A Review of Emerging Sensor Technologies for Facilitating Long-Term Ground Water Monitoring of Volatile Organic Compounds



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1.0 INTRODUCTION

1.1 PURPOSE OF THIS REPORT

This report summarizes the status of emerging sensor technologies for facilitating long-term ground water monitoring for a class of contaminants called volatile organic compounds (VOCs). It also describes a number of factors, including regulatory acceptance and cost-effectiveness, that influence the applicability of these technologies. The focus is on long-term ground water monitoring that is generally associated with a selected remedy, such as monitored natural attenuation or pump and treat.

The following three technology categories are considered:

- technologies that provide in-situ sampling and analysis of VOCs in ground water (i.e., sampling and analysis conducted within a monitoring well)
- commercialized technologies that automate both sampling and above-ground analysis of VOCs in ground water
- hand-held or otherwise field-portable instruments that can be used for the analysis of VOCs in ground water at the well where the sample is obtained

Both the sensor technologies and probes based on those technologies are discussed. Technologies specifically associated with cone penetrometers or direct-push samplers are not considered because these approaches are generally more applicable to site investigations and characterization rather than long-term monitoring.

1.2 BACKGROUND

1.2.1 THE ROLE OF GROUND WATER MONITORING

Ground water monitoring serves a number of vital roles in the characterization and remediation of contaminated ground water. During a remedial investigation, ground water samples are collected and analyzed to determine the types of contaminants present and the horizontal and vertical extent of those contaminants. The resulting data provide much of the information necessary to determine an effective remedial approach. Once a remedy is selected and operational, ground water monitoring is used to determine the progress of remediation and to ensure the remedy is operating effectively. This type of monitoring is frequently referred to as long-term ground water monitoring. It is often distinct from monitoring associated with site investigations and is the type of monitoring discussed in this report.

During long-term monitoring, samples may be collected from monitoring wells within a plume to determine the progress toward aquifer restoration, and samples may be collected from monitoring wells outside of the plume to ensure that contaminants are not migrating toward potential receptors. Samples may also be collected from actual receptors, including supply wells or surface water, to determine if contamination has reached them.

1.2.2 THE ESTIMATED MAGNITUDE OF THE GROUND WATER MONITORING MARKET

Ground water remediation and associated monitoring often takes decades, and ground water monitoring wells are generally sampled quarterly, semi-annually, or annually during a long-term ground water monitoring program. Depending on the size of a contaminated site, the hydrogeologic parameters, and the extent of the contamination, the number of samples collected from monitoring wells per sampling event may range from a few to over 100. A 2001 EPA report titled *Groundwater Pump and Treat Systems: Summary of Selected Cost and Performance Information at Superfund-financed Sites* (EPA 542-R-01-021a) indicates that, on average, a Superfund-financed pump and treat system has 23 monitoring wells that are sampled three to four times per year. Although this number of monitoring wells is not necessarily representative of all sites with ground water contamination, it provides an order of magnitude estimate.

There are thousands of sites with contaminated ground water, and volatile organic compounds (VOCs) are common ground water contaminants at these sites. Using the EPA NPL Advanced Query Form [*EPA OERR*, 2003], a June 2003 search listed 1,000 sites that are on, proposed for, or deleted from the National Priorities List (NPL) with ground water contamination and with VOCs as an identified constituent of concern. In addition, the EPA RCRA program identifies 1,714 sites in its RCRA Cleanup Baseline (i.e., high priority sites). In a study of 889 of these sites, 90% were identified as having ground water contamination and 85% were identified as having VOCs as an identified contaminant of concern [*EPA OSW*, 2002]. The EPA Office of Underground Storage Tanks (OUST) provides another indicator of the number of contaminated sites and the potential need for monitoring VOCs in ground water. In its Fiscal Year 2002 End of Year Activity Report (December 23, 2002), OUST indicated that approximately 143,000 UST sites still require cleanup. Beyond the sites mentioned above, there are others that are part of State programs.

Given that thousands contaminated sites exist through the country and many other contaminated sites exist throughout the world, it is conservative to estimate that long-term ground water monitoring programs result in millions of ground water samples collected and analyzed each year. In the United States, the large majority of these samples are analyzed in laboratories accredited by the National Environmental Laboratory Accreditation Program, which identified 1,680 individually accredited laboratories throughout the United States in May 2003 [*NELAP*, 2003].

1.2.3 LIMITATIONS OF CURRENT GROUND WATER MONITORING APPROACHES

The process of collecting ground water samples is time consuming and labor intensive, and analysis of the samples is generally conducted in off-site laboratories. Due to the required labor

and analysis, ground water monitoring is relatively expensive. In addition, due to the collection, preparation, and transportation of samples from monitoring wells to distant laboratories, ground water monitoring is prone to errors. The large number of samples collected and analyzed each year, the relatively high cost of collecting and analyzing each sample, and the potential for errors warrant research into new technologies for facilitating ground water monitoring.

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2.0 TRADITIONAL SAMPLING AND ANALYSIS

In order to evaluate the progress of emerging technologies, it is important to establish the currently utilized procedures for sampling and analysis and the associated costs.

2.1 TRADITIONAL OR CURRENTLY USED GROUND WATER SAMPLING METHODS

Ground water sampling from a monitoring well generally follows the procedure outlined below:

- 1. Determine the water level in well with an interface probe
- 2. Calculate the water volume in the well
- 3. Using either pumps or bailers, purge the well to remove at least three volumes of water
- 4. Collect a sample using a bailer or pump and transfer it to an appropriate sample bottle
- 5. Dispose of or decontaminate equipment

At the end of a sampling event, the water is disposed of properly and samples are packaged for shipment to an analytical laboratory. In general, anywhere from 3 to 10 wells can be sampled in a day by a single team of technicians, although this sampling rate depends heavily on site-specific conditions.

Low-flow or low-stress sampling has been introduced to provide a more accurate representation of ground water conditions under natural flow. This technique is generally used to reduce the presence of contaminants associated with particulates that may be mobilized during traditional sampling procedures but not mobilized under natural conditions. It is also beneficial because less purge water is generated compared to three-well volume purging. Low flow sampling requires the stabilization of various parameters including turbidity, dissolved oxygen, specific conductance, temperature, pH, and oxidation-reduction potential. Because of this stabilization process and other aspects of this procedure, the sampling rate is relatively similar to that of traditional sampling depending on site conditions.

Sampling with passive diffusion bags is another alternative to traditional sampling for VOCs. A typical passive diffusion bag sampler consists of low-density polyethylene tubing filled with distilled, deionized water and sealed at both ends. The bags are suspended in the monitoring well at specific elevations and allowed to equilibrate with the ground water flowing through the well. This equilibration period may last approximately two weeks. The bags are then retrieved from the well, and the enclosed water is transferred to sampling bottles for transport to the laboratory. This method is less labor intensive because it eliminates the time and water disposal associated with purging the wells. Interviews with environmental consultants conducted as part of the research for this report suggest that approximately 20 bags can be installed by two people in less than a day, and the bags can be retrieved and samples collected by two people in one day.

Interviews with environmental consultants suggest that a site with 20 wells can generally be sampled with three-well purging or low-flow sampling for approximately \$3,000 to \$8,000 per event. The variation is heavily dependent on site-specific conditions such as distance between and access to the wells and well-specific conditions such as depth, diameter, and yield. These costs include labor (with overhead) and equipment but assume extensive travel, per diem, and lodging are not required. They also do not account for laboratory analysis, data interpretation, or reporting. For passive diffusion bags, this cost can be significantly reduced. For example, the approximate cost of sampling 20 monitoring wells with this approach (including bag deployment and sample collection) is approximately \$2,000 to \$3,000. These costs are reasonable approximations based on 2003 dollars and may vary due to a number of factors. They are however, representative of typical sampling costs and are suitable for comparison to the new technologies described in this report.

2.2 CURRENTLY USED ANALYTICAL METHODS FOR VOCS

The above costs do not include actual analysis of the samples. Analysis is generally done using EPA SW-846 test methods, and for VOCs, the more widely used methods are 8260b and 8021b. Both techniques use gas chromatography, but 8260b uses mass spectrometry and 8021b uses a photoionization detector (PID) and/or a electrolytic conductivity detector. When combined with other approved methods to extract the contaminants from the water into the vapor phase, both methods are capable of detecting the more prevalent VOCs including halogenated hydrocarbons, such as trichloroethylene (TCE), and BTEX compounds (i.e., benzene, toluene, ethylbenzene, and xylenes).

Although costs of these samples may vary depending on location, number of samples, and service agreements or contracts, a competitive 2003 price for method 8260b is approximately \$110 per sample, and a competitive price for 8021b is approximately \$85 based on a standard turnaround time of approximately 3 weeks.

In addition to the ground water samples, other samples are require analysis for quality control. These samples include "trip blanks", "field blanks", and duplicates. The total cost of a sampling event should include the costs for these additional analyses.

Based on the above analytical costs, the cost of analyzing samples from 20 wells with traditional analytical methods is approximately \$2,500, bringing the estimated total cost for traditional sampling and analysis of 20 wells at a site to approximately \$5,500 to \$10,500 per event.

3.0 REQUIREMENTS FOR EFFECTIVE SENSOR-BASED INSTRUMENTS FOR LONG-TERM GROUND WATER MONITORING

A sensor-based instrument for ground water monitoring is designed for a target analyte or analytes. It distinguishes them from other chemicals present, determines the concentration of the analyte(s), and releases a measurable signal to the user or datalogger. A variety of technologies have been employed for this purpose, but to be effective for long-term ground water monitoring of VOCs, the sensor-based instrument should have the following characteristics:

- Sensitivity The sensors should be sufficiently sensitive to detect ground water contaminants at concentrations found at many sites. The federal maximum contaminant levels (MCLs) are often adopted as the remediation standards, though some states may have more stringent standards. Ideally, the detection limit for a particular compound should be lower than the MCL. However, instruments with less sensitivity could still provide meaningful results at many sites. In addition, because concentrations at a site might range from the low ug/L range to the high mg/L range, varying degrees of sensitivity are applicable and sensors with a dynamic range would be beneficial.
- Accuracy The concentrations measured by the sensor should closely match the actual concentrations of the constituents being measured. This requires that the sensor be repeatedly calibrated against known standards.
- Precision The concentration measurements from a particular sample or from samples with the same actual concentrations should be consistent with minimal variation.
- Reversibility Because the conditions in a particular monitoring well might change over time or the instrument might be moved from one well to another, one measurement should not be biased or influenced by a previous measurement. The instrument should be able to "reverse" back to a baseline between each sample.
- Speed The instrument should be able to make a measurement within an appropriate amount of time. If the instrument is to be left in place for long-term monitoring, only infrequent measurements might be necessary and the measurement time can be fairly long. However, if the instrument is moved from one well to another in a single sampling event, the measurements would be more frequent and the measurement time would need to be on the order of seconds or minutes.

