ESTCP
Cost and Performance Report

(CU-9716)

Site Characterization and Analysis Penetrometer System (SCAPS) Heavy Metal Sensors

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COST & PERFORMANCE REPORT
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LIST OF ACRONYMS

μsec	microsecond
As	Arsenic
bgs	below ground surface
Cal Cert	California EPA Department of Toxic Control's Technology Certification Program
cm	Centimeter
CPT	Cone Penetrometer Test
DL-LIBS	Downhole Laser – Laser-Induced Breakdown Spectroscopy
DLT	Detection Limit Threshold
DOE	Department of Energy
DOIT	Demonstrating Onsite Innovative Technology
DOT	Department of Transportation
EPA	Environmental Protection Agency
ERDC	U.S. Army Engineer Research and Development Center
ESTCP	Environmental Security Technology Certification Program
Fe	Iron
FO-LIBS	Fiber Optic – Laser-Induced Breakdown Spectroscopy
ft	feet
g	gram
GW/cm2	gigawatts per square centimeter
Hg	Mercury
hr	hour
Hz	Hertz
ICP	Inductively-Coupled-Plasma
ITRC	Interstate Technology Regulatory Cooperation
IWTP	Industrial Waste Treatment Plant
kV	kilovolt
LIBS	Laser-Induced Breakdown Spectroscopy
LIF	Laser-Induced Fluorescence
m	meter
msl	mean sea level

Nd	Neodymium
Nd:YAG	Neodymium: Yttrium Aluminum Garnet
NRL	Navy Research Lab
PIN	P-type/Intrinsic/N-type diode
ppm	parts per million
PTO	power take off
SCAPS	Site Characterization and Analysis Penetrometer System
sec	second
SERDP	Strategic Environmental Research and Development Program
Si	Silicon
SSC	Space and Naval Warfare System Center
TSTG	Technology Specific Task Group
U.S. EPA	United State Environmental Protection Agency
WGA	Western Governors Association
XRF	X-Ray Fluorescence
YAG	Yttrium Aluminum Garnet

ACKNOWLEDGMENTS

Technical material contained in this report has been approved for public release.

1.0   EXECUTIVE SUMMARY

1.1   BACKGROUND

The contamination at a hazardous waste site must first be delineated before clean up of the site can begin. Site characterization can be very costly, accounting for a third or more of the total cleanup cost. Until recently, the most common method in determining the extent of subsurface cleanup was to collect samples from either soil borings or monitoring wells, then sending them to a laboratory for analysis. This approach is inefficient and expensive.

1.2   OBJECTIVES OF THE DEMONSTRATION

The Site Characterization and Analysis Penetrometer System (SCAPS) was developed to address requirements for improved subsurface measurement of contaminants. SCAPS combines traditional cone penetrometer technology with real-time direct push chemical sensors to rapidly delineate the subsurface distribution of contaminants and hydrogeological conditions. In order to broaden the applicability of SCAPS, the Strategic Environmental Research and Development Program (SERDP) funded the development of several real-time *in situ* sensor technologies for screening of heavy metal contamination in soils. This technology demonstration report documents the performance and cost evaluation of three direct push metal sensor technologies conducted as part of a series of comprehensive side-by-side, field and laboratory evaluations supported by the Environmental Security Technology Certification Program (ESTCP). The technologies include two sensor systems based on Laser-Induced Breakdown Spectroscopy (LIBS) and one system based on X-Ray fluorescence (XRF).

1.3   DEMONSTRATION RESULTS

Field evaluations were conducted at four different sites selected to reflect varying hydrogeological conditions, metal contaminants, and modes of introduction of the metal contaminant into the environment (e.g., dissolved vs. particulate). Test sites included the Lake City Army Ammunition Plant in Independence, MO; Naval Air Station North Island at North Island, CA; Hunters Point Shipyard in San Francisco, CA; and Camp Keller in Biloxi, MS. Performance assessments in which results from the three sensors were compared against inductively-coupled-plasma (ICP) laboratory analysis of discrete samples showed mean accuracy of 91.7%, 97%, and 97%, respectively for XRF, Fiber Optic LIBS (FO-LIBS), and Downhole Laser LIBS (DL-LIBS) for the four site demonstrations. Cost comparison between SCAPS Metal Sensors with conventional Sampling and Discrete Push Sampling with off-site chemical analyses showed a cost advantage for the direct push sensors, on a cost per sample basis, of 98% compared with conventional soil borings and 95% compared to direct push sampling methods.

1.4   STAKEHOLDER/END-USER ISSUES

As a field-screening tool, the direct push metal sensor can delineate the distribution and boundaries of the contaminant source. At sites where the technology is applicable, results can be used to optimize the location, as well as reduce the number of soil borings and monitoring wells necessary to characterize a site. This information can significantly reduce both the overall number of samples

that need to be submitted for costly and time-consuming laboratory analyses and the costs associated with multiple and/or iterative field investigations.

2.0   TECHNOLOGY DESCRIPTION

2.1   TECHNOLOGY DEVELOPMENT AND APPLICATION

Three different direct push metal sensors are described in this report: Fiber Optic LIBS (FO-LIBS), Downhole Laser LIBS (DL-LIBS), and XRF. The following sections describe the motivation, technical details and use of the three-sensor systems.

2.1.1   Background

The contamination at a hazardous waste site must first be delineated before clean up of the site can begin. Site characterization can be very costly, accounting for a third or more of the total clean-up cost. Until recently, the most common way to determine the extent of subsurface contamination was to collect samples from soil borings or monitoring wells and send them to a laboratory for analysis. This approach has proven to be inefficient and expensive. Risk based clean-up strategies may dictate that the clean-up process will not require removal and/or treatment, but rather long-term monitoring to insure that there is no unexpected migration of the contaminant. Consequently, improved methods of monitoring contaminants in the subsurface are important for both the characterization and remediation of a site.

SCAPS (Site Characterization and Analysis Penetrometer System) was developed to address this requirement for improved subsurface measurement of contaminants. SCAPS combines traditional cone penetrometer technology with real-time chemical sensors to rapidly delineate the subsurface distribution of contaminants and hydrogeological conditions. The first chemical sensor fielded with SCAPS, the laser-induced fluorescence (LIF) sensor for petroleum, oils, and lubricants (POLs) has now been successfully commercialized. It also has achieved acceptance by the regulatory community as evidenced by its certification by the California Environmental Protection Agency (EPA), and verification by the U.S. EPA as well as numerous states via the Interstate Technology Regulatory Cooperation (ITRC) group.

In order to broaden the applicability of SCAPS, the Strategic Environmental Research and Development Program (SERDP) funded the development of sensor technologies for other contaminants. In particular, sensor systems have been developed for real-time *in situ* field screening of heavy metal contamination in soils. These three heavy metal sensor technologies include two sensor systems that are based on laser-induced breakdown spectroscopy (LIBS) and a third technology based on X-ray fluorescence (XRF). All three technologies emerged from the SERDP sponsored Accelerated Tri-Service SCAPS Sensor Development Program. This report describes the demonstration and validation of the capabilities of these three SCAPS metal sensing technologies to rapidly screen sites for the distribution of subsurface heavy metal contamination.

2.1.2   Laser Induced Breakdown Spectroscopy (LIBS)

LIBS involves the analysis of the spectral emission from a laser-induced spark. The spark is generated by focusing the high power emission from a pulsed laser onto a small spot on a sample material, resulting in a power density on the sample in excess of several gigawatts per square centimeter (GW/cm^2). Within the small volume about the focal point, rapid heating, vaporization, and ionization of a small amount of the sample material occurs. The subsequent laser-induced

plasma emission is spectroscopically analyzed to yield qualitative and quantitative information about the elemental species present in the sample.

The LIBS technique has been used successfully in the laboratory to identify and quantify elemental species in solids, liquids, and gases. The method is well suited to *in situ* detection of heavy metal contamination in soil because it is highly sensitive while requiring no sample preparation. Because the emission of different elements occurs at unique wavelengths, the method can be used for simultaneous analysis of multiple components.

The two LIBS probes developed under SERDP funding differ in the method of delivery of the excitation beam used to generate the laser-induced spark. The first configuration, fiber optic LIBS (FO-LIBS), utilizes optical fibers to deliver the excitation energy from a laser located in the truck to the sample. In the second configuration, downhole-laser LIBS (DL-LIBS), the laser is physically located in the CPT probe.

LIBS can generally be used to excite emission spectra from any atomic species with species dependant efficiency. In order to perform LIBS measurements remotely and in real time, as required by CPT-based sensor systems, several operational and design tradeoffs must be made between analytical precision/accuracy and timeliness of data collection. Because the two LIBS techniques evaluated in this study both use optical fibers to deliver the emitted spectra to an up-hole detection system, the choice of spectral lines used to characterize the species under study must fall in a spectral range that is consistent with the transmission capability of the optical fiber. Also, since the LIBS measurements are done *in situ*, there are matrix effects due to grain size or moisture content, which can affect the intensity of the response of the LIBS systems.

2.1.2.1 The FO-LIBS Sensor

The FO-LIBS sensor, shown schematically in Figure 1, utilizes the Q-switched output of a Nd:YAG laser operating at 30 Hz at 1064 nm which is delivered via a fused-silica fiber to the probe. A low f/# optical system (f/# ~1) is used in the probe to focus the laser output. This minimizes the size of the focused image of the optical fiber face on the sample and provides a power density at the sample that is sufficient to generate a laser-induced plasma.
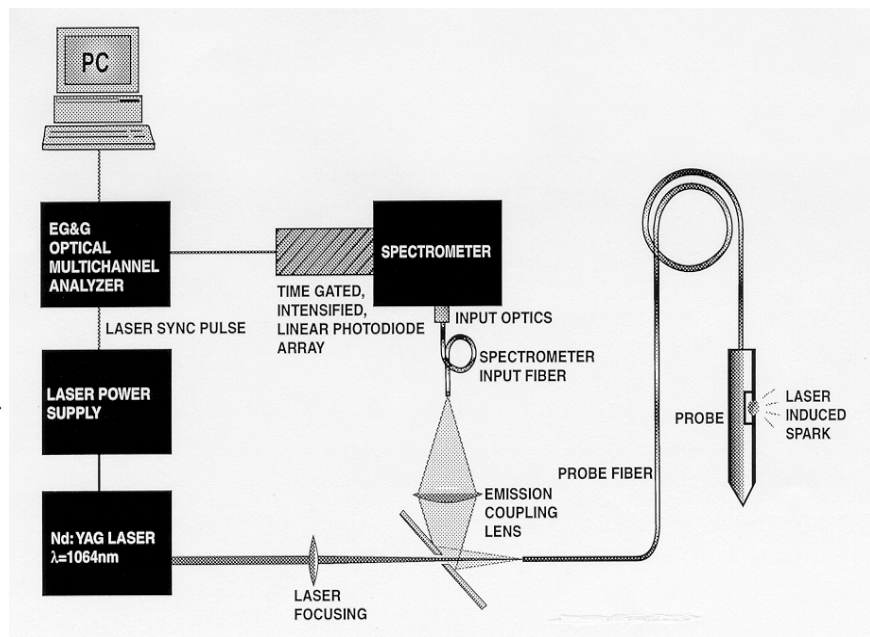

Figure 1.   Schematic of Fiber Optic LIBS (FO-LIBS) System.

