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A Review of Field Technologies for Long-Term Monitoring of Ordnance-Related Compounds in Groundwater

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ABSTRACT: Long-term monitoring (LTM) of remediated sites can be required on a quarterly basis for 30 or more years before site closure, with costs for sample collection, shipment, and analysis at an offsite fixed laboratory contributing 50 to 75 percent of the total expense. Cost-effective sampling techniques and field analysis could substantially reduce these costs. This technical report identifies and describes proven and promising sampling devices and onsite analytical instrumentation that potentially could be used now for LTM of ordnance-related compounds in groundwater. Instrumentation that generates data which can be used for regulatory decisions must be sufficiently sensitive to detect analytes of concern at action levels and must have excellent precision and accuracy to meet data quality requirements. Instrumentation for LTM must provide rigorous qualitative as well as quantitative identifications. The following general categories of field analytical technologies applicable to volatile organic chemicals and organic ordnance-related chemicals are included in this report: water quality monitors associated with low-flow purge techniques, discrete interval samplers, immunoassay for detection of explosives, gas chromatography with liquid compatible inlets, mass spectrometry with liquid compatible inlets, ion mobility spectrometry with liquid compatible inlets, chemical sensors, and colorimetric technologies.

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Preface

The Environmental Laboratory (EL) of the U.S. Army Engineer Research and Development Center (ERDC) prepared this report, which was sponsored by the Long-Term Monitoring Focus Area of the Environmental Quality and Technology Program. The Principal Investigator was Dr. Denise K. MacMillan, Environmental Chemistry Branch (ECB), Environmental Processes and Engineering Division (EPED), EL, Omaha, NE. Mr. David E. Splichal performed surveys of the environmental instrumentation market and project personnel.

This report was reviewed by Ms. Laura Percifield, ECB, and Ms. Louise V. Parker, Applied and Military Engineering Branch, Cold Regions Research and Engineering Laboratory, ERDC, Hanover, NH.

The EL studies were conducted under the general supervision of Dr. Douglas B. Taggart, Chief, ECB, Dr. Richard E. Price, Chief, EPED, and Dr. Elizabeth C. Fleming, Acting Director, EL.

At the time of the publication of this report, Dr. James R. Houston was Director of ERDC, and COL James R. Rowan, EN, was Commander.

1 Introduction

Long-term monitoring (LTM) of groundwater for environmental contaminants prior to closure or continued use of a remediated site is an expensive process mandated by State and Federal regulation. The costs associated with sampling and laboratory analysis over 10 years of monitoring on the more than 1,300 unique Army sites will be nearly $500M (*www.denix.osd.mil/denix/DOD/Policy/ Army/Aerta/tnstop.html*). The Department of Energy estimates spending $100M per year over the next 70 years, and the Navy estimates spending $80M per year in monitoring. Expenses for sample collection and laboratory analysis can contribute up to 70 percent of the total cost of groundwater monitoring and 50 percent of the total cost of a site investigation (ASCE 2003).

Manual collection of groundwater samples from monitoring wells is time consuming and expensive and may not give representative samples. Shipping and storage conditions can also negatively impact analytical results. Transportation of samples from the site to a fixed laboratory can cause compounds, such as vinyl chloride, to volatilize and degrade. Also, light-sensitive semivolatile compounds can degrade if not stored in appropriate bottles, and microbes present in the sample can degrade analytes of concern prior to analysis (Bayne et al. 1994). Sample storage can lead to sample loss through adsorption onto glass surfaces (Ranney and Parker 1998; Reynolds et al. 1990; Strachan and Hess 1982; Sharom and Solomon 1981; Ogan et al. 1978; Champion and Olsen 1971). Such events can lead to low bias for these analytes when analyzed at an offsite laboratory.

Labor, equipment, and transportation costs for sampling are added to the cost of analyses in a fixed laboratory using traditional instrumentation. Analyses are often performed days or weeks after samples are collected. Remobilization of the sampling crew and re-analysis may be required if problems are discovered with the data upon review by project personnel. These factors contribute to high overall cost and highlight the need for alternative processes.

In an effort to significantly reduce operational monitoring costs, the Engineer Research and Development Center (ERDC) of the United States Army Corps of Engineers (USACE), in partnership with the Army Environmental Center (AEC), initiated a program to develop processes and technologies for more effective groundwater monitoring which will be both acceptable to the regulatory community and meet the compliance and expense needs of the Army. Program requirements are detailed in the Army Environmental Requirements and Technologies Assessments (AERTA) document available on the DENIX website (*www.denix. osd.mil/denix/DOD/Policy/Army/Aerta/tnstop.html*) and were refined during an

LTM workshop held in Vicksburg, MS, 14-16 January 2003. Goals of the program are to develop and deploy field sampling and analytical technologies that will provide quick turn-around time for results (less than 4 hr), produce data that are acceptable to regulatory agencies, result in a 25 to 50 percent cost reduction compared to laboratory analysis, and apply to a wide variety of ordnance related compounds (ORC), including octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), 1,3,5-trinitrobenzene (TNB), 1,3-dinitrobenzene (1,3-DNB), methyl-2,4,6-trinitrophenylnitramine (tetryl), 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), 2-nitrotoluene (2-NT), 3-nitrotoluene (3-NT), 4-nitrotoluene (4-NT), ammonium perchlorate (NH_4ClO_4), propellants, and degradation products. The technologies should also be easy to operate and portable, meaning they should be sufficiently light enough in weight to be carried to the sampling site. In addition to providing cost savings for the Army, technologies that meet these goals are expected to be applicable to LTM performed by others.

The program goals will be addressed in three major work areas: (a) deployment of commercially available field sampling and analytical technologies that will reduce present operational costs, including development and implementation of new protocols for acquiring representative samples and definitive data in the field; (b) development and deployment of new and emerging technologies for a near-real-time in situ monitoring system (RTISMS) for detection of volatile organic compounds and ORC; and (c) method development for ORC that currently do not have acceptable analytical methods. As an element of the first major work area, this report describes commercial technologies that have been demonstrated to operate successfully in the field and may be appropriate for use with LTM projects that involve ordnance-related compounds.

For many projects, site managers are reluctant to implement field analytical methodologies due to the perception that field-generated data may not be acceptable to regulators. In 1986, the United States Environmental Protection Agency (USEPA) established an official compendium of analytical and sampling methods which have been evaluated and approved for use in complying with Resource Conservation and Recovery Act (RCRA) regulations: SW-846 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (*www.epa.gov/epaoswer/hazwaste/test/sw846.htm*). In 1990, the U.S. Army Corps of Engineers recommended, by issuing Engineer Regulation 1110-1-263 (USACE 1990), that SW-846 procedures be used as the primary analytical methods for projects that required USACE oversight. Procedures from SW-846 are widely used throughout the environmental analysis community and are readily accepted by regulators, but very few are field methods. Of the few field methods, most are considered screening methods, meaning they lack a critical component of data quality such as precision, accuracy, sensitivity, and/or specificity.

Instrumentation and procedures to acquire more reliable data from the field are available, especially for volatile organic compounds, and regulatory agencies are beginning to address the data quality issue. The California Environmental Protection Agency (CEPA) Department of Toxic Substances Control (Simmons 2004) published the following clarification: "…neither the federal court nor California standards for admissibility distinguish between analysis done in a fixed laboratory and analysis done in the field." The Departmental text continues:

"…in order for data to be accepted as evidence, whether the data come from a fixed laboratory or the field, the technique may need to (be) generally recognized in the scientific community (state standard), and must be shown to be relevant and reliable (federal standard). The rules for defensibility of field methods are no different than those for fixed laboratory methods."

Federal agencies are also beginning to advocate use of field data. Incorporation of field analytical technologies is a component of the USEPA Triad approach (Crumbling et al. 2001, Crumbling 2002) for managing environmental projects. This approach incorporates the elements of systematic planning, dynamic work plan strategies, and real-time field analytical measurement to reduce data uncertainty associated with limited sampling points (Interstate Technology and Regulatory Council (ITRC) 2003). Within the Triad approach, field analytical technologies are used to obtain reliable data quickly, eliminate sampling in unnecessary areas, and increase sampling frequency in contaminated areas to reduce uncertainty. The Triad approach is applicable to many measurement activities that occur onsite, including site characterization and monitoring. Onsite chemical analysis, rapid sampling, and real-time-data evaluation allow immediate access to information and enable dynamic work plans. Decisions on sampling locations and strategies can be made during sampling rather than during a redeployment of the sampling team. The use of less costly sampling techniques and field analytical methods that incorporate quality data parameters are keys to saving time and money during environmental assessment. The tools for limiting decision uncertainty include a broad category of analytical methods and equipment that can be applied either at the sample collection site or at a nearby laboratory capable of generating results more rapidly. They include field methods performed with hand-held, portable equipment, transportable technologies, and methods that require controlled laboratory conditions. As more field analytical tools are developed for site characterization, they should be readily adaptable to meet LTM requirements. The USEPA's advocacy of the Triad approach suggests growing regulatory acceptance of field-generated data.

This technical report identifies proven and promising sampling devices and onsite analytical instrumentation that could be used now for LTM of ordnance-related compounds in groundwater. Of the many field analytical technologies available commercially, not all are appropriate for meeting the needs of LTM for ORC. Appropriate instrumentation must be sufficiently sensitive to detect analytes of concern at action levels and must have excellent precision and accuracy to meet data quality requirements. Instrumentation for LTM must provide rigorous qualitative as well as quantitative identifications. Sites under LTM are presumably well characterized, however, so some leeway is possible in the steps toward qualitative analysis. For example, systems known to have chromatographic co-elutions may be acceptable for LTM if one of the co-eluting compounds is known not to be present at the site. The following general categories of technologies applicable to volatile organic chemicals and organic ORC are included in this report:

    a. water quality monitors associated with low-flow purge techniques
    b. discrete interval samplers
    c. immunoassay for detection of explosives
    d. gas chromatography with liquid compatible inlets

e.　mass spectrometry with liquid compatible inlets
　　　　f.　ion mobility spectrometry with liquid compatible inlets
　　　　g.　chemical sensors
　　　　h.　colorimetric technologies

　　　This report is not exhaustive in that some technologies that fit the above categories may not be included. Inclusion or inadvertent oversight of any instrumentation or technology does not represent positive or negative bias toward the technology. In addition, the report does not discuss technologies that are intended for detection of metals and inorganic compounds or solely for volatile organic compounds. The following technologies are beyond the scope of this report:

　　　　a.　sampling devices that are specific for soils or air
　　　　b.　instrumentation limited to detection of metals, inorganic chemicals, or volatile organic chemicals
　　　　c.　open-path vapor detection instrumentation
　　　　d.　technologies limited to detection of chemical warfare agents
　　　　e.　technologies limited to detection of biological agents
　　　　f.　technologies limited to detection of oil in water
　　　　g.　screening kits
　　　　h.　immunoassays and immunosensors specific for detection of pesticides, polychlorinated biphenyls (PCBs), and/or pentachlorophenol
　　　　i.　gas chromatographs that cannot analyze aqueous samples
　　　　j.　mobile laboratories
　　　　k.　emerging technologies

　　　Web site addresses for manufacturers of cited technologies are compiled in Appendix A. Also included in Appendix A are addresses for web sites of interest for additional information about field analytical technologies.

2 Methods

This technical report identifies sampling and analytical technologies that are available from commercial sources that have the potential to reduce long-term environmental monitoring costs for ORC and volatile organic compounds and to produce data that will be acceptable to site managers and regulators. The technologies included in the report are limited to those applicable to detection of ordnance-related organic chemicals in groundwater but are not limited to those with usefulness solely to the Army. The report consists of information obtained through many sources, including traditional literature searches (journals, periodicals, conference proceedings, and books), Internet searches (keywords, website browsing), conference attendance, and personal correspondence. To gather information from LTM users, a questionnaire on LTM practices was prepared and sent to USACE District chemists. District chemists were chosen for participation in this study because their duties include oversight of chemical data generated from LTM projects. In addition, District chemists must approve incorporation of innovative sampling and analysis techniques into USACE project work plans prior to regulatory approval. Also, due to their experience with a variety of environmental projects and the full range of analytes of concern, the responses provided by the Corps chemists should be applicable outside the Department of Defense.

A survey consisting of 18 questions was sent to approximately 90 project chemists throughout the Corps of Engineers on two occasions, May 2003 and September 2004, to help the LTM focus area team better understand user needs and gauge the extent of field analytical method use. Recipients had the discretion to forward this survey to others such as Corps geologists, risk assessors, other chemists, and project managers with responsibilities for LTM. Since the Corps of Engineers has extensive experience with LTM projects, and, since District personnel interact closely with the regulatory community, input from this group was considered essential. Survey questions were developed by the authors of this report. As shown in Appendix B, respondents were asked for input on a variety of questions ranging from the number of LTM sites in their project load to their opinions on including innovative sampling and/or analysis techniques in their projects.