- Durability The instruments should be able to withstand the harsh conditions of ground water and the handling associated with field activities. Depending on the site and the technology, a single instrument may be used for measurements in multiple wells or locations on the same day or it may be left in a single well indefinitely for measurements over an extended period of time. Specific consideration should be given to the potential for corrosion and biofouling.
- Reliability The instruments should operate reliably with minimal maintenance.
- Simplicity The instruments should be relatively easy to calibrate and utilize in the field.
- Selectivity Ground water at hazardous waste sites may contain a variety of contaminants, and a sensor should be able to determine concentrations of specific target contaminants with minimal interference from the other contaminants.
- Affordability The instrument and operating procedures should be affordable and cost-effective compared to the existing approach to traditional ground water sampling and analysis.
- Acceptability Sensors should be acceptable to both the party using the sensor and the agency that oversees or regulates the remedial activities. Such acceptability likely requires the sensor technology to be proven relative to the traditional methods and documented quality assurance and quality control measures.

4.0 EMERGING SENSOR TECHNOLOGIES FOR ANALYSIS OF VOCS IN GROUND WATER

This section describes emerging sensor technologies for long-term ground water monitoring of VOCs. Some technologies have been developed to collect and analyze a ground water sample within a well. Other technologies have been developed to automatically collect a sample, transport it out of the well, and analyze it either above-ground or in a separate subsurface chamber. In addition, some hand-held or otherwise field-portable analytical technologies are being developed for field analysis of ground water samples. Although the developers of the first two types of technologies classify to them as "in-situ" (i.e., sampled and analyzed in place rather than in an external environment), for the purposes of this paper, only the former type of technology (i.e., where both the sampling and analysis is conducted in the well) is classified as "in-situ".

Specific projects are presented for the three classes of technologies mentioned above. The information provided comes from publicly available literature and personal interviews with members of the project teams. Technologies and individual projects were identified by an internet search and discussions with professionals interested in identifying these technologies. The projects presented in this report are not necessarily the only projects involved in developing these technologies but represent the large majority of the efforts involved in developing sensor technologies for the facilitation of the sampling and analysis of VOCs in ground water. Additional project teams are likely involved in similar work but were either not identified or insufficient information was found. For example, projects were identified in both Japan and Germany, but detailed descriptions of them are not available in English as of the writing of this report.

A number of other qualifications regarding this list of technologies should also be noted:

- The field of sensor development is large and varied with projects devoted to developing instruments for exploration of other planets, quality control in the food and packaging industry, health and safety in the work place, homeland defense, and other fields. Some of these technologies may be transferable to ground water monitoring but because research efforts are not necessarily directed to ground water monitoring these technologies may not have been identified for this report.
- Some sensor technologies may be sufficiently early in their developmental stages such that the broad range of their application, which may or may not eventually include ground water monitoring, may not yet be known.
- Other sensor technologies are being developed for analysis of metals and explosives in ground water. Description of these technologies is beyond the scope of this report.

Although it is targeted for in-situ ground water monitoring, the 2001 Sandia Report titled *Review* of Chemical Sensors for In-Situ Monitoring of Volatile Contaminants [Ho, et al., 2001], provides a broader description of sensor technologies that are not necessarily limited to ground water monitoring for VOCs. Various gas analyzers, electrochemical sensors for analyzing metals, and other sensors are described and a number of links are provided.

4.1 TECHNOLOGIES FOR IN-SITU VOC SAMPLING AND ANALYSIS OF GROUND WATER

A number of technologies are currently being developed for in-situ sampling and analysis of VOCs in ground water and each technology faces the technical problem of distinguishing the target analyte from other chemicals in the surrounding environment and then accurately quantifying the amount present. The following technologies address these technical problems but are in various stages of development. For each technology a brief description and current efforts are provided.

4.1.1 CHEMIRESISTORS

This technology is based on chemically sensitive resistors that are comprised of a conductive polymer film applied to a micro-fabricated circuit. When specific chemical vapors come into contact with the polymer, it swells, changing its resistance and therefore providing a measurable electrical response. Each sensor includes an array of these resistors with different polymers, and mathematical analysis of the signals (chemometrics) from each resistor is used to determine the concentrations of multiple constituents in the sample. Because measurements are made in the vapor phase, the vapor phase concentration must be converted into a aqueous or liquid phase concentration using Henry's Law.

Sandia National Laboratories In-situ Chemiresistor Sensor

The Sandia chemiresistor probe includes a sensor that is isolated from the surrounding ground water by a selectively permeable membrane that allows vapors, but not water, into the sensing chamber. A variety of VOCs can be detected including BTEX (benzene, toluene, ethylbenzene, and xylenes) compounds and chlorinated compounds, such as trichloroethylene (TCE). The sensor, however, needs to be calibrated for specific contaminants. The actual measurement process with this technology is fast (a few minutes), but the sampling chamber would need time (on the order of hours) to equilibrate with the surrounding ground water if the environment were changed (i.e., if the probe was moved to a different depth in a well or moved to a different well).

The sensor includes an array of four chemiresistors with a temperature sensor and a heating element (for measuring/controlling temperature) encased in a waterproof package. Additional commercial devices have been included to provide measurements of pressure, ambient temperature, and relative humidity. A prototype probe without the heating element has been constructed and field tested at Edwards Air Force Base during FY02. The sensor probe

withstood a water pressure of up to 30 feet. It was able to operate continuously for four months at a depth of 5 feet below the water table powered by a 20 watt solar panel. The sensor polymers were unstable due to the high humidity and condensation in the sensor chamber. Including the heating element and temperature sensor on the chemiresistor chip can maintain the chip temperature above the ambient temperature to avoid condensation. This feature will implemented for the FY03 field tests. The sensor detection limit in laboratory conditions is approximately 0.1% of the saturated vapor pressure. For TCE this translates to an aqueous concentration of approximately 1,000 ug/L (compared to the MCL of 5 ug/L) and to xylene of approximately 2,000 ug/L (compared to the MCL of 10,000 ug/L). Because the TCE concentrations in the test well during the FY02 field tests were lower than this detection limit, the sensor and traditional analytical results could not be compared.

Sandia is in the process of adding a pre-concentrator to the probe to improve its sensitivity. Vapor phase contaminants collect on the concentrator over a specified time, and then the preconcentrator is flash heated to release the accumulation of contaminants onto the chemiresistors. With the pre-concentrator, the sensitivity of the probe will likely improve by an order of magnitude or more. The addition of a pre-concentrator and associated field testing of the probe will likely occur in FY04, but additional funding is required for this to occur.

Expected Cost per Unit

The expected cost of the probe cannot specifically be quantified at this time; however, the components are generally inexpensive. Although the costs of manufacturing the actual chemiresistors is low (i.e., well under \$100), the housing, cable, and other items will add to the cost. In addition, sale prices are higher than manufacturing costs and will depend on the number of units that can be sold. The project team does not yet include a commercial partner for manufacturing and distribution.

Project Contact

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4.1.2 QUARTZ CRYSTAL MICROBALANCES

The sensing technology consists of an array of quartz crystal microbalances (QCMs) coated with various polymers that selectively absorb the contaminants of concern. As the contaminants adsorb to the polymer, the mass on the surface of the QCM changes. This mass on the QCM affects its resonant frequency, which can be measured electronically. Different polymers can be developed to detect different compounds. Like the chemiresistor technology, a single sensor includes multiple QCMs and chemometrics of the resulting signals is used to determine the constituents and concentrations of the sample. A variety of VOCs can be detected, but the sensor requires calibration for specific contaminants.

Nomadics, Inc./General Electric Quartz Crystal Microbalance Sensor

Also like the chemiresistor technology, this sensor is isolated from the surrounding ground water by a selectively permeable membrane that allows vapors but not liquid to enter. Inside the chamber, the chlorinated compounds in the vapor phase adsorb to the polymers, and therefore create a QCM response that can be measured. Once again, the vapor phase concentration must be correlated to the aqueous or liquid phase concentration and time (on the order of hours) is required for equilibration if the probe is moved to a different location.

For this particular probe developed by Nomadics, the polymers (developed by General Electric) are designed to adsorb chlorinated compounds such as TCE and carbon tetrachloride. An array of QCMs, each coated with a different polymer, is isolated in a chamber within the submerged probe. Some of the sensing units have the ability to measure humidity and temperature so that these factors can be controlled when measuring the contaminant concentrations. When a measurement is completed, the vapor in the chamber is purged through a carbon canister to prevent VOC-laden air from leaving the probe.

The development status of this sensor technology is relatively mature. Field testing of a probe prototype is scheduled at two facilities for February and March of 2003. The probe is approximately 2 inches in diameter and 6 feet long and is designed to be used in monitoring wells that are 2 inches in diameter or more. The probe is designed to operate autonomously and has an induction link that allows data to be transferred and the on-board batteries to be charged. At this point, maintenance of a probe would be expected semi-annually.

Laboratory results suggest concentrations as low as 50 ug/L are feasible. If requested, probes could likely be manufactured and distributed for at least limited use by the end of FY03.

The current focus of this probe is to use it for vertical profiling of contaminant concentrations in a single well. The probe elevation is controlled by a winch and is lowered to various levels within the screened interval of the well. When a new level is reached, the probe is allowed to come to equilibrium with the new surroundings, which requires a few hours, and a measurement is taken. Currently, the probe can make one run of multiple measurements in a 24-hour period with the onboard battery requiring charging every 48 hours.

Although vertical profiling of concentrations is useful for some applications, long-term monitoring would generally involve a single measurement in a single well per sampling event.

Expected Cost per Unit

The expected cost per unit is unclear at this point. The crystals each cost approximately \$100 and at least three are required per probe. Additional costs are associated with the housing, cable, and electronic boards. Ultimately, the cost per unit is dependent on the market: the more probes that can be sold, the more inexpensive they will be. Nomadics handles the manufacturing and sales. They estimate that initial costs may be as high as \$7,500 per probe but that costs may be lower depending on the number of units that can be sold.

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4.1.3 HIGH RESOLUTION ION MOBILITY SPECTROMETRY (IMS)

This technology uses a radioactive foil to ionize contaminants in the vapor phase and then propels the ions through a drift tube toward a collector. The time of flight for the ion to travel the length of the drift tube is dependent on a number of factors including the mass of the ion. If other parameters are held constant, then the time of flight can be used to determine the mass of the ion and therefore the compound. The technology has sufficiently high sensitivity to detect contaminants below their MCLs and can distinguish between a variety contaminants (including chlorinated hydrocarbons and BTEX compounds) in a single sample. IMS units are generally large and reserved for laboratory or well-controlled field conditions. They are also used for detecting explosives or other trace chemicals as part of airport security.

Boise State and Washington State Universities Ion Mobility Spectrometer

A team of scientists at Boise State University and Washington State University are developing a ground water monitoring system that incorporates a miniaturized IMS unit. The unit is approximately 4 centimeters in diameter, which is small enough to fit in a direct-push probe or in a 2-inch monitoring well. The team is currently designing the unit to be installed with direct-push techniques into the vadose zone, but modifications can be made to house the unit in a probe that can be installed in the saturated zone. Samples would be collected, measurements would be made in the subsurface, and data would be transmitted to the surface. Once at the surface the data could be collected on-site or could be retrieved remotely by wireless communications. The data would then require interpretation, which can be automated, to convert the analysis results into specific contaminants and concentrations.

The team is in a relatively early phase of research and development. Work began in the Summer of 2002 and a prototype probe is expected during 2003. Additional funding will be required to further develop and improve the technology.

Expected Cost per Unit

The expected cost of the probe cannot specifically be quantified at this time; however, the components are generally inexpensive. Although the costs of manufacturing the sensor is low (i.e., under \$100), the housing, cable, and other items will add to the cost. In addition, sale prices are higher than manufacturing costs and will depend on the number of units that can be sold.