Details of the FO-LIBS probe are described in the ESTCP final report (Lieberman et al., 2001). Briefly, the light emitted from the fiber in the probe is collimated, turned by a quartz prism, and focused by a short-focal-length quartz

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lens through a sapphire window in the probe. Because the soil is pressed against the window, the lens-to-sample distance is held fixed. Contamination is not an issue because the probe is entirely sealed, allowing for operation below the water table.

It was observed that after several thousand laser pulses, the sapphire window became pitted by the LIBS spark, resulting in degradation of window transmission; therefore, a system was designed to reposition the spark on the window surface (Theriault et al., 1998). This design incorporates two stepping motors to drive a block that houses the optics and provides two-axis control of the position of the spark on the window surface. Due to the relatively small size of the focused spot, compared to the size of the sapphire window, the number of discrete positions available is in excess of 1,000. After the window surface has been completely scanned (typically one week), a new window is inserted in the probe window housing at a replacement cost of $17.00.

The excitation and emission light are decoupled using the configuration shown in Figure 1. The excitation beam is focused by a 25-cm focal length lens through a 2-inch aluminum mirror containing a small hole at 45°. Since the returning LIBS signal fills the entire numerical aperture of the fiber, most of the return signal is turned 90° by the mirror with only a small loss (~5%) through the hole. Like the probe design, this configuration is robust and can be operated over a large spectral range allowing the analysis of different spectral regions with no system adjustment or component substitution.

The spark emission is fiber-optically coupled to a spectrograph that disperses the light onto a time-gated, intensified, linear detector array. The time gating of the detector during data collection is crucial due to the initial broadband background continuum during the evolution of the plasma. Resolution of the signal from the metal emission is enhanced by delaying the application of the gate pulse to the detector until after the short-lived broadband background has decayed. The duration of the gate pulse is chosen to correspond with the duration of the metal emission to optimize the signal-to-noise ratio.

In order to reduce the standard deviation of the data, signal averaging is used. Typically, each measurement is the result of 300 single-shot spectra which are accumulated in the memory of the detector controller. For a laser with a 30Hz repetition rate, acquisition of 300 spectra requires 10 seconds. Depth resolution can be controlled by the operator and is typically 1 inch.

Detection limits for LIBS in general, and the FO-LIBS sensor in particular, are a function of several variables, including the intensity of the emission line(s) for a specific metal, plasma temperature, and detector signal to noise, etc. For *in situ* measurements, soil type and moisture content are also important variables. For dry soil, with a grain size of 600-800 µM, typical detection limits for the FO-LIBS sensor of 0.7, 5.2, and 19 ppm for lead, chromium and cadmium, respectively, have been reported (Theriault et al., 1998).

2.1.2.2 The DL-LIBS Sensor

There are two significant design differences between the FO-LIBS sensor and the DL-LIBS sensor system.

First, the DL-LIBS sensor has a compact Nd:YAG excitation laser located in the probe itself (Miles et al., 1997). This provides the capability for higher irradiances (1000 GW/cm2) and hotter plasmas than a fiber-illuminated system for two reasons. First, the fiber has a limit to the amount of energy that can be successfully transmitted through it without damage. Second, a multimode fiber system as used in FO-LIBS can never achieve diffraction-limited, focused spot sizes and must spread the laser energy over a larger area. This results in a weaker signal compared to a laser in the probe system such as DL-LIBS which has diffraction limited performance. Additionally, the DL-LIBS system uses a relatively slow F/3.2 optical transmit section allowing for a large depth of focus, minimizing any effect soil position has on irradiance.
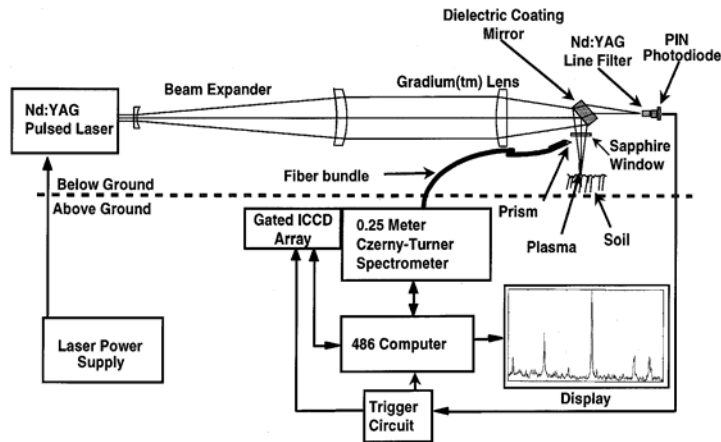
Figure 2. Schematic of Downhole Laser LIBS (DL-LIBS) System.

A second difference is that the sapphire window is recessed from the soil wall. Unlike a window in contact with the soil, a recessed window is not subject to damage from the plasma. See Figure 2. Laser energy is focused directly onto the soil (without passing through a fiber) as the probe is withdrawn from the push hole. This approach requires that measurements be made as the probe is withdrawn rather than advanced and uses a special probe design with a drop-off sacrificial sleeve that is left at the bottom of the hole.

DL-LIBS collects different data in the push and retraction modes. All downhole data is recorded on the computer's hard disk as it is acquired. During pushing, the following data is recorded as a function of depth: cone force, sleeve force, hydraulic ram force, soil type, soil dielectric constant, and volumetric soil moisture. During retraction, DL-LIBS data is collected again as a function of depth in the form of integer counts per unit time per wavelength interval for all wavelengths in the region of interest. Typically, the DL-LIBS probe integrates for 100 microseconds (μsec) to achieve the sensor detection limits for average concentrations. Currently, sampling is done every three seconds, resulting in a spatial resolution of about 0.8 cm per sample.

Detection limits for DL-LIBS are dependent on the standard deviation of the background or low concentration sample measurements. The three-sigma detection limit is defined as the concentration (determined via the instrument calibration curve) corresponding to three times the standard deviation of the normalized intensity of the metal peak of interest divided by the slope of the concentration curve. In DL-LIBS, the peak intensity of the metal transition of interest is divided by the integral of all intensities in the spectrum. This aids in reducing the effects of shot to shot pulse energy variations. A typical detection limit for the SCAPS DL-LIBS Metals Sensor is 10 ppm for lead.

2.1.2   The X-Ray Fluorescence (XRF) Sensor

X-ray fluorescence operates by detecting characteristic x-rays emitted by the atoms in a sample. An x-ray source bombards a sample with incident x-rays, where the atoms become excited and emit fluorescence x-rays, which are detected as a function of the energy of the x-rays. At the atomic level, an incident x-ray excites an electron from a core level, which then decays producing a

fluorescence x-ray. Since the electron energy states producing a fluorescence x-ray are entirely within the atom, the x-ray is produced with a constant and well known energy (different for each type of atom).

X-ray fluorescence is a well-established, non-destructive method of determining elemental concentrations at part per million (ppm) levels in complex samples. It operates with no sample preparation and is currently used as a laboratory analysis method for samples obtained from hazardous waste sites. Its characteristics are ideally suited to field analysis.

Recent advances in instrumentation have allowed the construction of a spectrometer, which will meet the size restrictions imposed by the diameter of the cone penetrometer probe. This configuration is shown in Figure 3. High sensitivities can be achieved while the head is stationary for several minutes. Continuous monitoring at lower sensitivities is possible, depending on descent rates, contaminant concentration, and soil type.
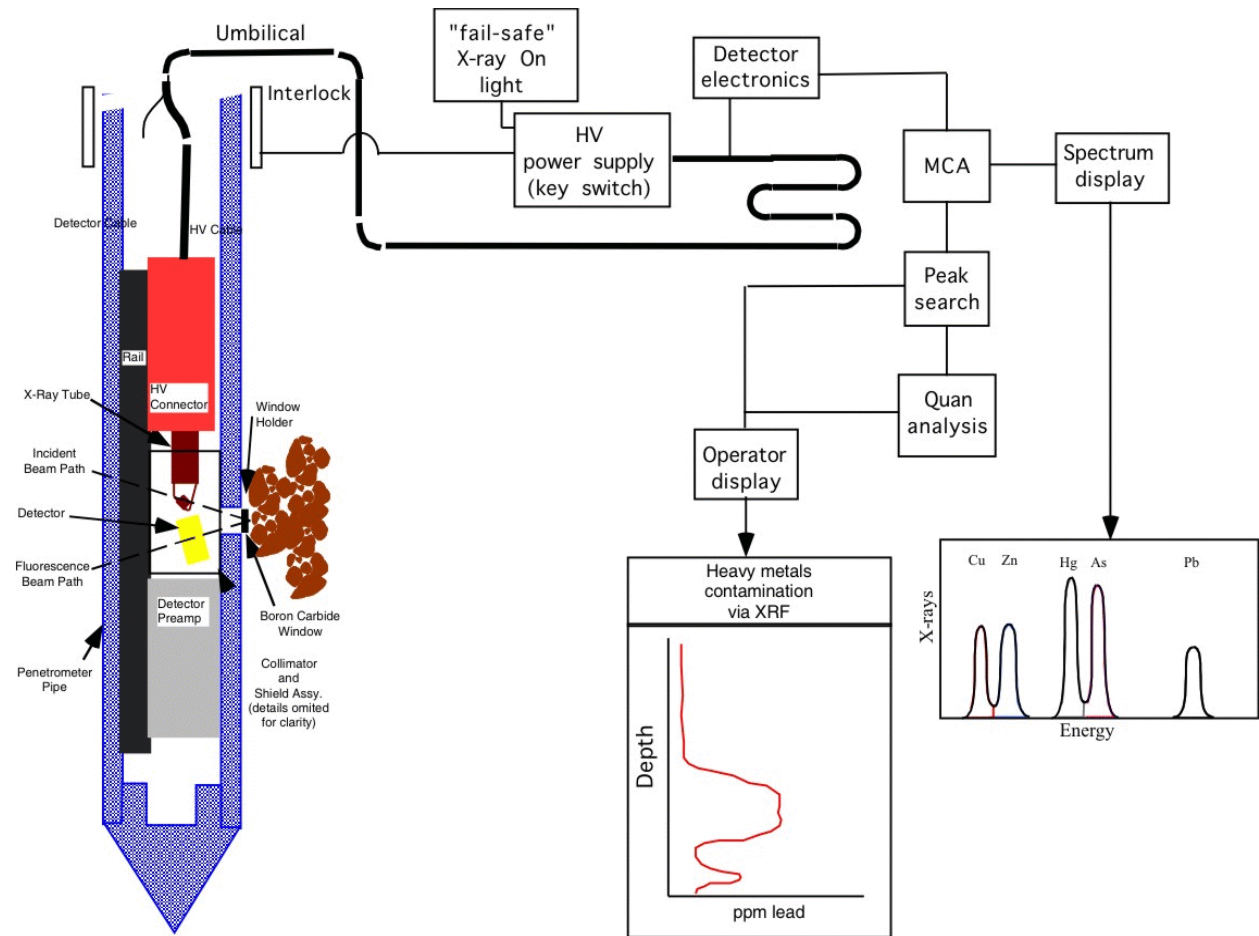
The XRF metals sensor consists of three subsystems (refer to Figure 3): the actual below-ground probe, the umbilical cable, and the above-ground electronics package (Elam et al., 1998). The probe contains the x-ray source, detector and preamp, appropriate x-ray optics, the mounting system, and the rugged x-ray window. A sealed x-ray tube is used as the excitation source, both to achieve adequate detection limits in the allotted time and to avoid the licensing and safety problems of a radioactive source. The detector is a silicon P-type/Intrinsic/N-type (Si-PIN) diode in a small case