3   Technology Reviews

Survey Results

Eight completed survey questionnaires representing six different Corps Districts were received for the May 2003 survey. Eighteen responses from ten Corps Districts were received for the September 2004 survey. Since initial recipients passed on the questionnaire to others, an accurate response rate could not be calculated. The tabulated results appear in Appendix B. The respondents are responsible for 1 to 30 LTM projects with total costs ranging from $30,000 to $500,000 per year per project. Six respondents monitor only groundwater for their projects, one monitors soil only, and the others monitor both soil and groundwater. One respondent reported monitoring biota for an LTM project. The analytes of concern for these projects include volatile organic compounds, metals, semivolatile organic chemicals, waste fuels, and ORC such as explosives and perchlorate. Volatile organic compounds were monitored for more projects than were the other compounds, followed by metals. Explosives and semivolatile compounds such as pesticides and polychlorinated biphenyls were reported to be monitored with the third highest frequency. Monitoring at these sites is scheduled to last from less than 5 years to more than 30 years. Samples are collected at predefined intervals (quarterly, semiannually, annually, etc.), with semiannual sampling being most frequent according to the respondents. All samples are analyzed at offsite laboratories, and two respondents indicated samples were also analyzed by onsite laboratories.

Responses to the questionnaire suggest project personnel perceive that regulators may not be willing to accept innovative field analytical methods. Respondents reported satisfaction with the time interval between sampling, data reporting from offsite laboratories, and review of data by project personnel. Three of eight respondents to the 2003 survey and twelve of eighteen respondents to the 2004 survey indicated that they would consider using field analytical methods for their projects if certain conditions were met such as cost savings, project data quality requirements, and availability of methods that would apply to all parameters. Some respondents did not consider field analytical methods for their projects because the projects were not time-critical in the way that site characterizations are. Others suggested they were satisfied with current procedures or thought field analytical methods would be too costly. Several respondents indicated that regulators required that analyses for LTM be performed in a fixed laboratory.

Commercial Technologies for LTM

LTM consists of several steps including sample collection, transport, laboratory analysis, and data evaluation. Opportunities for cost avoidance and reduction exist in each of the steps. Technologies that can create savings in collection, transport, and analysis will be discussed first.

Groundwater Sampling

Collection devices such as bailers or high-speed pumps are commonly used to sample well water for analysis at offsite laboratories. Older groundwater sampling techniques require purging the well casing to remove a minimum of three to five times the well volume prior to sample collection in order to collect a representative sample. This procedure can lead to differences in the physical and chemical properties of the water in the well compared to the water surrounding the casing (Puls and Barcelona 1996). For example, analyte concentrations may only reflect concentrations in the most permeable part of the screened interval. In some cases, the well "goes dry" or recharges so slowly that a representative sample cannot be collected. Delineation of analyte concentrations according to depth within a well may also be a concern to regulators because maximum concentrations within a plume should be monitored. Purge water must be stored onsite until laboratory results are received and appropriate disposal can occur. If the stored water is demonstrated by chemical analysis to be hazardous, sampling waste disposal costs add to the total cost of site cleanup.

Issues associated with purging a set volume and pumping at high flow rates led to development of low-flow sampling techniques to improve data quality (Puls and Barcelona 1996; Ritchey 2002). This technical report focuses on two new techniques: low-flow purging and sampling methods, with minimal drawdown, and discrete interval samplers, or passive samplers with little or no purging (Puls and Barcelona 1996; USEPA Region 1 1996; Nielsen and Nielsen 2002; ASTM 2003). The techniques provide cost savings and can produce more representative samples than the traditional methods.

Low-flow purging and sampling technologies

Low-flow purging refers to the low velocity with which water enters the pump intake. Typically, flow rates on the order of 0.1-0.5 L/min are used for low flow purging compared to the multiple L/min flow rates observed for older purging methods. The flow rate must be less than the rate of aquifer recharge so that water is not drawn from a different, more permeable zone in the formation. Water quality indicator parameters such as pH, specific conductance, dissolved oxygen, oxidation-reduction potential, temperature, and turbidity are measured to determine when formation water is accessed and purging is no longer required (Parker 1994). Water quality monitoring is typically performed by instrumentation manufactured specifically for this purpose. Representative technologies are described later in this section of the report.

Low-flow purging and sampling provides several advantages over older sampling techniques with set purge volumes. The low flow rate minimizes disturbance of the sampling point, thereby reducing sampling artifacts such as turbidity. Onsite sample filtration is generally not needed with low-flow techniques, thus less time is required for sample collection. Minimal drawdown produces less stress on the formation and should result in collection of a representative sample from the formation water (Puls and Barcelona 1996). Smaller purging volumes decrease sampling time, waste, and disposal costs.

A study comparing low-flow sampling with bailing was recently reported for the Brookhaven National Laboratory Groundwater Surveillance Program for which more than 1,000 wells are monitored for volatile organics and radionuclides (Paquette 2004). The study was limited to 21 wells and a total of 219 samples that were collected after set purge volumes were removed. Representative sample collection was observed after purging as little as 0.05 to 0.25 casing volumes, compared to the 3 to 5 well volumes purged for older sampling techniques. The Brookhaven program converted to low-purge sampling in 1999 as a result of the study. The change to low-flow techniques led to a 92 percent reduction in the volume of purge water generated and annual cost savings of $425,000 through reduced costs for labor involved in sampling and disposal of purge water. Table 1 presents some potential advantages and disadvantages of low-flow purging and sampling technologies.

Table 1
Potential Advantages and Disadvantages of Low-Flow Purging and Sampling Technologies Compared to Older Groundwater Techniques

Potential Advantages	Potential Disadvantages
Reduced turbidity at sampling point	Water quality parameters must be measured to indicate stabilization
Sample filtration not needed	Stabilization may not occur rapidly
Less stress on formation	Equipment may require additional training
Shorter sampling time due to smaller purging volumes	Higher capital costs due to use of dedicated pumps
Dedicated pumping equipment reduces cross contamination	

A variety of pumps are available for low-flow purging and sampling, including peristaltic pumps, bladder pumps, electrical submersible pumps, and gas-driven pumps. Initial capital costs for low-flow purging are equivalent to those for high-flow-rate purging. A one-time cost for a low-flow or high-flow pump, which can be used for multiple wells, with water quality monitor, is approximately $4,500. Often, with low-flow purging and sampling, dedicated equipment is recommended, which reduces cross contamination and eliminates the need for decontamination of pumps and tubing, but increases equipment costs. Low-flow purging also requires flow through cells and water quality sensors that are not used in high-flow techniques. For both low-flow and high-flow techniques, batteries and pumps must be transported to and from the sampling site. Low-flow equipment is more sophisticated and requires additional training

for proper operation. Also, when using newer purging technologies, parameters such as turbidity and dissolved oxygen may not stabilize quickly and could result in generation of a substantial volume of purge water, high disposal costs, and lengthy sample collection time. Other advantages and disadvantages associated with use of these devices are summarized in the literature (Lee 2002).

Flow-thru cells using sensors specific for each water quality (WQ) parameter are needed to measure and document stabilization of the well when using the low-flow sampling technique. Traditional high-flow techniques generally purge to a set volume and sample without evaluation of WQ parameters. The following paragraphs describe four representative systems currently available for use in monitoring of WQ parameters. The product descriptions were obtained from Internet-based marketing information. Characteristics were not consistently described between manufacturers and thus point-by-point comparisons between products were not possible. Performance evaluations by entities other than the manufacturers were not found in the literature.

a. **QED Environmental Systems MicroPurge Basics MP20 Flow Cell.** The MicroPurge Basics MP20 Flow Cell is manufactured by QED Environmental Systems (Ann Arbor, MI). The waterproof, microprocessor-based device signals when selected purge WQ parameters remain steady over successive readings at user-defined intervals. Readings are displayed and stored automatically. Up to 200 data points can be collected and downloaded to a personal computer with automatic date and time stamp. With an internal volume of 175 mL, the sensor gives a fast response at low-flow purge rates. The probe attaches with a bayonet-type mount to the flow cell. The cell is calibrated daily and monitors turbidity, oxidation-reduction potential, pH, dissolved oxygen, conductivity, temperature, and salinity. The meter uses standard C cell. It includes an additional turbidity sensor and data download capability.

b. **Omni Controls, Inc. YSI 556 Multiprobe System with 5083 Flow Cell.** The YSI 556 Multiprobe System with 5083 Flow Cell is produced by Omni Controls, Incorporated (Tampa, FL). The hand-held, waterproof unit simultaneously measures WQ parameters by using field replaceable electrodes for dissolved oxygen, pH, conductivity, temperature, and oxidation-reduction potential. The system requires custom data analysis software and can be interfaced to a personal computer. The unit stores up to 49,000 data sets that are time and date stamped. The cost for this unit is approximately $3,600.

c. **In-Situ, Inc. Multi-Parameter Troll 9000 with Low-Flow Cell.** The Multi-Parameter Troll 9000 with Low-Flow Cell is manufactured by In-Situ, Incorporated (Laramie, WY). This system can monitor up to seven sensors simultaneously for determination of dissolved oxygen, conductivity, temperature, pH, oxidation-reduction potential, salinity, pressure, nitrate, chloride, ammonia, or turbidity through a 248-mL flow cell. The device is precalibrated at the factory and uses a single solution to calibrate most sensors simultaneously in the field. The data logger allows recording up to 1,000,000 data points which are collected onto a hand-held computer. The cost for this unit ranges from a base price of $5,350, without the turbidity sensor, to $6,850, depending on features and number of sensors selected.

d. **Solinst Canada, Ltd. Model 475 Flow Cell.** Solinst Canada, Ltd. (Georgetown, Ontario, Canada) produces the Model 475 Flow Cell. This company does not sell sensors or probes, but retrofits existing monitoring technologies to their own flow cell, which has a 500-mL capacity. The cell is designed with re-sealable compression fittings for two to six analysis ports. A model that is compatible with more sensors is also available. The system can record pH, temperature, and conductivity measurements that can be downloaded onto a computer. Probes for other tests such as ion concentration analysis can be purchased. The cost for the Model 475 Flow Cell is $645. With the cost of the sensors included, the total system cost is likely to approximate the total cost for systems listed above.

Discrete interval samplers

Representative sample collection can be achieved without purging through use of discrete interval samplers, also called no-purge or minimal-purge samplers. There are two types of discrete interval samplers: grab-type samplers and passive diffusion samplers. Both types of samplers are easy to use, can be helpful in wells that recharge slowly, and reduce or eliminate costs associated with disposal of purge water. Discrete interval samplers are placed in the screened interval of the well. In wells with short screens, the groundwater flow is typically horizontal and laminar, with only minimal mixing with the water column above the screened interval (Puls and Barcelona 1996), which may contain stagnant water.

Parker and Clark (2002) studied performance of five discrete interval type samplers: the Kabis sampler from SIBAK Industries Limited, Inc. (Peoria, IL), the HydraSleeve™ by GeoInsight (Las Cruces, NM), the Discrete Interval Sampler from Solonist Canada, Ltd. (Ontario, Canada), the Passive Diffusion Bag Sampler developed by the United States Geological Survey (USGS) and marketed by Columbia Analytical Services, Inc. (Kelso, WA) or EON Products (Snellville, GA), and the Pneumo-Bailer™ from Best Environmental Subsurface Sampling Technologies, Inc. (Golden, CO). The devices were evaluated for representative collection of volatile organic compounds, pesticides, explosives, and metals from laboratory standpipes and for trichloroethene (TCE) from a field site. Each of the samplers gave acceptable recoveries for volatile compounds. For explosive analytes, the results were acceptable for all samplers evaluated except the passive diffusion bag (PDB) sampler (PDBS). For most explosives, recoveries from the PDBS correlated poorly with controls, and RDX and HMX could not be detected in samples collected with these devices.

Due to ease of use, low cost, and success with collection of volatile organic compounds, the PDBS and the HydraSleeve™ will be discussed further. These samplers also permit multiple devices to be deployed simultaneously in the well, and allow contamination to be profiled according to depth. The more comprehensive and accurate view of contamination produced through depth profiling lends greater accuracy to modeling and monitoring, which can lead to more effective remediation. Discrete interval samplers also minimize turbidity while taking a representative sample.

The PDBS can be used for sampling groundwater for volatile organic compounds and aromatic gasoline residues. Originally designed by Vroblesky and Hyde (1997), the PDB samplers are made of low-density polyethylene with 10 Å pores, are about 20-in long, and hold approximately 220 mL of deionized water. Most volatile organic compounds readily diffuse through the polyethylene membrane; some ketones, ethers, and alcohols are exceptions (Vroblesky 2001). Current literature (ITRC 2004) recommends this device for sampling groundwater for volatile organic compounds only. Parker and Clark (2002) reported no significant differences in recoveries of volatile organics from the PDBS versus recoveries from control samples from laboratory standpipe studies. Research to evaluate the compatibility of different polymers and a porous polyethylene pipe sampler with additional environmental contaminants is underway (Parker and MacMillan 2004).

