contamination in the area around and below the buildings measured by total petroleum hydrocarbons (TPH) in the soil and benzene in the groundwater. Free product LNAPL was detected in one of the initial three monitoring wells. Based on the initial results, Geosciences (1993) conducted further site assessment during 1993. Ten soil borings and nine monitoring wells were installed and sampled. Total petroleum hydrocarbon contamination was found in many of the soil boring samples, and LNAPL was detected in two of the monitoring wells (OHM Remediation Services Corporation 1997). Table 2 summarizes the groundwater monitoring effort.

Year	Monitoring Wells	Recovery Wells
1991	3	
1993	9	
1996-1997		67

Table 2. Initial Petroleum Hydrocarbon Characterization.

Based on these results, a LNAPL removal system was designed. During initial construction of this removal system in 1996, the extent of LNAPL contamination was found to be four times greater than originally estimated. Construction was halted and the extent of LNAPL contamination was further investigated and delineated in the summer of 1997. After the discovery of TCE in a number of monitoring wells, OHM Remediation Services Corporation recommended additional site characterization and a reevaluation of the proposed site remediation plan.

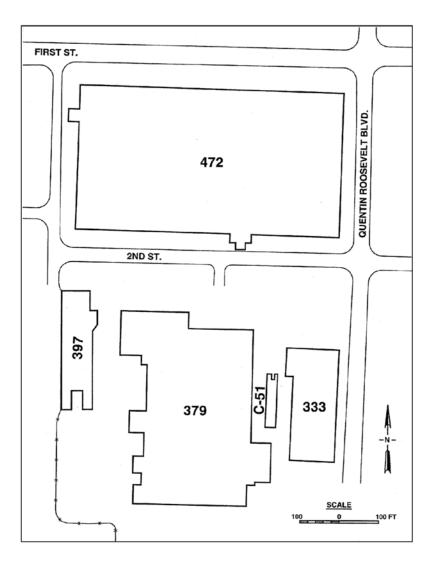


Figure 8. NAS North Island.

3.5.1 Hydrogeology

Previous investigations at the site have identified two primary geologic units at NAS North Island: an upper well graded sand to silty sand underlain by a poorly graded sand to silty sand. The upper unit of well-graded fine to medium sand and silty sand contains some coarse grains and is up to 20 percent silt. The upper unit extends from the surface to approximately 4.6 to 6 m (15 to 20 ft) below ground surface (BGS). The lower unit is a poorly graded very fine to fine grained sand and silty sand with less than 10 percent medium grains and up to 10 percent silt. The top of this unit is generally encountered 4.6 to 6 m (15 to 20 ft) BGS. The upper unit was hydraulically placed for the development of North Island. The lower unit was formed by natural deposition in a nearshore environment (Geosciences 1993).

Groundwater at the site appears to flow toward the north-northwest. The average hydraulic gradient across the site has been reported to be 0.0017 m/m (0.0017 ft/ft), and slug tests have measured the

hydraulic conductivity to be approximately 0.04 m/day (0.12 ft/day) in the lower geologic unit. These data have been used to conclude that the surficial aquifer is unconfined (Geosciences 1993).

3.5.2 Extent of Contamination

The extent of petroleum contamination had been defined in previous investigations (OHM Remediation Services Corporation 1997; Costanza, Myers, and Davis 2001). Additional investigation of soil and groundwater at depths between 6 and 12 m (20 and 40 ft) BGS in February 1998 indicated that free product TCE or DNAPL may be present at the site in the vicinity of monitoring well PW-62. Based on the February 1998 investigations, a contour map of the groundwater contamination at the Buildings 379 and 397 site was developed. The wide range of contaminant concentrations present at this site made it an ideal site to demonstrate the rapid site characterization capabilities of the SCAPS VOC sensing technologies. The Hydrosparge VOC sensor for groundwater was demonstrated in July 1998, completing 50 direct pushes and 115 sample analyses. This demonstration was credited with being instrumental in better characterizing the horizontal boundaries of the TCE plume above 12 m (40 ft) BGS (OHM Remediation Services Corporation 1999).

By design, the Hydrosparge VOC sensor cannot grout upon retraction. Thus, any push beyond an aquitard would leave open a potential migration pathway for contaminants. For this reason, the vertical extent of contamination at this site was still unknown after the Hydrosparge demonstration was completed.