with self-contained cooling, connected to a low-noise preamp in close proximity. The preamp provides sufficient signal to drive the umbilical cable. The x-ray window is 1 mm thick boron carbide, a low atomic number material that is relatively transparent to x-rays in the relevant energy range.

The umbilical cable conducts high voltage and filament power required by the x-ray tube, the electronics and cooling power for the detector and preamp, and the signal pulses from the detector. It is fully shielded both for noise immunity and high voltage safety. It also contains signal cables for stratigraphy sensors. The sensor has provisions for routing signal cables and grouting tubes through the sensor.

The above ground electronics package contains the x-ray tube power supply with safety interlocks and the driver electronics for the detector. The x-ray power supply for the x-ray tube provides adjustable high voltage (to 30kV) and filament voltage, which is regulated to provide constant emission current and thus constant x-ray output. The detector's electronics provides the necessary power supplies and contains pulse-shaping circuitry. Its output connects to a standard multichannel analyzer for data collection and analysis. The electronics package connects to an interlock shield insuring that the probe is inserted into the ground before the x-ray tube is energized. This shield also allows test samples to be measured above ground via a sample introduction port. This port allows calibration samples, blanks, and test samples to be run during field operations. The remainder of the above ground system consists of a multichannel analyzer and a portable computer to collect, interpret, and display the data.

Once the sensor window is brought into contact with the subsurface soils, the x-ray tube is energized and an XRF spectrum is collected for 100 seconds. This spectrum is then stored and analyzed in accordance with the methods outlined below. This takes a few seconds while the sensor is moved to a new depth, and the process repeated. This provides the best detection limits but requires collecting data at each depth. The sensor can also be used in a continuous mode where data is collected during descent. Any hot spots will be visible as rapid changes in the spectrum, and can be investigated as desired. The entire 100-second spectrum gives an indication of the average analyte concentration throughout the depth covered during spectrum collection. This provides a compromise between detection limits, quantitation, and rapid survey coverage. Experiments have determined that a push rate of 0.5 cm/sec is ideal for this purpose. Hot spots above 2000 ppm can be detected on-the-fly (Unsell, 1998) while the ability to achieve the sensor detection limits for average concentrations is retained.

Detection limits for x-ray fluorescence spectra depend almost entirely on counting statistics in the spectrum. The three-sigma detection limit is defined as the concentration (determined via the instrument calibration curve) corresponding to three times the standard deviation of the background intensity under the peak (measured on a low concentration sample or on the same region of the spectrum from a blank). The standard deviation is the square root of the number of x-ray counts. This method provides a reliable limit for detection by automated peak calculation algorithms. The limit of quantitation is ten times this standard deviation. A typical detection limit for the SCAPS XRF Metals Sensor is 100 ppm for lead.

XRF is a well-developed and widely accepted method for measuring metal content. Its capabilities are well known and its comparability to laboratory analysis results have been documented (MCDONALD et al., 1996). Matrix and interference effects are thoroughly understood and it is the

subject of a draft EPA method entitled "Field Portable X-ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment" (FORDHAM, 1997). Its only weakness is that detection limits for most metals are in the 10 ppm range with current instruments.

2.2   PROCESS DESCRIPTION

Figure 4.   Photograph of Navy Cone Penetrometer Test (CPT) Vehicle.

All three sensors were designed for deployment with a standard 20-ton cone penetrometer platform (Figure 4). Cone penetrometery has long been used to characterize soil for geotechnical parameters, including soil classification, strength, and liquefaction potential. This is accomplished by advancing (pushing) an instrumented probe into the ground using a truck mounted hydraulic system. The hydraulic system translates the weight of the truck (reaction mass) into pushing force. A standard 20-ton system can advance a 1 meter-long by 3.57-cm diameter probe into the ground at a rate of approximately 1 meter per minute in accordance with American Society of Testing and Materials (ASTM) Method D3441 (American Society for Testing and Materials, 2001). Probes can be pushed to depths in excess of 50-m in normally compacted soils. Because the cone penetrometer vehicle is designed as a stand-alone mobile system, the truck can be driven to the site and simply positioned over the selected push location. A generator operated off the truck diesel engine and regulated through an uninterruptible power supply with a battery bank supplies all power for equipment. Other than clearing the push location for utilities and obtaining "drilling" permits (requirements vary by locality), there are no other set-up requirements. After the sensor probe is withdrawn, the push hole can be grouted using a second probe containing an umbilical through which grout is pumped, thereby hydraulically sealing the push hole.

Typically, a minimum crew of at least three people is required for most field operations. This includes the sensor operator and two push room personnel. The required training for the push room personnel are similar to that required for the standard geotechnical cone penetrometer test (CPT). The sensor operator should be computer savvy, have a background in science or engineering, and have detailed system component training in order to diagnose and correct field equipment problems. All personnel conducting field investigations at potentially contaminated sites are required to complete the 40-hr. Hazardous Waste Worker Training and receive annual 8-hr Hazardous Waste Worker Update training.

2.3 PREVIOUS TESTING OF THE TECHNOLOGY

The sensitivities of all three technical approaches have been documented at or below the regulatory limits for metal contaminated soils under laboratory conditions. The FO-LIBS probe was successfully field tested in January, 1996. The tested probe used a 'fixed focal point' design (i.e., laser ablation occurred at the same place on the window). The initial test consisted of six pushes at uncontaminated sites with soils that ranged from medium to coarse grain silty sand. The emission of naturally occurring Fe in the soil was profiled at depths up to 20 ft. The spectra obtained from a pure Fe powder was shown to overlay with the emission lines observed from the *in situ* soil measurements in the region from 390 nm to 440 nm. In these initial tests, the same probe and window were used for the duration of the experiment and withstood several thousand laser pulses with no measurable loss in transmission. Subsequent tests encountered difficulties with severe transmission losses due to pitting of the sapphire window. The probe was redesigned to provide a capability to reposition the focusing optics onto an undamaged portion of the window. This 'scanning' FO-LIBS probe was field tested at a lead battery dumpsite at Mare Island Naval Shipyard in April 1997. The distribution of the battery waste at the site was variable. Several contaminated locations were identified that coincided with plastic battery casings and metal at the surface.

After fabrication of the DL-LIBS probe in 1996, it was installed in the SCAPS truck, and system checks were conducted at the ERDC to ensure system operability. The DL-LIBS probe was then tested at the Louisiana Army Ammunition Plant. Nine pushes were performed in a landfill, which was primarily used to dump chromium-bearing sludge. Chromium was readily detected in all holes pushed at the landfill. Field investigations also showed that no meaningful data could be obtained when the probe was pushed below the water table. In August of 1997, the DL-LIBS probe conducted field investigations at the Joliet Army Ammunition Plant in Joliet, IL. The DL-LIBS sensor detected lead contamination from lead azide, which was used during fuse manufacturing. Depth profiles indicated a high degree of lead contamination at 2 feet below ground surface (bgs). These field tests demonstrated the probe's capabilities in soil media ranging from sandy soil to expansive clay soil and its ability to detect two target metals of DoD concern: chromium and lead.

The XRF probe was also tested at the Joliet Army Ammunition Plant in 1997. Eleven pushes were performed. Acceptable data were obtained for all the holes pushed.

In these previous testing of the three sensors, confirmational laboratory data were not obtained. The purpose of these initial field investigations was (1) to demonstrate that the LIBS and XRF sensor systems had the capability to obtain field-screening data, and (2) to show that the probe configurations were robust.

2.4 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

2.4.1 Advantages of the Technology

The direct-push metal sensors were developed to provide real-time *in situ* measurements of subsurface metal contamination at hazardous waste sites. The method is not intended as a compete replacement for traditional soil borings and monitoring wells. Instead, the metals sensors are *in situ* filed screening techniques for qualitatively characterizing the pattern of subsurface metal contamination prior to the installation of groundwater monitoring wells or soil borings.

Subsequently, the site can be further characterized with limited numbers of carefully placed stab samplings, borings, or wells. In addition, characterization can be expedited based on immediate availability of results minimizing or eliminating the need for return sampling efforts to compete the delineation zone of contamination. Finally, direct-push sensors facilitated the characterization of contaminated sites with minimal exposure for site personnel and the community to toxic contaminants while minimizing the volume of investigation-derived waste normally generated by conventional site characterization activities.

2.4.1.1 Sensor Advantages

In general, the detection limits are lower for LIBS than XRF based sensors for on-the-fly measurements (approx 1-10 ppm for LBS vs. approx 1000 ppm for XRF). However, XRF detection limits can be improved to 100 ppm or better by using longer integration times.

It has been suggested that because of the very high irradiances ($1000 \ GW/cm^2$) that can be achieved with the down-hole laser used in the DL-LIBS system that the system would be expected to hotter plasmas and hence improved detection capabilities over fiber optic systems (Miles et al., 1997). However, recent evidence appears to indicate that optimal results are obtained using laser pulses with 20-50 mJ pulses of 5-20 ns duration to produce peak powers of a few megawatts (Winefordner, 2000).

The major advantage of XRF over LIBS technique is that the XRF method integrates a larger sample area (volume) than the LIBS methods.

