WORKSHOP REPORT:

Long-Term Monitoring Sensor and Analytical Methods Workshop

Orlando, FL
June 13-15, 2001

Characterization, Monitoring, and Sensor Technology
Crosscutting Program (CMST-CP) &
Subsurface Contaminants Focus Area
Office of Science and Technology
Office of Environmental Management
U.S. Department of Energy

LONG-TERM MONITORING SENSOR AND ANALYTICAL METHODS WORKSHOP

Executive Summary

The Long-Term Monitoring (LTM) Sensor and Analytical Methods Workshop, held June 13-15, 2001, in Orlando, FL, was conducted to evaluate available and newly emerging sensors and analytical instruments for use in LTM of contaminants in the subsurface. One hundred and twenty people participated in the workshop, which was sponsored by the Subsurface Contaminant Focus Area (SCFA) Program in the U.S. Department of Energy (DOE) Office of Science and Technology, representing both technology users and technology developers. During the workshop, DOE site-identified LTM needs were used as the basis for determining functional requirements for sensors and for assessing current technologies and approaches. From this assessment, technology gaps were determined and opportunities for LTM research and development (R&D) were identified.

While workshop discussions were originally intended to focus on chemical sensors and/or chemical field analytical methods that can be used to monitor contaminants for LTM programs, participants maintained that surrogate measurements or alternative approaches to measuring contaminants directly are equally, if not more, important for monitoring programs. Participants expressed uncertainty regarding the ability of point chemical measurements to provide an accurate assessment of site conditions, even with numerous measurements. Instead, the primary interest was in the broader goal of identifying what measurements need to be taken to support monitoring decisions. Participants with monitoring program experience stated that monitoring subsurface parameters such as moisture, pH, or oxygen levels can provide critical information about the condition and integrity of a remedial system. In many cases, monitoring changes in these parameters provide the best early warning for remedial system failure. Workshop conclusions regarding alternative approaches to contaminant measurements are summarized as follows:

- The design of integrated systems to measure moisture content, moisture flux, and moisture potential is a high priority for monitoring engineered isolation or waste storage facilities such as landfills, vaults, barriers, etc.
- Identification of natural analogs that can be used to monitor the condition of a site is a priority for identifying surrogate parameters. Surrogates can be monitored at sentinel locations at remediated sites. Changes in sentinel measurements can be used to trigger contaminant measurements, as opposed to reliance on predetermined contaminant monitoring schedules.
- Development of technologies that make measurements over extended areas, such as remote sensing methods or subsurface geophysical methods, have advantages over point sensors and should be a high priority in monitoring R&D programs.

The workshop participants concluded that most technologies needed for measuring surrogate parameters are well developed today. Thus, the near-term R&D focus in this area should be demonstrating the integration of these existing sensors and analytical methods for the purposes and objectives of environmental monitoring. In contrast, chemical environmental contaminant sensors are largely under developed, and thus recently emerging techniques were discussed. (See Sections 3.1.3, 3.2.3, and 3.3.3.) The primary focus, however, was identification of requirements for contaminant sensors. Requirements for each contaminant class were developed to guide the future R&D program. (See Sections 2.2 and Appendix G, H, and I.)

Whatever the monitoring measurements, the goal is to understand the entire site system transport processes and risks. This understanding will lead to strategies that determine where and how to put samplers and monitors, what to monitor, and how to understand the monitoring data. Additionally, all monitoring programs must stay flexible to change over time. Based on this underlying concept, participants drew the key conclusions presented in Exhibit 1.

Exhibit 1. Key Conclusions from Workshop

- There are three general monitoring approaches that will influence contaminant sensor designs: (1) sampling in monitoring wells, (2) sampling in small-diameter access tubes, and (3) implanting vadose zone monitors.
- The drawback to point sensors is the potential for non-representative data of site conditions. Limited data points can be misleading in heterogeneous environments.
- Integration of sample volume may be a means of dealing with heterogeneity and reducing the number of samples for LTM programs, particularly for mass transfer limited sites.
- Designing a sensor to meet all requirements identified for each class of contaminants sensors would be difficult and extremely expensive. However, individual emerging sensors identified in this workshop could meet identifiable application niches.
- Many sensors meet short-term needs for process and performance monitoring. Sensors developed for these purposes may be a stepping-stone to LTM sensors.
- To shorten the R&D cycle, new environment sensors should embody available industry standard protocols within the sensor deployment and integrated system (e.g., use of 4-20 mA, 0-10v, or RS-232 for data transmission).
- Development of a few standard deployment platforms and sampling protocols with open architecture would encourage use of multiple sensors from various developers. In addition, it would foster development speed, technology acceptance, and collaborations leading to multiple sensors working together.
- Engineering goals for LTM sensors include making them easy to understand, install, calibrate, operate, and maintain with a capability to survive the deployment environment.
- Monitoring systems should be automated with data transmission via telemetry for remote control and data processing capability.
- Given that costs drive the use of and govern the market for monitoring sensors, they must be cheaper than baseline methods.
- Difficult-to-access locations such as deep vadose zone or deep well environments are an ideal application for sensors.
- Real-time sensors should be considered only when increased monitoring frequency is required, such as in surface water monitoring, monitoring during active remediation activities, and special climatic episodic events such as floods, snow melts, etc. In general, sampling frequency requirements increase from monitoring soils to ground water to surface water.
- Automated sampling combined with developed analytical field methods may offer more opportunity in the short term for monitoring programs than relying on sensor development.
- LTM program strategies should incorporate investment in training for regulators, site managers, and field operators to help them understand current data and set the stage for progress and innovation.
- Mobile on-site radiological measurement technologies are available for gamma-emitting nuclides. However, development is required for similar capabilities for alpha- and beta-emitting nuclides.

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LONG-TERM MONITORING SENSOR AND ANALYTICAL METHODS WORKSHOP

1.0 Workshop Background and Organization of Report

Workshop Background. Recently, the focus on the importance of technologies for long-term monitoring (LTM) programs for environmental restoration projects in the U.S. Department of Energy (DOE) has increased. Long-term stewardship programs will employ a broad range of surveillance, monitoring, and data collection techniques, with one data subset being contaminant concentration levels in the subsurface. Contaminant concentrations are typically obtained monthly, quarterly, semi-annually, or annually by collecting samples from drilled monitoring wells and then sending samples to laboratories for standard analyses. However, reducing the cost of these routine monitoring analyses and avoiding drilling additional wells has become a high priority for site managers, as evidenced at a May 2001 Ground Water Issues Meeting at Fermi National Accelerator Laboratory attended by DOE ground water monitoring program managers. Possibilities for reducing monitoring costs include (1) using field measurement technologies and (2) automating sampling and measuring concentrations in the field with either field analytical methods or sensors.

In light of these issues, an important effort for DOE is to research and develop effective detection and contaminant measuring technologies as well as improved sampling techniques. Various optical, chemical, electrochemical, electrical, and mechanical techniques (or combinations of these) are available commercially and can be applied to LTM technologies or sensors. However, considering the long life cycle of performance monitoring required at DOE sites, the performance characteristics of monitoring technologies must be continually improved.

Based on these considerations, a workshop was conducted on June 13-15, 2001, in Orlando, FL, to evaluate currently available or newly emerging sensors and analytical instruments used for LTM in the subsurface. This effort was hosted by the Characterization, Monitoring, and Sensor Technology (CMST) Crosscutting Program and sponsored by the Subsurface Contaminant Focus Area (SCFA) Program, both managed by the Office of Science and Technology within the DOE Office of Environmental Management. The objective was to identify requirements for LTM technologies and to determine what technologies are available to meet the requirements. Where existing technologies do not meet the performance goals of LTM programs, the near-term and long-term objectives for research and development (R&D) programs were identified.

Organization of Report. This report describes the workshop's major findings. In Section 2, the contaminants of most concern and the functional requirements for sensors for LTM programs are identified for each class of contaminants (i.e., organics, metals, and radionuclides). In addition, a summary is presented of common themes that emerged across the three breakout groups regarding LTM measurement technologies. Section 3 presents the workshop findings regarding LTM issues for the three contaminant classes. Finally, to provide context for this report as well as to assist future workshop planners, Section 4 presents information on the workshop participants, topics and objectives, and overall process.

2.0 Summary Findings Regarding Contaminants of Most Concern, Functional Requirements, and Common Recommendations

2.1 Contaminants of Most Concern

In the area of radionuclide contaminants, those of greatest concern are the mobile isotopes or radionuclides that are not generally measured using gamma ray detectors. This includes uranium, technetium-99, tritium, strontium-90, cesium-137, plutonium, and americium. In the area of metals, those that will be most important to monitor are mercury, hexavalent chromium, lead, and beryllium. According to the National Research Council report "Research Needs in Subsurface Science" (2000) and the STCG needs statements, the most important volatile organic contaminants are TCE, PCE, dichloroethylene, chloroform, and carbon tetrachloride, while the important semivolatile organics are PCBs.