4.0 PERFORMANCE ASSESSMENT

SCAPS ITMS-MIP detection system performance was compared with that of conventional sampling and analytical methods using three specific criteria for comparison.

- a. Accuracy of analytical result.
- b. Time required to characterize extent of contamination.
- c. Reliability and ruggedness.

The results presented in this chapter are from the July 1999 ITMS-MIP system demonstration at NAS North Island and the April/May 2000 production work.

4.1 ACCURACY

The accuracy of the ITMS-MIP system in situ analysis results was determined by independent laboratory analysis of soil and water samples.

Figure 9 shows the typical measurements made at a single investigation location. The VOC concentration is plotted against the soil type with depth. In this example the soil classification scale ranges from 1 to 12 with clay ranging from 3 to 5, silt ranging from 5 to 8, and sand ranging from 8 to 11.

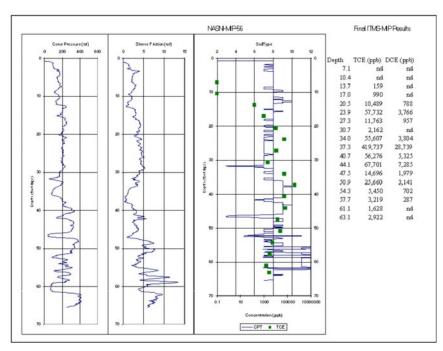


Figure 9. Typical In Situ Analysis Result for an Investigation Location. (VOC results are in μg/L of calibration solution.)

The results of validation sample analysis by EPA Method 8260 (USEPA 1993) for NAS North Island appear to be systematically biased toward the in situ ITMS-MIP results. Figure 10 shows that the ITMS-MIP results were greater than validation sample results for all soil types with a combined R^2 of 0.48 and a slope of 0.78. However, actual correlation bias cannot be determined when comparisons are based on different concentration units. Since the ITMS-MIP results are expressed in mg/L of calibration solution, which is an apparent concentration term, relative mass of contaminants between CPT pushes is measured and not the true soil concentrations as measured by conventional laboratory analysis.

Figure 10 presents data collected by two different operators from successive years. It is believed that some bias may be related to the process of collecting soil samples from the NAS North Island site. This belief is supported by the results obtained from collecting water samples from short screen length 0.6-m (2-ft) micro-wells as presented in Table 3. While there may not be exact agreement between the water sample results and the in situ ITMS-MIP results from the saturated zone, they compare more favorably with an R² of 0.95 compared to samples from the vadose zone with an R² of 0.60. The ITMS-MIP system correctly indicated the presence of contamination without false negative results. However, one false positive ITMS-MIP measurement was recorded at MIP41-70 (Table 3). It should be noted that sand matrix materials provided better correlation regarding the ITMS-MIP data reliability than other soil matrix materials.

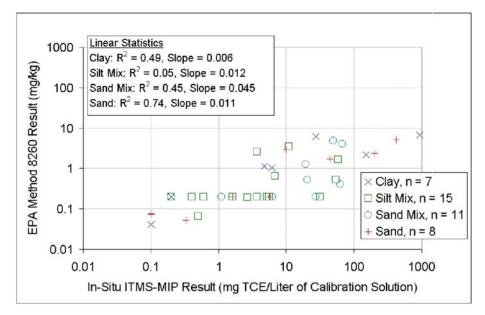


Figure 10. NAS North Island Validation Results.

Sample ID	MIP Sample Depth, ft BGS	ITMS-MIP µg/L	Screen Length ft BGS	EPA 5035/8260 μg/L	
MIP41-43	40.6	331	40-43	60	
MIP41-70	71.1	2294 ¹	68-70	<5	
MIP46-54	54.2	8785	54-56	15200	
MIP55-30	30.5	19923	30-32	25400	
MIP55-45	44.1	72688	45-47	22100	
MIP55	47.4	14839]		
¹ Soil sample collected from MIP41-70 had low moisture content; false positive.					

 Table 3.
 TCE Water Sample Comparison, NAS, North Island, May 2000.

The ITMS-MIP systems correctly indicated the presence of contamination without false negative results. A false positive result was recorded at MIP41-70.

