FEDERAL REMEDIATION TECHNOLOGIES ROUNDTABLE MEETING
Arlington, Virginia
December 7, 2005

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ACTION ITEMS

- ► EMS will make electronic copies of the presentations available on its FTP site by the Friday (December 9) following the meeting.
- ► John Kingscott will update the FRTR points of contact for DOE, replacing Skip Chamberlain with Beth Moore.
- ► All Roundtable participants will look for more cleanup projects that can be added to the innovative technology cost and performance case studies and send them to John Kingscott by April 1 for inclusion in the Spring 2006 update.

WELCOME/OPENING REMARKS

Walt Kovalick (U.S. EPA/OSRTI) welcomed the attendees and opened the 31st meeting of the Federal Remediation Technologies Roundtable (FRTR) with a brief overview of the agenda. He thanked Marti Otto (EPA/OSRTI) for her efforts to develop a robust program of measurement and monitoring presentations for the meeting. Participants introduced themselves

PROJECT UPDATES

Technology Cost and Performance

John Kingscott (EPA/OSRTI) provided an update on cost and performance-related FRTR activities and announced the addition of two new products to the FRTR resource library.

The Decision Support (Software) Tools (DST) Matrix is now available on the FRTR website (www.frtr.gov/decisionsupport). The DST Matrix contains publicly funded decision support software tools for environmental restoration activities from agencies such as EPA, DOE, and DoD. The selection team avoided including software products that require special training to use. The matrix displays the applicability of each tool to contaminant classes and media types. The matrix is not designed to compare the tools against one another, but instead to provide an evaluation of the capabilities and uses of the individual tools to help project managers better understand how to select the appropriate one(s) for their specific site needs. The matrix includes direct links to the tool software homepages, the matrix-development report, and case studies that show how select tools can be used as part of a cleanup project.

The second new product is the final version of the draft fact sheet presented for comment at the spring 2005 meeting, "Remediation Technology Assessment Reports: Summary of Selected Documents" (EPA 542-F-05-006). The fact sheet was developed to identify remediation technology assessment reports that reflect experience with innovative technologies gained through extensive field work. It identifies 14 reports that may be particularly useful to project managers. These reports are available on the FRTR website (http://www.frtr.gov/costperf.htm) under "Remediation Technology Assessment Reports":

- *Cost and Performance Report: Multi-Site Air Sparging* (Navy, 2005)
- *Principles and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents* (ESTCP, Air Force, Navy, and Army, 2004)
- *Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater, Second Edition* (ITRC, 2005)
- *In Situ Thermal Treatment of Chlorinated Solvents: Fundamentals and Field Applications* (EPA, March 2004)
- *Multi-Phase Extraction* (USACE, 1999)
- *Capstone Report on the Application, Monitoring, and Performance of Permeable Reactive Barriers for Ground-Water Remediation: Volume I and II* (EPA, 2003)
- *Permeable Reactive Barriers: Lessons Learned/New Directions* (ITRC, 2005)
- *Permeable Reactive Barriers for Contaminant Remediation* (EPA, 1998)
- *Engineering and Design: Soil Vapor Extraction and Bioventing* (USACE, 2002)
- *Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater* (AFCEE, 1999)
- *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water* (EPA, 1998)
- *Strategies for Monitoring the Performance of DNAPL Source Zone Remedies* (ITRC, 2004)
- *How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites: A Guide for Corrective Action Plan Reviewers* (EPA, 2004 update)
- *Evaluation of Subsurface Engineered Barriers at Waste Sites* (EPA, 1998)

To propose adding new reports to the compilation, or to provide feedback on existing reports, please send comments to Marti Otto (EPA/OSRTI, 703-603-8853, otto.martha@epa.gov).

Kingscott said that a total of 22 new case studies and reports are being prepared for addition to the FRTR Technology Cost and Performance case study database (www.frtr.gov/costperf.htm). The new case studies are in the following areas: treatment (10), site characterization (10), and technology assessments (2). EPA will continue to check web sites to locate new information for all categories of reports. He urged FRTR participants to alert him to any new or previously overlooked information concerning field implementation of innovative technologies that EPA might use to develop new case studies. If anyone has a new cost and performance report to add to the database, it should be turned in by April 1 for inclusion in Spring 2006 update.

The Navy and EPA recently met to discuss the topic of DNAPL remediation and the possibility of coordinating Navy/EPA efforts in that area. At present, no work plan or schedule has been developed, but the participants agreed that a great need exists for more field data and that reviewing the existing 50-60 FRTR DNAPL case studies and lessons learned might be a viable initial approach. The collaboration could involve (1) revisiting sites where DNAPLs have already been treated to examine how effective the remediation has been, biological activity at the site, and the effect on groundwater, and/or (2) examining mass flux of contaminants both before and after remediation at new sites. Other agencies wishing to take part will be welcomed.