Project Contact

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4.1.4 RESONANCE ENHANCED MULTIPHOTON IONINZATION (REMPI)

This is a spectroscopic approach to selectively detecting contaminants. Lasers of specific wavelengths with narrow bandwidths are used to ionize the contaminant of concern without ionizing other chemicals. The ionized chemical is then more easily detected. The measurement takes place directly in water.

University of South Carolina, REMPI Fiber-Optic Sensor

A fiber-optic probe has been developed that is capable of being submerged. The primary research focus is on lasers that are appropriate for detecting various compounds. Most of the work to date has been on BTEX compounds with detection in the \sim 1 ug/L range. Current efforts are to identify lasers for detecting chlorinated solvents like TCE and carbon tetrachloride.

Bench testing has been conducted, but additional bench testing and field testing is still required. The research group is currently working to renew the funding from DOE.

This group is also pursuing research based on the use of nanoparticle photocatalysts and fiber optics. A fiber-optic tip is coated with the photocatalyst and the VOC breaks down into simpler compounds upon exposure to light that is sent down the fiber.

Expected Cost per Unit

The cost of an individual unit, once manufactured, is difficult to estimate at this time, but the Characterization, Monitoring, and Sensor Technology Crosscutting Program [*CMST-CP*, 2001] reported that the cost of the commercial lasers is reportedly approximately \$7,500. The project team does not yet include a commercial partner for manufacturing and sales.

Project Contact

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4.1.5 WAVE-GUIDES

A laser provides a coherent beam of light that is split and sent across two strips on a fabricated wave guide: a test strip and a reference strip. The presence of contaminants changes the refractive index (an optical property) on the test strip, but the reference strip is unaffected. Because the light on the sample strip is altered, an interference pattern results when the two beams of light are recombined and the light intensity of the recombined beam is different than that of the original beam. This change in light intensity are analyzed to determine the contaminant concentration.

Selective polymers or reagents are used on the test strip to increase the sensitivity and selectivity of the instrument to specific contaminants. Measurements can be made directly in water; therefore, no conversion using Henry's Law is required.

Georgia Tech Bio-Optoelectronic Sensor System (BOSS)

Proto-type sensors have been developed but have not necessarily been incorporated into a testable probe. Current efforts funded by the Defense Advanced Research Projects Agency (DARPA) Optoelectronics Center are focused on miniaturizing the sensor onto a small microchip that can be mass produced at relatively low cost. Detection capabilities are approximately 50 ug/L to 100 ug/L. Laboratory results are promising but the chip-sized sensor will not be ready for field testing for a few years. The larger-scale technology has been licensed to a commercial partner. A member of that project team could not be reached for comment.

Expected Cost per Unit

The expected cost of the probe cannot specifically be quantified at this time; however, the components are generally inexpensive. Although the costs of manufacturing the sensor chip is under \$100, the housing, cable, and other items will add to the cost. In addition, sale prices are higher than manufacturing costs and will depend on the number of units that can be sold.

Project Contact(s)

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NJIT Integrated Photonic Sensor

Proof of concept has been completed in the laboratory using percent concentrations of ethanol and methanol. The ability to detect contaminants in 1 to 10 ug/L range is expected when selective polymers are used. Additional funding is required to move from the proof of concept phase to the applied phase.

Expected Cost Per Unit

The expected cost of the probe cannot specifically be quantified at this time; however, the components are generally inexpensive. Although the costs of manufacturing the sensor chip is under \$100, the housing, cable, and other items will add to the cost. In addition, sale prices are higher than manufacturing costs and will depend on the number of units that can be sold.

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Roland Levy, New Jersey Institute of Technology <u>LevyR@adm.njit.edu</u> (903) 596-3561

4.1.6 MID-INFRARED FIBEROPTIC SENSORS

This technology uses a mid-infrared light source, polymer coated silver halide optical fibers, and a Fourier transform infrared (FT-IR) spectrometer to detect chlorinated hydrocarbons and aromatics in water. Other variations involving hollow waveguides and gas phase analysis after stripping VOCs from the aqueous phase are also developed are also under development by this team. The coated fiber serves as a fiber-optic evanescent wave sensor (FEWS) and is exposed to the contaminated water. The chlorinated hydrocarbon contaminants adsorb to the polymer, and as mid-infrared light travels through the fibers, it is influenced by the contaminants adsorbed to the polymer. FT-IR spectroscopy, which has been used widely since the 1960s, is used to analyze the change in the light signal. The membranes that coat the fibers can be selected based on the target analyte. Alternatively, miniaturized evanescent field sensors based on quantum cascade lasers are currently in development.

Georgia Tech Mid-Infrared Fiberoptic Sensors

This project team is well diversified, working on sensors for monitoring constituents in ground water, surface water, and marine environments in both the United States and Europe. The same general technology is used for each of these efforts, so field tests in one environment lend pertinent information to development of probes for other environments. Ground water probes have been tested both in simulated/controlled environments and in the field. Currently, the technology can measure concentrations of 5 to 10 various VOCs (including TCE, tetrachloroethylene, and BTEX) in a single sample with detection limits of approximately 100 ug/L. Efforts with various lasers and membranes are focused on increasing the sensitivity to allow for detection in the 1 to 10 ug/L range.

Prototype sensors have been developed, and the team is pursuing additional opportunities for field testing. The currently developed "dip-probe" can be used to sample 2-inch wells to a depth of approximately 20 feet below ground surface. Below this depth, the light is increasingly attenuated by the increasing fiberoptic length. In this application, the FT-IR spectrometer remains above-ground and a probe is lowered into the well. Alternatively, ground water or VOCs purged from the ground water with air can be sent to the surface to be measured in a flow

through cell. Further developments of FT-IR detectors are leading to smaller units that will soon allow deployment of a probe to greater depths.

At least two applications are foreseen for ground water monitoring: the probe can either be submerged in a single well for a long duration or it can be moved from one well to another well. Use of the second application depends on the equilibrium time for the contaminants to adsorb to the polymer. Depending on the accuracy required, measurements with a probe may take from one minute (accuracies of approximately 10%) to 60 minutes (accuracies of 1% to 2%).

Current efforts include increasing the sensitivity, extending the lifetime of the polymers in water (they currently last approximately 3 weeks), designing a probe that can reach greater depths, and further refining the technical operation including chemometric data evaluation. Work is currently supported by the U.S.G.S. National Water Quality Initiative for surface water and ground water monitoring, the Department of Energy Gas Hydrates Program for deep sea spectroscopic sensing, and the European Union for landfill leachate monitoring.

Expected Cost per Unit

The expected cost to manufacture a probe is approximately \$1,000 to \$2,000 although the cost is dependent on the type of sensitivity and selectivity required. The actual price of a unit, however, will be higher, particularly if a fully featured FT-IR spectrometer is included (\$20,000 to \$40,000). The project team has a number of commercial partners for development efforts, but the current focus is not yet on manufacturing and sales. In addition, sale prices are higher than manufacturing costs and will depend on the number of units that can be sold.

Project Contact

Dr. Boris Mizaikoff, Georgia Institute of Technology boris.mizaikoff@chemistry.gatech.edu (404) 894-4030 http://asl.chemistry.gatech.edu/

4.1.7 UV-INDUCED FLUORESCENCE SPECTROSCOPY

Jet Propulsion Laboratory (JPL)

JPL has reportedly field tested a device that uses UV-induced fluorescence spectroscopy to detect contaminants in water. This technology uses UV light to cause compounds in the sample to fluoresce and measures the intensity of the fluorescence. The technology was originally developed for exploration on Mars, but has been modified for ground water analysis. A prototype instrument was reportedly tested at Edwards Air Force Base, but the project team was not available for comment.

Expected Cost per Unit

No expected cost was obtained.

Potential Project Contact

Arthur Lonne Lane, Jet Propulsion Laboratory 818-354-2725 Arthur.L.Lane@jpl.nasa.gov

4.2 COMMERCIALIZED AUTOMATED TECHNOLOGIES FOR VOC SAMPLING AND ABOVE-GROUND ANALYSIS OF GROUND WATER

The technologies described in this section are already commercialized but are under further development. They provide automated systems for sampling VOCs that transport the samples to automated analytical units that are located outside of the well, either at the surface or another subsurface chamber. This approach reduces the number of sensors required because a single analytical unit can serve more than one sampling probe. This approach also keeps the sensor readily available for servicing or calibration.

Waste Technologies of Australia VOC Monitor

This product incorporates both a sampling and a sensing technology. For sampling, VOCs in the subsurface (saturated or unsaturated zone) diffuse into semi-permeable tubing located inside a stainless steel probe. The tubing is purged with instrument grade air at a low flow rate (10 ml/minute) and the VOC-laden air is transported to the surface where it is analyzed. Analysis is provided by a metal oxide sensor (MOS). When a MOS is heated in air, oxygen reacts with the sensor surface creating a barrier or resistance to electron flow. When a reducing gas, such as TCE vapor, is present, the resistance to electron flow is lowered and a change in an electrical signal can be measured. Although this sensor can be calibrated for a specific compound, it is not selective to that particular compound. Therefore, if multiple reducing compounds are present, the reading will be a representative concentration of all of those compounds and not a specific concentration for each compound.

As with the chemiresistor and QCM technologies described previously, the VOC concentration of the sampled air must be converted into an aqueous concentration using Henry's Law.

The VOC monitor is commercialized. The concept was developed by Waste Technologies of Australia Party Limited, which is the commercialization arm of the Cooperative Research Centre for Waste Management and Pollution Control (CRC WMPC), in conjunction with collaborators at the Commonwealth Scientific and Industrial Research Organization (CSIRO). Initial versions of the technology were developed and marketed by Chemtronics, which is no longer in business. Greenspan Technologies has since been selected to manufacture the probes which are in use in Australia, Germany, and the United States. With Greenspan, the technology has been greatly

improved. The sample range has been improved, and the calibration time has decreased from 3 days to 2 hours. Additional versions of the probe are under development using different sensors.

Currently, the sensor detects all VOCs that enter the diffusion probe. Therefore, although this sensor can be calibrated for a specific compound, it is not selective to that particular compound. Sensitivities currently allow detection of both TCE and BTEX compounds to a level of approximately 100 ug/l to 20,000 ug/L.

The unit runs on a 12V DC power supply (e.g., batteries or solar panels) and provides a 4-20mA signal for storage in a data logger. The data logger can be accessed directly with a computer with Windows based software or remotely.

Expected Cost per Unit

Monitoring systems with one or four ports are available with a single probe feeding into each port. A probe costs approximately US\$950, a 1 port system (probe with detection sensor and software, all on a metal box) is around US\$9,500, and a 4 port system is approximately US\$11,500.

Project Contact

Geoff Borton, Waste Technologies of Australia, Party Limited <u>g.borton@unsw.edu.au</u> <u>g.borton@wastetechnologies.com</u> +612 9385 4886 <u>http://www.wastetechnologies.com</u>

Burge Environmental Ground Water Sampling System and TCE Optrode

This technology is comprised of both sampling and analytical modules. The sampling module collects samples (from up to eight locations in a single well) and transports them to a separate analytical module. The analytical module is currently designed to detect TCE although modifications are being made to analyze for chromium (VI) and other specific metals. This description only discusses the sampling and analysis of TCE.