4.2 TIME TO CHARACTERIZE EXTENT OF CONTAMINATION

Navy contractors took nearly 8 years to characterize the hydrocarbon plume using conventional groundwater monitoring wells. The SCAPS Hydrosparge VOC sensor took only 22 days in July 1998 to determine the horizontal extent of the shallow chlorinated hydrocarbon plume. The ITMS-MIP required just 15 days to determine complete vertical characterization in July of 1999 and April of 2000. Table 4 summarizes the number of in situ measurement locations and samples collected and analyzed during the SCAPS technology efforts. The major difference in the July 1999 and April-May 2000 production rates is related to the difference in investigation approaches. In the July 1999 effort, specific investigation depths were selected prior to the field deployment, while in April-May 2000 only the investigation locations were previously selected.

Table 4.	NAS North	Island Demonstration	Production Comparison.
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Date	Date Sensor		Samples	Sample/Location (Approx.)
July 1998	Hydrosparge VOC	50	115	2-3
July 1999	ITMS-MIP	40	207	5
April/May 2000	ITMS-MIP	28	493	18

4.3 RELIABILITY AND RUGGEDNESS

No production delays were caused by the ITMS or transfer lines during the July 1999 demonstration. The only delays were caused by logistical constraints such as clearance for the next sample location or striking an unmarked waterline. One of the major requirements for the ITMS-MIP system to work properly is to have facility personnel ready to accommodate changes as the work proceeds. Since analytical results are available as samples are collected, real-time decisions can be made, which means real-time changes in the investigation plan are necessary.

There were two lost production days during the April-May 2000 production deployment. The membrane was ruptured during retraction through gravel backfill material. One day was spent trying to repair the membrane, and another day was spent installing the new replacement probe that was shipped from ERDC. However, the average in situ analysis per day for the deployment was approximately 38 samples per day. Maximum push depth consistently exceeded 15 m (49.2 ft) BGS.

4.4 SUMMARY OF SITE-SPECIFIC INFLUENCES

The SCAPS ITMS-MIP system was evaluated under varying site conditions to determine if specific site conditions could be identified that affected system performance. Surface anomalies such as steep sloping terrain, paved surfaces, and permanent structures prevented the deployment of the SCAPS ITMS-MIP at some locations and were considered a logistics problem, not a technological problem.

Site conditions that varied during the deployment of the ITMS-MIP system were identified as variables and thus as potential problems. The specific variables identified at the demonstration sites were the number of subsurface interrogations per push location, soil type, saturated versus unsaturated soil, and seasonal temperature differences.

The number of subsurface interrogations per push location was not found to affect the performance of the ITMS-MIP system if adequate care was taken to remove (flush with carrier gas) analyte vapors from system transfer lines between sample interrogations. Since analyte vapors must be removed from system transfer lines to prevent cross-sample contamination, continuous push sampling was not evaluated and is not recommended.

The type of soil undergoing evaluation for VOC contamination was found to affect ITMS-MIP data correlation with validation samples. This may be a direct result of the calibration method that is based on a single groundwater-soil matrix (i.e., uses spiked, saturated sand to develop a calibration curve). At the Naval Air Station (NAS) North Island, a "silt mix" soil exhibited an R² correlation of 0.05, while a "sand" soil exhibited an R² correlation of 0.74. The effect of soil type on ITMS-MIP performance was also observed at the Savannah River Site (SRS). The effect of soil porosity was not investigated during this study, but it is thought to contribute to the variability of ITMS-MIP system performance.

The water content of the soil was also found to affect the ITMS-MIP system performance. The in situ ITMS-MIP deployed in the saturated zone of the NAS North Island exhibited an R^2 correlation of 0.95, as opposed to an R^2 correlation of 0.60 for vadose (unsaturated) zone deployment. The ITMS-MIP system was shown to provide optimal performance in saturated soil deployments.

The effects of site temperature did not produce a noticeable effect on ITMS-MIP performance. However, cold temperatures may cause vapor analytes to condense in long cold transfer lines. The effects of varying cold temperatures on analyte transfer were not evaluated during this study.