2.2 Functional Requirements

General technical or functional requirements for LTM sensor systems by contaminant class are provided below, with additional information in Appendix M and N.

<u>LTM Requirements for Organic Sensors</u>

- Capable of threshold measurements (e.g., 5 μg/L or MCL equivalent)
- Must be quantitative (+/- 20%)
- Must be reliable (2-year, stand-alone operation–including maintenance)
- Capable of appropriate dynamic range (based on problem)
- Capable of in-well performance (currently) and in-ground performance (future)
- Capable of point measurements (predominate application); flux measurements (some applications)
- Must be simple to operate and simple to understand (stakeholders)
- Must satisfy the evolving need—currently a remedial process, eventually LTM of completed remediation
- Must address compounds of interest including CVOCs (e.g., TCE, PCE, and CCl_4), hydrocarbons, breakdown products for toxicology considerations, indicator species, and co-contaminants such as hydraulic fluids, lard oil, and PCBs in oil
- Must be capable of measurements in the presence of interferences (assume target is 51% of mixture)
- Must be capable of measurements at a frequency of less than three months (quarterly sampling)
- Must be rugged given the specific field environment
- Must cost significantly less than the current baseline—maximum $4,000 for deployed system (current baseline of $500/sample is assumed, with a technology replacement cycle of every two years.)

LTM Requirements for Metals Sensors

- Must monitor for compliance (RCRA metals)
- Must monitor for performance (e.g., barrier failure)
- Capable of obtaining a representative sample
- Must be cost effective relative to baseline technology
- Capable of calibrated measurements
- Capable of accurate detection of metals to meet site regulatory requirements
- Must meet sensitivity of measurement determined by required application
- Must identify potential interferences
- Must be compatible with site deployment systems
- Must be rugged and reliable over design lifetime
- Must minimize waste generated

LTM Requirements for Radionuclides Sensors

- Capable of precision, reliability, accuracy, and selectivity
- Must be easy to use/understand/calibrate/maintain
- Capable of appropriate detection limit (0.1 MCL)
- Must employ integrated or qualitative sensors
- Must incorporate indicators of environment health, remediation control and effectiveness, engineered system performance, stabilization, etc.
- Capable of meeting regulatory levels or other drivers
- Capable of automated, remote telemetry (field, possibly in situ)
- Must have lower overall cost than baseline ($1-50 K)

2.3 Common Recommendations across All Workshop Breakout Groups

While LTM needs, requirements, and R&D solutions vary depending on the contaminant class and matrix involved, recommendations common across all classes and matrices emerged throughout the workshop. These recommendations are presented below. (For recommendations specific to contaminant class and matrix, see Section 3.0.)

Surrogate parameters. Many DOE LTM needs include requests for real-time, in situ sensors that measure contaminants to MCL detection levels reliably over extended periods via automated or unattended operations or in remote locations. However, meeting these requirements will be difficult and expensive and require long-term R&D programs. Thus, workshop participants concluded that designing sensors and integrated sensor systems for monitoring *surrogate* parameters that are good indicators of remedial system performance might be more easily achievable and therefore offer a better short-term R&D approach. Furthermore, surrogate measurements, such as moisture content, pH or redox conditions, and barometric pressure changes, might be better indicators of early system failures than contaminant measurements. Thus, there was general consensus that a focus on implementing and demonstrating sensors for these alternative measurements should be a high priority.

Moisture data. A significant issue for environmental remediation projects is identifying the best ways to detect early warning signs of system failures for containment or engineered isolation facilities such as landfills, vaults, and caps. Monitoring the moisture content and flux is emerging as a baseline monitoring approach through negotiation with regulators regarding DOE engineered facilities. Because moisture sensors are commercially available, many site managers would like to focus on developing integrated systems that monitor moisture flux, water content, and soil water potential below and around remedial systems. The monitored moisture data not only give an early indication of potential system failure, but also facilitate specific site understanding of the transport pathways and processes that influence contaminant movement.

Standard packaging and architecture. To accelerate the sensor development cycle, consideration must be given to the entire system from the outset, including elements such as the deployment and sampling system, data acquisition and processing system, and data transmission systems integrated with new sensors. The development process may be expedited through use of standard packaging designed for common environmental field applications and emplacements. Additionally, standard, open-architecture data acquisition and transmission systems already commercially available should be used. These industry standards should be adopted to allow all sensors to interface well with one another.

Two examples of existing environmental sensor systems are considered possible formats for use in integrating newly developed sensors. The first example is found in a U.S. Geological Service nationwide stream/river monitoring program, in which certain measurements such as stream flow or water level are automatically taken remotely on a periodic basis, with the data transmitted via telemetry to a central database. The data are then accessible to the public through the Internet. Standard commercial sensors and data acquisition systems are in place. DOE could leverage its resources by using these established systems as the 'backbone' for monitoring systems and adapting the sensors as required for environmental applications.

The second example is the E-SMART® network technology developed for the last decade by General Atomics with the support of the Air Force Research Laboratory, Defense Advanced Research Projects Agency, U.S. General Services Administration, and DOE. The present system employs a standard networking protocol capable of connecting sensors from various manufacturers into a single network for device monitoring, data logging, and peer-to-peer communications. One E-SMART® system in operation polls more than 100 sensor variables at ten-minute intervals. Variables include water level, pH, conductivity, dissolved oxygen, oxidation-reduction potential, turbidity, temperature, barometric pressure, humidity, wind speed, wind direction, rainfall, differential pressure, AC current, and total volatile organics (hydrocarbons and halocarbons, e.g., BTEXs, TCE, and PCE). Some signals are received directly via hardwire, while others are received via radio communication from remote sites (including sites at which sensors and radios are powered by solar panels). More information is available from the General Atomics website (http://www.ga.com/atg/html/environ.html).

Real-time analysis. Considering the timescale for contaminant migration in soils, groundwater, or subsurface vapor, obtaining real-time data appears unwarranted in most cases where quarterly monitoring is the norm. While episodic events, such as flash floods or downpours, would require more frequent data collection, in general no real benefits would result from the requirement for real-time analysis; this is particularly true in cases where it is unlikely that the volume of data generated would be fully reviewed on a regular basis. Exceptions to this conclusion include (1) situations when more frequent monitoring data would provide valuable information, such as monitoring rivers or other surface waters that are transient in nature and (2) situations when time-integrated information based on frequent data collection would provide a more accurate picture than quarterly information.

Sensors and field analytical methods. Many limitations and challenges exist in regard to sensor development. For example, can sensors self calibrate and stay calibrated over long periods of time? Are they reliable over periods on the order of years? Can they recognize site-specific interferences? In light of the significant investment required to overcome these concerns, alternatives to sensors might better serve monitoring programs. In regard to metals, for instance, advances in field analytical methods might be more cost effective in the short term because most issues cited here have already been overcome in commercially available field methods. In addition, automated sampling combined with advanced field methods may offer more opportunity for change in monitoring protocols. In contrast, sensors could be advantageous in several ways: (1) if inexpensive, they could be placed in numerous positions where previously only one data point was captured, (2) they could be designed to change out easily upon failure, (3) they could reduce the sampling waste created in monitoring programs, and (4) they could be placed in difficult-to-reach locations and possibly eliminate exposure to contaminated medium for field workers previously collecting samples.

Automated sampling systems. Given the significance of cost factors, focusing on automated sampling systems is a better first step than investing in integrated sensor systems that will initially be too costly to justify use. Currently, few sensor companies are willing to expend effort to develop environmental sensors due to the lack of a market. For instance, even demonstrated field-deployable instrumentation has not become part of existing monitoring programs. Thus, for sensors to become commonly used in routine monitoring systems, they must be more cost effective than the baseline of sample collection and laboratory analysis. This can only be achieved by creating a market for environmental sensors so that industrial investment in development and production is warranted.

Point sensors. Point sensors provide limited information and often do not provide data that truly represent actual site conditions or a subsurface formation such as an aquifer. Thus, a recent focus has been on capturing large areal information to better characterize true environmental conditions. The combination of point sensors with continuous, or multi-dimensional, methods can characterize the subsurface with less uncertainty.

Field tests. Sensor development programs should place high priority on providing developers with multiple opportunities to test technologies in the field. This would allow for initial 'failures' and subsequent adjustments to innovative detection systems early in development under real site conditions.

Available measurement systems. Many innovative, handheld, easy-to-use, field-deployable contaminant measurement systems are rarely used in cleanup or monitoring programs throughout the DOE complex. In many cases these new field analytical methods, which have been tested and demonstrated under rigorous independent performance verification programs, could significantly reduce monitoring costs and provide data on a more timely basis than standard quarterly monitoring programs. Thus, a high priority should be placed on increasing the awareness of site operations personnel, site managers, and regulators about these methods and their potential uses.