The TCE optrode optically analyzes the sample. A clear reagent is introduced that reacts with TCE and turns red. Pulses of green light are introduced into the chamber and the attenuation of that light is proportional to the concentration of the TCE/reagent product (and therefore the concentration of TCE). Chloroform is the only known chemical that interferes with the analysis of TCE. In the absence of chloroform, TCE measurements are accurate with a limit of detection of 1 ug/L, which is below the MCL. In the absence of TCE, chloroform measurements are accurate.

The sensor repeatedly analyzes TCE in the headspace of the analytical module chamber until an equilibrium between the sample water and the headspace is achieved. This measurement is then

compared to the results from regularly analyzed blanks and calibration standards. A three point calibration, including a blank is used with the calibration standards depending on the concentration range of interest. The two calibrations that are used: the low (0 ug/L, 6 ug/L, and 12 ug/L) and the high (0 ug/L, 30 ug/L, and 60 ug/L). After each sample, the chamber is purged with an inert gas to ensure that cross contamination between samples does not occur. All of the sampling, analyses, purging, and calibration runs are programmable and fully automated, and the analytical system is capable of several quality control checks including splits, duplicates, and mid-point calibration checks.

The technology has been field tested at Homestead Air Force Base (with EPA Technology Innovation Office) and the Savannah River Site and has historically had valve problems. Alternative valves are being tried, system improvements are underway, and subsequent field tests have been successful. The unit has been installed operational for as long as nine months and has been used to sample influent and effluent at a treatment plant for over one year.

Cost Per Unit

For a single well, the sampling and analytical unit cost for field deployment in a remote location is approximately \$15,000. Additional sampling units can be purchased for approximately \$3,000 per unit, which would lower the cost per well, and a single analytical unit can support up to 4 to 6 sampling units. Therefore, using an analytical unit for multiple wells could reduce the cost per well to as little as \$5,500 per well. The cost of the sensor itself is approximately \$250 per unit, which is comparable to sensor costs of the technologies discussed in Section 4.1, which have sensor manufacturing costs on the order of \$100 to \$200 per unit.

Project Contact

Scott Burge, Burge Environmental <u>burgenv@primenet.com</u> (480) 968-5141 <u>http://www.burgenv.com</u>

4.3 HAND-HELD AND OTHERWISE FIELD-PORTABLE ANALYTICAL UNITS FOR FIELD ANALYSIS OF VOCS IN GROUND WATER

A third approach that can facilitate ground water sampling is the development of field-portable analytical tools that can be used manually on-site. Many of the projects in this category utilize a miniaturized gas chromatrograph (GC) for separating the contaminants of concern prior to detection. This provides the benefit of being able to detect multiple contaminants. It is also similar to the technology used in accepted EPA test methods and may be more readily accepted by the regulatory community. In addition, because the sensor is above-ground and easily portable, calibration with blanks and various standards are likely easier than with sensors that are located in a monitoring well. As an aside, such units might potentially facilitate remedial investigations where sampling can be done on-site to provide investigators with immediate

results rather than using a mobile lab or sending samples of site. Further discussion of this application is beyond the scope of this report.

As described, the technologies in this section cannot automate ground water monitoring because groundwater samples need to be collected by traditional sampling methods, passive diffusion bags, or other sampling technologies (such as those in Section 4.2). However, these technologies could replace the need for sending samples to off-site laboratories, which may help reduce costs, especially for sites in remote locations. Ideally, some of the field portable units described in this section could be further miniaturized, simplified, or automated and combined with sampling instruments to further facilitate ground water monitoring.

This section includes two classes of instruments with varying degrees of portability. The first class includes two instruments that are considered "hand-held". The second class includes five instruments that are field-portable instruments but are two large to be considered hand-held. They are, however, under 100 pounds, can be operated by a technician with only a few days of training, and cost less than \$100,000 per unit. These five instruments documented in this report are not necessarily fully inclusive of the technologies in this class, but they demonstrate the development status of instruments in this class. In addition, they have all been evaluated by the EPA Environmental Technology Verification (ETV) Program specifically for monitoring VOCs in ground water.

A third class of field-portable technologies are not discussed here for the following reasons:

- they are over 100 pounds and therefore more difficult to transport in the field
- they require experienced scientists for operation
- the cost of an instrument is approximately \$100,000 or higher

Although these technologies may be appropriate for monitoring during site investigations, relative to the other technologies discussed, these instruments do not appear to have the same potential to facilitate long-term, routine ground water monitoring at the majority of sites.

Other comparable analytical technologies and instruments exist and are used in a variety of industries, but they are not included in this report if the associated efforts have not been directed at groundwater monitoring. In addition, although non-portable units could be installed at a fixed location at a site and used for on-site analysis, this type of unit is not described here.

4.3.1 HAND-HELD INSTRUMENTS UNDER DEVELOPMENT

Sandia National Laboratories : ChemLabTM

This instrument is in a relatively mature research and development phase. It comfortably fits in one hand (similar in size to a personal digital assistant). It uses a three stage process for analysis:

pre-concentration - During this phase, contaminants in the vapor phase collect on membrane over an established period of time. The membrane is then flash heated to

release all of the contaminants in one concentrated pulse. Different membranes can be used to pre-concentrate different classes of chemicals. A sol-gel is used that absorbs semi-volatile organic compounds very well. Other membranes can be used for VOCs.

separation - During this phase, the concentrated contaminants are separated through a miniaturized GC column. This separation will allow each contaminant to be detected individually. The column is approximately 86 cm long but is oriented in a spiral and only takes up approximately 1 cm² (i.e., the size of a dime). To help separate the contaminants, the inside of the column is coated with a polymer or the column. A miniaturized packed column can also be used. Different types of columns can be used for different classes of contaminants (i.e., a packed column would likely be used for VOCs and the coated column may be used for explosives).

detection - This stage uses an array of surface acoustic wave (SAW) sensors. SAW sensors include an input transducer that sends an acoustic signal to vibrate a crystal and an output transducer that converts the vibrations into a measurable electrical signal. Contaminants pass over three detectors coated with different polymer adsorbents and one uncoated detector. The presence of contaminants on the detectors changes the frequency of the vibrations and therefore the electrical signal. Detection is accomplished when a phase shift is found between the signals of the coated and uncoated detectors.

Each sample can be analyzed in approximately 2 minutes and can provide concentrations for multiple chlorinated hydrocarbons and BTEX compounds. Detection capabilities are in the sub ppm level in the vapor phase, but specific information is not available on the detection of typical ground water contaminants since that is not the true focus of the technology at this point. By comparison, using Henry's Law at 20 C, a ground water TCE concentration of 5 ug/L (i.e., the MCL) translates to a vapor phase concentration of approximately 270 ppb. Therefore, this technology is likely sufficient for measuring ground water contaminants at the MCL or near MCL level. Efforts are currently underway to develop modules for transferring contaminants from the dissolved phase into the vapor phase for analysis. There are plans to demonstrate the system within a municipal water supply system with a water interface in early 2005. Prototypes should be available for testing in early to late 2004. The project team has a commercialization partner for manufacturing and sales of the : ChemLabTM.

Expected Cost Per Unit

At this stage of development it is difficult to estimate cost; however, project contacts estimate that if manufactured optimally and in bulk each unit could cost between \$2,000 and \$5,000.

Project Contact

Richard Cernosek, Sandia National Laboratories <u>rwcerno@sandia.gov</u> 505-845-8818 <u>http://www.sandia.gov/microchemlab</u>

Advanced Field System, Inc. Hand-held GC

This instrument weighs approximately 8 pounds and has dimensions of 8 inches by 5 inches by 3 inches. It accepts both liquid and gas samples. Like the : ChemLabTM, it uses a micromachined GC to separate the chemicals to be analyzed. This unit, however, has a GC column length of 5 meters to provide additional separation. This unit also uses a glow discharge detector (GDD) for detection. A GDD uses a high voltage to create an electric field that ionizes the contaminants that have been separated by the GC. The ionized contaminants then affect the electric field creating a measurable response. Hydrocarbons in the two-carbon to 14-carbon range can be detected at the ppb level in the vapor phase and chlorinated compounds can be detected in the ppt (part per trillion range) in the vapor phase. A supplemental unit is available so that liquid samples can be analyzed. The concentration in the vapor phase would need to be converted, using Henry's Law, to the liquid phase. As stated earlier, a ground water concentration for TCE of 5 ug/L, translates to a vapor phase concentration of approximately 270 ppb.

A fully performing prototype has been made and the commercialization partner is prepared to begin manufacturing, but funding is required. Once funding is obtained the project team envisions 4 to 6 months for manufacturing.

Expected Cost Per Unit

At this stage of development it is difficult to estimate cost. The costs provided by the project team were based on the costs of other commercially available gas chromatographs, which range in price from \$20,000 to \$50,000 per unit. The commercialization partner, Advanced Field Systems, Inc., estimated \$30,000 per unit, but specified that the cost could be lower.

Project Contacts

Conrad Yu	Terrence Cullen
Lawrence Livermore National Laboratories	Advanced Field Systems, Inc.
Center for Microtechnology	terrencecullen@handheldgc.com
<u>yu1@llnl.gov</u>	530-521-9270
(925) 422-7356 (voice)	http://www.handheldgc.com

4.3.2 PREVIOUSLY EPA EVALUATED FIELD-PORTABLE INSTRUMENTS

The following five instruments were evaluated together through the EPA ETV Program in September 1997 for their ability to detect chlorinated VOCs in ground water. The evaluation included analysis of performance evaluation (PE) samples with known concentrations and ground water samples from monitoring wells. For both types of samples, the instrument results were compared to laboratory results.

Many of the instruments are primarily designed as gas analyzers but were evaluated for their potential to analyze ground water samples by either sampling the head space above a water

sample or using on-board equipment to purge and then trap the VOCs from a water sample. Specifications for the instruments, including estimated costs, are provided based on information obtained from current brochures or from the ETV report.

Electronic Sensor Technology (ESTCAL) Model 4100 and 4200

This instrument, referred to as the zNose[™], combines a gas chromatograph with an array of SAW detectors. Therefore, the analysis is conducted in a similar manner to that of the Sandia National Laboratories : ChemLab[™]. VOC concentrations in water samples are measured by analyzing the head space above the water sample and then converting the vapor phase concentrations into aqueous phase concentrations. The Model 4100 was evaluated by the ETV program in 1997, and the Model 4200 has since been developed. The specifications for the zNose[™], as determined by a brochure for the Model 4200 or from the ETV study for the Model 4100, are as follows:

Parameter	Value or description	Information Source
Total weight:	service module: 20 poundsanalytical module: 7 pounds	brochure
Size:	service module: 12 inches x 10 inches x 6 inchesanalytical module: not provided (smaller than the service module)	brochure
Power:	50 watts, typical	brochure
Analysis time:	10 to 60 seconds	brochure
Cost:	\$26,200	brochure
Operator requirements:	chemical technician	ETV study
Deployment time:	ready to sample within 30 minutes	ETV study
Detection limits:	10 ug/L to 100 ug/L (for chlorinated VOCs in a water sample)	ETV study
Versatility:	42 of the 68 compounds present in ETV study	ETV study
Precision:	 The median relative standard deviation of all ETV PE samples 15% for the Model 4100 7% for the reference laboratory 	ETV study
Accuracy:	The median absolute percent difference for all ETV PE samples44% for the Model 41007% for the reference laboratory	ETV study
Comparability:	The median absolute percent difference between the Model 4100 and the laboratory measurements for all ground water samples from the ETV study was 30%.	ETV study

The ETV program concluded the following:

Under appropriate applications, the Model 4100 field-portable gas chromatograph with surface acoustic wave detector can provide useful, cost-effective data for environmental site characterization and routine monitoring. The results of this demonstration show that the instrument is best suited for routine monitoring of water samples contaminated with relatively few chlorinated VOCs....