In general, these types of samplers are placed in the well and allowed to equilibrate with the water inside the screen. Vroblesky and Campbell (2001) determined that equilibration required as long as six days for some volatile compounds, though one to four days were sufficient for most. A two-week interval is recommended before retrieving the sampler from the well (ITRC 2004). For some LTM projects, new bags are deployed immediately after sample collection and allowed to remain in the well until the next sampling event (O'Neill and Rieck 2003). Upon retrieval, the top of the bag is cut and the equilibrated water is poured from it into the appropriate container for shipment. Pasteur pipets can also be used to pierce the bag and allow the sample to be poured.

The PDBS (Figure 1) presents some advantages versus use of bailers or pumping techniques, including ease of deployment and operation and relatively low cost (approximately $20 per bag). The bags can be placed end-to-end to delineate contaminant stratification. Since the bags cannot be reused, decontamination of sampling equipment is not necessary. The small pore size does not allow sediment to pass into the bag, thus eliminating sample turbidity. Other advantages include reduction or elimination of purge water, option for use with slowly recharging wells, and quick collection time after equilibration. The ITRC (2004) reported a 40-70 percent potential savings on sampling costs with use of the PDBS.

Users should be aware of some constraints when using these sampling techniques. Samplers must be placed in the appropriate physical location in the well and not collected until after an equilibration period. Analyte measurements reflect the concentration over time, rather than a concentration for a particular point in time, as is obtained with traditional sampling techniques. The device depends upon diffusion of analytes in and out of the sampler; thus, rapid changes in concentration may not be detected.

Figure 1. The passive diffusion bag sampler. Photo used with permission. (*http://www.caslab.com/products.php*)

The HydraSleeve™ (Figure 2) is a grab-type sampling device comprised of a long polyethylene bag with a reed valve at the top and a weight attached to the bottom. The sampler dimensions can be customized to meet project-specific sample volume requirements and well diameters. To initiate the collection process, the closed sampler is lowered into the screened interval by a suspension line attached to a stainless steel weight. The sampler is allowed to sit undisturbed for a minimum of 12 hr to allow for equilibration. After the prescribed time, the sampler is pulled upward at a minimum rate of 1 ft/min. The upward motion causes the reed valve to open and water to enter the sleeve. Earlier versions of the HydraSleeve™ were equipped with a check valve, which required that the device be moved up and down in the well to bring water into the bag. This practice disrupted the water column and increased turbidity in some wells.

With the reed valve, the HydraSleeve™ induces only minimal agitation of the well water. The internal water pressure keeps the reed valve closed when the bag is filled so that mixing with water above the screened interval cannot occur. Once withdrawn from the well, the sample should be squeezed out of the bag into appropriate containers through a tube inserted below the check valve. For sampling of LTM wells at regular frequency, the HydraSleeve™ can be left sealed in the screened well interval for indefinite periods between sampling events.
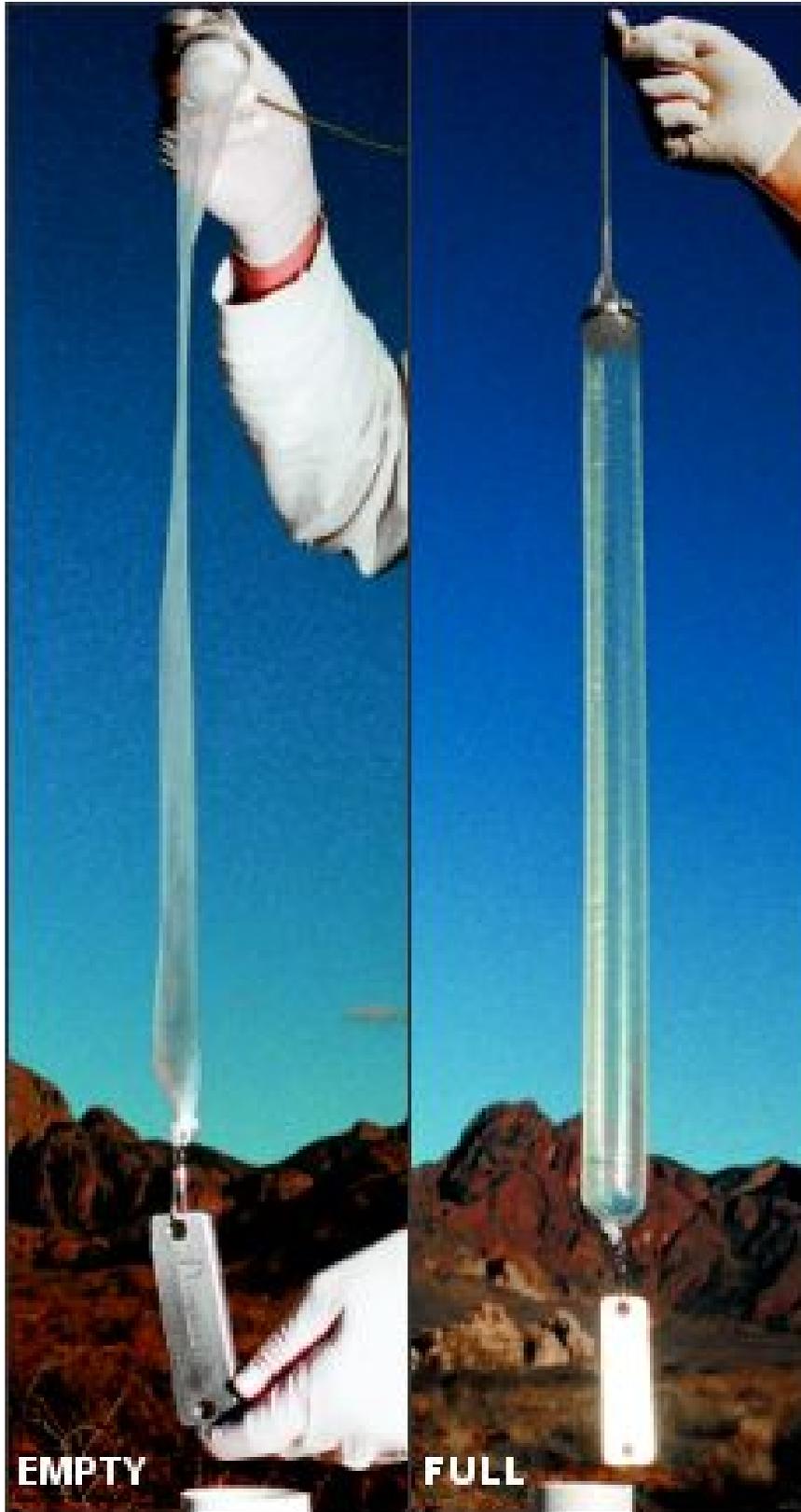
Figure 2.   The HydraSleeve™. Photo used with permission.
(*http://www.hydrasleeve.com/*)

This sampling technique has been demonstrated for many environmental contaminants of concern to the military, including volatile organics and explosives. No significant differences in recoveries of volatile organic compounds and explosives were observed between samples collected with the HydraSleeve™ versus control samples (Parker and Clark 2002). There are many advantages to using the HydraSleeve™ over other sampling techniques, including its compatibility with deployment in a monitoring well for long periods of time prior to sample collection. Bio-fouling is not a factor since compounds do not diffuse into the bags. The manufacturer reports 50 to 80 percent sampling costs savings can be obtained using this device (*http://www.hydrasleeve.com/pages/intro_to_ hydrasleeve.html*). Since the bags can be reused in the same well, decontamination of sampling equipment is not necessary. As with the PDBS, the bags cost approximately $25 each and only minimal training is required to become proficient in their use.

Field Analytical Technologies

Performing quantitative analytical determinations in the field requires highly specialized instrumentation. For example, unlike instruments operated in an air-conditioned fixed laboratory, field instruments must be able to withstand variable temperature and humidity conditions. Ideally, the equipment would have reliability that is equal to or greater than that observed for typical laboratory instrumentation, requiring little hardware or software maintenance. The instrumentation should be powered in the field by battery or generator and should require minimal peripheral components such as bulky gas tanks that would make deployment more cumbersome. Portable instrumentation should be sufficiently light to be carried to the monitoring site, if needed. Transportable instrumentation that can be driven to the site is also appropriate in many instances, though reaching some remote sites may be difficult.

Along with additional requirements compared to fixed laboratory equipment and processes, field analytical technologies and methods need to be cost effective. Capital costs for portable or transportable instrumentation, plus costs associated with analyst labor and expendable supplies, may initially exceed fixed laboratory costs. The point in time at which field analytical technologies become cost effective depends on several factors, including installation costs, the number of samples analyzed per event, the number of wells associated with each instrument, data handling and access methods, frequency of sampling, traditional sampling costs, sample shipment expenses, and laboratory analytical charges. Some of these factors, along with technical descriptions and examples of field use, will be discussed for select field technologies in the following sections.

Immunoassay

Immunoassay is a popular, effective, and inexpensive method for onsite environmental analysis. Four types of immunoassay technologies are generally used for various industries: enzyme immunoassay (EI), radioimmunoassay (RIA), fluorescent immunoassay (FIA), and enzyme-linked immunosorbent assay

(ELISA). Of the four, the ELISA technique is most often used for environmental field analysis due to high sample throughput, low detection limits, and high selectivity for the analyte of interest. The ELISA reagents are safe and easy to use, and, as with other immunoassay procedures, the ELISA methods generate a very small amount of nontoxic waste. The ELISA kits generally have long shelf lives. The kits are lightweight and highly portable and can be hand-carried to sites. Instrumentation for RIA is not as field portable as the equipment for other immunoassay methods. Also, the half-life of ^{125}I, commonly used with RIA, is short, and radioactive materials can be difficult to handle. Both EI and FIA are effective for detection of polychlorinated biphenyls, and FIA can be used for pesticides. But since these classes of compounds are not ordnance related, further descriptions of EI and FIA will not be provided here.

With the ELISA technique, contaminants of interest are determined through a competition between the analyte antigen and a tagged standard antigen for a limited number of antibody binding sites on a solid surface. In some instances, compounds with structural similarities to the analyte of interest also compete for the antibody sites. For example, compounds such as 1,3,5-trinitrobenzene, 2,4-dinitrotoluene, or tetryl can mimic TNT by binding to a TNT antibody. The kits are supplied with tables that indicate the potential for data quality impacts. Binding of the tagged standard antigen to the adsorbed antibodies induces a colorimetric reaction, but binding of the analyte antigen alone does not. Thus, the intensity of the observed color is inversely proportional to the concentration of the analyte in the sample. The concentration of the target analyte can be determined approximately by visually comparing the color intensity to a standardized color card. The ELISA method can provide quantitative, definitive data when a calibrated photometer or spectrophotometer is used to accurately and precisely detect absorbances. The photometer can be interfaced to a computer to electronically record results, or the analyst can manually record the results. Battery-operated photometers are available so that the immunoassay kits can be used in the field. As with other analytical methods, quality control samples such as blanks and matrix spikes are also required for generation of definitive data.

Immunoassay kits are commercially available for a limited number of contaminants, including trichloroethylene, tetrachloroethylene, TNT, RDX, and total petroleum hydrocarbons. Examples of these kits are the D TECH® TNT Explosives Field Kit, EnviroGard® TNT kit, and the RaPID® TPH/BTEX Assay, all now produced by Strategic Diagnostics Incorporated (Newark, DE). Explosive-specific antibodies are bound to the surface of a tube for identification and quantitation with the EnviroGard® kits. For the RaPID® kit (Figure 3), antibodies to petroleum hydrocarbons are bound to magnetic beads. For the D TECH® kits (Figure 3), antibodies are bound to nonmagnetic beads. Sample analysis by immunoassay requires multiple steps, including addition and removal of reagents, timed incubations and stirring, and time for color development.

Figure 3.   (A) RaPID TPH/BTEX assay kit; (B) D Tech TNT field kit. Photos used with permission.
(*http://www.sdix.com/ProductSpecs.asp?nProductID=33*;
http://www.sdix.com/ProductSpecs.asp?nProductID=21)

Thorne and Myers (1997) evaluated immunoassay kits for determination of TNT and RDX in groundwater from monitoring wells at three military sites. Results obtained with the immunoassay kits were compared to those obtained by a reference laboratory using reverse phase high performance liquid chromatography (RP-HPLC) according to SW-846 Method 8330 (USEPA 1986). The D TECH® kits for detection of TNT and RDX were observed to provide results within 10 min, approximately three times faster than other kits tested. The immunoassay results for TNT showed a high bias and a 30 percent false positive rate when compared to the results obtained by the reference laboratory. The Enviro-Gard® kit also had a high bias for TNT. Other investigators reported that matrix interferences such as particulates led to a high bias in TNT concentrations measured by the D TECH® kit (Craig et al. 1996). The D TECH® kit for analysis of RDX gave such poor results that a calibration curve could not be constructed by Thorne and Myers (1997). Detection limits for TNT and RDX with the D TECH® kits both exceeded the advisory limit of 2 μg/L for each analyte as determined by the USEPA (1988, 1989), which suggests the kits would be acceptable for use for site screening but not appropriate for monitoring to ensure regulatory compliance.