3.0 Summary Findings Regarding LTM for Specific Contaminant Classes

The workshop focused on obtaining LTM information regarding three contaminant classes, i.e., organics, metals, and radionuclides. Considerations in defining these classes included the following: (1) although radionuclides are a subset of metals, radionuclide measurement methods focus on the decay property of the nuclides, (2) the mobility of organics is significantly different than that of metals and radionuclides, and (3) sampling and detection approaches are unique to each contaminant class.

During the workshop, participants separated into three breakout groups to address each contaminant class. Each group addressed a common set of six workshop objectives (see Appendix B). The findings of these groups regarding each objective are presented here by contaminant class.

3.1 Organics

3.1.1 Objective: Assess current LTM chemical sensor and analytical needs

One assessment of user needs for LTM presented in this session involved an analogy equating the meeting room with a site (including the subsurface) and contending that users only need to know if contaminants are leaving the room. While this analogy implies the need to determine current and future fate and transport of contaminants at a site and action levels predicated on human health and environmental risk, it also underlines the simplicity of stewardship objectives.

Discussions focused on the following documented applied end-user needs compiled from the STCG needs database (see Appendix E): AL-01-06-04-SC; AL-01-06-01-SC; OH-AB-013; OR-BW-10/19A; OK-01-29/31; OK-99-01; ORHY-01/01A/01Bd; ORHY-04/04A/04B; RF-ER-14; RL-SS02/SS03; SR-00317; and SR-3027.

End-user descriptions of needs categorized by DOE Field Office are presented in Table 3.1.1. Note: Not all DOE sites were represented at the workshop; thus, discussions covered only certain DOE site needs.

3.1.2 Objective: Define the technical functional requirements for those needs

This objective involves distinctions between what is desired by end users and what is required by regulators and required to support decision making. The group separated VOC needs into three categories: (1) collection of measurements as required to fulfill state and/or federal requirements, (2) performance assessment of remedial systems, and (3) detection for sentinel purposes. The performance requirements for each category will significantly differ.

During the last twenty years of sensor development, most activities have focused on development of sensors that yield point measurements. For LTM applications, however, the point measurement approach may not be the most efficient. Under regulatory guidance, several types of measurements may be required: (1) point measurements, e.g., monitoring wells, etc., (2) integrating flux sensors, and (3) overall biological toxicity.

Table 3.1.1 End-User Descriptions of Needs by DOE Field Office

Field Office	**Need Descriptions**
Idaho	ID61-36: - Containment integrity of shallow barriers for contaminants such as carbon tetrachloride and VOCs - Release of liquids through barrier walls - Change in rate migration of soil gas
Albuquerque	Need higher frequency data (more than once a year) because the public is not satisfied with the current sampling frequency. This frequency should be based on rate of ground water flow. AL-01-06-04SC: - Need measurement of toxicology associated with the presence of compounds rather than specific compounds - "Effect sensor" may be more appropriate than contaminant sensor - Magnification and synergies of compound - Capture speciation of more toxic daughter products
Oak Ridge	- VOCs are not a high priority - Shallow PCB drums are filled with solid materials
Savannah River	The MCL (EPA Maximum Contaminant Level) for TCE and PCE in groundwater is 5 micrograms per liter. In addition to issues associated with the low detection level, there are purge requirements and Investigative Derived Waste (IDW) issues for both sensors and baseline technologies used in existing wells. Typical deployment platforms include drilling and direct push technologies. In general, the sensors need the following attributes: - Standardized data logger - Robustness - Reliable calibration protocols - Cost effectiveness
Richland	The RL-SS02 Need Statement documents a need to optimize pump-and-treat systems. This is an example of a long-term application with a near-term solution. A "threshold value" sensor that is significantly less sensitive than the MCL may be appropriate for this and many applications; however, obtaining an accurate and defensible value remains important. There is also a need for co-contaminants sensors that can operate in complex chemical matrices, such as PCBs in machine oil.

Discussions revolved around the paradigm shift from the characterization and monitoring mode, where industry is today, to efficient LTM. The changes that are necessary under this paradigm shift to begin gathering of different data or use of other methods must be negotiated with stakeholders and regulators. Key issues to be considered for LTM sensors include:

- Data quality of the measurements
- Necessity of measuring threshold values versus actual concentrations
- Required sensitivity or detection limit
- Sampling rate (continuous, hourly, weekly, monthly, quarterly, annually)
- Potential of low-cost measurement of surrogates versus contaminants of concern
- Sensor life expectancy and maintenance issues

In regard to the issue of whether concentration or contaminant flux drives risk management, the answer involves consideration of the following:

- Flux is needed as input for modeling
- Actual risk considers the contaminant concentration

The identified technical functional requirements for LTM sensors for organic contaminants are as follows:

- Capable of threshold measurements (e.g., 5 µg/L or MCL equivalent)
- Must be quantitative (+/- 20%)
- Must be reliable (2-year, stand-alone operation, including maintenance)
- Capable of appropriate dynamic range (based on problem)
- Capable of in-well performance (currently) and in-ground performance (future)
- Capable of point measurements (predominant application) and flux measurements (some applications)
- Must be simple to operate and simple to understand (stakeholders)
- Must satisfy the evolving need—currently a remedial process, eventually LTM of completed remediation
- Must address compounds of interest including CVOCs (e.g., TCE, PCE, and CCl4), hydrocarbons, breakdown products for toxicology considerations, indicator species, and co-contaminants such as hydraulic fluids, lard oil, and PCBs in oil
- Must be capable of measurements in the presence of interferences (assume target is 51% of mixture)
- Must be capable of measurements at a frequency of less than 3 months (quarterly sampling)
- Must be rugged given the specific field environment
- Must cost significantly less than the current baseline—maximum $4,000 for deployed system; current baseline of $500/sample is assumed, with a technology replacement cycle of every two years

Highlights of the discussions leading to identification of the technical functional requirements listed above are as follows:

- Sensor development should be a step process, from easy to more difficult problems. It should follow an evolutionary process of development. The DOE and other federal agencies have made a significant investment in technology development of VOC sensors. DOE should leverage this investment now by 'picking the low-hanging fruit' or applying previously developed technologies that may need only minimal modification. The intent should be to pay only for innovative parts of the technology development.
- There should be a process to determine criteria for LTM sensors. The sensors need to be designed so that key decisions can be based on the data generated from them. Consequently, this requires regulatory approval of the sensors. End users feel that cost will be the main driver for sensor selection.
- Sensors must have an appropriate dynamic range to address the problem; in operation, users do not want to exceed the calibrated range. Continuous measurements far exceed needs of users, who will be swamped by data. There is a need for real-time measurements for field screening under characterization or active monitoring scenarios. Frequently the measurement of trends is most important. Ultimately, the expected frequency of change will dictate the sampling interval; the appropriate interval is shorter than quarterly.
- Major issues to consider regarding maintenance requirements for sensors are continuous and reliable calibration, useful sensor lifetime, easy retrieval, and easy repair of sensors.
- Concentration versus flux: During soil vapor extraction (SVE) monitoring, the flux and composite number are important rather than single, one-time measurements. Attention is placed on tracking patterns of soil gas rebound. Also, effective monitored natural attenuation remedies need flux measurements. However, concentration measurements are more common, and most sites do not measure both flow and concentration values needed to calculate flux. Additionally, modelers need flux values that are calculated from measurement of flow rate and concentration.
- Three possibilities for what the monitoring environment will be like five years down the road are: (1) monitoring wells, (2) implanted vadose zone monitors, and (3) small-diameter access tubes.

3.1.3 Objective: Evaluate current technologies against functional requirements

This objective involves evaluation of what technologies are available that might meet the functional requirements established in the previous subsection. The group selected eight sensors and monitors, which are discussed in Table 3.1.3. Additional discussion highlights are provided in Appendix N.1, which also contains a summary of how many of the eight technologies meet each of the identified functional requirements. (Note: A system using a horizontal permeable pipe that can be used as a perimeter sentry was also discussed as an alternative to the point sampling or sensing methods. The system can be used with directional drilling or installed in trenches. It uses a leak alarm system for detecting pollutants.)