More detailed information regarding the evaluation can be found in the report titled *Environmental Technology Verification Report, Field-Portable Gas Chromatograph, Electronic Sensor Technology, Model 4100* (EPA-600-R-98-141).

Electronic Sensor Technology 805-480-1994 http://www.estcal.com

Inficon, Inc. HAPSITE

This instrument combines a gas chromatograph with a mass spectrometer, which are the technologies used in EPA Method 8260b. VOC concentrations in water samples are measured by analyzing the head space above the water sample and then converting the vapor phase concentrations into aqueous phase concentrations. The specifications for the HAPSITE, as determined from either the current brochure or from the ETV study, are as follows:

Parameter	Value or description	Information Source
Total weight:	service module: 45 poundsanalytical module: 35 pounds	brochure
Size:	 service module: 18 inches x 17 inches x 8.5 inches analytical module: 18 inches x 17 inches x 7 inches 	brochure
Power:	30 watts, typical	brochure
Analysis time:	30 to 60 seconds	brochure
Cost:	\$76,000	ETV study
Operator requirements:	chemist with GC/MS experience and 3 days of training	ETV study
Deployment time:	ready to sample within 30 minutes	ETV study
Detection limits:	5 ug/L to 10 ug/L (for chlorinated VOCs in a water sample)	ETV study
Versatility:	59 of the 68 compounds present in ETV study	ETV study
Precision:	The median relative standard deviation of all ETV PE samples12% for the HAPSITE7% for the reference laboratory	ETV study
Accuracy:	The median absolute percent difference for all ETV PE samples8% for the HAPSITE7% for the reference laboratory	ETV study
Comparability:	The median absolute percent difference between the HAPSITE and the laboratory measurements for all ground water samples from the ETV study was 13%.	ETV study

The ETV program concluded the following:

The results of this demonstration show that the HAPSITE can provide useful, cost-effective data for environmental site characterization and routine monitoring. The instrument could be employed in a variety of applications, ranging from producing rapid analytical results in screening investigations, to producing

accurate and precise data that are directly comparable with that obtained from an off-site laboratory. These data could be used to develop risk assessment information, support a remediation process, or fulfill monitoring requirements....

More detailed information regarding the evaluation can be found in the report titled *Environmental Technology Verification Report, Field-Portable Gas Chromatograph/Mass Spectrometer, Inficon, Inc., HAPSITE* (EPA-600-R-98-142).

Inficon, Inc. 315-434-1100 http://www.inficon.com

Innova AirTech Instruments, Type 1312 Multi-gas Monitor

This instrument incorporates photoacoustic infrared detection, which means the device can theoretically detect any gas that absorbs infrared radiation. Infrared light is pulsed into the sample chamber and the gas absorbs and emits radiation causing it to increase and decrease in temperature. The changes in temperature cause changes in pressure (an acoustical signal) that are then analyzed. Optical filters are used to select up to five gases and water vapor to be analyzed at a time. VOC concentrations in water samples are measured by analyzing the head space above the water sample and then converting the vapor phase concentrations into aqueous phase concentrations. The specifications for the Type 1312, as determined from either the current brochure or from the ETV study, are as follows:

Parameter	Value or description	Information Source
Total weight:	30 pounds with accessories	ETV study
Size:	15.6 inches x 11.8 inches x 6.9 inches (without accessories)	brochure
Power:	100 watts, typical	brochure
Analysis time:	15 to 75 seconds	brochure
Cost:	\$28,000	ETV study
Operator requirements:	technician with 1 day of training	ETV study
Deployment time:	ready to sample within 30 minutes (ETV study)	ETV study
Detection limits:	approximately 5 ug/L (for TCE and PCE in a water sample)	ETV study
Versatility:	up to 5 VOCs (ETV evaluated for TCE and PCE only)	ETV study
Precision:	The median relative standard deviation of all ETV PE samples15% for the Type 13127% for the reference laboratory	ETV study
Accuracy:	The median absolute percent difference for all ETV PE samples29% for the Type 131210% for the reference laboratory	ETV study
Comparability:	The median absolute percent difference between the Type 1312 and the laboratory measurements for all ground water samples from the ETV study was 29%.	ETV study

The ETV program concluded the following:

The results of this demonstration show that the Innova AirTech Instruments Type 1312 Multi-gas Monitor can provide useful, cost-effective data for routine groundwater monitoring when the composition of the samples is known. Since the composition of the sample must be known to avoid spectral interference, the instrument is not well suited for site characterization applications where VOC content of the samples is unknown....

More detailed information regarding the evaluation can be found in the report titled *Environmental Technology Verification Report, Photoacoustic Spectrophotometer, Innova AirTech Instruments, Type 1312 Multi-gas Monitor* (EPA-600-R-98-143).

Innova AirTech Instruments (Denmark) (+45) 44 20 01 00 http://www.innova.dk

Perkin-Elmer Corporation - Voyager Photovac Monitoring Instruments

This instrument combines a GC with a photoionization detector and/or an electron capture detector. VOC concentrations in water samples are measured by analyzing the head space above the water sample and then converting the vapor phase concentrations into aqueous phase concentrations. The specifications for the Voyager, as determined from either the current brochure or from the ETV study, are as follows:

Parameter	Value or description	Information Source
Total weight:	33 pounds with accessories	ETV study
Size:	15.4 inches x 10.6 inches x 5.9 inches (without accessories)	brochure
Power:	10-18 volts DC, 115 AC or 240 VAC	brochure
Analysis time:	not provided, but likely less than one minute	brochure
Cost:	\$24,000	ETV study
Operator requirements:	technician with 1 day of training	ETV study
Deployment time:	ready to sample within 60 minutes	ETV study
Detection limits:	5 ug/L to 10 ug/L (for chlorinated VOCs in a water sample)	ETV study
Versatility:	39 of 68 compounds present in the samples from the ETV study	ETV study
Precision:	The median relative standard deviation of all PE samples from the ETV study was 20% for the Voyager compared to 7% for the reference laboratory.	
Accuracy:	The median absolute percent difference for all PE samples frm the ETV study was 41% for the Voyager compared to 10% for the reference laboratory.	ETV study
Comparability:	The median absolute percent difference between the Voyager and the laboratory measurements for all ground water samples from the ETV study was 74%.	ETV study

The ETV program concluded the following:

The results of this demonstration revealed that sample handling methodologies may have adversely affected the observed precision and accuracy of the instrument. Perkin-Elmer Photovac has developed an improved field method for sample preparation and handling that includes the use of an internal standard. The new method is expected to result in improved instrument precision and accuracy. The Voyager may be suitable for both field screening and routine analysis applications....

More detailed information regarding the evaluation can be found in the report titled *Environmental Technology Verification Report, Field-Portable Gas Chromatograph, Perkin-Elmer Photovac, Voyager.* (EPA-600-R-98-144).

Perkin-Elmer Instruments 800-762-4000 http://www.photovac.com

Sentex Systems, Inc. Scentograph Plus II

This instrument combines a GC with an electron capture detector. The VOCs are extracted from the water sample by a an on-board "purge-and-trap" mechanism. Sentex also has developed the SituProbe (not evaluated by the ETV program), which does the purge-and-trap in-situ and eliminates the need for direct handling of the samples. The specifications for the Scentograph Plus II as determined from either the current brochure or from the ETV study, are as follows:

Parameter	Value or description	Information Source
Total weight:	80 pounds including purge-and-trap unit, laptop, and GC	ETV study
Size:	approximately the size of a large suitcase	brochure
Power:	vehicle battery or line power	brochure
Analysis time:	not provided, but likely less than one minute	brochure
Cost:	\$35,000	ETV study
Operator requirements:	technician with 1 day of training	ETV study
Deployment time:	ready to sample within 60 minutes	ETV study
Detection limits:	0.1 ug/L to 50 ug/L (for chlorinated VOCs in a water sample)	ETV study
Versatility:	35 of 68 compounds present in the samples from the ETV study	ETV study
Precision:	 The median relative standard deviation of all ETV PE samples 8% for the Scentograph Plus II 7% for the reference laboratory 	ETV study
Accuracy:	 The median absolute percent difference for all ETV PE samples 10% for the Voyager 7% for the reference laboratory 	ETV study
Comparability:	The median absolute percent difference between the Voyager and the laboratory measurements for all ground water samples from the ETV study was 12%.	ETV study

The ETV program concluded the following:

The results of this demonstration show that the Sentex Systems, Inc. Scentograph Plus II field-portable GC with electron capture detector can provide useful, cost-effective data for environmental site screening and routine monitoring. The instrument could be employed in a variety of applications, ranging from producing rapid analytical results in screening investigations, to producing accurate and precise data that are directly comparable with that obtained from an off-site laboratory. These data could be used to develop risk assessment information, support a remediation process, or fulfill monitoring requirements....

More detailed information regarding the evaluation can be found in the report titled *Environmental Technology Verification Report, Field-Portable Gas Chromatograph, Sentex-Systems, Inc., Scentograph Plus II.* (EPA-600-R-98-145).

Sentex Systems, Inc. 973-439-0140 or 800-736-8394 http://www.sentexinc.com

4.4 SUMMARY OF TECHNOLOGY STATUS

The ability to detect VOCs in-situ or to otherwise technically facilitate the process of long-term monitoring is feasible. Summaries of the various highlighted projects are provided in Tables 4-1 through 4-4. The projects are in varying stages of development. Instruments where analysis is conducted above-ground are already commercially available, and instruments where analysis is conducted in-situ are primarily in the research and development stage.

The capabilities and estimated costs of the instruments vary. For example, some instruments may be developed to analyze one or two compounds in-situ while others have built-in gas chromatographs are developed to analyze a wide range of compounds above ground. In general, the instruments with built-in gas chromatographs are more expensive than the other sensor technologies described. Some teams that are in the research stage of their project suggest a sensor might cost \$100 to manufacture, but this cost is not necessarily representative of the cost of a fully-functional instrument that incorporates the overhead and profit of the manufacturer and/or vendor. A fully developed sensor for one or two parameters might cost \$7,500 (e.g., the Nomadics/GE instrument). An automated sampling and analysis system for four monitoring wells might cost \$15,000 to \$30,000. A hand-held or field-portable unit with a gas chromatograph might cost \$5,000 to \$76,000, with most units costing approximately \$30,000.

Although the detection limits for many of these technologies are generally above typical cleanup standards or MCLs, they are sufficiently low to provide screening level data at many sites with elevated concentrations. Some of the technologies appear ready for extensive field testing and potential use at some sites (for screening level data), and some technologies have already been evaluated by the EPA ETV program. Applicability for use at sites will depend on a number factors, including cost-effectiveness and regulatory acceptance, that are discussed in the following section.

Many of the project teams interviewed mentioned that funding is required to either further the research on the devices, to move the devices from the research and development stage to commercialization and manufacturing, or to begin manufacturing.