5.0 COST ASSESSMENT

The costs associated with ITMS-MIP operation include daily equipment cost for the SCAPS truck, expendable supplies, crew travel expenses, and labor. While these costs vary from site to site, the average cost of operating a SCAPS truck and four-person crew in the field during production work, regardless of sensor type, is approximately \$4,500 per day.

The number of in situ measurements per day at a particular site depends on site mobility, subsurface geology, and depth of penetration. As previously discussed, the ITMS-MIP analysis is very fast (less than 5 min per measurement). The majority of the time associated with the ITMS-MIP system operation is the time associated with pushing the sensor to the depth of interest.

5.1 COST COMPARISON WITH CONVENTIONAL TECHNOLOGIES

Table 5 shows typical cost comparisons between the ITMS-MIP technology and conventional drilling/soil sampling. Cost savings are realized from SCAPS direct push methods due to a number of factors: (a) the speed with which direct push techniques access depth compared with drilling; (b) the low amount of IDW produced by the direct push methods; and (c) the rapid availability of near real-time information to make additional sample placement decisions. As can be seen from Table 5, the MIP provides significant cost savings compared with conventional drilling/soil sampling with offsite analysis.

5.2 COST COMPARISONS FROM THE APRIL-MAY 2000 NAS NORTH ISLAND INVESTIGATION

The production rate from the April-May 2000 ITMS-MIP deployment was approximately 38 in situ measurements per day from 2 to 4 investigation locations per day. Table 6 shows cost comparisons between the ITMS-MIP system and conventional drilling and soil sampling techniques with offsite sample analysis for the NAS North Island April-May 2000 demonstration. These costs are compared with estimated cost of installing an equivalent number of monitoring wells.

The estimated cost savings for the NAS North Island April-May 2000 investigation is 25 percent with a 1600 percent increase in the number of samples produced in one-fourth the amount of time. As a qualitative screening tool, the ITMS-MIP aids in optimizing the number and location of monitoring wells needed to delineate a contaminant plume. The real cost savings of this quick screening technology will be realized in terms of reducing the number of monitoring wells required for a site.

SCAPS ITMS-MIP In Situ Measurement		Conventional D (Hollow Stem Aug Spoon, and Offsite	er, Split	Direct Push and Analysis	Offsite
10 Pushes to 30 ft, MIP VOC Analysis Every 3 ft	Cost	10 Borings to 30 ft (100 Soil Samples for VOC Analysis)	Cost	10 Borings to 30 ft (100 Soil Samples for VOC Analysis)	Cost
2 field days @ \$4,500/day	\$9,000	Drilling for 300 ft @ \$30/ft	\$9,000	Drilling for 300 ft @ \$10/ft	\$3,000
Analysis for 100 samples	Included in cost	VOC analysis for 100 samples @ \$200/ sample	\$20,000	VOC analysis for 100 samples @ \$200/ sample	\$20,000
Geotechnical data: CPT continuous data for 300 ft	Included in cost	Geotechnical analysis for 10 samples @ \$100/sample	\$1,000	Geotechnical analysis for 10 samples @ \$100/sample	\$1,000
1 waste drum @ \$40/drum	\$40	28 waste drums @ \$40/drum	\$1,120	1 waste drum @ \$40/drum	\$40
Decon water testing	\$1,000	Decon water testing	\$1,000	Decon water testing	\$1,000
Waste soil testing	\$0	Waste soil testing	\$3,000	Waste soil testing	\$0
Waste soil disposal	\$0 (none produced)	Waste soil disposal for 20 drums @ \$100/ drum	\$2,000	Waste soil disposal	\$0 (none produced)
Decon water disposal for 1 drum @ \$100/ drum	\$100	Decon water disposal for 8 drums @ \$100/ drum	\$800	Decon water disposal for 1 drum @ \$100/ drum	\$100
4-man crew	Included in cost	Geologist for 40 hr @ \$60/hr	\$2,400	Geologist for 24 hr @ \$60/hr	\$1,440
		Technician for 40 hr @ \$40/hr	\$1,600		
Total	\$10,140		\$41,920		\$26,580
Unit cost per sample	\$101		\$419		\$266
Note: to convert feet to m	eters, multipl	y by 0.3048.			

Table 5. Comparison of Unit Costs for the ITMS-MIP Systemand Conventional Technologies.