Table 3.1.3 Available Technologies That May Meet Functional Requirements

Sensor / Monitor	**Issues / Recommendations**
Chemiresistors Under development by C. Ho, Sandia National Laboratory. These are polymer resistors that sorb chemicals. Swelling causes changes in resistance. They are passive and reversible.	Detection capabilities not at MCL ~ ppm (mg/L) levels for water. Interferences are an issue. Will use matrix analysis of an array of sensors of different polymers with different sorbing and resistance properties. Has built-in thermocouple. Requires specific calibration for target compounds and background matrix. Works below water <10 m using semi-permeable membrane. Very inexpensive to make. Does not work in NAPLs; unclear if microbes or biofouling will be an issue. **Recommendation:** This sensor should be taken to the field quickly to determine actual field performance. To determine commercial costs, compare to existing commercial technologies with similar, simple operating principles and fabrication requirements.
Planar Waveguide Under development by B. Martin, Georgia Tech. Etched planar wave guide using index of refraction changes with optical interferometer. A matrix of separate polymer coatings with different responses to different chemicals will be used to speciate the target compound. They are passive and reversible.	Detection capabilities (BTEX ~ 50 μg/L; CVOC ~ 100 μg/L) are not at MCL. Can also measure pH, ammonia, proteins, and bacteria concentration <10 cfu (colony forming units); an antibody coating produces reaction. Requires specific calibration for target compounds. Dynamic range may be an issue. Small size. Approximately $500 per sensor. Doesn't work in NAPLs. May have difficulties in some mixtures, e.g., BTEX. Long-term stability is unknown. Licensed technology to commercial partner. **Recommendation:** This sensor should be taken to a well-characterized site quickly to determine actual field performance.
REMPI (Resonance Enhanced Multiphoton Ionization) Under development by M. Angel, U.S.C. (angel@mail.chem.sc.edu). This is a direct spectroscopic technique that uses selective ionization to analyze specific compounds.	Uses a small laser and dye system for selectivity. Detection capabilities at MCL: benzene ~ 2 μg/L. Dynamic range is approximately 4 orders of magnitude. Laser wavelengths for some compounds are not yet commercially available. Easy to understand. Bench tested, but not field tested yet. Cost data are unknown, but commercially available laser is $7,500. **Recommendation:** More bench testing required for relevant compounds. This sensor should be taken to the field to determine actual field performance.

Table 3.1.3 (Continued)

Sensor / Monitor	**Issues / Recommendations**
CPT Sensors for Membrane Interface Probe (MIP) Under development by Dakota Technologies, Dan Engebretson. Several existing sensor technologies have been reconfigured for operation with the direct push MIP for volatile organics.	Three technologies are being developed to interface with the MIP: photoionization, halogen specific, and downhole gas chromatograph. Detection capabilities not at MCL: VOCs ~ 50 ug/L. The response is matrix dependent. Not designed for long-term, unattended use. Continuous monitoring and depth profiling. Very rugged. Quantitation capabilities and performance in presence of interference is not yet well understood. Bench tested, but not yet field tested. Cost data are not yet known, but the system purchase cost will probably be between $20-50 K to purchase. **Recommendation:** Applicable to LTM as a periodic testing of the subsurface at different stages of treatment, e.g., during cleanup, polishing, and at intervals following active cleanup
Quartz Crystal Microbalance Under development by Tim Sivavec, General Electric. Uses an array of quartz crystal microbalance sensors with a series of proprietary coatings that respond in different ways to different compounds.	Has funding from within GE as well as from EM-50 for development and commercialization. Nomadics is the commercial partner. Detection capabilities are near MCL for individual VOCs ~ 5 µg/L. The limit of detection is higher in mixtures of VOCs. The long-term reliability, potential interferences, and commercial cost are unknown; however, the probe itself costs $1 K. A membrane is used to isolate the sensor from moisture. It is small enough to fit in a 2"-diameter well. It has been tested in a 2"-diameter well. **Recommendation:** Conduct more field testing in different contaminant scenarios.
Fast Gas Chromatography (GC) on CPT POC: Al Robbat, Tufts University. Uses heated sampling probe/line and Peltier-cooled trap on CPT with interface to fast GC with 500°/min ramp. Measures soil mass fraction in zone of influence of probe.	Can speciate and quantitatively analyze VOCs, semi VOCs, PAHs, PCBs, pesticides, and petroleum compounds in approximately 3 minutes per analysis. Is sensitive to .5 mg/kg PAH, .2 mg/kg PCBs. Volume of sample is unknown. Similar to Membrane Interface Probe based sensors; this technology is not left in ground, but deployed periodically to measure progress at a site. Reliability is probably good. Can analyze 5 samples/hr @ $5 K/day (including CPT): $150-200/sample. Is rugged, but currently only used in the vadose zone. **Recommendation:** This detection system is more representative of typical characterization technologies vs. monitoring sensors. However, at $200 per sample, such classical approaches may be cost-effective alternatives to monitoring. More testing in the field in different contaminant scenarios is recommended.

Table 3.1.3 (Continued)

Sensor / Monitor	Issues / Recommendations
Automated Sampling system and TCE sensor Under development by S. Burge, Burge Environmental. This is a licensed technology from Lawrence Livermore National Laboratory. It is a reagent - based detection system using the Fujiwara reaction for TCE analysis.	Can quantify TCE to MCL < 5 µg/L. Large dynamic range. The analysis occurs above ground, but the system can sample wells automatically. Has operated in the field for nine months to date. The analysis reaction only occurs with TCE and chloroform. It costs between $12 K and $15 K. **Recommendation:** This sensor is being tested at Homestead AFB and is scheduled for field testing at Savannah River Site this year.
Continuous Flow Immunosensor Developed at NRL; commercially available at Research International, Inc. This is a continuous flow immunosensor technique requiring no reagent addition. There are two versions: the FAST 2000 and the FAST 6000.	<200 µl sample. Can analyze TNT and RDX to 20 µg/L in 2 minutes, but is semi-quantitative. TCE, PAH, and Estradiol are being studied. Can perform 50 tests per membrane. It is amenable to automation, but currently cannot operate unattended. It has a large dynamic range, i.e., approximately 2 orders of magnitude. The cost is $20 K for the instrument and $4/sample. **Recommendation:** This technology (FAST 2000) was tested for response to explosive contamination as part of the EPA ETV program, and results were mixed. The newer version should be field tested.

3.1.4 Objective: Assess technology shortcomings and gaps

A significant issue addressed was that technology developers spend a significant portion of their resources on developing a package that will house and protect a sensor with appropriate dimensions for the specific application, e.g., inside a 2"-diameter well. There was a call for a standard package designed for common environmental field applications and emplacements. Besides the standard emplacement package, the need exists for a standard interface, open architecture, and user-friendly output, as well as a standard bus for control and feedback. The U.S. Department of Defense E-Smart® system is an example of a useful architecture to promulgate in the DOE. Another example of a standard data acquisition and transmission system that DOE could adopt is found in the U.S. Geological Service national network of surface water sensors that record various parameters of streams and rivers, with data available to citizens on the Internet. In regard to the observation that standardization already existed for most sensors (e.g., 0-10 volt; 4-20 mAmp; 0-30 mVolt, RS-232, IEEE 488), it was agreed that non-unique functionality should conform to one of the popular standards in existence to reduce sensor development costs. Also in regard to common interfaces and their definitions, it was suggested that a common enclosure for sensors be developed because nearly all applications require a small footprint and the capability of stand-alone operation.

Additional discussion on the definition and structure of LTM followed. Most participants agreed that the LTM method must satisfy regulators, which may require confidence-building activities and comparisons to baseline techniques. Sending some portion of samples (e.g., 10%) for SW-846 analysis is a commonly accepted way of accomplishing this. Additionally, some outreach efforts may be required to educate stakeholders on the high-resolution data available from in situ sensors so that correct, objective decisions can be made.

3.1.5 Objective: Identify LTM strategies

The group agreed unanimously on the need for testing sensors and monitors under actual field conditions at well-characterized sites. More funding should be spent on application R&D to bridge the gap between the bench top and the field. Several commercially available sensors can satisfy many of the identified requirements; however, many users and stakeholders do not understand these technologies. Thus, resources should be used to educate users and stakeholders on the operating principles, advantages, and limitations of these technologies as well as what the measurement means in the larger scope of the cleanup objectives. In addition, funding should be used to develop generic platforms for multisensor deployment with standardized architecture wherever possible. Another consideration is that a technology should match the data quality objective for the situation. For instance, in many cases where likely concentration fluctuations are well understood and data are only required on an infrequent basis, a requirement, nonetheless, for real-time, high-frequency data is presented. Finally, long-term strategies should include funding for the development of inexpensive sensors that satisfy the LTM requirements identified in this report.

The following issues were unresolved and should be addressed in future LTM monitoring strategy sessions: Does LTM require that technologies be left in place? Are periodic field campaigns part of the LTM strategy? Are there other alternatives to the traditional point sampling sensing, e.g., long integrating samplers or horizontal arrangements? Should LTM be simply threshold detection and signaling for collection of a baseline sample? Are high-resolution data better or worse for effective site cleanup and final disposition?

3.1.6 Objective: Identify LTM R&D program

The following suggestions regarding identification of an LTM R&D Program were offered by individual participants:

- Development of multi-sensor platforms.
- Small, inexpensive sensors that are cheap and easily last two years, potentially biodegradable. Deployment platforms are still an issue.
- Commit $1million to train regulators and site engineers on how to use current information.
- Fund application engineering, i.e., fund the development portion of R&D.
- Fund field-testing of sensors that have done well on the bench top. Take advantage of low hanging fruit. This is important because during testing and deployment things fail. This is one part of the "Valley of Death" when taking a technology from basic research to commercial product.
- Fund multiple deployments. Do many deployments, not three.