Table 4-1. Summary of Emerging In-situ Sensors for Sampling and Analysis of VOCs in Ground Water (Part 1 of 2)

Technology	Developer and Contact Information	Development Status	Selectivity/Sensitivity	Current Focus
Chemiresistors	Clifford K. HoSandia National Laboratory <u>ckho@sandia.gov</u> 505-844-2384 <u>www.sandia.gov/sensor</u>	Prototype field tested Additional field testing required in FY03 and FY04 with new features	TCE at ~1,000 ug/L (current) TCE at ~50 ug/L (expected with pre- concentrator) Needs to be calibrated to specific compounds being detected	Heating element to be added reduce effects from humidity Pre-concentration to improve sensitivity Additional funding required for further research and development
Quartz Crystal Microbalances (QCMs)	Joel Roark Nomadics, Inc. jroark@nomadics.com 405-372-9535 www.nomadics.com Joseph Salvo GE Global Research Center salvo@research.ge.com 518-387-6123 www.crd.ge.com	Field testing in February and March 2003 Commercialization underway and manufacturing possible within months	TCE at ~50 ug/L	Initial field testing Additional funding required to continue development and begin manufacturing
High Resolution Ion Mobility Spectrometer (IMS)	Joe Hartman Boise State University Boise, ID 83725-2075 208-426-5714 <u>joehartman@ieee.org</u> <u>jhartman@boisestate.edu</u> <u>http://coen.boisestate.edu/sensor/sens</u> <u>orweb.html</u>	Prototype probe for vadose zone expected in 2003 Additional funding will be required beyond 2004	Sensitivity is expected to be sufficient to meet MCLs for multiple contaminants (including chlorinated hydrocarbons and BTEX compounds) in a single sample	Prototype development Transfer technology from vadose zone to saturated zone Reduce the amount of transmitted data from probe so that wireless communications will be effective for data transfer

Technology	Developer and Contact Information	Development Status	Selectivity/Sensitivity	Current Focus
Resonance Enhanced Multiphoton Ionization (REMPI)	Mike Angel University of South Carolina <u>angel@mail.chem.sc.edu</u> 803-777-2779 <u>www.chem.sc.edu/graduate/ANGEL3.</u> <u>HTML</u>	Proof-of-concept phase, but prototype probe has been developed Bench tests conducted with BTEX Basic research on lasers for the detection of chlorinated compounds	BTEX at ~1 ug/L	Bench testing with various lasers Additional funding required
Wave guides and interferometry	Dr. Martin A. Brooke Georgia Institute of Technology martin.brooke@ece.gatech.edu (404) 894-3304	Prototype sensor but no prototype probe	Sensor provides VOC detection at the 50 ug/L to 100 ug/L	Field testing Additional funding required
	Roland Levy New Jersey Institute of Technology <u>LevyR@adm.njit.edu</u> (903) 596-3561	Proof of concept complete	~10 ug/L expected	Prototype development Additional funding required
Mid-Infrared fiberoptic sensors	Dr. Boris Mizaikoff Georgia Institute of Technology boris.mizaikoff@chemistry.gatech.edu (404) 894 4030 <u>http://asl.chemistry.gatech.edu/</u>	Mid-infrared prototype probe developed and field tested Beyond proof-of-concept but not yet ready for commercialization	Chlorinated compounds at or below 100 ug/L Other compounds also in the 100 ug/L range	Increasing sensitivity, further miniaturizing probe, and extending the lifetime of the adsorbent polymers
UV-Induced Fluorescence Spectroscopy	Arthur Lonne Lane Jet Propulsion Laboratory <u>Arthur.L.Lane@jpl.nasa.gov</u> (818) 354-2725	Prototype instrument reportedly tested in the field	Unknown	Unknown

Table 4-1. Summary of Emerging In-situ Sensors for Sampling and Analysis of VOCs in Ground Water (Part 2 of 2)

Table 4-2. Summary	of Commercialized	Automated Systems	for Sampling an	d Analysis of V	OCs in Ground Water
			1 0	•	

Developer and Contact Information	Description/Cost	Selectivity/Sensitivity	Current/Future Efforts
Geoff Borton Waste Technologies of Australia, Party Limited g.borton@unsw.edu.au g.borton@wastetechnologies.com +612 9385 4886 <u>www.wastetechnologies.com</u>	 \$950 US per probe ~\$9,500 US for one probe, analyzer with one port, software, and datalogger ~\$11,500 US for analyzer with four ports, software, and datalogger 	Measures the cumulative concentration of all VOCs present to a total concentration of approximately 100 ug/L and higher	Broadening the range of detection Incorporating other sensors for more selectivity
Scott Burge Burge Environmental <u>burgenv@primenet.com</u> (480) 968-5141 <u>www.burgenv.com</u>	Sampling and analytical system costs ~\$15,000 Additional sampling unit can be purchased for ~\$3,000	TCE as low as 1 ug/L	Continue improving valves Investigate sensors for other contaminants

Developer and Contact Information	Description/Cost	Description/Cost Selectivity/Sensitivity Current/Fut	
: ChemLab [™] Richard Cernosek Sandia National Laboratories <u>rwcerno@sandia.gov</u> 505-845-8818 <u>www.sandia.gov/microchemlab</u>	Utilizes a micromachined pre- concentrator, GC, and SAW detectors Approximately \$2,000 to \$5,000 if manufactured in bulk Commercialization underway but approximately 1-year away from ability to analyze liquid samples	Can detect multiple contaminants (e.g., BTEX and chlorinated solvents) in a single sample Sensitivity likely at or near MCLs	Water analysis for municipal water supplies A wide range of applications appropriate, including ground water monitoring
Hand-Held GC Conrad Yu Lawrence Livermore National Laboratories Center for Microtechnology <u>yu1@llnl.gov</u> (925) 422-7356 (voice) Terrence Cullen Advanced Field Systems,Inc. <u>terrencecullen@handheldgc.com</u> 530-521-9270 <u>www.handheldgc.com</u>	Utilizes a micromachined GC and a glow discharge detector The estimated cost for the unit is based on the cost of currently available GC systems that cost on the order of \$30,000. However, costs could potentially be lower. Commercialization underway and manufacturing can begin	Can detect multiple contaminants (e.g., BTEX and chlorinated solvents) in a single sample Sensitivity at or near MCLs.	Water analysis, but not specifically for ground water analysis A wide range of applications appropriate, including ground water monitoring

Table 4-3. Summary of Hand-Held Systems for On-Site Analysis of VOCs in Ground Water

Table 4-4. Summary of Field-Portable Systems Evaluated by EPA ETV Program for
On-Site Analysis of VOCs in Ground Water (Part 1 of 3)

Technology and Vendor	Description/Cost/Status	Detection Capabilities	ETV Conclusion
zNose [™] Electronic Sensor Technology 805-480-1994 <u>www.estcal.com</u>	Utilizes a GC and SAW detector and samples water by purging and trapping the VOCs. The cost of the unit is approximately \$26,000 The system is commercially available.	Can detect multiple VOCs including BTEX and chlorinated compounds. The technology has been evaluated by the EPA ETV program. Detection limits for many VOCs range from approximately 10 ug/L to 100 ug/L	can provide useful, cost-effective data for environmental site characterization and routine monitoring under appropriate applications best suited for routine monitoring of water samples contaminated with relatively few chlorinated VOCs
HAPSITE Inficon, Inc. 315-434-1100 <u>www.inficon.com</u>	Utilizes a GC and mass spectrometer and samples water by sampling head space above sample The cost of the unit is approximately \$76,000. The system is commercially available.	Can detect multiple VOCs including BTEX and chlorinated compounds. The technology has been evaluated by the EPA ETV program. Detection limits for many VOCs range from approximately 5 ug/L to 10 ug/L	can provide useful, cost-effective data for environmental site characterization and routine monitoring. could be employed in a variety of applications, ranging from producing rapid analytical results in screening investigations produces accurate and precise data that are directly comparable with that obtained from an off-site laboratory data could be used to develop risk assessment information, support a remediation process, or fulfill monitoring requirements

Table 4-4. Summary of Field-Portable Systems Evaluated by EPA ETV I	Program for
On-Site Analysis of VOCs in Ground Water (Part 2 of 3)	

Type 1312 Multi-gas Monitor Innova AirTech Instruments (Denmark) (+45) 44 20 01 00 <u>www.innova.dk</u>	Utilizes photoacoustic infrared detection to analyze up to five gases at a time. Water samples are analyzed by analyzing the head space above the sample. The cost of the unit is approximately \$28,000. The system is commercially available.	Can detect up to five VOCs including TCE and PCE. The technology has been evaluated by the EPA ETV program for analyzing TCE and PCE. Detection limits for TCE and PCE are approximately 5 ug/L.	can provide useful, cost-effective data for routine groundwater monitoring when the composition of the samples is known. is not well suited for site characterization applications where VOC content of the samples is unknown.
Photovac Voyager Perkin-Elmer Instruments 800-762-4000 www.photovac.com	Utilizes a GC with photoionization and/or electron capture detection and analyzes water samples by analyzing the head space above sample The cost of the unit is approixmately \$24,000 The system is commercially available.	Can detect multiple VOCs including TCE and PCE. The technology has been evaluated by the EPA ETV program for analyzing multiple chlorinated hydrocarbons. Detection limits for most chlorinated compounds is are approximately 5 ug/L to 10 ug/L	sample handling methodologies may have adversely affected the observed precision and accuracy of the instrument (an improved method has been developed) may be suitable for both field screening and routine analysis applications

Table 4-4. Summary of Field-Portable Systems Evaluated by EPA ETV Program for
On-Site Analysis of VOCs in Ground Water (Part 3 of 3)

Scentograph Plus II Sentex Systems, Inc. 973-439-0140 or 800-736-8394 <u>www.sentexinc.com</u>	Utilizes a GC with electron capture detection and analyzes water samples by on-board purge and trap or through an in-situ probe. The cost of the unit is approximately \$35,000	Can detect multiple VOCs including TCE and PCE. The technology has been evaluated by the EPA ETV program for analyzing multiple chlorinated hydrocarbons.	can provide useful, cost-effective data for environmental site screening and routine monitoring. could be employed in a variety of applications, ranging from producing rapid analytical results in screening investigations
	The system is commercially available.	Detection limits for most chlorinated compounds is are approximately 0.1 ug/L to 50 ug/L	produces accurate and precise data that are directly comparable with that obtained from an off-site laboratory data could be used to develop risk assessment information, support a remediation process, or fulfill monitoring requirements

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5.0 IMPLEMENTING GROUND WATER MONITORING SENSOR TECHNOLOGIES

The previous section outlined multiple emerging technologies for facilitating ground water monitoring. Some of these technologies are still in the research and development phase and some have already been commercialized. Even those that have been commercialized are not in widespread use for long-term ground water monitoring. The following are some of the factors to consider for implementation of sensor technologies for long-term ground water monitoring.

- demonstration of reliability
- consideration of site-specific conditions
- achievement of regulatory approval
- demonstration of cost-effectiveness

5.1 DEMONSTRATION OF RELIABILITY

Although these technologies are tested repeatedly in the laboratory and in the field, additional technological challenges are faced once technologies make it to the marketplace. This has been evident in the marketing of the two technologies described in Section 4.2 and one of the technologies described in Section 4.3.