2.4.2 Limitations of the Technology

2.4.2.1 CPT Limitations

The three sensor technologies were designed for cone penetrometer truck deployment. Consequently, all are subject to the push limits of this particular type of CPT platform. The dimensions of the truck require a minimum access width of 10 feet, and a height clearance of 15 feet The access limits for a 20-ton CPT vehicle are similar to those for conventional drill rigs and other heavy excavation equipment. The CPT sensors and sampling tools may be difficult to advance in subsurface lithologies containing cemented sands and clays, buried debris, gravel, cobbles, boulders, and shallow bedrock. As with all intrusive site characterization methods, it is extremely important that all underground utilities and structures be located before undertaking site characterization activities.

2.4.2.2 Sensor Limitations

Because of the high specificity of the line spectra obtainable from LIBS measurements, the method is, in general, qualitatively very good for identification of most metal contaminants. The primary limitation on the qualitative *in situ* identification of a particular species is the presence of other species that may have interfering spectra. For example, a naturally occurring species that contains a high density of lines throughout the visible spectrum is iron. Resolution of the spectrum of a given contaminant above the background (primarily iron) is a matter of using a spectrometer with adequate dispersion in the spectral region of interest and is not generally a problem. Because of the manner

in which the two LIBS methods ablate a small sample (typically ~10-9g) of soil per measurement, they are essentially point measurement methods that are subject to sampling errors which can be reduced by spatial signal averaging. This can be achieved by sampling with high spatial resolution. Also, due to the relatively high standard deviation associated with a single LIBS measurement, temporal signal averaging is utilized to reduce the detection limit. Variation in soil matrix is another factor that potentially limits the analytical precision and accuracy associated with LIBS measurements. As discussed in Section 5 of this report, site-specific calibration curves are used to minimize the affect of variations in the soil matrix. Another potential limitation of using optical fibers for transmitting the emission signal to the detector system is the relatively high attenuation of the optical fibers in the deep ultra-violet spectral range. This may limit the use of some emission lines for some elements. However, most elements have multiple emission lines and provide usable lines within the working range of the fiber.

The major limitation of the FO-LIBS sensor was degradation of the window that was overcome use of the scanning optical system. There are no specific limitations other than those typical of LIBS by in general, as listed in the previous section.

Because DL-LIBS utilizes a compact laser in the probe, it has certain restrictions due to its ultra-small size. The primary limitation is pulse rate where the laser is currently limited to 1/3 Hz with ambient laser cooling. If the laser is cooled by liquid, the pulse rate can reach 1-2 Hz. For the current DL-LIBS configuration, the lifetime of the laser will be dramatically reduced if pulse rates exceed 1/3 Hz.

The optical window, which protects the interior of the DL-LIBS probe from water leakage, is recessed. The laser energy used to create the micro plasma is focused in front of this window. Consequently, there is a gap between the focal point and the optical window. Should the probe be pushed into non-cohesive soil (e.g., free-flowing water borne soils in the saturated zone or free-flowing soils in the vadose zone), this slot may fill with soil and the sensor may not be able to obtain data.

Certain x-ray lines from different elements occur at energies very close in energy and thus overlap in the spectrum. The cooled Si-PIN detector in the SCAPS XRF Metals Sensor has an energy resolution of 250 eV, which resolves all but the most severe overlaps. A typical example is the overlap of the K-beta line of an element with the K-alpha line of an element with one lower atomic number. Since the interfering K-beta line is 5 to 10 times weaker than the K-alpha line, the interfering metal must be present at large concentrations to cause a problem. Another example is the lead (Pb) L-alpha line interference with the Arsenic (As) K-alpha line. Lead can be measured using the L-beta line to avoid interference with little or no loss of sensitivity. In the presence of large amounts of lead, arsenic must be measured with the As K-beta line, whose lower intensity causes a corresponding loss of sensitivity.

2.4.2.3 Matrix and Moisture Effects

XRF sensor response is affected to some extent by the composition and particle size of the soil matrix, but the effect is not serious for field screening usage. For the XRF sensor, soil moisture effects for zero to about 20% moisture are negligible. For saturated soils the effect is about 20%. The most significant effects are from other heavy metals present and from the size of the metal

particles. Since lead oxide is 98% lead by weight, lead present in the form of lead oxide particles will absorb x-rays depending on their size and affect the signal accordingly. For example, lead sulfide with a particle size of 12 microns reduces the signal by about 20% (Criss, 1976). If the lead is dispersed on the soil then the signal is not affected. Since the soil consists mostly of low atomic number materials, the particle size of the soil has little effect.

Matrix and moisture also affect the LIBS technology sensors. The primary variables affecting quantification of the LIBS measurement are soil moisture and soil grain size ((Miles et al., 1992), (Theriault et al., 1999)). Specifically, given two soils with the same contamination level, a clay soil will exhibit a weaker LIBS signal than a sandy soil. Likewise, a wet soil will exhibit a weaker signal than a dry soil of the same contamination. For these reasons, LIBS sensor responses are more accurate in dry soil and when the effects of soil moisture and soil grain size are monitored and used in the calibration algorithms. Other research has indicated that soil pH may also have an effect on LIBS signals (Cortes et al., 1996).

The presence of complex mixtures of contaminants (e.g., a site where organic contaminants are present along with heavy metals) is not expected to significantly affect the performance of either the LIBS or XRF metal sensors. Both sensor technologies are highly specific for the target analytes. In addition, because extremely high temperatures are generated during plasma in the LIBS analysis, it is expected that organic compounds will be broken down to elemental species during the analysis. In fact, LIBS has been used successfully to quantify metals directly in oil (Fichet et al., 2001). For XRF, the presence of organic contaminants, in addition to heavy metals, would not impact the detection abilities of the XRF sensor significantly. High levels of organics may cause as much as 10 to 15% errors in quantitation due to the difference in matrix absorption versus typical (aluminosilicate) soils.

Physical "smearing" or "drag-down" of contamination by either the LIBS sapphire window or the XRF boron carbide window is not a problem (even when the probe is pushed through layers of free product) as long as the window is properly designed (i.e., the window must not be recessed relative to the surface of the probe). Both sapphire and boron carbide are very hard materials (nearly as hard as diamond) and do not tend to absorb contaminants. Years of experience with Laser-Induced Fluorescence (LIF) probes employing sapphire window has shown that there is no memory effect when the probe is pushed through thin layers of soil heavily impacted with POLs (petroleum, oils and lubricants) (Lieberman et al., 1991). Similarly, measurements with the XRF probe showed that when the probe is pushed through a layer containing greater than 10% lead oxide, the signal returns to below detection limit a few centimeters past the layer. Finally, visual data collected with a video imaging probe equipped with a sapphire window, show conclusively that even when a probe is pushed through a layer of free product consisting of petroleum hydrocarbons and chlorinated solvents, there is no "smearing" of the window by the contaminant (Lieberman et al., 1998).

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3.0   DEMONSTRATION DESIGN

3.1   PERFORMANCE OBJECTIVES

The primary performance objective for each of the metal sensors tested in this evaluation is that they provide semi-quantitative data on the *in situ* presence of heavy metal contamination. Specific claims for the three SCAPS metal sensors are noted below.

1.   Near continuous measurements generated by the sensor provide detailed mapping of the distribution of subsurface heavy metal contamination. These three metal sensors typically collect data at 0.2 ft intervals.

2.   Good qualitative agreement with the pattern of contamination derived from analytical measurements (EPA Method 6010) of semi continuous soil samples.

3.   Direct comparison of sensor data with samples collected using conventional CPT soil sampler tools by pushing in close proximity to the metal sensors' pushes show good agreement with conventional laboratory methods (EPA Method 6010).

4.   Collection and storage of multi-channel atomic emission spectra throughout each push.

5.   Data from the three SCAPS metal sensors is available in real time as the sensor is advanced into the ground or retracted from the subsurface. This allows real time decisions on how deep to collect verification samples on the site.

6.   The location of future pushes can also be decided in real time at the site using the information available from previous pushes. This can greatly speed the delineation of the contamination plumes.

7.   The three SCAPS metal sensors can detect the presence of heavy metals which includes, but may not be limited to, lead, cadmium, chromium, mercury, arsenic, zinc and copper in the bulk soil matrix.

8.   Measurements can be made to depths up to 150 feet in normally compacted soil, when the three SCAPS metal sensors are used in conjunction with an industry-standard 20-ton penetrometer push vehicle.

9.   Geotechnical sensors (cone pressure, sleeve friction) may be integrated with the three SCAPS metal sensors to provide simultaneous continuous geotechnical and stratigraphic information to aid in interpreting contaminant distributions.

10.   The *in situ* nature of the three SCAPS metal sensors minimizes possibilities for contaminating or altering soil samples that are inherent with traditional collection, transport and analysis procedures.

11.   The three SCAPS metal sensors provide more accurate measurement of the depth of the contaminant because the three SCAPS metal sensors do not suffer from sampling difficulties

encountered by other common methods such as soil boring/split spoon sampling and stab sampling.

12.   The SCAPS sensor probes produce minimal IDW. A typical 6-meter push with the SCAPS probes produces approximately 40 liters of water IDW (used to clean the push rods). A typical 6-meter boring produces 210-285 liters of soil IDW as well as 40 liters of water used to clean the augers. Furthermore, the penetrometer rods are steam cleaned directly upon removal from the ground, reducing potential contamination hazards to site personnel.

3.2   SELECTION OF TEST SITE(S)

Test site were selected using the following criteria.

•   The U.S. Department of Defense (DoD) (as site owner) agreed to allow access to the site for the demonstration.

•   The site is accessible to two-wheel drive vehicles.

•   The soils at the site have been contaminated by heavy metals that are detectable by the three SCAPS metal sensor technologies.

•   The soil types at the site consist of unconsolidated sediments of native sands, silts, clays, and gravel. These soil types are suitable for CPT pushing and present good subsurface matrices for the three SCAPS metal sensor technologies.

•   The soil contaminant levels identified during previous investigations ranged from below analytical laboratory detection limits to heavily impacted. These data indicate contamination in the subsurface in concentration ranges comparable with the SCAPS metal sensing technologies to be demonstrated.

3.3   TEST SITE HISTORY AND CHARACTERISTICS

Demonstration of the SCAPS Metal Sensors was conducted at four different test sites (Table 1). Each of the four test sites is described in the following sections.

Table 1.   Metal Sensor Test Sites and Target Contaminant.

Site Name	Location	Site Designation	Target Contamination
Lake City Army Ammunition Plant	Independence, MO	LCAAP	Lead
Naval Air Station North Island	North Island, CA	NASNI	Chromium
Hunters Point Shipyard	San Francisco, CA	HPS	Chromium
Camp Keller	Biloxi, MS	Camp Keller	Lead

3.3.1   Lake City Army Ammunition Plant, Independence, Missouri

Lake City Army Ammunition Plant (LCAAP) is located in Jackson County, Missouri, mostly within the eastern corporate boundary of Independence, Missouri, and 23 miles east of Kansas City, Missouri. The SCAPS metal sensors were evaluated LCAAP Site 30, a Demolition Dump.