Regarding the current state of sensors and fundamental philosophies on LTM, the following questions and statements were offered:

- Are the new technologies and sensor solutions looking for problems?
- Where is the true cost-saving opportunity? Is it in new technologies or being smarter about current methods?
- Sites need to prioritize and determine the essence of their needs. For example:
    1. "I don't want the plume to leave the room, not a sensor hanging down the well" is a clear requirement from the user.
    2. Community stakeholders are ultimate end users.
    3. Perhaps a cultural anthropologist is needed to help anticipate the long-term needs for a particular site.
- How should one communicate the intangibles that are largely covered by professional judgment, e.g., the true radius of influence and the confidence level in measurement and the reported value? Can the "What would I do if this were my house?" approach be incorporated in professional judgment?
- Should DOE look harder for new, non-conventional technologies (paradigm shift) as opposed to point, concentration measurements?
- Are more deployments really going to make it?
- There are existing technologies that can work!
- Is it necessary to develop and standardize new architecture?
- The U.S. Geological Service has developed systems and approaches that can be used.
- What about the commercialization issue? Should DOE focus on pushing technologies into the market, or fund development to address their own problems in a cost-effective manner?

3.2 Metals

3.2.1 Objective: Assess current LTM chemical sensor and analytical needs

Typical needs statements cite a need for reliable, real-time monitoring information with in situ sensors in both soils and groundwater. For example, "Devices or sensors are needed to detect below ground releases in the vadose zone from leaks, spills, or releases of contaminants before reaching ground/surface water. The envisioned device will be field rugged, long-lived, require minimal maintenance, and networked via wireless technology to a central alert system" (ID-6.1.37). Needs for real-time, in situ monitoring of metals include several citations for mercury and hexavalent chromium, but lead and other heavy metals were also cited, as well as some locations with beryllium contamination.

During this session, the true need for real-time measurements for LTM was discussed. John Kubarewicz from Bechtel Jacobs Oak Ridge stated that he has never had a request for real-time monitoring. He noted that most wells are sampled quarterly and surface waters are typically sampled monthly. Surface water sampling also may be done in response to episodic events such as floods. Khris Olsen from Pacific Northwest National Laboratory stated that real-time monitoring for chromium levels may be required for the Columbia River, but that away from the river the chromium levels have been steady for years; thus, quarterly or monthly monitoring seems to be adequate. The frequency of sampling at most sites increases from soils to groundwater to surface waters. It was generally agreed that there is little need for real-time, continuous measurements of metal contamination in soils for LTM and surveillance. As an alternative to sensors or field analytical methods, automated sample processing in the field can provide major cost savings. For example, the use of 3M Empore™ disks for the collection of certain metals or radionuclides from water samples could avoid the considerable expense of transporting large water samples back to a laboratory.

The most common citations of needs for rapid determinations of metals were in remediation activities or when preparing a site for transfer to industrial use, i.e., remediation activities may mobilize a contaminant, and rapid analyses may be particularly useful to avoid harm to workers during these activities. Even in these cases, it was noted that field analytical methods could provide substantial savings for many metal determinations, particularly if analyses could be done quickly.

Obtaining a representative sample is important for all analytical determinations, and a question was raised regarding whether it is possible for in situ sensors to obtain useful information about metals in soils unless numerous sensors are distributed over a large volume. In situ sensors in monitoring wells also may not provide useful information about the aquifer unless the well is adequately purged, and this is particularly true for reactive species such as Cr(VI).

Overall, the primary concern is monitoring mercury and hexavalent chromium in ground and surface waters in a manner that provides useful information with respect to regulatory compliance and the integrity of containment systems. Measurement of beryllium concentrations on surfaces and in air particulates is also of significant interest.

3.2.2 Objective: Define the technical functional requirements for those needs

Many determinations of metals are driven by needs for regulatory compliance. Thus, determinations of RCRA metals in ground and surface waters may be required with analytical limits of determination typically set at half of the drinking water standard. It was observed that there might be reluctance at many sites to collect data that is not required by a regulator because of potential retroactive compliance penalties.

The other principal driver for LTM is performance monitoring, particularly for containment structures. Thus, almost every major DOE site has needs for monitoring landfills and other storage facilities as well as reactive barriers and plumes with no active remediation activities.

A major requirement for all types of monitoring is obtaining a representative sample. This need, along with the necessity of doing the calibrations required to meet regulatory accuracy requirements, suggests that it will be difficult to develop in situ sensors that will be cost effective for most applications.

The use of in situ sensors will also be determined by whether they are cost effective relative to baseline methods. As described above, most soil and groundwater determinations are required at monthly or quarterly intervals. Thus, the cost for maintaining calibrations over long times may not be justified if only infrequent reporting is required. Participants were not aware of any current sensors that can meet calibration requirements for several years, and they anticipate that developing sensors to meet these requirements in a cost-effective manner would be a major challenge for sensor developers.

The accuracy and sensitivity of measurements are most often determined by regulatory requirements, as noted above. Limits of detection for mercury, for example, may be as low as

10 to 50 parts per trillion, and determinations of specific species (such as methyl mercury chloride or dimethyl mercury) may be much more useful than simply obtaining the total elemental composition.

The calibrations of most sensors or analytical methods may be affected by other metals in the samples, so the general range of concentrations of potential interferences must be known. Thus, most analytical determinations require on-site personnel with sufficient expertise to modify the sensor or analytical method for local conditions.

The analytical system or device must be rugged and reliable over its design lifetime. Another requirement for most determinations, particularly for field or in situ measurements, is that there be minimal or no waste materials produced by the analytical procedure.

Finally, any analytical system must be compatible with site deployment systems. This includes obvious requirements for a sensor or sampling device to fit into a monitoring well, but it may also require that a monitor for soil contamination be deployable in a cone penetrometer system. If in situ sensors with wireless communications become available, then there will be a need for standard communication protocols, power supplies, and other standards for plug-in sensor modules.

The summary of this discussion as presented during the workshop is presented in Appendix M.2.

3.2.3 Objective: Evaluate current technologies against functional requirements

The participants were not aware of any in situ, LTM systems currently available for accurate determinations of metals at the levels required for regulatory compliance or performance monitoring. Discussions of available methods focused on field analytical methods and did not review the numerous methods available for fixed laboratories (see Table 3.2.3).

The primary analytes considered by the group were mercury, lead, chromium, and beryllium. Most discussions focused on the workshop-provided list of available technologies. In addition, a list of techniques is also available in a report, *Recommendations on the Development of Chemical Sensors and Field Deployable Instrumentation for DOE Needs,* available at the Characterization, Monitoring, and Sensor Technology website (http://www.cmst.org/cmst/reports.html). Field analytical methods for metals are described in a standard book on the subject, *Current Protocols in Field Analytical Chemistry (http://www.wiley.com/legacy/cp/cpfc/fctoc.htm#3)*. The only methods for metals that are extensively discussed in this book are anodic stripping analysis, x-ray fluorescence, and immunoassays. The latest editions of two biannual reviews on Water Analysis and Environmental Analysis have recently been published (S. D. Richardson, Anal. Chem., **2001**, 73(12), 2719; R. E. Clement, P. W. Yang, C. J. Koester, Anal. Chem., **2001**, 73(12), 2761). These reviews describe new developments and more extensive reviews of methods used for both laboratory and field-deployable analysis of contaminants.

3.2.4 Objective: Assess technology shortcomings and gaps

As described in the previous subsection, there are currently no widely available, real-time, in situ sensors for LTM of metals in any medium. Although the need for such sensors is often cited in STCG needs statements, the participants contend that simpler and faster field analytical methods may be more cost effective in the near future. The only field methods for metals cited in a recent standard reference book were x-ray fluorescence, anodic stripping voltammetry, and immunoassays. Although there are commercial sources for each of these methods, they require considerable expertise to obtain reliable results.