The VOC Monitor constructed by Chemtronics for Waste Technologies of Australia originally had prohibitively long periods for calibration and was difficult to use. The later models from Greenspan, however, are reportedly improved with calibration times as low as two hours. Initial tests with the Burge Environmental system had valve problems that have since been corrected. The Photovac Voyager had problems with the sample handling during the ETV study. Those issues have reportedly been corrected but indicate the types of problems faced by sensor technologies as they move to the market place or are adapted to ground water monitoring from another application.

None of these issues faced by the developers involved the sensor technology itself; rather, they involved the logistics and other more commonplace technologies that surround the sensors. Such logistics (including routine calibration procedures) are likely to face the other technologies under development as they emerge from the laboratory. Because many consumers are unlikely to pay for unreliable instruments, additional funding will likely be necessary to help bridge the gap between development of the sensing technology and the multiple iterations that are required for establishing reliability.

5.2 CONSIDERATION OF SITE-SPECIFIC CONDITIONS

The contaminants of concern and other ground water parameters may affect the applicability of a sensor technology at a particular site. This is especially true for long-term ground water monitoring where sensor may remain in place for months or years.

The sensitivity of the sensor should be appropriate for the data quality requirements for the site and the concentrations in the wells where it would be used. Sensors with relatively low sensitivities may be appropriate for monitoring near a source area while sensors with higher sensitivities would be required for monitoring near the plume fringe. Many of the sensor technologies discussed in Sections 4.1 and 4.2 are capable of providing screening-level data at sites where wells routinely have concentrations above 100 ug/L and the contaminants of interest are limited. Many of the technologies discussed in Sections 4.3 are capable of providing screening-level data at sites with a variety of contaminants that have concentrations near MCLs. Moreover, the ETV studies for two of the five technologies described in Section 4.3 concluded that the two technologies were capable of providing data quality comparable to an off-site laboratory.

Although the sensor technologies described in Sections 4.1 and 4.2 can be modified to detect various contaminants, perhaps by changing a polymer or laser, a single probe (for many of the technologies) can generally only detect one contaminant of one class of contaminants. The Burge Environmental system, for example, can only detect TCE, and other sampling and analysis would be required if the monitoring of TCE breakdown products (i.e, 1,2 DCE and vinyl chloride) were required. The Waste Technologies of Australia system detects combined VOCs and does not give concentrations of the individual constituents. Although sampling one contaminant of concern or one class of contaminants is helpful at most sites, many sites may have multiple contaminants of concern and would require either additional sensors or traditional sampling and analysis. In many cases, the presence of one compound may interfere with the analysis of another compound. In such cases, the analysis of the target compound would only be reliable if the other compound is not present.

In addition to contaminants such as VOCs, ground water contains other constituents or has other properties that may affect the functionality of a sensor. For example, the presence of bacteria, iron, magnesium, and calcium has led to fouling of monitoring and extraction wells at many sites. Such fouling will also likely affect sensors that are in place for months or years at a time. A high or low pH may also contribute to corrosion of the sensor. Although fouling of wells can often be addressed with chemical treatment, that treatment may not be suitable for sensors, which may have to be routinely removed and cleaned.

Finally, some wells can be sampled relatively quickly while sampling of other wells may be relatively slow or may generate large volumes of water during purging. For wells that can be sampled relatively quickly, sensors might not be as applicable or cost-effective. However, for the latter type of wells, sensors may be particularly applicable. Consultants interviewed during the research for this report found passive diffusion bags particularly useful for this latter type of well.

5.3 ACHIEVEMENT OF REGULATORY APPROVAL

Although current monitoring techniques have a number features that might compromise the results, these traditional methods are widely accepted by the regulatory community. For example, current sampling methods and procedures are designed to ensure that sample water is representative of the surrounding aquifer rather than the potentially stagnant water in wells. Sensors that remain in the well for an extended period of time might be accepted if the instrument is located in the screened portion of the well and intercepts ground water from the surrounding aquifer as it flows through the well. Sensors that are designed to be dipped into each well during a sampling event may not be accepted if the instrument is relatively large and displaces water in the well, causing water to flow from the well into the surrounding aquifer during a measurement.

Current laboratory analytical methods are accepted by the regulatory community for a number reasons including the demonstrated precision and accuracy of the methods. An instrument's detection limit will not be the only criteria considered when the instrument is being considered for regulatory approval. Among other items, regulators will likely require similar precision and accuracy to the currently used analytical methods. Two of the five field-portable technologies evaluated by the EPA ETV program provided precision, accuracy, and selectivity suitable for the ETV study to conclude that the technologies were comparable to laboratory methods. Most of the instruments described in Sections 4.1 and 4.2 have not yet been evaluated by such a program.

In addition, data quality is frequently questioned, analytical laboratories often require strict certification, and laboratory reports generated under the traditional monitoring approach often include calibration curves and other information used in the analysis. With each group of samples sent to a laboratory, field blanks, duplicates, and calibration standards are run. If sensor technologies are to replace existing practices, they will also need to be able to provide similar quality assurance information. For the technologies where the sensor is permanently in place within the well, routine calibration will likely be difficult compared to technologies where the sensor is above-ground or the calibration is automated. The Burge Environmental system considers these rigorous data quality procedures and incorporates calibrations and other quality assurance samples during automated operation. In addition, the instruments in Section 4.3 with above-ground analysis also have the ability to incorporate calibrations and quality assurance samples.

Because many decisions at a site involve regulatory agencies, the application of new technologies to replace existing methods would require regulator approval. New technologies would likely first be used for screening-level data. After years of testing and validation, the technologies may be appropriate for replacing traditional sampling and/or evaluating compliance. Therefore, it is appropriate to begin using these technologies, where applicable, alongside current monitoring methods.

5.4 DEMONSTRATION OF COST-EFFECTIVENESS

Cost-effectiveness will likely be a primary driver in adopting sensor technologies, but to be costeffective, sensors should provide life-cycle savings and a relatively fast return on the capital used to purchase the sensors. A cost comparison of the sensor technologies to traditional methods should account for the capital costs of purchasing the sensors and supporting equipment as well as the costs for routine maintenance. The following three sections provide preliminary cost comparisons of traditional methods to each of the three classes of technologies described in Section 4.0. A hypothetical site is used, and the following assumptions are made:

- The hypothetical site has one or one class of VOC contaminants such that only one type of sensor is required.
- The site has 20 monitoring wells that must be sampled quarterly.
- The data quality and regulatory climate is such that sensor technologies, as applied, can completely replace traditional sampling and analysis methods.
- Costs for traditional sampling and analysis at the site are consistent with those presented in Section 2.0 of this report. An assumed low-end cost for sampling is estimated at \$3,000 per quarterly event, and an assumed high-end cost for sampling is estimated at \$8,000 per quarterly event. An average cost of approximately \$2,500 for analysis is assumed per quarterly sampling event. As discussed in Section 2.0, this is a reasonable approximate cost, but may not assume per diem or other travel costs. These unit costs per event translate to a low-end annual cost of \$22,000 per year and a high-end cost of \$42,000 per year for quarterly monitoring.

The results of these cost comparisons are heavily dependent on the assumptions that are made regarding site parameters, instrument performance, assumed costs, and other factors. For example, a requirement for semi-annual or annual sampling (which is common) instead of quarterly sampling would reduce the annual cost for traditional sampling by a factor of two or four, respectively. These comparisons are only intended to provide a preliminary analysis for the sensor technology developers, environmental professionals, and other individuals and organizations potentially affected by these sensor technologies.

5.4.1 COST COMPARISONS OF EMERGING IN-SITU TECHNOLOGIES VS. LONG-TERM TRADITIONAL MONITORING

Although manufacturing a sensor may cost on the order of \$100 as stated in Section 4.0, the market cost of a complete probe with housing and cable is likely greater than \$1,000. In the early stages of marketing the technologies when fewer units are sold, the cost will likely be higher. For example, Nomadics estimated that the costs for QCM probe may be has high as \$7,500 per unit. Additional costs are also necessary for dataloggers, power sources, and other supporting equipment or activities. For example, if data are to be accessed remotely, telemetry equipment is necessary. Routine maintenance is difficult to estimate for the emerging technologies at this

early stage; however, routine calibration, cleaning, battery charging, or replacement of materials (i.e., an air supply, activated carbon, reagent, etc.) will likely be required.

For the purpose of this cost comparison the following assumptions are made regarding the costs of the sensor technologies:

- Each well requires a sensor for a total of 20 sensors at the site.
- Each sensor and necessary supplementary equipment can be purchased and installed for a cost of \$5,000 per well. This includes the sensor and cable, power supply, datalogger, telemetry equipment (if necessary), installation, and startup.
- Routine maintenance of all 20 sensors at the site can be accomplished for approximately \$5,000 per year. This includes a field technician providing service, cleaning, and calibration of each sensor 2 times per year. Approximately 2 hours per sensor per visit is assumed plus up to \$1,000 per year for materials.
- Non-routine maintenance or replacement of the sensors does not occur within the first 5 years. Fouling or other factors can be addressed during the routine service estimated above.

raditional monitoring methods for these cost assumptions.							
Year	Low-End Traditi	onal Monitoring	High-End Tradi	tional Monitoring	Sensor Technology		
	Annual	Cumulative	Annual	Cumulative	Annual	Cumulative	
1	\$22,000	\$22,000	\$42,000	\$42,000	\$105,000	\$105,000	

\$42,000

\$42,000

\$42,000

\$42,000

\$84,000

\$126,000

\$168,000

\$210,000

\$5,000

\$5,000

\$5,000

\$5,000

\$110,000

\$115,000

\$120,000

\$125,000

2

3

4

5

\$22,000

\$22,000

\$22,000

\$22,000

\$44,000

\$66,000

\$88,000

\$110,000

The table on the following page summarizes the life-cycle costs for sensor technology and the traditional monitoring methods for these cost assumptions.

Provided the above assumptions and no discounting, the sensor technologies appear to result in cost savings relative to the high-end costs for traditional monitoring around year 3 but do not become cost-effective relative to the low-end costs for traditional monitoring within 5 years. The results of this analysis would vary with different assumptions. For example, if the cost per unit was cheaper and/or more frequent monitoring was required, then the sensor technology would become more cost-effective. However, if the monitoring frequency was reduced to semi-annual, which is fairly common, the sensor technology would not be cost-effective within 5 years, even compared to the high-end costs for traditional sampling.

An alternative approach to implementing these sensor technologies is to use a few probes that can be moved from well to well so that only a few probes are needed to sample and analyze many wells. This approach would not likely be cost-effective for the chemiresistor or QCM approaches because long equilibrium times would extend the length of the sampling event; however, it may be cost-effective for the mid-infrared fiberoptic and waveguide sensors that have shorter sampling and analysis times. However, these sensors would likely need to be rather small so that water in the well is not displaced, which would disrupt equilibrium conditions and cause some of the water in the well to flow into the surrounding aquifer. A second cost comparison is provided with the following assumptions.

- Two technicians, each with a probe, can sample/analyze all 20 wells for approximately \$3,000 per event. This assumes approximately 1 hour per well, including any decontamination that is required between wells, and costs for limited additional equipment.
- Each probe, with supplemental equipment, costs \$5,000. Routine maintenance costs \$1,000 per year for the two probes.
- Non-routine maintenance/ replacement of sensors does not occur within the first 5 years.