Gas chromatography

Analytical laboratories routinely use gas chromatography (GC) for the identification and quantitation of organic environmental contaminants. The technology provides highly sensitive and economical analysis with high resolution for a wide range of analytes, including volatile organics, polychlorinated biphenyls, pesticides, dioxins, furans, and explosives. Use of chemical class-specific detectors and columns can increase the selectivity of the analysis. Purchase prices for field or laboratory compatible GC instruments can range from $10,000 to $40,000. This section discusses field gas chromatography systems that generate definitive data and are already commercially available.

In a gas chromatographic system, target analytes in an inert carrier gas flow from an introduction system into a coated capillary column situated inside a temperature-programmable oven. Sample analytes undergo compound-specific interactions with the solid phase coating of the capillary column. The specificity

of the interactions cause the analytes to group together according to common characteristics and separate from compounds with different characteristics. Analytes elute from the column according to degree of interaction with the coating material so that compounds with little affinity for the material elute first and impinge upon a detector. Analyte concentrations are calculated according to the detector response as represented by peak area or height. Qualitative identification of analytes is based on column retention time.

Recent advances in gas chromatograph instrumentation have increased the practicality of field analysis (Santos and Galceran 2002). For example, high-speed GC technology with short columns enables near-real-time analysis of environmental samples. Also, multidimensional GC, which uses two differently coated columns in sequence, can lead to improved separation for highly complex mixtures such as PCBs. The use of ambient air as a carrier gas creates a significant advancement since it eliminates the need for heavy gas cylinders that supply only a few hours of operation (Grall et al. 2001). Nontraditional detectors, such as the surface acoustic wave device, can tolerate higher pressure than other detectors, such as the photoionization detector, so that smaller size pumps can be used (Whiting et al. 2001).

a. **Detectors.** Several detectors are compatible with gas chromatography for field detection of contaminants in water. These include highly specific detectors such as electron capture detector (ECD) for nitrogen-, oxygen-, and/or halogen-containing compounds and thermionic ionization detector (TID) for nitrogen- and/or phosphorus-containing molecules. Less specific detectors, such as the surface acoustic wave (SAW) detector, ion mobility spectrometer (IMS), and mass spectrometer (MS), that are applicable to a wider variety of analytes can also be coupled to GCs for field analysis. GC/IMS and GC/MS provide additional selectivity for analyte detection and will be discussed in sections that follow. GC technologies coupled to the other detectors listed will be discussed here.

The ECD is a highly sensitive detector for applicable compounds and, when used with GC, provides determination of organochlorine pesticides by SW-846 Method 8081B, polychlorinated biphenyls (PCBs) by Method 8082 and explosives by Method 8095 (USEPA 1986). Low µg/L quantitation limits are observed with the technology. The ECD employs a radioactive ^{63}Ni source that emits a continuous stream of beta particles that ionize the carrier gas and form a stable electron cloud in the ECD cell. Analytes are directed from the GC column to the ECD cell where they capture free electrons. The detector pulses at a faster rate to maintain constant current in the cell, and the pulse rate is translated to an analog output that is recorded as a peak when the rate increases.

The TID, also called the nitrogen-phosphorus detector (NPD), is another highly sensitive detector for GC, but is only compatible with compounds that contain nitrogen or phosphorous. The detector uses a glass bead containing alkali metals that is heated to high temperatures under low hydrogen flow to ionize the sample as it elutes in nitrogen carrier gas from the GC column. The hydrogen flow conditions are optimized so that compounds that do not contain nitrogen or phosphorous are not ionized. The ionized components are collected and counted to provide a peak with height or area used to determine analyte concentration.

b. **SRI Instruments Model 8610C GC-TID.** Hewitt and Jenkins (1999) demonstrated the feasibility of determination of explosives in the field with an SRI Instruments (Torrance, CA) Model 8610 GC (Figure 4) with dual TID and ECD. Extractions were performed by preconcentrating 1-L water samples onto membrane solid phase extraction filters and eluting with 5 mL acetone. Gas chromatography with an ECD can be used effectively for determination of explosives in water, as demonstrated in the laboratory by Walsh and Ranney (1998). The ERDC Cold Regions Research and Engineering Laboratory scientists used solid phase extraction to concentrate explosives analytes from water samples into acetonitrile (Jenkins et al. 1995) for analysis on a Hewlett Packard (Wilmington, DE) HP 5890 GC in the laboratory. For the field study, the ECD gave a nonlinear response for calibration standards, and HMX, though spiked, was not detected. System response with the TID was more linear. With the TID, HMX was observed, but, due to losses during the analysis, data quality was sufficient only for qualitative identification of HMX in unknown samples. The GC-TID method detection limits for explosives were approximately 500 ng/L, as compared with laboratory observed limits in the range of 40-400 ng/L from 0.5-L samples by GC-ECD (Walsh and Ranney 1998). Detection limits for the field GC-ECD system were not determined due to the nonlinear response.

A comparison of the field GC-TID method to explosives determination by RP-HPLC gave a correlation coefficient, r^2, of 0.998 for all explosives analytes (Hewitt and Jenkins 1999). The dinitrotoluenes were difficult to separate from HMX present at high concentrations, however. Also, the analyte recoveries of 61-71 percent that were observed from water samples spiked at low concentrations and extracted in the field were less than recoveries obtained during typical laboratory extractions of explosives. Hewitt and Jenkins concluded that analysis of explosives in the field with a transportable GC with TID could provide sufficient sensitivity and faster results than could be obtained in the laboratory, plus the method could detect a wider concentration range than could other current field methodologies. Sample throughput statistics were not reported, but analytical run times were less than 10 min. An electrical power source and the need for gas supplies were noted as constraints on operation in the field.

The SRI Instruments Model 8610C GC-TID system was evaluated by the USEPA Environmental Technology Verification (ETV) program for analysis of RDX, TNT, and 2,4-DNT in acetone extracts of soils in 2000 (Dindal et al. 2001b). Field data were evaluated against data produced by SW-846 Method 8330 at a fixed laboratory. The Model 8610C system weighed 75 lb and was operated at the sampling site. Two operators were able to prepare and analyze approximately three samples per hour. Daily set-up time in preparation for analysis was 1 hr.

Figure 4. Model 8610 GC. Photo used with permission.
(http://www.spectrolab.co.uk/gas_chromatography/gc8160.htm)

Through the study, the technology was shown to be highly accurate for RDX and TNT, giving average percent recoveries of 91 and 97 percent, respectively. Similarly, Hewitt and Jenkins (1999) reported recoveries of 94-113 percent for explosives extracted from soils in the field. Dindal and coworkers reported high method precision with mean relative standard deviations (RSD) of less than 25 percent for each of the three study analytes. Comparison of the field study results to results from the reference laboratory gave correlation coefficients of 0.95 for TNT, 0.85 for RDX, and 0.44 for 2,4-DNT. The low correlation for 2, 4-DNT was attributed to a low number of samples. Quantitation limits obtained by both the field method and the fixed laboratory analysis were 0.5 mg/kg for explosives in the study. The GC-TID data gave a 3-5 percent rate for false positives and a 2-4 percent rate of false negatives when compared to data reported by the reference laboratory.

Based on the evaluation study results, the USEPA concluded that the Model 8610C generated accurate and precise results for RDX, TNT, and 2, 4-DNT in soil extracts. Other explosives analytes included on the SW-846 Method 8330 target analyte list were not evaluated.

c. **Sentex Systems, Inc. Scentograph Plus II.** Another field-transportable gas chromatograph, the Scentograph Plus II manufactured by Sentex Systems, Inc. (Ridgefield, NJ), underwent ETV program verification for detection of chlorinated volatile compounds of groundwater at two sites in 1997 (Einfield 1998D). The target analytes at one site were limited to trichloroethene and tetrachloroethene, while contaminants at the second site also included chlorinated ethanes, 1,2-dichloropropane, and *trans*-1,3-dichloropropene. In addition to the actual site samples, 165 performance evaluation samples spiked with known concentrations of chlorinated volatile compounds were included in the study. The system was equipped with an ECD and a microargon ionization detector, however, only detection with the ECD was evaluated. Sample introduction was accomplished by continuous purge-and-trap followed by analyte preconcentration on Tenax or other adsorbent material. The system used a gas cylinder for carrier gas that provided 10-hr continuous operation before needing to be replaced. The technology gave practical quantitation limits of 1 μg/L for most volatile organic analytes when a 50-sec purge was used. The practical quantitation limit decreased to 0.1 μg/L with a 200-sec purge. Carbon tetrachloride and 1, 2-dichloropropane co-eluted.

The Sentograph Plus II GC weighed approximately 80 lb, was operated from a small van, and exhibited throughput capacity of two samples per hour. Data generated in the field for the groundwater samples was compared with data produced by a reference laboratory that received split samples. Notably, the reference laboratory analyzed samples by SW-846 Method 8260A (USEPA 1986) which is a GC/MS method. In both the field and the laboratory analysis, the median RSD for results was less than 10 percent. The correlation coefficients for low concentration analytes detected in the field and by the reference laboratory exceeded 0.95. The field analytical method gave results for only 35 of the 68 compounds present at concentrations greater than or equal to 1 μg/L that were detected by using the reference method. Of the 68 compounds included in the study, the field GC was only calibrated to quantitate 62. The field method pro-

duced high rates of false negative detections for 1,2-dichloropropane and 1,2-dichloroethane when present at 10 μg/L.

The ETV report noted that a technician could accomplish basic instrument operation but a more experienced analyst would be required for calibration, method development, and data handling. During the study, the purge-and-trap unit malfunctioned, as did the instrument-computer interface. Replacement of the purge-and-trap unit, followed by instrument recalibration, was required. The USEPA concluded that the Scentograph Plus II technology was appropriate for routine monitoring for regulatory compliance and also for screening during site characterization.

d. **Perkin-Elmer Corporation-Photovac Monitoring Instruments Voyager.** The ETV program also evaluated the Perkin-Elmer Corporation-Photovac Monitoring Instruments (Wilton, CT) Voyager field portable GC equipped with an ECD (Einfield 1998c) and the Model 4100 GC with SAW (Enfield 1998a) produced by Electronic Sensor Technology (Newbury Park, CA) at the same two sites used for the evaluation of the Scentograph Plus II described above.

The Voyager system, equipped for analysis of chlorinated volatile analytes in water, weighed approximately 50 lb and was operated from a small van. Sample throughput was estimated at three samples per hour, which is comparable to that achieved at a fixed laboratory. Data generated in the field were compared to results obtained by a reference laboratory that performed SW-846 Method 8260A. The field instrument falsely identified trichloroethene at both Federal sites and failed to detect five different compounds in more than 80 percent of the performance evaluation samples spiked at 10 μg/L. The reference laboratory reported no false positives and no false negatives. The field instrument correctly identified 89 percent of the analytes detected by the reference laboratory at concentrations above 1 μg/L in the site samples. The reference laboratory method detection limits were on the order of 0.1 μg/L for most chlorinated volatile compounds, and thus the reference laboratory was able to detect 68 compounds as present in the groundwater samples while the field instrument, with presumably higher detection limits, was only able to detect 39. Three pairs of analytes were observed to co-elute on the Voyager system and thus could not be differentiated. The reference laboratory method did not have such a significant problem with co-elutions because the GC/MS method uses both analyte retention time and spectrum to assign compound identification.

Data acquired with the Voyager portable GC were less accurate and less precise than data produced by the fixed laboratory. The average percent difference for select analytes of interest from replicate performance evaluation samples analyzed by the portable system was 41 percent, while the value was 7 percent for the reference laboratory. Median RSD in the performance evaluation samples was 20 percent with the Voyager and 7 percent at the reference laboratory. Precision improved to 15 percent median RSD with the Voyager analysis of the site samples, while the reference laboratory median RSD remained comparatively stable at 6 percent. Accuracy with the GC method would likely improve with incorporation of internal standard calibration rather than external calibration. Also, the field analyst may have reduced method performance by heating the

samples and then pouring them into containers for analysis, potentially losing volatilized analytes in the process.