Table 3.2.3 Current Field Analytical Methods That Meet Functional Requirements

Technologies	Descriptions
X-ray Fluorescence (XRF) Instruments	Both field-screening and field-transportable systems are commercially available. XRF methods have multielement capabilities and are primarily useful for heavy metals. Perhaps the best application of these techniques is for soil samples, and it was emphasized that standard techniques to obtain representative samples are essential when using these instruments. It was noted that it is possible to determine metals in water samples by drying the samples on support films and then performing the determination on the residues.
Laser-Induced-Breakdown Spectroscopy (LIBS)	One example is a LIBS system built by Science and Engineering Associates for use at a Brush Beryllium Company site in Ohio for determinations of beryllium in soil. Both backpack and van-mounted instruments were constructed, with the latter having higher sensitivity. The LIBS performed adequately for this characterization activity and was more effective for beryllium determinations than for heavier metals. However, LIBS systems have been used for a wide variety of metals by this and other groups. Even though there is an extensive literature on applications of LIBS for metal determinations, most systems have been custom made at a cost of $80-100 K. Some sample preparation is usually required to obtain uniform samples with properties similar to those used for calibration, and past experience with direct evaporation of soil samples has suggested that this method is difficult to calibrate.
Anodic Stripping Voltammetry (ASV); Electrochemical Techniques	ASV can be used directly to measure ppb levels of some metals, and ASTM or EPA standard methods exist for cadmium, lead, arsenic, selenium, and chromium (VI), for example. Commercial instruments are available. The technique is not useful for alkali or alkaline earth metals, such as sodium, lithium, calcium, and magnesium, but it can be used either directly or with complexing agents for most other metals. Based on work conducted in an Environmental Management Science Program (EMSP) project to develop a method for chromium and uranium in water, considerable hurdles exist to develop an in situ instrument that would maintain calibration stability over long terms.
Colorimetric and Fluorescence Methods	Numerous methods are available for most metals, and many classical metal determinations using complexing agents have been adapted for use in fieldable kits or simple instruments. These methods are useful for field screening of metals in water and are relatively inexpensive.
Immunoassay Methods	Tulane University has developed antibodies for numerous metal complexes with EDTA and other complexing agents. These methods are useful for field screening and have detection limits for cadmium, mercury, lead, and uranium(VI) at parts-per-billion levels. The analyses of water samples can be completed in 10 minutes. The methods are being commercialized by Sapidyne Instruments, and other immunoassay methods are described in *Current Protocols in Field Analytical Chemistry,* as cited at the beginning of this subsection.

3.2.5 Objective: Identify LTM strategies

Recommendations for general research strategies include maintenance of research programs that are balanced among the three areas of basic research, applied research, and demonstrations and deployments. More support is needed for applied research to bring basic developments from the laboratory to the ready-for-deployment stage. In addition, despite the reluctance of technology users and technology development program managers to commit funds for long-term demonstrations, continued support for such demonstrations or deployments is essential.

Another recommendation is to provide more adequate response times for submission of proposals after a call has been issued, particularly for the latter stages of technology developments that require extensive cooperation between developers and users. The call for proposals should address specific contaminants of concern and should have user input to describe the accuracy and detection limits expected for a successful method.

The primary basic research support within the DOE Office of Environmental Management (EM) is in EMSP and SBIR Phase I programs. Basic research objectives should, of course, be oriented toward developing innovative applications of advances in analytical measurements. Goals particularly important for DOE applications include minimization of waste generation by analysis methods, development of new field or sensor methods with lower costs than baseline methods, and development of in situ technologies to access difficult locations, such as the deep vadose zone or deep wells. Specific research areas include micro-electro-mechanical (MEMS) devices, miniature chromatographic methods ("laboratory on a chip"), disposable test kits, and membranes for sampling and analysis of specific metals from aqueous solutions. Remote sensing optical and geophysical methods are also of continued basic research interest because such methods offer the hope of being able to monitor large areas.

Applied research within EM is mostly supported by EM50 Applied Research calls to industry and the DOE laboratories whose goals are set by the EM50 focus area programs and by SBIR Phase II projects. The principal goal of such projects is to produce field prototypes based on prior proof-of-principle laboratory work. A key aspect of this work, particularly as it nears completion, is development of partnerships with groups experienced in deployments. Emerging technologies that may be ready for more extensive applied research include microcantilever detectors for mercury, LIBS for mercury and other metals, and optrodes for metal determinations.

Research leading to demonstrations and deployments is supported by core project funding from the EM50 focus area programs, by "Quick Win" funding to sites from EM50, and by SBIR phase III projects. Potential "quick wins" for advancing applied research efforts include an exploration of whether surrogate measurements (such as pH, conductivity, and moisture determinations) can provide adequate performance monitoring for containment integrity without more expensive determinations of the actual contaminants. Additional development of sensors for mercury based on anodic stripping voltammetry may also be possible without major revisions of available instrumentation.

General conclusions from this session:

- Real-time sensors or monitoring systems are generally not needed for most LTM of soils and groundwater.
- Real-time sensors should be considered only when increased monitoring frequency is required, such as in surface water monitoring, monitoring during active remediation activities, and impoundment monitoring. Although development of inexpensive sensor systems for in situ, real-time determinations of metals in soils and groundwater is desired, success in such development is unlikely in the near future.
- High initial development costs can be expected for real-time, in situ sensors, and users should carefully consider whether such sensors can be made available in sufficient numbers to obtain useful measurements of contaminants without the use of the traditional screening and/or purging methods to obtain representative samples. If manual sampling methods are required to obtain representative samples, then development of improved field analytical methods may be more cost effective than that of unattended sensors.

3.2.6 Objective: Identify LTM R&D for chemical sensors

The summary of this discussion is incorporated into the previous subsection. The summary report listing basic and applied research objectives and quick win/core program objectives is presented in Appendix N.2.

3.3 Radionuclides

3.3.1 Objective: Assess current LTM chemical sensor and analytical needs

During this session, participants identified radionuclide contaminant LTM needs at various sites. The results are presented in Table 3.3.1A.

Table 3.3.1A Radionuclide LTM Chemical Sensor and Analytical Needs

Site	LTM Needs
Nevada Test Site	Small, durable, sensors capable of deep, downhole application Sensor systems with remote communication capability Cheap pumps capable of bringing up ground water samples from depths ranging from hundreds of feet to four thousand feet below ground surface Both continuous monitoring and episodic monitoring Current monitoring frequencies (ranging from quarterly to every three years) Tritium (HTO), with sensitivity sufficient for conservative indication of tritium migration to the ground water Ability to monitor soil water content below caps (as an indicator of effectiveness for protecting ground water), as required by regulators Drivers: - DOE Orders - Citizens' Advisory Board and strong stakeholder involvement - Federal Facilities Compliance Agreement and Consent Order (risk management is the stated objective; species that must be monitored are not specified) - The above also apply at the off-site test locations managed by DOE/NV Radionuclides may not be the only monitoring need at those locations

Table 3.3.1A (Continued)

Site	LTM Needs
Savannah River Site	Tritium (HTO) and Strontium-90 At depths between 0 and 200 feet Drivers: Federal Facility Compliance Agreement (FFCA), Tri-Party Agreement (TPA), RCRA, and CERCLA Nonintrusive monitors Detection limits sufficient for measurement at MCLs for drinking water and other Applicable or Relevant and Appropriate Requirements (ARARs) Sensors/methods for monitoring phytoremediation sites Frequency: ranges from quarterly, to semi-annually, to annually, mostly episodic Continuous monitoring may be useful for characterization of contaminant release and transport processes
Hanford	LTM in place Ground water: determination of new contaminant impacts, e.g., from tanks and landfills - Semi-annual - Transient releases (also a challenge) Monitor existing plumes (technetium-99, tritium (HTO), uranium, iodine-129) - At depth of up to 300 feet below ground surface Technetium-99 (get better site-specific information on mobility and risk) - Technetium-99 correlates with the results of gross beta measurements - In situ detectors for beta emitters such as technetium-99 (present methods require coring and laboratory analysis; costs are $1-3 M/borehole in the Hanford tank farm area) - Strontium-90 localized Drivers: TPA, RCRA, CERCLA, and DOE Orders
Los Alamos; Rocky Flats Environmental Technology Site	Deep ground water monitoring Episodic monitoring (impact of large flows from canyons) Sensitivity down to sub-pCi levels for Pu and Am Sampling issue for colloid transport (hot particles) Surface water: vent based or seeps, near real-time measurements needed, flow-paced - Rocky Flats: over month At Los Alamos: uranium, cesium, strontium Need to distinguish between natural levels and anthropogenic contamination - Anthropogenic is approximately 40 ppb - Natural is 10 ppb up to ppm levels - Monitoring solution may be combination of laboratory work with field monitoring - Facilities as well; e.g., waste water treatment plants Sensors to address non-proliferation monitoring Drivers: agreements, operating permits

Table 3.3.1A (Continued)

Site	LTM Needs
Fernald	Real-time monitor for uranium in groundwater Monitor for uranium in leachate from on-site disposal facility Measure to levels <20 ppm Remote monitoring of short episodes Must function in presence of interference from varying pH; redox potential also varies Uranyl carbonate is a species of interest Must be able to monitor uranium in the range from 2 ppm to 30 ppb
INEEL	Radionuclides have been measured and monitored by chasing plumes; emphasis is shifting to focus on sources; want to catch transport of contamination from burial trenches Want to use vadose zone monitoring for that purpose; currently using suction lysimeter (with porous cup) to try to capture moisture and contaminants escaping from burial trenches Monitoring of episodic events (e.g., snow melts, downpours) may be important Characterization and monitoring forensics, e.g., isotopic analysis, is important for understanding contaminant origin and transport Vadose zone has the "slows" (less mobile sources) Drivers: No regulations drive vadose zone monitoring; regulations are driven principally by groundwater considerations

General comments from users concerning radionuclide LTM needs at DOE Sites are as follows:

- There is no regulatory driver for monitoring the vadose zone; however, there are known vadose zone contaminants at Hanford (and many other DOE sites). The need to monitor contaminant transport in the vadose seems intuitive. Regulations do require protection of the ground water, which can be interpreted as requiring vadose zone monitoring.
- There is a need to monitor surface barriers and post-closure covers.
- There is a need to monitor soil water flux and/or soil water potential. These are the driving forces for movement of contaminants from the vadose zone to the groundwater. The Alternative Cover Assessment Program (ACAP), an EPA program with involvement of DOE (Subsurface Contaminants Focus Area), Sandia National Laboratory, University of Wisconsin, Pacific Northwest National Laboratory, Desert Research Institute, and DoD, is looking at the performance of various caps in different soil and climate environments by observing soil water flux.
    - There is a need to update capping technology since some of the methods date back a hundred years.
- There is a need to know the relationship between hydrologic factors and the transport of radionuclides.
- There is a need to know the distribution of radionuclide contamination in the vadose zone and how it is changing.