LCAAP was the first new government-owned facility in the early 1940's to expand small arms ammunition production. Operations at LCAAP (i.e., the manufacture, storage, and testing of ammunition) have resulted in the use of various process waste treatment systems and onsite disposal. Chemicals used onsite in the production process includes soaps, detergents, bleaches, hydrochloric acid, sulfuric acid, nitric acid, explosive compounds (e.g., lead azide and lead styphnate), phosphate cleaners, petroleum and lubricating oils, trichloroethane, trichloroethene, and other cleaning solvents. The waste for the production areas includes mixtures and reaction products of these chemicals. Previous investigations have indicated that heavy metals, including arsenic (As), barium (Ba), beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), silver (Ag) and zinc (Zn), are present on the surface and/or at depths up to 10 feet.

The Area 30 Demolition Dump is located in the northwest portion of LCAAP. This site is near the LCAAP boundary and adjacent to the community of Lake City. It was used by the LCAAP fire department from 1951 to 1967 to burn wooden boxes. Antimony, barium, cadmium, copper, lead, mercury, silver and zinc have been detected above background. Antimony, lead, and copper have been found in high levels, both on the surface and 5 to 7.5 feet bgs. Detection of lead ranged from 200,000 ppm at depth to 25,000 ppm on the surface. Lead contamination was evaluated at this site by the three SCAPS heavy metal sensors.

Lake City Army Ammunition Plant Area 30 is above alluvial sediments of the main paleochannel, underlain by 10 feet of silty clay which grades sharply into medium grained sand. Subsurface media at Area 30 fluctuates between medium and coarse-grained sand until bedrock is encountered at 88 feet. The surficial soil underlying the area is Napier silt loam. Ground water is from 4 to 8 feet bgs. Ground water flow direction is in general to the south at a gradient of 0.0066 ft/ft. The terrain is gently sloping to the east with a total relief of less than 5 feet. Vegetation is mowed grass.

3.3.2   IWTP at Naval Air Station, North Island, California

The Industrial Waste Treatment Plant (IWTP) is located in the northern end of Naval Air Station, North Island (NASNI), which is in southern San Diego County, California, across the San Diego Bay from the city of San Diego. Until the middle 1940s, North Island and Coronado Island were separated by a narrow tidally influenced inlet, or bight, at which time the Navy filled this area with dredge material. The city of Coronado adjoins NASNI to the southeast and is the nearest civilian population center. The SCAPS metal sensors evaluated the Paint Waste Sludge Basin of the IWTP at NASNI.

NASNI was commissioned in 1917 and used to train pilots and aircraft mechanics. Operations at NASNI, including the repair and service of fleet squadrons, have resulted in the use of various waste processing systems and onsite disposal. The IWTP was built in 1972 and used to process nine waste streams containing hazardous materials.

Initially, most of the wastes were disposed of in unlined impoundments. In 1976, the unlined surface impoundments were lined with either concrete or PVC. Prior to liner installation, approximately 12 inches of contaminated soils were removed from the surface of each impoundment. The Paint Basin is one of four waste sludge basins built in 1973 on the east side of the IWTP. It was used for evaporation of paint chip sludge from water curtain spray booths and consisted of one concrete-lined basin that measured 25 feet by 25 feet by 3 feet deep. The concrete liners were reinforced with steel rods, with each liner being approximately 4 inches thick. However, several cracks were found along the joints where the basin floors intersected the sidewalls. These cracks provided the most probable conduits for contaminant leakage and migration into the underlying sediments. Previous investigations have indicated that heavy metals, including primarily chromium (Cr) with much smaller amounts of barium (Ba), cadmium (Cd), copper (Cu), lead (Pb), nickel (Ni), and zinc (Zn), are present beneath the Paint basin. The three SCAPS heavy metal sensors were deployed to evaluate chromium contamination at this site.

The NASNI Industrial Waste Treatment Paint Basin is above sand and silt sediments of the Late Pleistocene Bay Point Formation which is composed primarily of marine, fossiliferous, loosely consolidated fine to medium grained brown sand, underlain by undifferentiated granitic rocks of the Southern California Batholith and prebatholithic metavolcanic rocks. Ground water is present at approximately 20 feet bgs, but is subject to minor fluctuations as a result of tidal forces. The terrain is topographically flat. The concrete liner of the paint basin is in place and contains holes drilled from previous investigations.

3.3.3 The Former Ship Repair Area (Parcel D), Hunters Point Shipyard, San Francisco, California

The main portion of Hunters Point Shipyard (HPS) is situated on a long promontory located in the southeastern part of San Francisco extending eastward into San Francisco Bay. The HPS property consists of about 936 acres; 493 of which are on land, and 443 of which are below bay waters. Parcel D is a 128-acre tract of land located in the southeast central portion of HPS.

The land at HPS can be divided into three functional areas: (1) the industrial production area, which consists of the waterfront and shop facilities for the structural machinery, electrical, and HPS service groups; (2) the industrial support area, which consists of supply and public works facility; and (3) the non-industrial area, which consists of former Navy personnel residential facilities and recreation areas. The former ship repair area in the south and southwest portions of HPS (Parcel D) was investigated.

The promontory on which HPS is located has been recorded in maritime history since 1776, first as Spanish mission lands used for cattle grazing and later, in the 1840s, for its dry dock facilities. The Treasure Island Naval Station-Hunters Point Annex also known as the Hunters Point Naval Shipyard was established in 1869 as the first dry dock on the Pacific Coast. In 1940, the Navy obtained ownership of the shipyard for shipbuilding, repair, and maintenance activities. After World War II, activities shifted from ship repair to submarine servicing and testing. The Navy operated Hunters Point Annex as a shipbuilding and repair facility from 1941 until 1976. Between 1976 and 1986, the Navy leased most of the shipyard to Triple A, a private ship-repair company. The shipyard was an annex of Naval Station Treasure Island until 1974 when the Navy's Engineering Field Activity West assumed the management of it. In 1987, PCBs, trichloroethylene and other solvents,

pesticides, petroleum hydrocarbons, and metals including lead were confirmed at a number of shipyard locations. These findings and the shipyard's proximity to an off-site drinking water source (the aquifer used by a water bottling company) resulted in the EPA placing HPS on the National Priority List in 1989. However, subsequent Navy investigations indicate that the aquifers beneath HPS and that used by the bottling company do not appear to be connected. In 1991, the Department of Defense listed the shipyard for closure.

During the 1960s, zinc chromate had been used extensively as a primer for aluminum. Consequently, there are elevated concentrations of chromium present. For example, in IR-09 of Parcel D where zinc chromate spraying operations took place, chromium concentrations as high as 2700 ppm have been reported. The three SCAPS heavy metal sensors were deployed to evaluate chromium concentration at this site.

Parcel D at HPS consists of about 128 acres of southeast central shoreline and lowland coast. The land surface at Parcel D is mostly covered by asphalt, buildings, or other structures. Between 70 and 80 percent of HPS land consists of relatively level lowlands constructed by excavating portions of surrounding hills and placing non-engineered fill materials along the margin of San Francisco Bay. Parcel D is located in the lowlands with surface elevations ranging from 10 to 40 feet above mean sea level (msl).

The peninsula forming HPS is within a northwest-trending belt of Franciscan Complex bedrock known as the Hunters Point Shear Zone. The depth to Franciscan Complex Bedrock from the ground surface in Parcel D varies from less than 1 foot in the northern area to greater than 200 feet in the southeastern area. Directly south of the Parcel D boundary is an outcrop of bedrock called Shag Rock. Undifferentiated Sedimentary Deposits cover the bedrock over much of Parcel D, occurring beneath Bay Mud Deposits or, rarely, directly beneath Artificial Fill. These deposits range up to 110 feet in thickness. Bay Mud Deposits underlie most (about 80 percent) of Parcel D except for a strip along the northern margin of the site and over the bedrock high point directly south of Parcel D. Where present, Bay Mud Deposits range up to 100 feet thick. Undifferentiated Upper Sand Deposits are rather scattered in occurrence beneath Parcel D. Where existent, these sands generally overlie Bay Mud Deposits but may be interfingered with Bay Mud Deposits, and, in a few localities, directly overlie Undifferentiated Sedimentary Deposits. These sands range in thickness up to 20 feet. Artificial Fill overlies all of the naturally occurring units and ranges in thickness up to 80 feet. The thickness of the Artificial Fill and all naturally occurring surficial deposits generally increases toward the bay, with the exception of the bedrock high point in the southern part of Parcel D.

3.3.4 Camp Keller Small Arms Range, Keesler Air Force Base, Biloxi, Mississippi

Keesler Air Force Base is located in Biloxi, MS. Camp Keller, which is part of Keesler Air Force Base, is located 15 miles north of Keesler on state route 67. Several small arms firing ranges are located within Camp Keller. These firing ranges are currently in use by the Air Force, Navy, and reserve units. Each firing range consists of a firing area, a clear standoff area providing distance to the target, and an impact berm. Due to firing range activities, the primary contaminant of concern is lead. In October of 1996, the ERDC SCAPS truck was used in field investigations utilizing the DL-LIBS metal sensor at Camp Keller in front of the Air Force impact berm. Measurements showed that the highest lead concentrations (up to 6000 ppm) were found near the surface. However, leached lead contamination was detected from the surface to depths of four feet. No

difficulties were encountered during pushing. The water table was encountered at 10 feet below ground surface.

The landmass of Camp Keller consists of the Gulf Coastal Plain, a continuation of the Atlantic Plain, and borders the Gulf of Mexico from Florida to Mexico, stretching northward to include the lowlands of the Mississippi Valley as far as St. Louis, Missouri. Geologically, the coastal plain is an extension of the submerged continental shelf. The Atlantic and Gulf coastal plains have subsided and emerged several times since the end of the Mesozoic era, as shown by the types of sedimentary deposits (Cretaceous age and younger), that underlie and comprise them. During the last Ice Age, when sea level was hundreds of feet lower, coastal plains were much broader and shorelines were far offshore of their present positions. The coastal lowlands consist of a gulf-ward-thickening, heterogeneous, unconsolidated to poorly consolidated wedge of discontinuous beds of sand, silt, and clay.