The ETV report concluded that the Voyager portable GC was an appropriate technology for routine monitoring. Also, the report indicated that a trained technician could successfully accomplish basic instrument operation but a more experienced analyst would be required for calibration, method development, and data handling.

e. **Electronic Sensor Technology Model 4100.** As with the ETV evaluation of the Voyager field-portable GC, data generated in the field by the Model 4100 system (Enfield 1998a) were compared to results obtained by a reference laboratory that performed SW-846 Method 8260A. The Model 4100 GC with SAW detector uses an air sparge to remove volatile analytes from water samples. Analytes are directed to a trap and then thermally desorbed onto the head of the GC column. The instrument is equipped with a short chromatographic column so that data can be collected in about 30 sec for each sample. Analytes exit the column at the detector. The SAW device is coated with a nonspecific absorbing polymer that resonates at 500 MHz in the absence of analyte. Interaction of analytes with the polymer coating alters the resonance frequency. The frequency change is translated to a signal that is translated into a chromatogram by the instrument's proprietary processing and control software. The Model 4100 instrument, including a gas canister with a 5-day helium supply and a laptop computer, weighs only 35 lb. A more recently developed system is reported by the manufacturer to weigh less and perform sample analysis in only 10 sec (*http://www.estcal.com/Products.html*). The Model 4100 instrument showed a sample throughput capacity of two to three samples per hour, despite rapid data acquisition. Delays were attributed to sample complexity and data processing. The instrument was operated from a van that also supplied power to the instrument through an inverter connected to the van's battery. The instrument was ready to operate in only 20 min upon arrival at the site.

The Model 4100 portable GC identified only 64 percent of the target analytes that were identified by the reference laboratory for the same groundwater samples but identified 78 percent of the analytes spiked into performance evaluation samples. Six pairs of compounds were observed to co-elute, including trichloroethene that eluted with 1,2-dichloropropane. The median absolute percent difference for field analytical results compared to actual concentrations of spiked samples was low at 44 percent. The reference laboratory GC/MS performed with greater accuracy, giving a median absolute percent difference of only 7 percent. Comparison of results from the field analysis with those from the fixed laboratory showed excellent correlation at high and low concentrations of target analytes. No false positive results were reported, but false negatives were reported for 11 compounds in each of 10 performance evaluation samples spiked at 10 μg/L. A twelfth compound gave a 20 percent false negative rate. Typical GC/MS laboratory reporting limits for each of the compounds are below 10 μg/L, however, and, therefore, those compounds would be expected to be detected by the reference laboratory.

Data acquired with the Model 4100 system exhibited good precision with a median RSD of 15 percent for select target analytes in replicate analyses of per-

formance evaluation samples. The laboratory data gave a median RSD of 7 percent. The field data were considerably less accurate than the laboratory data; median average percent differences were 44 percent and 7 percent for the field and laboratory, respectively. The ETV report cited the need for improved sample handling procedures that could improve data quality.

As with the other GC systems discussed here, the ETV report noted that a technician could accomplish basic instrument operation but a more experienced analyst would be required for calibration, method development, and data handling. The system was judged to be an acceptable technology for groundwater monitoring for regulatory purposes and for site screening.

Mass spectrometry

Mass spectrometry is an essential tool for identification of organic contaminants in complex mixtures such as environmental samples. Due to generation of highly specific and characteristic spectra, wide dynamic range, and excellent sensitivity, mass spectrometry is widely considered to be the premiere analytical technique for acquisition of definitive data. Mass spectrometers can be interfaced to a number of sample introduction devices including GCs, liquid chromatographs (LC), solid phase micro-extraction fibers (SPME), membrane inlets, and direct sampling inlets. Of these, GC/MS is the most popular system and is used in today's laboratory for identification and quantification of volatile organics according to SW-846 Method 8260C and semivolatile organics by Method 8270D (USEPA 1986). Liquid chromatography/mass spectrometry (LC/MS) methods promulgated by the EPA include SW-846 Method 8231 (USEPA 1986) for detection of semivolatile analytes. For environmental samples in which detectors such as the ECD cannot identify target analytes due to background interference, use of the MS may provide confirmation through the characteristic mass spectral pattern generated for each individual analyte. Quantitation limits from GC/MS analyses are slightly higher for most analytes (1 μg/L vs. 0.1 μg/L) when compared to other GC detectors, but the high specificity of analyte identification is often a compensating factor.

A mass spectrometer is a system with five basic parts: vacuum system, sample introduction device, ionization source, mass analyzer, and ion detector. When coupled to a GC, the analyte molecules being eluted through the chromatography column by the carrier gas are directed to the MS. Unlike GC detectors for which identification of an analyte is based solely on column retention time, the MS allows the peaks eluting from the GC to be positively identified using their mass spectra and retention times. In GC/MS analysis for environmental contaminants, mass spectra are normally generated by electron impact ionization. The ionization occurs in the ion source by analyte interaction with an electron beam. As the 70 eV beam bombards the analytes, electrons are ejected from analyte molecules to generate positive ions known as molecular ions. With sufficient energy, molecular ions can dissociate into characteristic fragment ions and nondetected neutral molecules. The positive ions produced by electron impact are attracted through the slits of the ion source and mass analyzer. Ions are differentiated according to their mass-to-charge ratios. Ions are detected by an electron

multiplier, and the resulting ion count signal is used to create the mass spectrum for the analyte.

Manufacturers of mass spectrometer have recently reduced the overall size and increased ruggedness of the instruments, enabling analyses that were once only associated with fixed laboratories to be performed in the field. Laboratory GC/MS bench scale instruments, minus the computer and peripherals, are typically much larger in both weight and physical dimensions than field-deployable units. For instance, the dimensions of an Agilent Technologies (Palo Alto, CA) 6890 GC coupled to a 5973 MS are $20 \times 58 \times 22$ in. with a weight of approximately 194 lb. A typical compressed helium gas cylinder used in the laboratory is 4.5 ft tall, weighs approximately 200 lb, and must be securely fastened to a wall or other fixture to remain upright. Some portable GC/MS systems, including a gas canister and rechargeable battery, weigh approximately 50 lb and have size dimensions that are approximately one third those for laboratory fixed instruments, allowing deployment to remote sites to be accomplished much more readily. Purchase prices for portable instruments are typically in the range of $100,000 to $200,000.

Each component of the mass spectrometer system must maintain functionality when miniaturized. Technical advances that have enabled operation at reduced size for mass analyzers, instrument electronics, control computers, ion sources, and sample inlets have been achieved more readily than advances in vacuum technology (Badman and Cooks 2000). Low pressures are required so that ions can pass through the analyzer with minimal impedance from background gases. Since the pressure inside the instrument strongly influences detection parameters, the inability of current technology vacuum pumps to support the optimal performance of other system components has held back overall system development. A small number of field portable or transportable instruments are commercially available and have been demonstrated to be effective for collection of definitive environmental data.

a. **INFICON® HAPSITE® GC/MS.** The HAPSITE® quadrupole GC/MS (Figure 5) is manufactured by INFICON® (East Syracuse, NY) for determination of volatile organic compounds in the field. When equipped with a headspace sampling modification, 20-mL water and 10-g soil samples can be analyzed in standard 40-mL vials. The HAPSITE® can be outfitted with small gas canisters and a proprietary nonevaporable getter pump to give approximately 5 days of vacuum for analysis in the field. The field-portable model uses rechargeable batteries that provide approximately 3 hr of power. In the portable configuration, the system weighs 35 lb, or 51 lb when the headspace sampling modification is included. The system can be modified to a transportable vehicle-based version that weighs 75 lb by replacing the getter pump with a turbo molecular pump and rough pump and upgrading the power supply. The system provides laboratory-comparable data when operated according to procedures described in SW-846 Method 8260B (CEPA 2004). Twenty to twenty-five samples can be analyzed in an 8-hr day by this method. The quadrupole mass spectrometer utilizes electron impact ionization in the positive ion mode and can perform full scans or selected ion monitoring over a mass range of 45-300 daltons. The data handling system, which is equipped with the National Institute of Standards and Technology (NIST) library for automated compound identification, records the chromatogram

and spectra for each analysis. The system is calibrated in the same manner as a GC/MS at a fixed laboratory and can analyze quality control samples onsite to provide data of known quality. Detection limits for most volatile compounds range are in the range of sub-μg/L to 50 μg/L and are comparable to fixed laboratory limits. Improved detection limits for the HAPSITE® quadrupole GC/MS can be achieved through modification with a microtrap. The system is ruggedized to withstand field conditions from 0 to 45 °C and up to 100 percent humidity.

Figure 5.   The HAPSITE® Quadrupole GC/MS. Photo used with permission. (http://www.inficonchemicalidentificationsystems.com/hapsitechemical identification.html)

The HAPSITE® was evaluated by the USEPA in 1997 (Einfield 1998b) and more recently by the California EPA (CEPA 2004). The USEPA evaluated the transportable system at two sites contaminated with chlorinated volatile compounds. The system was observed to be operational within 30 min and throughput was 3 samples per hour. The absolute percent difference for compounds in standard mixtures was calculated to be 8 percent for the HAPSITE® and 7 percent for a parallel fixed-laboratory analysis by Method 8260B. Comparison of results obtained in the field and at the reference laboratory for groundwater samples with analyte concentrations both above and below 100 μg/L gave a linear correlation above 0.98. In a similar study using groundwater samples from the sites used by the USEPA, CEPA observed a linear correlation greater than 0.97. The USEPA concluded that the HAPSITE® could generate data comparable to those from a fixed laboratory and was appropriate for site screening and monitoring. The CEPA concluded that the HAPSITE® could generate data comparable to those produced in a fixed laboratory according to Method 8260B when the instrument was calibrated and appropriate quality control samples were included. The CEPA study also noted that the HAPSITE® is not accepted by the California Environmental Laboratory Accreditation Program. Successful use of the instrument requires approximately 3 days training for an operator already familiar with mass spectrometry, and up to a month may be needed to successfully modify method parameters to meet new applications. Benefits such as high

dynamic range, savings in cost and time, operation in harsh environments, and use for incident response were also noted.

    b. **Bruker Daltonics, Inc. EM640™ GC/MS.** The EM640™ mobile GC/MS (Figure 6a) manufactured by Bruker-Franzen Analytical Systems, Inc., now Bruker Daltonics, Inc. (Billerica, MA) and the SpectraTrak™ 672 GC/MS manufactured by Viking Instruments Corporation, now also part of Bruker Daltonics, Inc., were both evaluated by the USEPA in 1995 (Einfield et al. 1997a,b). The SpectraTrak™ 672 GC/MS is no longer commercially available. The EM640™ mobile GC/MS uses an optional sampler accessory to spray 250-mL aqueous samples through a nebulizer into a chamber with air as a carrier gas that transports the sample to a sorbent trap. After trapping, the sample is desorbed onto the GC column. Several sample inlet modules are available to extend the instrument's ability for analysis of different sample matrices. Due to the short GC column length, instrument throughput is high, with capacity for analysis of eight samples per hour. The manufacturer indicated that mathematical processing compensates for analyte co-elutions that result from the short column (Einfield et al. 1997a). The instrument has a mass range of 1-640 amu and wide dynamic range. The instrument can withstand harsh environmental conditions and operates over a temperature range of -10 to 45 °C. The system weighs approximately 140 lb, is operated from a vehicle, and can be powered by battery or generator. The manufacturer recommends a training period of 1 week for an experienced GC/MS chemist prior to operation.

A. **B.**
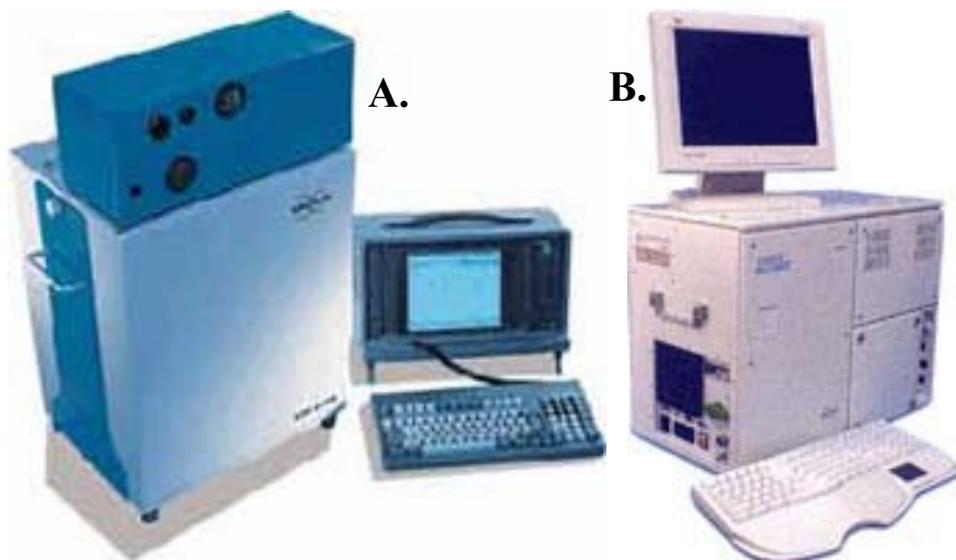
Figure 6.   Transportable GC/MS instruments (A) EM640^TM Mobile GC/MS; (B) The Viking 573 GC/MS. (*http://www.bdal.de/modux3/*). Photos used with permission.