Table 6. NAS North Island April-May 2000 Investigation.

Activity	Monitoring Wells (Estimated)	ITMS-MIP (Actual)
Locations investigated	28	28
Cost for sample access	\$133,514 ¹	\$90,556
Number of samples collected	28	493
Cost for sample analysis ²	\$5,600	\$22,000
Cost for IDW disposal	\$11,218	included
Total cost	\$150,332	\$112,556
Cost per sample	\$5,369	\$228
Elapsed time	2 months	15 days
¹ Estimated using the Bioventing Cost ² EPA 8260 sample analysis at \$200/s		

6.0 CONCLUSIONS

The ITMS-MIP system is a rapid in situ qualitative analytical tool for gathering large amounts of data in a short period of time. This type of data can be synthesized onsite for immediate use in the decision-making process for site characterization. During the April-May NAS North Island investigation, the SCAPS ITMS-MIP crew analyzed 493 individual MIP samples in situ from 28 sites in 15 days. Using the Bioventing Cost Estimator, it was estimated that the placing of 28 monitoring wells to evaluate the same 28 locations would take a drill crew 2 months. The large difference in the number of samples made available by the ITMS-MIP system provides a broader profile of the contaminant plume than does sampling by conventional methods.

The sample matrices investigated were soil and soil gas in the vadose zone and soil and water in the saturated sand zone. The ITMS-MIP system response in saturated and vadose zone soils was different from validation sample results. Correlations were higher in saturated zone sand that had $R^2 = 0.74$. The ITMS-MIP exhibited poorer correlation in vadose zone soils (clay $R^2 = 0.49$ and silt $R^2 = 0.05$). The ITMS-MIP data for unsaturated soils consistently underestimated contaminant concentrations for clay type vadose zone soils at both the NAS North Island site and the DOE Savannah River Site. This may be due to the method used to calibrate the MIP in saturated sand. Combined data for the five ITMS-MIP sites show an R^2 of 0.34 and a slope of 0.14.

Use of the ITMS-MIP system for site investigation results in a considerable cost savings compared with conventional drilling and soil sampling/well placement. A cost comparison between the actual costs from the April 2000 effort and the estimated cost of completing a similar effort with monitoring wells showed that using the ITMS-MIP system potentially saved \$38,000, a 25 percent cost savings. The ITMS-MIP produced 493 samples versus the 28 samples that would have been analyzed by installing and sampling conventional monitoring wells.

Timesaving may be the greatest value added. The complete characterization screening of the TCE plume required 15 days versus 2 months for well installation. The timesaving was possible because the MIP was able to sample and analyze approximately 38 samples each day allowing the crew to complete the characterization in one field deployment. The site managers are now at a decision point that they may not have reached for another 2 years if they had completed the characterization using conventional methods.

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APPENDIX A

POINTS OF CONTACT

List of Demonstration Participants:

Mr. George Robitaille, Technical Monitor U.S. Army Environmental Center Technical Support Division SFIM-AEC-ETD Aberdeen Proving Ground, MD 21020-5401 Telephone: (410) 612-6865 Fax: (410) 612-6836 E-Mail: gerobita@aec1.apgea.army.mil

Dr. William Davis, ERDC Principal Investigator 220 Kathryn Avenue Decatur, GA 30030 Telephone: (404) 377-6835 E-Mail: mmbdavis@bellsouth.net

Ms. Karen F. Myers, ERDC CEERD-EP-C Environmental Chemistry Branch Vicksburg, MS 39180 Telephone: (601) 634-3652 Fax: (601) 634-2742 E-Mail: myersk@wes.army.mil Mr. Jed Costanza Naval Facilities Engineering Service Center 1100 23rd Avenue Port Hueneme, CA 93043

Dr. Marc Wise Chemical and Analytical Sciences Division Oak Ridge National Laboratory Bethel Valley Road Bldg. 4500-s, Room s-139 Oak Ridge, TN 37831-6120 Telephone: (615) 574-4861 Fax: (615) 576-7956 E-Mail: wisemb@ornl.gov



ESTCP Program Office

901 North Stuart Street Suite 303 Arlington, Virginia 22203 (703) 696-2117 (Phone) (703) 696-2114 (Fax)

e-mail: estcp@estcp.org www.estcp.org