Showing participants a list of cost and performance contacts in the various FRTR agencies, Kingscott said that he will add Beth Moore to the list as the Department of Energy (DOE) point of contact to replace Skip Chamberlain.

Workshop on Nanotechnology for Site Remediation

Marti Otto (EPA/OSRTI) provided a report on the nanotechnology workshop held in Washington, DC, October 20-21, 2005. The workshop was held to present the latest nanotechnology research results and to stimulate collaboration among attendees. Approximately 180 U.S. and international registrants from academia, industry, and government attended the workshop, which was sponsored by nine government organizations. The presentations addressed the state of the science of the use of nanoscale zero-valent iron for DNAPL-contaminated groundwater, research on other types of nanomaterials, fate and transport of nanomaterials, potential toxicity, public perceptions, and case studies of nanoscale materials applied to remediate Navy and NASA sites.

The workshop breakout sessions produced numerous recommendations, including:

(1) Increase research in the following areas:

- Fate and transport of nanomaterials,
- Detection methods,
- Contaminant destruction processes using nanomaterials,
- Treatment trains that include nanotechnology,
- Toxicity of nanoparticles, and
- Applied research and field implementation.

(2) Improve technology transfer and validation by developing simplified information to compare technologies using cost and benefits, and present technology developers with incentives to contribute to risk understanding.

(3) Improve public perception of environmental use of nanotechnology by increasing outreach to the states and the public, adapting current community relations protocols for nanotechnology, and gathering and presenting more data on exposure and toxicity to reassure the public. These efforts would also include the development of a “Citizen's Guide” to nanotechnology for site remediation.

The workshop proceedings and presentations will be available shortly on the FRTR website. EPA hopes to develop additional cost and performance case studies from some of these materials and is seeking collaborators to pursue the breakout session recommendations, particularly with regard to increasing the knowledge of nanoparticle fate and transport in the environment and the efficacy of the technology.

One of the recommendations was to make the nanotechnology meeting a biannual event, but the sponsors have made no decision on this yet.

FRTR Remediation Technologies Screening Matrix and Reference Guide

Layne Young (U.S. Army Environmental Center) began with background information on the development of the *Remediation Technologies Screening Matrix and Reference Guide*. The Matrix was designed to be a user-friendly tool for screening potentially applicable remediation technologies. It presently contains information on 59 *in situ* and *ex situ* technologies for soil or groundwater remediation.

This resource was developed with member agency support. USAEC manages product updates in coordination with a Screening Matrix Committee, which includes members from FRTR member agencies and ITRC. The Screening Matrix Committee provides direction and final approval for updates. Current revisions to the Matrix were initiated by the Committee early in FY 2004. These revisions are designed to create a more user-friendly format to compare and contrast multiple remediation technologies by establishing a consistent and uniform rating scale that displays only three main ranking symbols (similar to the circles used in *Consumer Reports*), indicating that for a particular type of site or circumstance a technology is considered above average, average, or below average. Some categories have been eliminated or consolidated to simplify use of legend and definitions.

Cost estimates for selected soil and groundwater technologies have been updated in the Resource Guide section. Cost data in the reference guide were outdated, oversimplified, and, in some cases, nonexistent. The Screening Matrix Committee directed the developers to estimate costs for several newer technologies and update technology profile cost sections; use a standardized cost estimating tool (RACER) to provide a systematic, reproducible process to develop ranges of cost estimates for technologies at sites of varying complexity; and present cost results in three tiers to aid all levels of Screening Matrix users.

In FY 2005, the Matrix developers drafted 14 RACER-based cost updates. Eight soil technologies (bioventing, phytoremediation, soil vapor extraction, chemical extraction, soil washing, incineration, thermal desorption, and solidification/stabilization) and six groundwater technologies (phytoremediation, air sparging, chemical oxidation, air stripping via packed towers, air stripping via low-profile towers, and passive/reactive treatment walls) were updated. Estimating the costs for groundwater remediation was especially complex. RACER software was used to develop ranges of cost estimates for multiple site condition scenarios (usually four) for technology application. The scenarios developed varied in complexity and scale of application. A standard "mini-matrix" was established that defines technology application scenarios for sites that are small/easy, small/difficult, large/easy, and large/difficult. The RACER exercise enabled the developers to identify the primary cost drivers.

The new matrix has been approved by the Committee, and it should be posted shortly on the FRTR website. As the cost estimates are reviewed and approved, they will also be posted. The Committee is continuing discussions to determine what portions of this tool will be updated in 2006.