After generally surveying the LTM needs, participants identified the most important radionuclide LTM problems and corresponding drivers at DOE Sites (see Table 3.3.1B).

Table 3.3.1B The Most Important Radionuclide LTM problems and Corresponding Drivers

Site	Most Important Radionuclide LTM Problem	Driver(s)
Savannah River Site	Tritium (HTO)	Regulations and cost of monitoring (compliance)
Nevada Test Site	Tritium (HTO) at depth	Regulations, cost of monitoring (compliance), need to understand
Idaho National Engineering and Environmental Laboratory	Need to understand the potential mobility and transport of contaminants from source term (buried waste)	Need to protect ground water below burial sites
Hanford	Vadose zone (this is new territory; lack of understanding is considerable) Vadose zone sampling is the most important area to interrogate Monitored natural attenuation of radionuclides is important	Need to protect ground water below the site Compliance with RODs
Fernald	Uranium in water (ground water and leachate from on-site disposal facility)	Cost of monitoring (compliance)
Los Alamos	Actinides	Cost and sampling issues Also need more measurements to help understand transport

3.3.2 Objective: Define the technical functional requirements for the needs

Discussion of this topic was based in part on the functional requirements included in the workshop-provided need statements (see Appendix C) and in part on information provided by the site users and other breakout session participants. The participants were not subject to the regulatory, budgetary, and schedule requirements and constraints that actual DOE site managers are subject to. Therefore, the results, in Table 3.3.2 tabulated below, are functional performance goals for radionuclide LTM sensors rather than the functional performance requirements. Clearly, the actual functional performance requirements for application of specific sensors at specific DOE sites will likely differ considerably from site to site because of the broad range of applications and application conditions at the different sites. Decision quality objectives / data quality objectives (DQOs) for those applications are crucial, and they are application- and site-specific.

Performance requirements have been specified for tritium (HTO) measurements at the Nevada Test Site and at the Lawrence Livermore National Laboratory site, and for uranium measurements at the Fernald site and in the UMTRA program. The group's summary presentation is provided in Appendix M.3.

Table 3.3.2 Radionuclide Functional Performance Goals

Area	Goals
Information	Measures composition Reports concentration or dose (integrated for regulators) Integrating or qualitative sensors are important; these may serve as indicators for environment health, remediation control/progress/effectiveness, engineered system performance, stabilization, etc. Measures extent of change (from norm, set point, or regulatory level) Reports in terms understood by public, stakeholders (some education may be required) Provides measures of variability in space, time (important parameters are integration time, reporting interval, standard deviation of results); sensor sampling and/or diameter/sphere of influence characteristics are important; sensor stability is an issue for change detection Provides an alarm when a threat occurs
Technical	Sensitivity sufficient for measurement at regulatory levels or to satisfy other drivers Detection limit of 0.1 MCL is typically desired At the Nevada Test Site, tritium (HTO) must be measured to levels much lower than the drinking water standard – 1,000 pCi/liter Dynamic range sufficient to satisfy DQOs for the application Selectivity sufficient to provide accuracy in presence of potential interference Precision, reliability, accuracy, and comparability (PARC) sufficient to satisfy DQOs for the application; laboratory quality data is often required Has adequate response time and measurement frequency Required frequency of calibration is acceptable
Engineering	Easy to understand, install, calibrate, operate, and maintain (training may be required) Field deployable: in situ (e.g., downhole), at site (e.g., at well), or remote; deployable in small spaces Survives deployment environment (temperature, pressure, humidity, radiation, corrosives, etc.) Automated, with telemetry for remote control and data reporting Employs standard data communication equipment and protocols Minimum consumables requirements (power, reagents); minimum waste generation Low overall cost (equipment cost plus operating cost) as compared to the baseline cost Equipment cost (depending on the application) may be in the range of $1-50 K. Vendor support will likely be needed to meet Reliability, Availability, and Maintainability (RAM) requirements Includes fault tolerance for critical components Regularly verifies the essential characteristics of its own performance; reports (alarms) on failure - Useful operating life of at least two years (unattended)

3.3.3 Objective: Evaluate current technologies against functional requirements

This discussion was based on the technology information in Appendix I, Radionuclide Detection Technologies, and additional technology information from participants.

Current Technologies

- Although small gamma ray detectors have been deployed in the subsurface using a cone penetrometer (ARA, Corp of Engineers), most existing radionuclide measurement technologies cannot be deployed downhole.
- Most existing radionuclide measurement technologies do not operate unattended for long periods of time in the field.
- Few monitors are available for field detection/LTM of alpha- and beta-emitting radionuclides, e.g., tritium (HTO), technetium-99, strontium-90.
- No sampling techniques and deployment platforms appear suitable for LTM of radionuclides.

Emerging Technologies

Two emerging technologies appear to have potential for addressing previously identified radionuclide LTM site needs:

- The Field Deployable Tritium Analysis System (FDTAS): This system is both emerging and existing (OST TMS database Tech. ID 161). It has been demonstrated at Brookhaven.
- Technetium-99 monitoring system (OST TMS Tech. ID 1514, for rapid field sampling and monitoring): This system is also both emerging and existing (Innovative Technology Summary Report published January 2000, DOE/EM –0501, *Rapid Sampling Using 3M Membrane Technology*).

3.3.4 Objective: Assess technology shortcomings and gaps

In general, the sensors/analytical methods needed to address the most important radionuclide LTM needs at DOE sites are not available. Either they do not exist or they do not satisfy key functional performance goals for LTM (e.g., the capability of providing data with the required quality in long-term, unattended field operation). Specific gaps identified are listed below:

- Sensors are needed for tritium (HTO) and mobile radionuclides, especially for those radionuclides not commonly measured using gamma ray detection (e.g., uranium, iodine-129, technetium-99, strontium-90, cesium-137, plutonium, americium).
- Sensors are needed for moisture (moisture flux and moisture content).
- Sensors are needed to provide measurement data for assurance of barrier performance as well as early indication of barrier problems, i.e., before potentially errant radionuclides can be detected.
- Methods are needed for sampling the unsaturated zone, especially for deep vadose zone sampling.
- There is a need for smart, multi-sensing systems, e.g., where one sensor meeting a trigger level activates one or more other sensors to begin their monitoring.
- There is a need for sampling and monitoring systems for episodic events (e.g., meteorologic events such as wind storms, downpours, snow melt, flash floods, canyon flow).

3.3.5 Objective: Identify LTM strategies

Strategies for advancing the application of sensors in support of LTM are listed below:

- Plan the use of sensors (and other measurements) so the resulting data can facilitate quality decisions concerning the maintenance and/or corrective actions that may be necessary to maintain the effectiveness of waste isolation/containment facilities.
- Use sensors of various types (physical, moisture, chemical, radionuclide) to gain the earliest possible warning of the failure of isolation/containment facilities such as landfills, caps, and vaults. The earlier the warning, the earlier appropriate maintenance or corrective action can be taken. Also, the earlier such action can be taken, the less costly it is likely to be. Pollution prevention is easier and cheaper than pollution cleanup.
- Design the sensors and reusable sensor access points into and around those facilities so sensors can be replaced with ease when failure and/or sensor upgrade opportunities occur.
- Begin applying and improving monitoring technologies now on the larger scale, higher concentration concerns (e.g., monitoring performance of waste disposal facilities as with the Savannah River Site Vadose Zone Monitoring System). Then, move on to more difficult LTM problems, such as monitoring the migration of Hanford UST radionuclides in the vadose zone.
- Monitor the movement of soil moisture (water flux) in the vadose zone below waste storage and disposal locations. It is the key to and conservative indicator of the potential for movement of radionuclides in the vadose zone (to groundwater).

3.3.6 Objective: Identify LTM R&D for chemical sensors

This objective was addressed by considering the questions listed below. Participant answers are provided immediately after each question. (The summary presentation is provided in Appendix N.3)

What potential quick wins should be pursued immediately?