    The USEPA evaluated the EM640™ mobile GC/MS at one site known to be contaminated with benzene, toluene, xylenes, and chlorinated organic solvents over a wide range of concentrations and at a second site which was contaminated primarily with trichloroethene and tetrachloroethene (Einfield et al. 1997a). The system was operable within an hour of arrival at each site after warm-up and

calibration en route. Approximately five samples could be analyzed per hour in the field. The median absolute percent differences for results for compounds in standard mixtures were calculated to be less than 50 percent for both the EM640™ and the fixed laboratory used as a reference. Relative percent differences for results of replicate samples were less than 50 percent. Detection limits for most volatile compounds were approximately 1 μg/L. As a result of the evaluation, the USEPA concluded that the EM640™ mobile GC/MS generated good quality data in the field.

　　　c. **Bruker Daltonics, Inc. Viking 573.** The Viking 573 (Figure 6b), a mobile GC/MS manufactured by Bruker Daltonics, Inc., is also designed to perform high-quality analytical chemistry in the field. The system uses a purge-and-trap sample inlet for analysis of volatile compounds. Direct injection is used for analysis of samples for explosives. The computer system operates on popular analytical software that contains the NIST mass spectral library. The system is capable of transmitting data offsite via a wireless Internet connection or modem. Detection limits for volatile organics approach low μg/L levels. For explosives, low mg/L levels are expected. The system is calibrated with procedures similar to those used in fixed laboratories and can analyze quality control samples as prescribed in EPA SW-846 methods. This unit utilizes the Hewlett-Packard 5973 Mass Selective Detector with a quadrupole mass filter. With an overall size of approximately 3 ft^3 and weight of 86 lb, the instrument is more transportable than portable. The Viking 573 is usually operated from a vehicle rather than directly at a sampling point. The instrument operates on 110-volt AC power. The manufacturer claims excellent precision and accuracy, comparable to fixed laboratory instrument performance. Two to three samples can be analyzed per hour in the field, which is similar to laboratory throughput capacity. The Viking 573 has not been evaluated by the ETV program.

　　　d. **Direct Sampling Ion Trap Mass Spectrometry.** Mass spectrometry can be performed in the field without a GC through use of alternative sample introduction techniques such as direct sampling ion trap mass spectrometry (DSITMS) (Figure 7), membrane interface mass spectrometry (MIMS), and fiber introduction mass spectrometry (FIMS). Direct sampling mass spectrometry was developed at Oak Ridge National Laboratory (ORNL) (Oak Ridge, TN) (United States Department of Energy (USDOE) 1998). Researchers at ORNL developed simple introduction devices that allowed a sample to be let into the mass spectrometer with little or no prior preparation and interfaced the inlets to a commercial ion trap instrument (USDOE 1998, Wise and Guerin 1997, Wise et al. 1997). The sample mixture does not undergo chromatographic separation into component analytes, so all analytes are detected at once and analytical response time is very short. The technology was licensed by ORNL to Tri-Corders Environmental, Inc. (McLean, VA). Instruments typically weigh approximately 120 lb and are operated on a table top or other comparably sized space. The system components can be powered by batteries or 110 Volt AC. For analysis of volatiles in water, analytes are sampled in headspace or purged with helium into a fused silica capillary restrictor. Other sample introduction devices can be interfaced to the capillary restrictor to broaden the analytical capabilities (Wise and Guerin 1997). For example, semivolatile analytes can be collected on sorbent tubes and thermally desorbed. Analytes are ionized by either electron impact or chemical ionization and analyzed in the ion trap. Analytes with the same

molecular ion and qualifying ion masses will not be differentiated by this method since chromatographic separation is not performed. For additional identification specificity, analyte ions can be isolated in the trap and provided sufficient energy to dissociate into characteristic fragment ions. The USEPA promulgated a DSITMS analytical method, SW-846 Method 8265, in 2002 for screening volatile organic analytes (USEPA 1986). Sensitivity for analyte detection is generally adequate for acquisition of quantitative data by this method; for well-characterized sites, qualitative identification of target analytes by this method should be sufficiently rigorous for the data to be acceptable to regulators as definitive.

Figure 7.   A vehicle-based DSITMS system
             (http://apps.em.doe.gov/ost/pubs/itsrs/itsr69.pdf)

The Department of Energy reported the performance of a vehicle-based DSITMS system at multiple sites in1998 (USDOE 1998). The USDOE noted a linear dynamic range of at least two orders of magnitude for volatile organic analytes. A comparison of in situ sparge DSITMS with SW-846 Method 8260 analysis by a fixed laboratory gave a linear correlation of 0.84. The USDOE considered the technology to be acceptable for multiple applications, including site characterization screening, remediation process monitoring, and periodic monitoring of volatiles in groundwater. A cost analysis for a field screening project showed that savings of more than $150,000 were achieved in one year for analysis of 643 samples compared to fixed laboratory costs. The performance evaluation also noted additional cost savings based on the need to drill fewer wells than planned by using the DSITMS method during site characterization.

The technology was demonstrated by the Environmental Security Technology Certification Program as a component technology of the site characterization

and analysis cone penetrometer system (SCAPS) (Davis et al. 2001, Myers et al. 2002). The DSITMS was also certified by the California EPA (CEPA 2000). Both studies showed that the technology performed analysis quickly and gave detection limits for volatile analytes comparable to values observed by EPA SW-846 Method 8260 performed in a fixed laboratory setting. The CEPA concluded that DSITMS should be considered a qualitative to semiquantitative method for many volatile analytes and recommended that a fixed laboratory analyze confirmation samples.

As with other transportable instrumentation, the DSITMS may have limited access to remote sites. Also, instrument operation requires an experienced GC/MS chemist with onsite training. If the in situ sparge probe is used, a tank of helium is needed onsite. Small tanks are available, but last for only a few days of continuous operation. Since the DSITMS does not use a separation technique prior to mass analysis, analysis is very fast, and several samples can be analyzed per hour. The technology is not adequate for complex mixtures of multiple analytes of concern and interferences, however.

e. **Griffin Analytical Technologies, Inc., Minotaur 400.** The portable Minotaur 400 cylindrical ion trap mass spectrometer (Figure 8) from Griffin Analytical Technologies, Incorporated (West Lafayette, IN) is an emerging technology with several options for sample introduction including SPME, MIMS, and GC. The cylindrical ion trap, having only end-cap electrodes and a cylinder-shaped ring electrode, is a simpler design than the traditional Paul trap used in many other ion trap instruments and is easier to miniaturize (Badman and Cooks 2000). A laboratory prototype system with SPME/GC interface is currently being evaluated for determination of explosives and PAHs by the authors of this report. The manufacturer suggests that the field system will have dimensions similar to a suitcase with a weight of approximately 50 lb. The instrument employs custom control software with files that are compatible with a popular analytical software package for additional data processing. The instrument provides increased selectivity through use of multidimensional mass analysis, MS/MS or MS^n scanning. For the MS/MS scan, the analyte of interest is isolated in the ion trap and then provided with sufficient energy to dissociate into characteristic fragments. The fragments are detected and displayed in the mass spectrum for the selected analyte. The MS^n scan allows for further selection of a fragment ion, followed by another stage of energy addition and subsequent fragmentation. These scan types increase confidence for analyte identification. The laboratory research grade instrument, the Minotaur 300, is approximately 1.7 ft^3 and can operate using 110-V AC or battery power. Operator training will be an important consideration for this instrument due to the novelty of the software as well as the hardware.

Ion mobility spectrometry

Ion mobility spectrometry (IMS) is a familiar technology due to its widespread use in screening baggage for explosives at airports. The technology can generate highly sensitive, precise, and accurate data that are accepted by the judicial system as well as environmental regulatory agencies. Sample analysis can be generally accomplished in seconds or in minutes if the spectrometer is coupled to a GC. Analytes are ionized, enter a drift tube, and travel along the tube at mass-

dependent rates to the detector. Ion counts are directly proportional to analyte concentrations. Analyte identities are derived from travel times. Several hand-held instruments are available for detection of organic compounds in vapors, but instruments that employ inlets other than headspace samplers for detection of contaminants in groundwater or soil samples are rarer.

Figure 8.   Minotaur 400 cylindrical ion trap mass spectrometer. Photo used with permission. (*http://www.griffinanalytical.com/main_products.html*)

The **GC-IONSCAN™** portable ion mobility spectrometer (Figure 9), originally developed by Barringer Instruments (Warren, NJ), now Smiths Detection, was evaluated by the ETV and Environmental Security Technology Certification (ESTCP) programs in 1999 for field determination of RDX and TNT in performance evaluation samples and in real-world groundwater and soil samples from five DoD sites (Dindal et al. 2000b). The instrument can be used for screening purposes by direct injection of samples followed by thermal desorption, or it can be used for more sensitive, quantitative data acquisition with injection onto the head of the GC column. Samples were subjected to a rapid solvent extraction prior to analysis on the GC-IONSCAN™ ion mobility spectrometer. Analytical results for performance evaluation samples indicated that the method was biased low for RDX and TNT in water, giving only a 46 percent recovery maximum for the samples evaluated. The GC-IONSCAN™ produced no false positive results for water samples but yielded a 39 percent false positive detection for RDX and 21 percent for TNT due to the high report-ing limit for both analytes.

Figure 9.   The GC-IONSCAN^{TM} portable ion mobility spectrometer . Photo used
             with permission.
             (*http://194.105.117.18/Documents/LifeSciences/GCIonScan_LS.pdf*)

Sensor technologies

Chemical sensors are devices that provide information about the chemical composition of the surrounding environment. They often combine physical transducers such as thermocouples or photodiodes with membranes or films that are selective and specific for the analyte of interest. The devices are generally small and lightweight, require low power, respond quickly, can be arrayed, and have high sensitivity. These characteristics make chemical sensors an attractive option for LTM.

Sensor technologies are not as readily available as the previously discussed field analytical technologies but are undergoing rapid development. Sensor technologies for environmental analysis fall into four primary categories: fiber optics, piezoelectric crystals, biosensors, and electrochemical detectors. Few full-scale commercial sensors are currently available for use for LTM. The Burge Environmental (Tempe, AZ) Ground Water Sampling System and TCE Optrode is an optical sampling and analysis device for TCE. With an observed limit of detection of 1 μg/L, sensitivity appears adequate for LTM of TCE. Several sensors such as the micro-ChemLab^{TM} hand-held instrument being developed by Sandia National Laboratories that will preconcentrate vapors onto a membrane, separate the contaminants through a miniaturized GC column, and detect the compounds through an array of SAW sensors or the Quartz Crystal Microbalance

under development by Nomadics (Stillwater, OK) show promise but are not yet beyond the prototype stage.

a. **Research International Fast 2000™ and Analyte 2000™.** In the sense considered here, biosensors use biological molecules such as DNA or antibodies to detect small molecules in a nonbiological environment. This definition excludes sensors that detect biomolecules such as glucose and also excludes sensors for microorganisms such as anthrax and tularemia. The Fast 2000™ and Analyte 2000™ immunosensors (Figure 10) were developed by the Naval Research Laboratory (Shriver-Lake et al. 1995; Bart et al. 1997) and licensed by Research International (Woodinville, WA). The Fast 2000™, a continuous flow sensor, and the Analyte 2000™, a fiber optic sensor, both use fluorescent immunoassay as a detection mechanism for field determination of TNT and RDX. For the Fast 2000™, an analyte-specific antibody is attached to a porous support material. Samples are introduced through injection into a flowing buffer. A fluorophore-tagged antigen, with chemical structure similar to the analyte of interest, binds to the antibody surface until displaced through competition with the target analyte in the sample. The fluorescent signal is monitored with a fluorometer and is inversely proportional to the concentration of analyte. Similarly for the Analyte 2000™, analyte-specific antibody is immobilized on the tapered tip of a fiber optic probe and binds to a fluorophore-tagged antigen. When exposed to the sample, the fluorophore-tagged antigen is displaced by the target analyte. The fluorophore is induced to fluoresce by the electromagnetic field known as the evanescent wave, which is generated by the fiber. The fluorescent light travels through the fiber to a detector. With multiple fibers coated with different antibodies, the probe can detect multiple target analytes simultaneously.
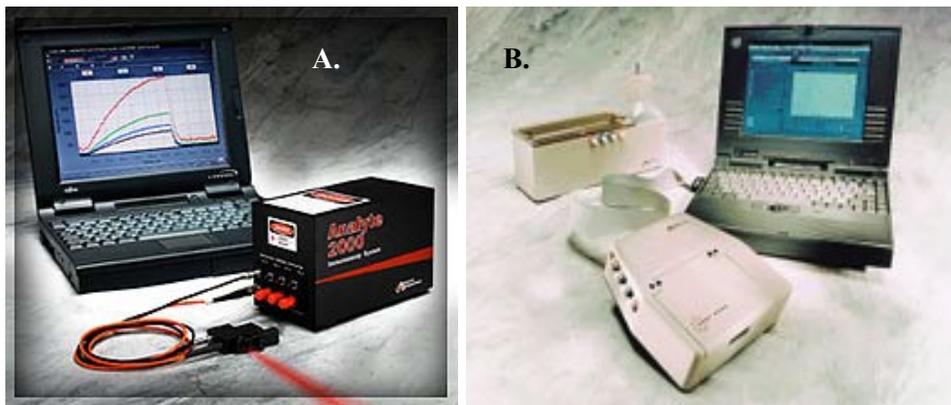
Figure 10. (A) The Fast 2000™ and (B) Analyte 2000™ immunosensors. Photos used with permission.
(*http://www.ornl.gov/sci/csd/Research_areas/etv/researchint.htm*)
(*http://www.resrchintl.com/analyte2000.html*)