3.4   PHYSICAL SET-UP AND OPERATION

The SCAPS truck mounted CPT platform is a stand-alone unit that requires no outside sources of electrical power during operation. No special structures, either temporary or permanent are required for operation. All power is supplied from a generator operated by the "power take off" (PTO) of the truck diesel motor and is regulated through an uninterruptible power supply with a bank of batteries. An external electrical power connection is also available. A hydraulic system, integrated into the truck, provides the force to push the probe into the ground and also powers a grout pump. Water, from onboard tanks, is consumed in the steam cleaning system and during grouting. Retraction grouting is currently not configured in the three metals sensor probes but may be included in operational configurations. A local source of water is required for refilling the onboard tanks. Another consumable is grout. These items may be acquired locally or carried along in the SCAPS support vehicles. Steam cleaning rinsate water is collected in DOT-rated 208 liters (55 gallon) drums and handled as potentially hazardous waste. Operations yield approximately half a drum of rinsate waste a day. Wastewater disposal is coordinated with site personnel and handled locally after results of rinsate sampling are completed.

3.5   SAMPLING/MONITORING PROCEDURES

To assess the comparability of data acquired by the three SCAPS metal-sensing technologies to data generated by established, conventional analytical methods, the SCAPS metal sensors data were compared to analysis results of sampled soil. A series of pushes and comparison borings were conducted. Sets of co-located pushes (i.e., one SCAPS XRF metal sensor push, one SCAPS FO-LIBS metal sensor push, one SCAPS DL-LIBS metal sensor push, and one CPT soil sampler push) were performed both inside and outside of the heavy metal contaminated plume area. Six sets of pushes along a transect from impacted to non-impacted were made to delineate the plume at each demonstration site. Soil samples were obtained either by hand-augering or by using the CPT soil sampling probe, and are included as a push in each set of pushes. The three SCAPS sensor pushes were triangulated around each CPT soil sample location in a manner to co-locate within approximately 8 inches of the verification sample.

During demonstration sampling, the SCAPS CPT pushed the three SCAPS metal probes as they acquired data (the DL-LIBS probe acquired data as the probe was retracted from the hole). Each

probe push was above ground water. After each push, the SCAPS metal probe was retracted, and the CPT push hole was backfilled with a dilute Portland cement, bentonite, and Sikament mixture using the "trimmy grout" method.

After the real-time metal sensor data was collected from each set of sensor interrogation holes, verification samples for that push hole were obtained either by pushing a CPT soil sampling probe or by hand-augering. Typically, three 6.6-inch long, 1.5-inch diameter stainless steel tubes of sample soils were collected from every 1 to 1.5 feet of boring using a Mostap 35PS sampler with a fishtool. The soil samples were collected at depths determined from review of the metal sensors' profile data. Only tubes containing sample soils which appeared relatively undisturbed were used. The sampler was pushed using the SCAPS truck, in accordance with the ASTM D3441, the standard for CPT soil sampling. The Mostap 35PS sampler itself is an approximately 34-inch long, 2-inch diameter steel penetrometer tip, which includes a 21-inch long sample barrel containing three 6.6-inch long stainless steel soil sampling tube. Samples for confirmatory analysis were collected from the lower and middle (deeper) 6.6-inch soil tubes in the 21-inch sampler. Each soil-sampling hole was backfilled with a dilute Portland cement, bentonite, and Sikament mixture. Each soil sample was handled as described in the following paragraphs. The hand-auger was used in those instances where groundwater was shallow (less than or equal to about 6 feet).

3.6   ANALYTICAL PROCEDURES

The inductively coupled plasma (ICP), EPA Method 6010 (U.S. Environmental Protection Agency), method for determining metal contaminants was used as the standard analytical laboratory method. It was selected as the confirmatory analytical method for the three SCAPS metal technologies due to its widespread and generally accepted use in delineating heavy metal contamination. This method requires that the solid soil sample be solubilized or digested prior to evaluation. Although this analytical method does measure the same metal constituents that are targeted by the three SCAPS metal sensors, some variability will occur due to the fact that the analytical technique is carried out on an "average" digested sample, while the SCAPS metal sensors are evaluating only a spot location of the sample. However, this analytical method was chosen because it represents technology that is currently used on a day-to-day basis to make decisions about the distribution of subsurface heavy metal contamination.

The ICP method measures element-emitted light by optical spectroscopy. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific atomic-line emission spectra are produced by a radio frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the lines are monitored by photomultiplier tubes. ICP can determine the presence of several metals simultaneously. Standard solutions of each metal of interest are prepared and evaluated. Then, mixed calibration standard solutions are prepared from those individual metal standard solutions and evaluated. For quality control, a calibration blank and at least three standards must be run to generate a calibration curve. At least one matrix spike and one matrix spike duplicate are run to determine digestion recoveries.

One of the main difficulties in comparing the methods is due to differences in small-scale spatial heterogeneity. Each metal sensing probe was pushed in close proximity to each other and to the soil verification sample location. However, there is some uncertainty in establishing the depth from which the soil sample is obtained. Due to the sharp vertical boundaries of the contamination plume,

an error of 6 inches or less in the sample depth can change from strongly impacted (greater than 10,000 ppm) to clean (less than 100 ppm for most metals). Additionally, it is important to reiterate that the analytical method tests a digested sample that represents an "average" result for that sample, whereas, the SCAPS metal sensors interrogate a small and discrete sample spot. For this reason, prior to shipping the soil samples to the analytical laboratory, each soil sample was homogenized on site and split into 4 aliquots. Then, one of the homogenized aliquots was reevaluated by each of the three SCAPS metal sensors as quickly as possible after completion of the field demonstration. At the same time, the samples were properly packaged and sent to the laboratory for analysis.

4.0 PERFORMANCE ASSESSMENT

4.1 PERFORMANCE DATA

The validation process for the two LIBS and XRF sensors consisted of deploying each probe at four predetermined sites. For each site, two sets of measurements were conducted. In the first set, *in situ* measurements were conducted at a number of locations (usually a transect of six separate push locations). These measurements provided a general qualitative picture of the contaminant distribution at the site. In the second set of measurements, discrete samples, gathered at each site, were homogenized. Splits of each homogenized sample were sent to the respective sensor laboratory and to an analytical laboratory for analysis.

At each site, a sample of uncontaminated soil was collected. The sample was homogenized, and splits were sent to each sensor laboratory. The sample of uncontaminated soil was assumed to be representative of the grain size distribution of the site and was used by each of the respective sensor laboratories to prepare calibration standards. The soil was allowed to air dry and standards were prepared by spiking aliquots of soil with known quantities of a solution containing 10000 ppm of the metal contaminant of interest undergoing investigation. Using these standards, a site-specific calibration curve was generated to minimize soil matrix effects.

These SCAPS metal sensors are intended as semi-quantitative field screening tools, not as quantitative analytical methods. Therefore, the performances of the sensor systems were evaluated using a standard contingency analysis. In a contingency analysis, the results from ex-situ sensor measurements performed on splits of homogenized discrete sample collected for the laboratory validations are plotted versus the concentration reported by the analytical laboratory. The resultant scatter plot has a format similar to that shown in Figure 5. The final results for each technology at each site were stated in the site report in terms of percent (%) agreement with the laboratory results by summing the number of true positive and true negative points from the scatter plot and dividing by the total number of samples. The final report includes the overall percent agreement for each technology summed over all site verification data.
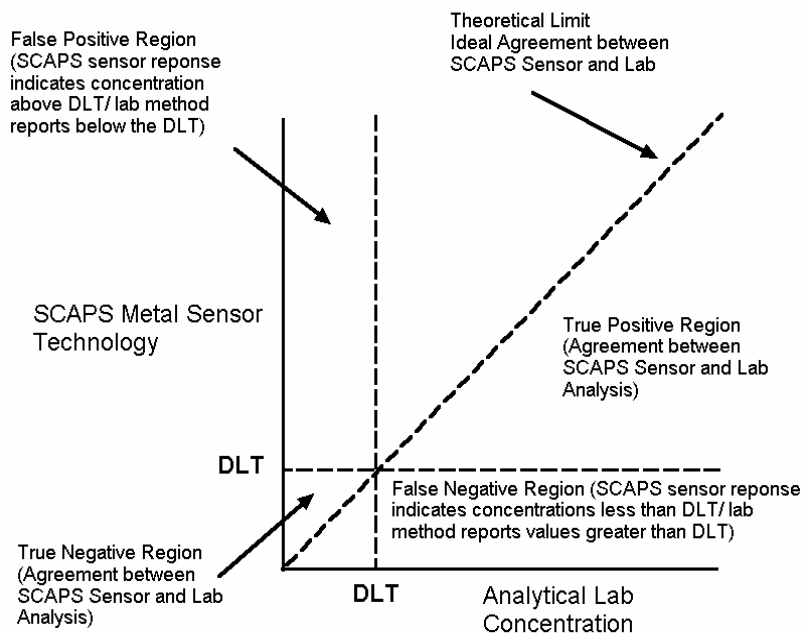
Figure 5. Contingency Plot Analysis where DLT is the Detection Limit Threshold.

Data reports have been completed for LCAAP, NASNI, HPS, and Camp Keller. The reports summarize the *in situ* sensor data, laboratory *ex situ* sensor data obtained for the three-sensor systems, off-site laboratory results, and notes and observations from field operations. Copies of

these reports may be obtained from Dr. S. Lieberman (address provided in Appendix A, Contacts). The raw and processed data for the pushes and laboratory data for each sensor at each site has been archived electronically on CD-ROM and is available in the ESTCP Final Report (LIEBERMAN et al., 2001).

The validation effort produced comparison data to support the effectiveness of the three SCAPS deployed metal sensor probe configurations. In general, detailed comparisons of the laboratory ICP results agree well with the patterns of contamination derived from *in situ* metal sensor data and agree semi-quantitatively with *ex situ* sensor data. Table 2 contains the contingency analysis summarizing results for the four site demonstrations for comparison of the ICP results with the benchtop sensor measurements.

**Table 2. Summary of Contingency Analysis Results for Comparison of
Benchtop Laboratory Data Obtained by the Three Sensors with ICP Results
for the Four Site Demonstrations.**

	XRF	FO-LIBS	DL-LIBS
True Positive	116/127	124/127	125/127
True Negative	38/41	39/41	38/41
False Positive	3	2	3
False Negative	11	3	2
% Agreement	91.7%	97.0%	97.0%

4.2   PERFORMANCE CRITERIA

The data presented above provides realistic comparisons to assess the demonstration's objectives. The primary objective of this demonstration was to evaluate the performance of three *in situ* SCAPS metal sensing technologies compared to conventional sampling and analytical methods. The *in situ* measurements of the three-sensor systems compare favorably with laboratory measurements of validation soil samples. Additionally, the above data show that each of the systems (i.e., the DL-LIBS, the FO-LIBS, and the XRF) successfully detected and differentiated heavy metal contamination in varying soil matrices. In all cases, data quality exceeded acceptable standards to meet the objectives. Design of the sampling scheme for verification of an *in situ* measurement by *ex situ* analysis remains the biggest problem. Varying contaminant distribution and small-scale soil heterogeneity can lead to samples which are not representative of the soil measured *in situ*.