- Highest priority:
  - Field Deployable Tritium Analysis System
  - Technetium-99 monitoring with auto-sampler, using EMPORE™ disks, and automatic disk cartridge changer at the surface (perhaps the measuring instrument as well); Chemical speciation is important for the technetium-99 measurement
  - Integrated system for monitoring soil water content, soil water tension (soil water flux), and contaminants (radionuclides); potentially and ideally with cone penetrometer deployment
  - Monitor soil water movement as an indicator of likely contaminant transport
- Lower priority:
  - Begin deploying auto-samplers in support of monitoring
  - Begin monitoring gross gamma as an indicator of contaminant transport
  - Employ colloid collection for actinide monitoring
  - Test the applicability of Cadmium Zinc Telluride (CZT) detectors for low-energy gamma ray monitoring

- Test the applicability of Mercuric Iodide detectors for low energy gamma ray monitoring
- Test the applicability of Portable Isotopic Neutron Spectroscopy (PINS) with Xenon detector for gamma ray measurement

What applied research will likely yield LTM success in the next three to five years?

— Automation of sampling techniques

What research is needed to address key LTM technical deficiencies?

— Development of sensors/methods for LTM of mobile radionuclides not ordinarily measured by gamma ray detection methods (e.g., tritium (HTO), uranium, iodine-129, technetium-99, strontium-90, cesium-137, plutonium, americium)

— Address the gaps identified earlier in this breakout session report (Section 3.3.4); (Note: Most of these are DOE-specific)

— Effects of drilling/pushing to emplace sensors/take samples; effects on the system; effects on the data

— Monitoring of soil water flux for verification of containment

— Automation of sampling techniques

— Assuring vertical isolation of sensors

— Deployment of LTM technologies with push technologies

— Field-scale verification of results from models

— Current EMSP projects

What administrative support is required to achieve LTM success?

— Guidance on cap design and LTM considerations in the 2003 guidance manual

4.0 Workshop Information

4.1 Workshop Participants

To successfully meet the workshop objectives, it was critical that two groups of participants attend: the users and developers of LTM technologies. Many DOE sites have completed or active on-going environmental remediation projects. These projects employ active systems, such as pump and treat or bioremediation; passive systems, such as permeable or non-permeable barriers; or disposal systems, such as landfills with caps. All of these systems need to be monitored over the long-term. Those most familiar with the systems and with the conditions of the sites are the respective LTM managers, who also actively negotiate closure agreements with regulators. Thus, it was extremely important that these site managers attend the workshop to describe their site needs and the functional requirements for technologies they might use.

In turn, once the site needs and requirements were established, the technology R&D workshop participants could respond by describing what technologies are available that meet, or could be modified to meet, the demands. They could also describe emerging technologies in various sensor fields and recommend R&D areas that offer promise for future LTM methods.

Of the 107 people that pre-registered for the workshop, 48 identified themselves as technology users and 73 were researchers or developers. (These numbers do not correspond directly because some participants identified themselves in both categories, while some did not select either.) Of those identified as researchers, 17 were from academia, 34 from federal laboratories, 15 from industry, and 6 from technology vendor companies. The researchers also identified their associated level of development, with 20 involved in basic research, 58 in applied research, and 21 in engineering development. On-site registration increased the total attendance to 120 participants. (See Appendix C for a list of participants with contact information.)

4.2 Scope of Workshop Topics, Objectives, and Background Information

Scope. Although many areas of emphasis exist for sensors and measurement technologies for subsurface monitoring programs, this workshop limited the scope of discussions to sampling and measurements of subsurface contaminants. Analytical methods and sensors for measuring all contaminants (organics, metals, and radionuclides) in all matrices (vapor, soil, and ground water) were included in the discussions. In addition, all sensor/technology delivery systems were considered, including downhole methods, emplacement methods for subsurface sensors, or aboveground methods associated either with wells or direct push technologies.

Objectives. The six pre-established objectives identified below (and in Appendix B) built on each other and were thus discussed in the order shown:

1. Assess current LTM chemical sensor and analytical needs
2. Define the technical functional requirements for those needs
3. Evaluate current technologies against the functional requirements
4. Assess technology shortcomings and gaps
5. Identify LTM strategies
6. Identify LTM R&D for chemical sensors

Objectives 1 and 2 provided opportunity for site users to identify specific needs and requirements for LTM technologies, while objectives 3, 4, and 6 dealt with information from the participants involved in technology R&D. In contrast, objective 5 required significant input from all participants to develop an understanding of the design of LTM programs and how their strategic goals might be met.

Background information. To facilitate discussions for each topic, several documents were provided for participant reference during the meeting. Each is described below.

— *Needs statements:* The most recent Site Technology Coordination Group (STCG) needs statements assigned to the SC-01 and SC-11 Work Packages under the SCFA program were listed in table format. The SC-01 Work Package includes technologies for subsurface characterization, monitoring, modeling, and analysis. The SC-11 Work Package includes technologies for validation, verification, and LTM of containment and treatment. The needs were separated into the categories of applied technology (Appendix E) and basic/other (Appendix F). Most workshop discussions centered on applied technology needs, given the assigned objectives. Appendix E contains an explanation regarding the use of the need statements information.

— *Technology lists:* Three lists of commercially available field technologies and corresponding parameter information were provided for the detection categories of (1) organic contaminants including volatile and semivolatile compounds, (2) RCRA metals, and (3) radionuclides. Where information gaps existed for particular technologies, participants were requested to provide information if possible. In addition, they were asked to add appropriate missing technologies. As these lists are exemplary in nature, they should not be considered as all-inclusive, nor do they serve as an endorsement of any technology. The lists may, however, serve as references for site managers looking for alternative measurement methods. See Appendix G, H, and I for measurement technologies for organic compounds, metals, and radionuclides, respectively. An explanation about the information contained in these lists is provided in Appendix G.

— *Summary sheets of contaminants at each site:* Two summary sheets were extracted from the document "Vadose Zone and Ground Water Characteristics and Contamination at Selected Department of Energy Sites" (www.em.doe.gov/vadose/index.html), which was compiled by EM-22, Office of Integration. The first sheet lists the major contaminants and plumes at 21 DOE sites as well as the ground water cleanup strategy being considered or used at each site. The second sheet lists the primary ground water and vadose zone contaminants for the same 21 sites. These lists were used as a reference for the major contaminants of concern at each site to allow discussion to concentrate on techniques to address the highest priority contaminants.

4.3 Workshop Process

Initial presentations at the workshop provided context for subsequent discussions. Bob Wood, the RPM and Chief of the Environmental Restoration Branch at Edwards Air Force Base, gave the first presentation (Appendix J) as a strong proponent and user of LTM sensors. Tom Schneider, a regulator from the Office of Federal Facilities Oversight, Ohio EPA, gave the second presentation from the regulator's perspective (Appendix K). Mr. Schneider is involved with one of the first DOE sites (Fernald) to formally undergo closure and LTM activities. Kathy Yager, from the EPA Technology Innovation Office, gave the third presentation, describing industry and responsible party receptiveness to sensors for LTM (Appendix L). The final presentation was given by Joe Rossabi and Roger Jenkins, who have extensive experience in testing and demonstrating environmental monitoring technologies in the field. They presented the major obstacles and issues that every developer must consider to successfully operate technologies in the field over long periods.

Following this opening session, each participant selected to join one of four breakout groups based on contaminant classes:

— VOCs and semi-VOCs in groundwater with Joe Rossabi and Roger Jenkins as moderators

— VOCs and semi-VOCs in soil and vapor with Carol Eddy-Dilek and Brian Looney as moderators

— Metals in soil and ground water with Glenn Bastiaans and Bruce Friedrich as moderators

— Radionuclides in ground water and soil with Bill Haas and John Plodinec as moderators

During the first day, the two VOCs groups decided to combine into the Organic group, leaving three breakout groups for the remainder of the workshop. Although participants could move between groups, participation can be estimated as follows: (1) Organic: 46 participants, with

10 users, 30 developers, and 6 technology supporters, (2) Metals: 12 participants, with 4 users and 8 developers, and (3) Radionuclides: 25 participants, with 11 users, 4 developers, and 10 technology facilitators or supporters.

The agenda, given in Appendix A, shows the topics covered and typical questions discussed in each session. The discussions addressed two major topic areas. In the first breakout session, groups focused on site user descriptions of site problems, LTM programs, and technology needs for those programs. Groups then moved into defining a list of functional requirements for technologies to meet site needs. Extensive discussions addressed identification of the most difficult monitoring problems facing site managers and the primary drivers behind these monitoring issues, such as regulatory requirements, costs, or need for better understanding of subsurface contaminant transport at the site. Following these discussions, all workshop participants reconvened together to hear summary statements from each breakout group regarding the major site problems and needs, and requirements for technologies to meet those needs. The summary slides presented by each group for this breakout session are provided in Appendix M.

The second breakout session focused primarily on developers. Discussion centered on issues such as identifying commercially available and emerging technologies that might meet user needs, determining strategies to provide solutions quickly, and recommending future R&D areas to quickly provide appropriate LTM technologies. Again, all participants reconvened to hear summaries from each group. (See Appendix N.) A final Question & Answer session concluded the workshop.