Both systems were evaluated by the ESTCP (2000). Performance for detection of TNT and RDX in groundwater was demonstrated at three sites with known explosives contamination. Performance evaluation samples spiked with known contamination levels were also analyzed as part of the study. The ESTCP found that both systems were lightweight, portable, and easy to use. The Analyte

2000™ fiber optic assay for RDX was shown to be accurate with an average relative percent difference (RPD) of -8 for field results compared to fixed laboratory results obtained by SW-846 Method 8330. The average relative percent difference (RPD) for the TNT analysis with the fiber optic immunosensor was 74, which indicates a high bias and poor accuracy. Determination of TNT gave a 38 percent false positive rate while reporting no false negatives. Analysis of RDX gave 9 percent for both the false positive rate and false negative rate. Analysis of RDX and TNT with the FAST 2000™ continuous flow immunosensor gave acceptable average RPDs. The false positive rate for detection of TNT was observed to be 30 percent, while the false negative detection rate was shown to be 11 percent. False negative and false positive rates for RDX detection by the continuous flow sensor were 6 percent and 13 percent, respectively. Both devices were subject to matrix effects. Calibration with standards dissolved in clean matrix may lessen this problem. Sample throughput was greater for the continuous flow sensor, which required only 2-4 min per analysis, as compared to the fiber optic system, which required 12-17 min analysis time per sample. The start-up costs for each system were approximately $20,000-$25,000. Limited availability of the antibodies for RDX and TNT was noted and could be an impediment to use of the systems.

The Fast 2000™ was also evaluated by the ETV program in 1999 (Dindal et al. 2000a). Groundwater samples from four sites and performance evaluation samples with known concentrations of TNT and RDX were brought to a central field location and analyzed. For this study, sample results for the continuous flow immunosensor compared poorly with results from the reference laboratory. The percent difference values for both TNT and RDX were greater than 75 percent, whereas acceptable results would be in a range of ± 25 percent. The results for performance evaluation samples demonstrated poor accuracy with average recoveries for TNT and RDX at 316 and 192 percent, respectively. False positive detections for TNT were reported for 80 percent of the blank samples; RDX gave a 24 percent false positive rate. The reference laboratory also produced high false positive rates for both analytes when analyzed according to SW-846 Method 8330. False negative rates for both analytes were low at 3 percent compared to the reference laboratory results. Operators with minimal training could analyze three samples per hour. Overall, the system was considered imprecise and biased high for both analytes.

Research International, Inc., attributed some of the poor performance to operator errors in data handling and subsequently revised the software. The manufacturer also upgraded the analytical system to a new product called the FAST 6000™. The new system is reported to have better signal-to-noise ratios, multiple detection channels, and enhanced flow-system performance (Dindal et al. 2000a). Demonstrations or evaluations of the upgraded system were not found in the literature.

b. **Texas Instruments/Nomadics, Inc. Spreeta™ Sensor.** Detection of TNT in the field is possible with the Spreeta™ Sensor (Figure 11) developed by Texas Instruments (Dallas, TX) and marketed by Nomadics, Inc. (Stillwater, OK). The device is a miniature optical biosensor based on competitive immunoassay and the surface plasmon resonance (SPR) phenomenon. For the immunoassay component of the sensor, trinitrobenzene (TNB) is immobilized onto a thin

gold film on a sensor chip surface through a bovine serum albumin (BSA) link. Antibodies to TNT are cross-reactive with TNB and will adhere to the TNB-BSA-gold film surface. The antibodies preferentially bind to TNT when it is present in a solution. An aliquot of TNT-specific antibody solution is added to samples prior to analysis. The antibodies will bind with TNT present in the sample, or in the absence of TNT, to the TNB complex adhered to the chip surface. Antibody binding causes an increase in the refractive index of the aqueous layer near the surface of the chip. Reflected light from a critical angle of incidence at the chip surface induces an evanescent field in the gold layer of the chip that leads to propagation of surface plasmon waves. The surface plasmon waves increase the amplitude of the evanescent wave, which induces resonance absorption of energy from the reflected light and decreases its intensity. The increase in refractive index that occurs with antibody binding alters the critical angle of incidence for surface plasmon resonance to occur. Changes to the angle of incidence are monitored and converted to analyte concentration.
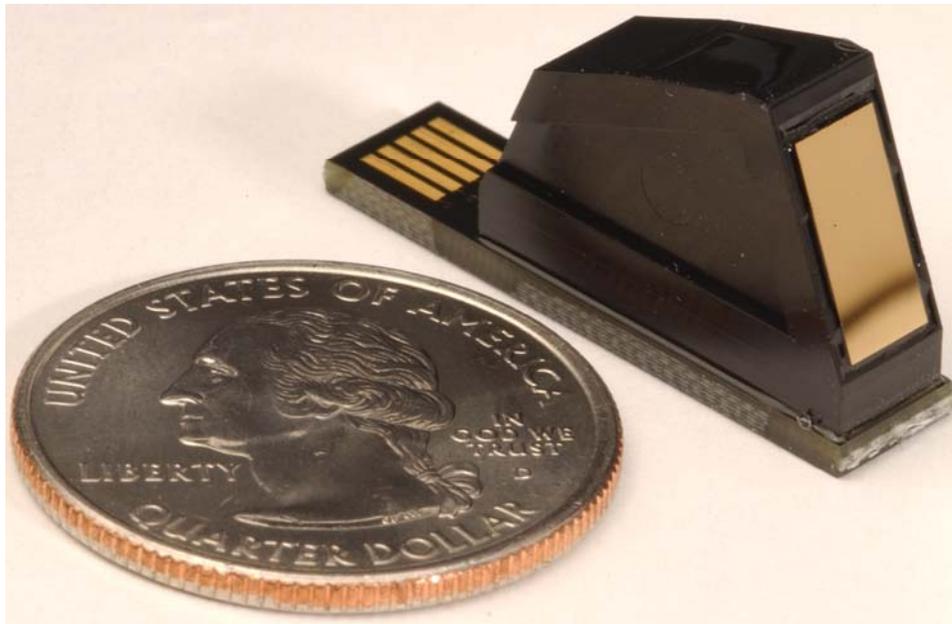
Figure 11. Spreeta™ TSPR2KXY biosensor. Photo used with permission.
(*http://www.ti.com/snc/pdf/spreeta-tspr2kxy-product-bulletin.pdf*)

The Spreeta™ Sensor was evaluated by the ETV in 2000 for field detection of TNT in soils (Dindal et al. 2001a). For the ETV study, soil samples from five different DoD sites were analyzed in a mobile laboratory on Oak Ridge National Laboratory. Samples were contaminated with multiple explosives compounds including TNT, DNT, RDX, and HMX but only analyzed for determination of TNT. Performance evaluation samples were included in the study, and all samples were also analyzed by a reference laboratory using SW-846 Method 8330. The Spreeta™ Sensor was calibrated over a range of small intervals rather than over a linear range. Performance evaluation sample results were comparable to expected results for 75 percent of the samples. A low bias was observed for 21 percent of the spiked samples. For real-world samples, the surface plasmon resonance sensor gave results that agreed with those from the reference labora-

tory for 65 percent of the samples. A low bias was observed for 32 percent of the samples. The sensor result was within 10 mg/kg of the result obtained by the reference laboratory for a majority of those samples, however. The sensor gave no false positive results and only a 3 percent false negative rate when compared with results from the reference laboratory. A single instrument had a sample throughput capacity of six samples per day. The device was easy to operate and easy to transport, weighing less than 3 lb.

The ETV study concluded that the Spreeta™ Sensor was an acceptable technology for determination of TNT at concentrations less than 10,000 mg/kg in the field. Since the soil samples were extracted with water, and the water extract was analyzed, the Spreeta™ Sensor technology should also be applicable to direct analysis of groundwater samples.

Colorimetric methods

A colorimetric method originally developed by Jenkins and coworkers at the ERDC Cold Regions Research and Engineering Laboratory, Hanover, NH (Jenkins and Schumacher 1990, Jenkins et al. 1994), was developed into a field kit for detection of RDX and TNT by EnSys (now Strategic Diagnostics, Inc., Newark, DE). Water samples are passed sequentially through two solid phase extraction filters and eluted with acetone. The extract from the first filter is reacted with base to generate highly colored species that absorb at 540 nm. The extract from the second filter is reacted with zinc after acidification. Under these conditions, RDX will yield nitrous acid. Further reaction of nitrous acid with Griess reagent will form an azo dye that absorbs at 510 nm. Results from the kits correlate well with SW-846 Method 8330 but are subject to interferences from humic acids, nitrates, and molecular sulfur (Jenkins and Walsh 1991). Detection limits for TNT and RDX in water are 1 μg/L and 4 μg/L, respectively. The detection limit for RDX is above typical action levels.

4   Conclusions

Commercially available technologies could be implemented for LTM to reduce costs and maintain data quality, but they must be assessed for compatibility with project requirements prior to selection. Detection of semivolatile analytes, such as ordnance-related compounds, in groundwater is not a capability that is as prevalent in analytical instrumentation as the ability to detect gases and volatile organic compounds. Current technologies also have limited capability for identification and quantitation of multiple analytes and are often more suitable for projects with only a single analyte of concern. Project-specific factors such as regulatory action levels, sampling frequency, number of monitoring wells, and data quality objectives must also be evaluated. Site-specific factors such as accessibility, analytical interferences, and number and types of analytes to be monitored must be considered when selecting a technology. Personnel with sufficient training must be available to operate field analytical instrumentation. Current monitoring costs must be compared to projected costs, keeping in mind that initial capital expenses for implementation of field monitoring are likely to exceed the costs for analysis at a fixed laboratory. Overall cost savings will be achieved through reduced wastewater generation, elimination of sample shipment, multiplexed technologies, lower labor costs for sampling personnel, and minimized fixed laboratory analysis.

Innovative sampling techniques, such as the passive diffusion bag sampler and the Hydrasleeve™, appear to have high potential for successful implementation at LTM sites. The relative ease of use and reduction of purge water volume, along with the ability to allow profile contamination of the well at different depths, should encourage acceptance by project management. The ability to deploy samplers months prior to a sampling event is also an advantage of these devices. Low-flow purge sampling is now the industry standard, primarily because only small volumes of wastewater are produced.

Field technologies for analysis of LTM groundwater samples are also available. Immunoassay techniques can provide semiquantitative screening data that may satisfy requirements for some projects. Incorporation of quality control samples such as duplicates and spikes could increase data quality for regulatory acceptance. Immunoassay would not be appropriate for sites with significant concentrations of cross-reactive species present that could interfere with accurate quantitation of the analyte of interest. Also, some kits are not appropriate for regulatory monitoring due to high detection limits.

Field-portable analytical instrumentation has advantages over analysis of samples at offsite laboratories including fast data turnaround. Quality control procedures can be incorporated onsite with many of the new miniaturized gas chromatographs and mass spectrometers. Instrumentation for analysis of volatile organics has been widely demonstrated, but the availability of instrumentation for effective determination of semivolatile analytes in water is more limited. Field extraction is an issue which must be resolved to enable analysis of semi-volatile compounds in the field. Also, some of the instruments for detecting volatile organics may not have sufficient mass range to detect semivolatile organics.

Barriers for implementation of field analytical methods include a potentially large initial capital investment and limited availability of trained personnel. These factors may not be the responsibility of a specific project but of some other entity such as a laboratory or architectural engineering firm, however. The need for determination of multiple parameters per site and limited availability of devices for detection of wide distributions of analytes are significant impediments to incorporation of field analytical methods for ordnance-related compounds. The small market for field analytical instrumentation is another disadvantage. Resolution of these and other barriers will require investment in development and demonstration of versatile, reliable, easy-to-use, multipurpose, and cost-effective technologies.

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Appendix A
Long-Term Monitoring Resources on the Internet

All website addresses were verified as accessible as of September 17, 2004.