Secondary objectives for this demonstration were to evaluate the SCAPS metal sensing technologies for their reliability, ruggedness, and ease of operation. For the most part, all three sensors displayed good reliability and ruggedness. The greatest difficulty was encountered at HPS where pushing was very difficult. Both the XRF and DL-LIBS sensors were compromised by water entering the probes. For CPT deployed sensors, it is common practice to have backup probes on hand in case a probe breaks below the ground surface and cannot be retrieved. ERDC successfully deployed a backup DL-LIBS probe and completed the scheduled six *in situ* pushes. The backup XRF probe was not functional, while the XRF sensor completed two of the six *in situ* pushes. After the HPS demonstration, the NRL sensor group repaired both XRF probes and successfully conducted the Camp Keller demonstration. With regards to ease of operation, typically a four-person crew (a field

site manager, two push-room personnel, and a metal sensor system operator) is employed to complete all aspects of field operations. A trained technician should operate all three SCAPS metal sensors. It should be noted that key personnel in both the DL-LIBS and FO-LIBS sensor groups left prior to completion of the demonstrations. Qualified personnel took over the projects and completed the remaining field demonstrations, *ex situ* laboratory analyses, and data processing.

4.3   DATA ASSESSMENT

In general, the overall accuracy (ranging from 92 to 97%) of the three sensor technologies as determined from comparison with laboratory results was adequate for use as a filed screening method. Precision was predominantly controlled by spatial heterogeneity rather than instrumental factors. Heterogeneity varied from site to site and appeared to be correlated with the manner in which the metal contaminant was introduced to the soil (i.e., particulate versus dissolved). This was documented with ICP laboratory analyses of five 1-g aliquots of six soil samples from each site (Table 3).

Table 3.   Precision Results for Replicate ICP Analyses of Soil Samples from Each Test Site.

Site	Precision
LCAAP	24-147%
NASNI	2-24%
HPS	10-30%
Camp Keller	8-113%

High standard deviations (>100%) were observed for replicate analyses of samples where the contaminant was introduced in particulate form (LCAAP and Camp Keller) with much lower standard deviations observed at NASNI and HPS where the contaminant was introduced in dissolved form. These results illustrate the difficulty of delineating contaminant zones using the results from a limited number of discrete samples. This difference in sample heterogeneity related to the nature of the contaminant would tend to mask variations in sensor performance related to variations in local geological conditions.

4.4   TECHNOLOGY COMPARISON

The SCAPS metal sensors provide real-time data as the probe is either pushed or retracted from the soil enables field modifications to the sampling plan. This capability provides a more timely and thorough investigation while avoiding the drawn-out iterative process, typical of conventional site characterization methods (e.g., traditional sampling and off-site laboratory analysis).

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5.0   COST ASSESSMENT

5.1   COST REPORTING

Cost comparisons are reported on a fee-for service basis. The estimate of the fee-for-service rate is based on an average obtained from several sources including both government (U.S. Navy Public Works Centers and U.S. Army Corps of Engineers District SCAPS operational systems) and commercial service providers for similar operations with laser-induced fluorescence sensor system. Although quoted rates can vary by approximately a factor of two, the average rate used for cost comparisons in this report of $6380/10-hr day appears to represent a fairly conservative estimate that would cover not only operations, but also account for basic data analysis and reporting. This rate is based on an equipment rate of $3,700/day, which includes the SCAPS LIF-equipped, 20-ton penetrometer system plus two support vehicles. The labor portion of this daily rate covers a four-person crew, including a push- room operator, a push-room helper, a data acquisition specialist, and a project geologist or project manager charged at $67.50/hr for a 10-hr day. Previously, the average cost of operating a SCAPS truck with a four-person crew in the field, during production work, was reported at $4,500 per day (ESTCP, 2001).

5.2   COST ANALYSIS

Major cost drivers for the metal sensor/CPT operations include equipment charges (including capital equipment costs, equipment repair and maintenance), labor, material (including grout material, misc. expendables), permitting, utility location, location surveying, IDW disposal, work plan/report preparation, and equipment mobilization/demobilization. As described in Section 5.1, costs are reported here on a fee-per-service basis in order to facilitate comparisons with conventional site assessment methodology. The primary source of uncertainties in cost estimates provided here is related to variations in the number of feet pushed per day that result from pushing in different geological materials. At sites where pushing is difficult due to tough geological material or a large number of cobbles, the push rate may be reduced or the probe may be refused, and it may be necessary to move the push vehicle to a new push location to achieve penetration.   In these situations, the push rate could be reduced by a factor of 25 to 50% or more.   A decrease in production rate of 50% would increase the cost per sample reported in Table 5 by a factor of two. It should be noted however, that if pushing is difficult or limited for the SCAPS push Metal *In Situ* Sensor, it will also be equally difficult for the direct-push sampling system, and may slow the conventional hollow-stem auger and split-spoon sampler system. Although all the metal sensor probes used in this study were equipped with strain gauges to monitor the tip and sleeve friction during pushes (also useful for avoiding breaking the probe), pushing in difficult geology also puts the probes at greater risk while increasing the chance of damaging or breaking the sensor probe. In extreme cases, it may become necessary to charge a surcharge for repair of damaged probes (the equipment charges cover normal "wear and tear" which includes periodic replacement of windows and other wear items). Other variations in production rate (number of feet pushed per day) arise from differences in the depth pushed at each push location. In general, production rate increases as the depth of the push increases because the setup time required to move the truck to a new location is reduced.

The fee for service costs reported include the capital equipment costs and costs for normal wear and tear and maintenance. Table 4 provides estimates of the capital costs of each SCAPS metal sensor

technology. Estimates provided in Table 4 indicate that the capital equipment costs for all three-sensor systems are similar (ranging from approximately $70K for the XRF sensor to approximately $90K for the LIBS sensors). These numbers are comparable to the commercial LIF system currently available from Dakota Technologies, Inc. (GERMAIN, 2002). Because the XRF and DL-LIBS sensor systems have more equipment downhole than the FO-IBS system, probe costs represent approximately 50%, and 29% of the total system costs for the XRF and DL-LIBS systems, compared to approximately 20% for the FO-LIBS system. Based on experience with LIF systems operated by government and commercial service providers, it is estimated that the life cycle for the instrumentation system is expected to be approximately five to seven years. Environmental/Safety training is also expected to be similar to that for LIF systems currently in operation in government and commercial systems.

Table 4.   Capital Equipment Costs for the Three SCAPS Metal Sensor Systems and a Commercial LIF System.

	XRF	FO-LIBS	DL-LIBS	LIF
Up Hole Instrumentation System	$30K	$72.5K	$62K	$97.5K
Probe/Umbilical	$35K	$19K	$27K	$15K
TOTAL	$65K	$91.5K	$89K	$112K

5.3   COST COMPARISON

This demonstration has focused on comparing the effectiveness of three CPT based metal sensor technologies to perform field screening at a heavy metal impacted hazardous waste site. Table 5 presents a direct comparison between the costs using a CPT/metal sensor technology versus conventional drilling, sampling, and laboratory analysis for field screening. Because the production rate for the three SCAPS metal sensor technologies is very similar, costs for the three metal sensor technologies are comparable.

This demonstration program has focused on the effectiveness of the CPT/Metal Sensor technology to perform field screening at hazardous waste sites with metal contamination. Table 5 presents a direct cost comparison using CPT/Metal Sensor versus conventional sampling and direct-push sampling. For a site investigation with 10 holes to a depth of 30 feet, the table shows the cost for SCAPS CPT/Metal Sensor at approximately 47% of the cost of conventional sampling with a sampling ratio of 30 to 1 in favor of CPT/Metal Sensor. On a per sample basis, Table 5 shows that SCAPS metals sensor technologies offer approximately a 98% cost savings compared with conventional soil borings and laboratory analyses. The cost savings realized from direct-push methods compared to conventional drill rigs are due to: (1) the speed with which direct-push techniques access depth versus drilling methods; (2) the low amount of investigation-derived waste produced by the direct-push methods; and (3) the ability of the direct-push technique to acquire near continuous data. Further savings not documented in Table 4 may be realized using the SCAPS sensors because onsite real-time data acquisition allows the sampling strategy to be modified in the field to more accurately delineate the extent of contamination. In contrast, traditional sampling strategies depend on results from laboratory analyses that are usually not available for days or weeks after samples are collected, and often require return trips to the field when initial results indicate that

further sampling is required to complete delineation of the contaminated zone. Also, the greater vertical sampling rates provided by the SCAPS sensors compared to conventional sampling methods (every 2 inches compared to every 5 feet) minimizes the chances that significant zones of contamination are missed because 5-foot sampling intervals performed with soil boring do not provide the resolution necessary to resolve some contaminant layers. For the CPT/ Metal Sensor technique, regulators may require a minimum number of confirmatory samples, which can be obtained using CPT sampling devices. This will increase the SCAPS CPT/Metal Sensor cost as presented in the table, but only three or four samples would be required at less than $1,000 additional cost.

Table 5. Cost Comparison of SCAPS Metal Sensors with Conventional Sampling and Direct-Push Sampling.

SCAPS Metal Sensor *In Situ* Measurement		Conventional Drilling (Hollow Stem Auger, Split Spoon, and Off-Site Analyses)		Direct-Push and Off-Site Analyses	
10 pushes to 30 ft. Metals and geotechnical data	COST	10 borings to 30 ft (60 soil samples for ICP analysis)	COST	10 borings to 30 ft (60 soil samples for ICP analysis)	COST
Two 10-hr field days @ $6,380/day	$12,760	Drilling & sampling @ $50/ft for 300 ft (approx. three 10-hr days)	$15,000	Drilling & sampling for 300 ft (approx. two 10-hr days)	$3,000
1 sample/2 inches for metals = 1,800 total samples	Included in basic cost	ICP laboratory @ $50 per sample x 60 samples	$3,000	ICP laboratory @ $50 per sample x 60 samples	$3,000
1 sample/inch for geotechnical data	Included in basic cost	Geotechnical laboratory analysis @ $100/sample x 5 samples	$500	Geotechnical laboratory analysis @ $100/sample x 5 samples	$500
4 waste drums @ $40/drum	$160	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 not produced	$0	Waste soil disposal, 20 drums @ $100/drum	$2,000	Waste soil not produced	$0
Decon water disposal for 4 drums @ $100/ drum	$400	Decon water disposal	$800	Decon water disposal for 1 drum @ $100/ drum	$100
4 man crew	Included in basic cost	Geologist @ $75/hr x 36 hrs	$2,700	Geologist @ $75/hr x 36 hrs	$2,700
		Technician @ $40/hr x 40 hrs	$1,600		
TOTAL	**$14,320**	**TOTAL**	**$30,720**	**TOTAL**	**$10,340**
Per Sample Cost for 1,800 samples	$7.95/sample	Per Sample Cost for 60 samples	$512/sample	Per Sample Cost for 60 samples	$172/sample

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6.0   IMPLEMENTATION ISSUES

6.1   COST OBSERVATIONS

Factors affecting the cost of the metal sensor/CPT operations include labor, material, travel, permitting, utility location, location surveying, work plan and report preparation, and equipment mobilization. Additional cost may be incurred for coring if the media surface is too hard for penetration (cement) or when the sensor probe is frequently refused due to lithologies which are difficult to push. SCAPS CPT/METAL SENSOR or SCAPS Membrane Interface Probe (MIP) costs have been quoted as approximately $6,380 per 10-hour day, plus per diem. It is expected that the operating costs for the SCAPS metal sensor systems will be comparable.