Year	Low-End Traditional Monitoring		High-End Traditional Monitoring		Sensor Technology	
	Annual	Cumulative	Annual	Cumulative	Annual	Cumulative
1	\$22,000	\$22,000	\$42,000	\$42,000	\$23,000	\$23,000
2	\$22,000	\$44,000	\$42,000	\$84,000	\$13,000	\$36,000
3	\$22,000	\$66,000	\$42,000	\$126,000	\$13,000	\$49,000
4	\$22,000	\$88,000	\$42,000	\$168,000	\$13,000	\$62,000
5	\$22,000	\$110,000	\$42,000	\$210,000	\$13,000	\$75,000

Provided the above assumptions and no discounting, this approach demonstrates cost savings relative to both the low and high costs of traditional sampling after the first year. Because these sensors are not dedicated to a particular well or site, they could be used at multiple sites. The capital costs would then be distributed over more sites and monitoring wells making the sensor more cost-effective. If widely available, some environmental consultants may choose to rent an instrument, as is often done with other environmental equipment. In this type cost analysis, renting the instrument would convert the capital costs of purchasing the instrument into annualized costs based on use.

5.4.2 COST COMPARISONS FOR COMMERCIALIZED AUTOMATED TECHNOLOGIES VS. LONG-TERM TRADITIONAL MONITORING

The approximate costs for these technologies are provided in Section 4.0 by the developers. Therefore, not as many assumptions need to be made regarding capital costs. The costs for the VOC Monitor technology are assumed here.

• For 20 wells, 5 of the 4-port systems would be required at a cost of \$12,000 each. This is a total purchase cost of \$60,000.

- Installation of these probes and analytical units (including calibration) will likely require an additional \$10,000 in labor and materials. This cost would likely be higher if the wells are far apart because sample lines would be required between each well and its respective analytical unit. A total approximate upfront cost is assumed to be on the order of \$75,000.
- Routine maintenance and calibration may be less than the in-situ technologies because fewer analytical units require calibration and service. A cost of \$3,000 per year is assumed.

Year	Low-End Traditional Monitoring		High-End Traditional Monitoring		Sensor Technology	
	Annual	Cumulative	Annual	Cumulative	Annual	Cumulative
1	\$22,000	\$22,000	\$42,000	\$42,000	\$78,000	\$78,000
2	\$22,000	\$44,000	\$42,000	\$84,000	\$3,000	\$81,000
3	\$22,000	\$66,000	\$42,000	\$126,000	\$3,000	\$84,000
4	\$22,000	\$88,000	\$42,000	\$168,000	\$3,000	\$87,000
5	\$22,000	\$110,000	\$42,000	\$210,000	\$3,000	\$90,000

Therefore, provided the above assumptions and no discounting, an automated unit such as the VOC monitor appears to be cost-effective within 3 to 4 years, even compared to the low-end costs for traditional methods. Once again, if the capital costs decrease or the monitoring requirements increase, the sensor technology becomes more cost-effective. However, if the monitoring requirements decrease to semi-annual or annual, the sensor technology becomes less cost-effective.

5.4.3 COST COMPARISONS FOR HAND-HELD AND FIELD-PORTABLE ANALYTICAL TECHNOLOGIES VS. LONG-TERM TRADITIONAL MONITORING

The hand-held and field-portable analytical technologies facilitate ground water sampling and analysis by reducing the preparation time for bottling samples and the costs associated with analyzing the samples in an offsite laboratory. For the upfront capital costs of purchasing the instruments, these technologies could theoretically eliminate the analytical costs of monitoring the hypothetical site. The following cost comparison makes the following assumptions:

- The purchase cost of a hand-held unit is approximately \$15,000, which is midway between the approximate costs provided by the project teams for the described instruments. The purchase cost of a field-portable unit (such as those evaluated by the ETV program) is approximately \$30,000, which is common for these technologies.
- Utilization of the sensor technology results in the same sampling costs as the traditional methods but eliminates the analytical costs. Only the low-end traditional costs are presented because it is the more rigorous comparison.

- Low-End Traditional Hand-held Sensor **Field-Portable Sensor** Year Monitoring Technology Technology Annual Cumulative Annual Cumulative Annual Cumulative \$31,000 1 \$22,000 \$22,000 \$31,000 \$46,000 \$46,000 \$44,000 2 \$22,000 \$16,000 \$47,000 \$16,000 \$62,000 3 \$22,000 \$66,000 \$16,000 \$63,000 \$16,000 \$78,000 4 \$16,000 \$79,000 \$94,000 \$22,000 \$88,000 \$16,000 5 \$22,000 \$110,000 \$16,000 \$91,000 \$16,000 \$110,000
- Calibration of the sensor instrument and interpretation of the analytical data can be accomplished for under \$1,000 per sampling event.

Provided the above assumptions, the hand-held sensor technology appears to provide cost savings during year 3 and the field-portable technology appears to provide cost savings during year 5. The primary difference is due to the capital cost of the instrument. Therefore, if the cost of the field-portable sensors can be reduced, the expected payoff time would decrease.

As with some of the in-situ instruments, these instruments are not dedicated to a particular well or site and can be used at multiple sites. The capital costs would then be distributed over more sites and monitoring wells, making the sensor more cost-effective. These instruments might also be appropriate to rent on an as needed basis.

6.0 FINDINGS

Numerous emerging technologies can technically facilitate the sampling and analysis of ground water. This report classifies these technologies in the following three categories:

- technologies that provide in-situ sampling and analysis of VOCs in ground water (i.e., sampling and analysis provided within a monitoring well)
- commercialized technologies that automate both sampling and above-ground analysis of VOCs in ground water
- hand-held or otherwise field-portable instruments that can be used for the analysis of VOCs in ground water

A total of 17 specific sensor projects are discussed to demonstrate the relative status, capabilities, obstacles, and costs associated with each technology. The applicability of the sensors at individual sites depends heavily on site-specific conditions, long-term monitoring objectives, regulatory approval, and cost-effectiveness. Regardless of the site, however, sensors provide real-time results that can be compared to historical values, and can be used to collect additional samples immediately, if necessary. This is a benefit over traditional methods where results are generally not available for a week and inconsistencies in sampling data may be left unresolved.

The report discusses a number of factors to consider when implementing the sensor technologies. Reliability, site specific conditions, regulatory approval, and cost-effectiveness are all discussed. Although some of the sensor technologies may soon be ready to provide screening level data at some sites, for any of the technologies to replace traditional methods, the necessary quality assurance and quality control measures will need to be incorporated. For example, a sensor technology will likely need to provide calibration and quality assurance data that are currently provided by analytical laboratories. It will also need to demonstrate accuracy and precision for specific contaminants of concern that are comparable to laboratory analytical methods. Some of the technologies that are intended to provide in-situ analysis in a single well over a period of time face a greater technical challenge than those technologies where analysis is either conducted at the surface or the instrument is routinely brought to the surface.

To explore the cost-effectiveness of these technologies, the report provides preliminary cost comparisons (based on a number of assumptions) between the sensor technologies and traditional methods. These cost comparisons and consideration of the capabilities/limitations of the various sensor technologies yields the following conclusions, which are dependent on the cost and other assumptions made in the analysis.

• Based on the preliminary cost comparison in this report and the associated assumptions, conducting long-term monitoring with a sensor permanently

installed at each well (even with remote access to data) might not be cost-effective relative to traditional sampling. However, this depends heavily on the cost of the traditional sampling, the cost of purchasing and installing those probes, and the sampling frequency. Permanent installation of sensors in monitoring wells may also make it difficult or expensive to routinely calibrate or service the sensors.

- Based on the preliminary cost comparison in this report and the associated assumptions, automated sampling and analysis systems with centralized aboveground analytical units, such as the VOC Monitor by Waste Technologies of Australia, appears be more cost-effective than placing a sensor in each well and appears to demonstrate cost savings relative to low-end costs associated with traditional methods. Once again, this determination of cost-effectiveness depends heavily on the actual cost of the traditional sampling, the cost of purchasing and installing the sensor instruments, and the requirements for sampling frequency. These technologies with above-ground analysis also appear easier to calibrate, either manually or automatically, and are probably more likely to meet the rigorous quality assurance standards required by regulators.
- Based on the preliminary cost comparison in this report and the associated assumptions (e.g., 20 samples are collected four times per year), using hand-held analytical instruments, such as the : ChemLabTM and the Hand-Held GC, would likely result in life-cycle cost savings relative to traditional methods during the second year of monitoring. These technologies can be calibrated routinely and can also likely be used for health and safety purposes or to greatly facilitate remedial investigations. In addition, these technologies have a wide variety of applications, which may help increase funding for further research, increase the total number of units sold, and decrease the cost per unit. These units could also potentially be combined with the automated sampling systems described above.
- Based on the preliminary cost comparison in this report and the associated assumptions, using a few probes to monitor many wells during a sampling event appears to provide the greatest potential cost savings relative to traditional long-term monitoring methods. This approach allows for routine calibration but requires that the probes equilibrate with the ground water quickly and that measurements can be made on the order of minutes. This is applicable to some of the in-situ instruments and all of the hand-held or field-portable instruments. In-situ technologies that appear to have this capability are the mid-infrared fiberoptic sensors, ion mobility spectrometers, and the wave-guide interferometry fiberoptic sensors. However, some of these instruments are fairly large and might disrupt the equilibrium in the well when they are submerged.

The following recommendations are provided given that some of the reviewed technologies are currently capable of providing screening level data at many sites, have the potential to one day provide data quality comparable to traditional methods, and have the potential to greatly reduce long-term monitoring costs.

- Research and development of sensor technologies should continue. Consideration should be given to the above conclusions and to communication with environmental professionals to ensure that the sensors are appropriate to various site conditions, are capable of meeting the site-specific data quality requirements, and are cost-effective relative to traditional approaches. Further development of mid-infrared and waveguide probes, automated sampling systems (that would utilize above-ground analysis), and hand-held and/or field-portable analytical instruments is particularly encouraged.
- Potential linkages between the various hand-held and/or field-portable analytical technologies and sampling technologies (such as the VOC Monitor, Burge Environmental system, or Sentex SituProbe) should be considered. These combinations could potentially be used as automated systems or as manual systems in which the sampling has been facilitated. Analyzing samples in the field makes it practical to employ sampling devices in which the VOCs are extracted from the water within the well rather than above-ground or in the laboratory.
- Comprehensive field tests of select technologies should be conducted by environmental professionals to provide researchers and the hydrogeological community with specific feedback on how the instruments can best be tailored for long-term monitoring. This is particularly encouraged for the hand-held and fieldportable units because the instruments are applicable to both long-term monitoring and remedial investigations and also have other applications that may divert researchers from further considering ground water monitoring.
- The regulatory community should be educated on these emerging technologies so they can provide feedback during the research and development stage are prepared and knowledgeable about them once they are ready for more widespread use.

Potential next steps for implementing these recommendations are as follows:

- The specific parameters of a comprehensive field test should be developed. Specific parameters include the conditions, types of contaminants, concentrations, test duration, etc. The field tests should incorporate multiple technologies, multiple wells with various conditions, and traditional monitoring methods to use for comparison. Sites where long-term monitoring is funded by EPA (i.e, Fund-lead sites) could be screened as potential test sites.
- Once the parameters of the field test have been documented, they can be circulated to the various sensor project teams to obtain cost estimates for participating in the field test and an appropriate time frame to prepare for the test.
- The results of the test should be shared with the state regulatory community as a first step toward educating it on the technologies as well as the current and expected capabilities.

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