General

1. Interstate Technology Regulatory Council, *http://www.itrcweb.org*.
2. List of Contaminants and their MCLs, *http://epa.gov/safewater/mcl.html#mcls*.
3. Strategic Environmental Research and Development Program (SERDP), *http://www.serdp.org*.
4. Environmental Security Technology Certification Program (ESTCP), *http://www.estcp.org*
5. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, *http://www.epa.gov/epaoswer/hazwaste/test/sw846.htm*
6. USEPA Field Analytic Technologies Encyclopedia (FATE), *http://fate.clu-in.org*.
7. United States Army Corps of Engineers, *http://www.environmental.usace.army.mil*
8. EPA Remediation and Characterization Innovative Technologies, *http://www.epareachit.org*
9. The Federal Remediation Technology Roundtable Field and Innovative Sampling and Analysis Technology Matrix, *http://www.frtr.gov*
10. Groundwater Central, *http://www.Groundwatercentral.info*

Low-Flow Purge Technologies

11. MP20 Flow-Through Cell, *http://www.qedenv.com*.
12. YSI 556 Multiprobe System, *http://omnicontrols.com/lists/ysi_556.htm*.
13. Multi Parameter TROLL 9000, *http://www.in-situ.com/In-Situ/Products/MPTROLL9000/TROLL9000.html*.
14. Flow-Through Cell System, *http://www.solinst.com/Prod/475/475.html*
15. Standard Practice for Low-Flow Purging and Sampling for Wells and Devices Used for Ground-Water Quality Investigations, ASTM Standard D6771-02. *http://www.astm.org*.

16. A Tale of Two Samplers – Parts I and II, *Pollution Engineering Online*. *http://www.etpproducts.com/bailers_vs._low_flow1.htm*.
17. Low-Flow Purging and Sampling Ground Water – Evolution of Technology and Standards, *ASTM Standardization News*. *http://www.qedenv.com/pdfs/astm_low-flow.pdf*.

Discrete Interval Samplers

18. HydraSleeve, *http://www.hydrasleeve.com/pages/intro_to_hydrasleeve.html*.
19. Columbia Analytical Services, *http://www.caslab.com*
20. EonProducts, Inc., *http://www.eonpro.com*
21. United States Geological Survey, *http://www.usgs.gov*

Immunoassay Technologies

22. Immunoassays for Environmental Contaminants (Pesticides) in Food and Water, *http://www.sdix.com/TechSupport/bulletins/T00037.pdf*.
23. EPA – Immunochemical Analysis, *http://www.epa.gov/heasdweb/edrb/chemistry/immochem/user-guide.htm*

Gas Chromatographs

24. Baseline-MOCON, Inc., *http://www.baselineindustries.com*.
25. SRI Instruments, *http://www.srigc.com*.
26. Environmental Technology Verification Program, *http://www.epa.gov/etv/verifications/verification-index.html*.
27. ISC Buyers' Guide – Portable Gas Chromatographs, *http://www.iscpubs.com/bg/us/prod/prod1642.html*

Mass Spectrometers

28. Introduction to Mass Spectrometry, *http://masspec.scripps.edu/information/intro/chapter1.html*.
29. Agilent Technologies, *http://www.chem.agilent.com*.
30. HAPSITE SituProbe Purge and Trap GC/MS System, *www.inficon.com*.
31. Viking 573 – Immediately Usable Mobile Mass Spectrometer, *www.bdal.com/viking573.html*.
32. Minotaur 400, *www.griffinanalytical.com/main_products.html*
33. Direct Sampling Ion Trap Mass Spectrometer (DSITMS), *http://www.tri-corders.com*.
34. "EPA Adopts an ORNL method for screening VOCs in the field," *http://www.wpi.biz/initiatives/2002/20020903.asp*.
35. GC-IONSCAN, *www.smithsdetection.com*

Sensors

36. Sandia National Laboratories, *http://www.sandia.gov*
37. National Exposure Research Laboratory, *http://www.epa.gov/nerl*
38. Oak Ridge National Laboratory, *http://www.ornl.gov*

Appendix B
Corps of Engineers Chemists Survey

A survey was sent to project chemists throughout the Corps of Engineers on two occasions to help the long-term monitoring focus area team better understand user needs and gauge the extent of field analytical method use.

Table B1 presents the results of the May 2003 survey, and Table B2 presents the results of the September 2004 survey.

Table B1
Survey Results of Long-Term Monitoring Practices, May 2003 Survey

Question	1. Project	2. Projects	3. Projects	4. Projects	5. Projects
1. How many Long Term Monitoring projects are you personally involved with at the present time?	2	1	3	0	2
	Unknown	$30,000-$40,000	$100,000-$200,000	$200,000-$300,000	>$1,000,000
2. What is the total approximate cost per year (including sampling, analysis, data review, etc.) of the Long Term Monitoring projects?	1	2	1	2	2
	Groundwater only	Soil only	Both Groundwater and Soil		
3. What are the matrices of concern for the LTM projects?	6	1	1		

(Continued)

Table B1 (Continued)

	VOA	Metals	Exp.	BNA	P/PCB	Other
4. What are the analytes of concern?	6	5	2	6	6	3

	SW-846/Other EPA Sampling Procedures	Passive Diffusion Samplers	Low Flow Pumps	Others		
5. What types of sampling methods are used?	5	1	5	2		

	<5 Years	5-10 Years	10-20 Years	20-30 Years	>30 Years	
6. In general, for how many years is the monitoring planned?	3	2	2	2	2	

	Quarterly	Semi-Annually	Bi-annually	Annually	Multi-Annually	3 Times a Year
7. What is the sampling frequency?	3	3	1	2	1	1

	State Environmental Department	Federal-EPA	Federal-DOD	Local	Tribal	
8. What authority is the source of the monitoring requirement?	6	7	1	0	0	

	Yes	No	Hydrosleeve™	GeoProbe	Passive Diffusion Bags	DITMS
9. Are any of the following innovative technologies used on the Long Term Monitoring projects?	2	6	0	1	1	0

	At the Sampling Location	On-Site Laboratory	Off-site Laboratory			
10. Where are the samples analyzed?	0	0	8			

(Continued)

Table B1 (Continued)

	Yes	No		Reason
11. Are field analytical methods (FAMS) used?	1	0		Costs are not known.
		0		Trained personnel are not available.
		1		FAMS are not available for the analytes of interests.
		2		FAMS are not available that can meet the necessary detection limits.
		3		FAMS only give screening data and the project needs definitive data.
		5		Regulatory requirement for off-site analysis.
		1		The analysis has always been done off-site.
		0		Never considered using FAMS

	Electronic Data Base	Paper Results Report Received Through the Mail	Faxed Paper Results Report	Narrative Summary of Results	Other
12. What is the format of the reported data?	5	4	0	1	2

	Electronic Database	Hard Copy	Verbal, then Hard Copy Reports	No Preference Indicated
13. What is the preferred format for the reported data?	4	2	1	1

	<24 Hours	1-6 Days	1-2 Weeks	2-4 Weeks	1-2 Months	2-3 Months	>3 Months
14. What is the typical time interval between sample acquisition and data reporting?	0	0	2	1	2	3	1

	Yes	No					
15. Does the typical time interval between sample acquisition and data reporting meet your needs?	8	0					

	<24 Hours	1-6 Days	1-2 Weeks	2-4 Weeks	1-2 Months	2-3 Months	>3 Months
16. What is the typical time interval between receipt of the data and review for project decision making:	0	2	1	0	2	1	2

(Continued)

Table B1 (Concluded)

	Yes	Comment	No	Comment
17. Is real time data reporting desirable for your Long Term Monitoring projects?	1	If it is acceptable to regulators and saves money	1	Not required
			1	Unless it could save money
			1	Doesn't require dense real-time data.
			1	This is LTM, not RI work.
			1	LTM data is to assess trend, not make field decisions.
			1	Mostly driven by regulatory requirements.

	Yes	No	Comment
18. If a field analytical method could meet project requirements, would you use it for your Long Term Monitoring project?	3	1	The customer is not likely to allow the change.
		5	The regulator is not likely to allow the change.
		1	Both the customer and the regulator would have to allow the change.
		1	There are accountability benefits with using an independent lab and validator

Table B2
Survey Results of Long-Term Monitoring Practices, September 2004 Survey

Question	1-5 Projects	6-10 Projects	More than 10 Projects			
1. How many Long Term Monitoring projects are you personally involved with at the present time?	13	3	2			

	Unknown	<$100,000	$100,000-$199,000	$200,000-$300,000	>$300,000	
2. What is the total approximate cost per year (including sampling, analysis, data review, etc.) of the Long Term Monitoring projects?	2	6	3	5	2	

	Groundwater	Groundwater & Soil	Air	Biota	Sediment	
3. What are the matrices of concern for the LTM projects?	13	6	1	1	1	

	VOA	Metals	Exp.	Anions	BNA	P/PCB	Others
4. What are the analytes of concern?	13	10	8	6	10	10	7

(Continued)

Table B2 (Continued)

	Encore Samplers	SW-846/Other EPA Sampling Procedure	Passive Diffusion Samplers	Low Flow Pumps	Others		
5. What types of sampling methods are used?	1	7	0	17	5		
	<5 Years	**5-10 Years**	**10-20 Years**	**20-30 Years**	**>30 Years**		
6. In general, for how many years is the monitoring planned?	3	3	1	8	4		
	Quarterly	**Semi-annually**	**Annually**	**Other**			
7. What is the sampling frequency?	7	15	12	1			
	State Environmental Department	**Federal-EPA**	**Federal-DOD**	**Local**	**Tribal**	**Other (DOE)**	
8. What authority is the source of the monitoring requirement?	11	9	4	0	0	1	
	Yes	**No**	**Hydrosleeve**[TM]	**GeoProbe**	**Passive Diffusion Bags**	**DITMS**	**Other**
9. Are any of the following innovative technologies used on the Long Term Monitoring projects?	6	12	0	2	1	0	5
	At the Sampling Location	**On-Site Laboratory**	**Off-site Laboratory**				
10. Where are the samples analyzed?	2	1	18				

(Continued)

Table B2 (Continued)

	Yes	No	Reason
11. Are field analytical methods (FAMS) used?	3	1	Costs are not known.
		0	Trained personnel are not available.
		1	FAMS are not available for the analytes of interests.
		2	FAMS are not available that can meet the necessary detection limits.
		3	FAMS only give screening data and the project needs definitive data.
		7	Regulatory requirement for off-site analysis.
		7	The analysis has always been done off-site.
		3	Never considered using FAMS.
		1	Turnaround time is not a factor

	Electronic Data Base	Paper Results Report Received Through the Mail	Faxed Paper Results Report	Narrative Summary of Results	Other		
12. What is the format of the reported data?	15	12	1	5	2		

	Electronic Data Base	Hard Copy	No Preference Indicated				
13. What is the preferred format for the reported data?	15	3	3				

	<24 Hours	1-6 Days	1-2 Weeks	2-4 Weeks	1-2 Months	2-3 Months	>3 Months
14. What is the typical time interval between sample acquisition and data reporting?	0	0	0	8	6	4	1

	Yes	No	Usually				
15. Does the typical time interval between sample acquisition and data reporting meet your needs?	12	1	5				

	<24 Hours	1-6 Days	1-2 Weeks	2-4 Weeks	1-2 Months	2-3 Months	>3 Months
16. What is the typical time interval between receipt of the data and review for project decision making:	0	2	3	6	1	4	1

(Continued)

Table B2 (Concluded)

	Yes	Comment	No	Reason	Unknown
17. Is real time data reporting desirable for your Long Term Monitoring projects?	1	Potential to impact drinking water	8	Not time critical	1
	1	Important for system optimization	1	No risk to health or life	
	1	If all parameters could be measured	2	No reason given	

	Unknown	Yes	Comment	No	Reason
18. If a field analytical method could meet project requirements, would you use it for your Long Term Monitoring project?	1	5	If methods were approved by Regulators	1	Off-site analysis required by Regulators
		6	No reason given	5	Regulator is not likely to approve change
				2	Happy with current system

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14. ABSTRACT

Long-term monitoring (LTM) of remediated sites can be required on a quarterly basis for 30 or more years before site closure, with costs for sample collection, shipment, and analysis at an offsite fixed laboratory contributing 50 to 75 percent of the total expense. Cost-effective sampling techniques and field analysis could substantially reduce these costs. This technical report identifies and describes proven and promising sampling devices and onsite analytical instrumentation that potentially could be used now for LTM of ordnance-related compounds in groundwater. Instrumentation that generates data which can be used for regulatory decisions must be sufficiently sensitive to detect analytes of concern at action levels and must have excellent precision and accuracy to meet data quality requirements. Instrumentation for LTM must provide rigorous qualitative as well as quantitative identifications. The following general categories of field analytical technologies applicable to volatile organic chemicals and organic ordnance-related chemicals are included in this report: water quality monitors associated with low-flow purge techniques, discrete interval samplers, immunoassay for detection of explosives, gas chromatography with liquid compatible inlets, mass spectrometry with liquid compatible inlets, ion mobility spectrometry with liquid compatible inlets, chemical sensors, and colorimetric technologies.

15. SUBJECT TERMS	Commercial off-the-shelf technologies	Field portable technology	Miniature gas chromatograph
Chemical sensors	Discrete interval sampler	Groundwater monitoring	Miniature mass spectrometer
Colorimetric	Field analytical method	Immunoassay	Ordnance related compounds

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