6.2   PERFORMANCE OBSERVATIONS

The primary performance objective for each of the metal sensors tested in this evaluation is that they provide semi-quantitative data on the presence or absence of heavy metal contamination. As summarized in Table 2, results from comparisons of the three sensor technologies show good agreement (>90%) for semi-quantitative comparisons (presence/absence) with the standard laboratory ICP results. These results indicate that all three-sensor technologies met the primary performance criteria as field screening methods. Results also showed that spatial heterogeneity can contribute to high variability in results even for standard laboratory methods. Higher sampling rates associated with *in situ* sensor systems may provide improved delineation of contaminant zones compared to estimates derived from a small number of discrete samples.

6.3   SCALE-UP

Unlike remediation technologies, very few scale-up issues are anticipated in moving from demonstration to full-scale implementation. Direct push platforms capable of deploying the sensor systems used in these demonstrations are readily available from several commercial vendors. The capability for deploying the three sensor technologies from platforms of opportunity was demonstrated during this project by deploying the sensors from two different penetrometer platforms (the SSC San Diego SCAPS system and the U.S. Army ERDC SCAPS system). Also, the capability to transition the sensor technologies to new technical personnel was demonstrated during the course of this program because all three-sensor programs experienced departures of key personnel that necessitated hand-off operation of the sensor systems from the original developer to new operators. Although direct push LIBS and XRF sensor systems are not currently available, several companies have expressed interest in the technologies, and negotiations are currently in progress for the technology transfer of at least one LIBS sensor system and the XRF sensor.

6.4   OTHER SIGNIFICANT OBSERVATIONS

Quantification of sensor response for all three-sensor systems suffered to some degree from sample moisture and matrix effects (LIBS to greater extent that XRF). Decrease in the response of the LIBS sensor, due the moisture effects, particularly limits the utility of the LIBS sensors for measurement in the saturated zone. In addition, the DL-LIBS sensor is subject to clogging from flowing sands in the saturated zone. It is possible that quantification of LIBS sensor response could be improved by correcting for variations soil moisture using an independent soil moisture content sensor. It is

important to note, however, that results demonstrated that this correction was not required for field screening level data for measurements made in the vadose zone.

6.5   LESSONS LEARNED

Because many metal contaminants are released into the environment in particulate form rather than in liquid form, as is the case for most other chemical contaminants (especially petroleum or solvent based contaminants), the subsurface distribution of many metals may be very heterogeneous and may be limited to shallow depths bgs. This suggests that in many cases it might be more appropriate to use a smaller push system than the 20-ton push vehicle used in this study. Pick-up truck size push systems are available and could be used to push the probes used in this study to depths of approximately 6 feet or more. Even though metals that are released in particulate form (e.g., bullets, batteries, etc.), rather than liquid form (e.g., plating solutions), may be limited to relatively shallow depths, the ability of the sensors to make many high density measurements is an important advantage because of the difficulty of delineating regions of contamination from a limited number of discrete samples provided by traditional methods.

6.6   END-USER ISSUES

As part of this ESTCP funded Dem/Val effort, efforts were taken to facilitate the transition of the SCAPS metal sensor technologies to the operational SCAPS systems. Currently, three SCAPS systems are operated by the Army Corps of Engineers — two by the Naval Public Works Centers; one by the Department of Energy (DOE) at the Savannah River Site in South Carolina; and one by the U.S. EPA. Because there is no formal mechanism or institutional support for technology transition, each transition is negotiated with and funded by individual DoD or other government users. Although there has been interest from commercial vendors in commercializing both direct push LIBS and XRF sensors, at present none of the sensors have been commercialized. Currently, each of these technologies is only available from the original technology developer.

6.7   APPROACHES TO REGULATORY COMPLIANCE AND ACCEPTANCE

As described earlier, the metal sensors evaluated as part of this effort represent one of a suite of sensor systems that have been developed or that are still under development for deployment with direct push systems. The LIF sensor for petroleum hydrocarbons was the first major chemical sensor system developed for this system. During the early stages of technology transfer of the LIF sensor, a common question raised by a potential user was, "Is the technology approved by the regulators?" From this question grew the concept that if the LIF technology were "approved" by the regulatory community, users would then embrace it. The quest for regulatory approval led to a successful multi-year effort (partially funded by ESTCP) to gain regulatory acceptance for the SCAPS LIF sensor technology based on assembling a comprehensive set of field measurements that directly compare the performance of the sensor system with traditional EPA methods for a variety of contaminants under different hydrogeological conditions. The cornerstone of obtaining as broad an acceptance as possible is linking these technical efforts with multi-state and national certification/ verification programs such as the U.S. EPA Consortium for Site Characterization Technology "verification" program and "certification" by the California EPA Department of Toxic Substance Control's Technology Certification Program (Cal Cert). For the case of the SCAPS nitrogen laser LIF sensor system, these opportunities were subsequently linked to the Western Governors

Association, Demonstrating Onsite Innovative Technologies (WGA/DOIT) project. Interest by the WGA/DOIT project subsequently led to the establishment of a SCAPS-LIF Interstate Technology and Regulatory Cooperation (ITRC) workgroup, Technology Specific Task Group (TSTG) with the goal to achieve acceptance by each of the seven TSTG member-states (Utah, Nebraska, New Mexico, Louisiana, New Jersey, Idaho, California) and using California Certification (Cal Cert) as the protocol. For the SCAPS nitrogen laser LIF system, these efforts resulted in the successful certification by the Cal Cert Program (California Environmental Protection Agency Department of Toxic Substances Control, 1996), verification by the U.S. EPA (Bujewski and Rutherford, 1997) and endorsement of the Cal Cert certification by the WGA (Cone Penetrometer Task Group Report, 1996).

Significant lessons were learned from the Tri-Service SCAPS Program in the process of obtaining regulatory acceptance of the SCAPS LIF sensor. Specifically, there appears to be no single path to gain universal acceptance of new technology by the regulatory community. However, and probably more importantly, it was learned that obtaining regulatory acceptance does not guarantee user acceptance. While regulatory acceptance is a desirable goal, if the users cannot be convinced that the new technology will enable them to do their jobs faster, better, and cheaper, it will be slow to establish itself in the marketplace. Experience from the SCAPS LIF program suggests that user acceptance is achieved one user at a time. Discussions with both government and commercial LIF service providers indicate that the key to growing a business is to provide a product that meets the customers' needs at a competitive price (personal communications, Tim Shields, PWC San Diego, San Diego California; Racyp Yilmaz, Fugro Geoscience, Inc., Houston, Texas). Satisfied users generate repeat business and tell other perspective customers. Regulatory approval by itself may not generate user acceptance. In retrospect, experience seems to suggest that many perspective users that initially expressed reluctance to use SCAPS LIF because of "lack of regulatory acceptance" may have found other reasons not to use a new technology even if the regulatory community approved the technology.

Based on lessons learned from the SCAPS LIF sensor technology, it appears the most effective means to promote acceptance of a new field screening technology is to aggressively market the technology and grow a user base for that technology. Experience suggests the need to convince individual users and regulators of the merits of the technology coupled with the fact that there is often high turnover in both communities requires a long-term and persistent marketing effort. In general, a motivated commercial vendor has the capability to rally more marketing savvy (knowledge and experience) for a product or service than does a government technology developer. While the SCAPS LIF ESTCP project focused almost exclusively on gaining acceptance of the technology by regulators, the efforts of the SCAPS metal sensors ESTCP project were directed more towards generating a link with commercial partners that ultimately would take the lead for marketing the technologies to both users and regulators. It is believed that this strategy has the advantage of offering a longer term solution to the difficult problem of nurturing a new technology through its' infancy than the previous approach that focused almost exclusively on the single issue of regulatory acceptance at the expense of other factors required for successfully establishing a new technology in the marketplace.

During the SCAPS LIF ESTCP project, it also became apparent that, in general, regulators and users are often slow to accept new methods and technologies due to limited exposure, inadequate technical understanding, and lack of high quality validation data that support developers and/or vendor claims.

Ultimately, acceptance requires exposure leading to understanding, as well as comprehensive data validation. With the goal to document the performance of these sensor systems under various conditions with "hard data," a comprehensive effort was conducted to make available the results of this demonstration/validation program as well as related work. To inform regulators, government agencies, and commercial users, the SCAPS metal sensing technologies have been presented in national and international environmental conferences and peer-reviewed, scientific journals. The publications/presentations for each metals sensor are summarized in the ESTCP final report (Lieberman et al., 2001). The SCAPS metals sensor technologies were also demonstrated at the annual SCAPS User's meetings.

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APPENDIX A

POINTS OF CONTACT

Point of Contact (Name)	Organization (Name & Address)	Phone/Fax/E-mail	Role in Project
Dr. Stephen Lieberman	SSC San Diego Code D361 49575 Beluga Rd. San Diego, CA 92152-6325	(619) 553-2778 (603) 909-8049 (Fax) lieberma@spawar.navy.mil	Project Coordinator FO-LIBS POC
Dr. Pamela A. Boss	SSC San Diego Code D363 45650 Lassing Rd. San Diego, CA 92152-6171	(619) 553-1603 (619) 553-1269 (Fax) bossp@spawar.navy.mil	F0-LIBS Technical Lead
Dr. W. Tim Elam	10551 158th Ave. NE Redmond, WA 98052-2659	(425) 867-9002 wtelam@his.com	XRF Technical Lead
Mr. John H. Ballard	U.S. Army Engineer Research and Development Center (ERDC) 3909 Halls Ferry Rd. Vicksburg, MS 39180-6199	(601) 634-2446 (601) 634 2854 (Fax) john.h.ballard@erdc.usace.army.mil	DL-LIBS POC
Mr. Javier Cortes	U.S. Army Engineer Research and Development Center (ERDC) 3909 Halls Ferry Rd. Vicksburg, MS 39180-6199	(601) 634-2447 (601) 634-3518 (Fax) javier.cortes@erdc.usace.army.mil	DL-LIBS Technical Lead

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