Really Simple Syndication (RSS)

Walt Kovalick provided a short overview of Really Simple Syndication, or Rich Site Summary, (RSS) technology. RSS is designed for sharing headlines and other Web content. RSS is like a mini database containing headlines and descriptions of what's new on a site, making it easy to expand new services. On EPA's Clu-In site, a user can open up the URL containing the RSS feed text to read updates at will (see example at www.clu-in.org/rss/). RSS can reach PDAs and cell phones and can be used to quickly prepare email ticklers, voice updates, and automated email newsletters. For example, subscribers can receive information about the latest updates to Clu-In as a banner across the screen when they open their browsers. It not only displays news, but also lists news on other sites.

An Internet browser or separate aggregator software is needed to read the RSS feed. An example of an RSS reader can be found at Feedalot Reader (www.feedalot.com). Examples of RSS aggregators can be found at Awasu (awasu.com) A large list of aggregators is available on line at en.wikipedia.org/wiki/List_of_news_aggregators. Once constructed, the RSS structure is automatic and requires little or no effort to maintain.

RSS would not replace services like TechDirect or "What's Hot" on Clu-In; it would simply add a new service to those already in place. Kovalick urged members of the Roundtable to take this concept back to their various agency webmasters in the hope that by the next meeting it will be possible to generate a listing of RSS feeds for environmental websites across the member agencies.

Technology Innovation: Additional Updates

Walt Kovalick provided updates on other ongoing FRTR projects. He said that a recently developed resource, *Sensor Technologies Used During Site Remediation Activities: Selected Experiences* (EPA 542-R-05-007) is now available on Clu-In at www.clu-in.org/download/remed/542r05007.pdf. The report provides an overview of several types of sensor technologies and summarizes selected experiences with using these technologies in the field. The following technologies are discussed in case studies: the Membrane Interface Probe (MIP) to determine contaminant concentrations, geophysical surveys to evaluate hydrocarbon contamination, a capacitance probe for soil moisture content, VECTOR technology to determine groundwater flow velocity, the Burge system for sampling and analysis, Supervisory Control and Data Acquisition (SCADA) with Programmable Logic Controllers (PLC) for groundwater pump-and-treat, and SCADA with PLC and ozone analyzers for groundwater pump-and-treat.

A new Environmental Cost Engineering section (www.frtr.gov/ec2/index.htm) has been developed by the Environmental Cost Engineering Committee (EC2) over the last two years. The new section highlights guidance, software, and other tools to support sound cost estimating; provides cost engineering contacts for EPA, DOE, Air Force, Army, Navy, Coast Guard, NASA, and DOI; and includes helpful document references and links.

Kovalick announced that the topic for the Spring 2006 FRTR meeting will be "Industry and International Environmental Development Initiatives." He proposed inviting speakers from the European Union (EU) Environmental Technology Development Initiative, the Sustainable Development Technology Corporation of Canada (a private entity created by the Canadian government with $450M to devote to applied environmental technologies over a 5-year period), the Petroleum Environmental Research Foundation, ITRC, the Remediation Technologies Development Forum, and the FRTR Panel on Technical Investments.

Kovalick went on to introduce the technical session for this meeting. He said that nanosensors were the technical topic of the Roundtable meeting held in December 2004, and the emphasis was primarily on basic research. This meeting on sensor technology is intended to identify technologies that are currently available or will be in the near future. Kovalick recalled that during the last PittCon (a very large annual chemistry conference) that he attended, the number of vendor booths advertising environmental technologies was small, and they were located in a backwater of the vendor floor. The main market for monitoring technology is not for environmental uses but for industrial processes, medical uses, and food safety. To improve the scope of development of technologies suitable for environmental monitoring, products adaptable for dual use must be scrutinized. For example, Kovalick has been in contact with several German scientists who are adapting food monitoring technology for environmental sensing. With increasing promotion of research and development in contaminant monitoring by the Office of Homeland Security, opportunities seem to be expanding.

CONTAMINANT MONITORING AND SENSOR TECHNOLOGY

Measurement and Monitoring for the 21st Century (21M^2)

Michael Adam (EPA/OSRTI) reviewed EPA's 21M^2 initiative. 21M^2 is designed to identify future program technology requirements in the areas of site characterization, process control, waste testing, and monitoring. Through 21M^2, EPA's Office of Solid Waste and Emergency Response encourages the deployment of promising measurement and monitoring technologies. The initiative identifies technology needs and sponsors research and demonstration of new technologies. It is supported by a website (clu-in.org/programs/21m2/) that houses user's guides, sponsored technology demonstration updates and reports, and a literature database that contains over 4,600 abstracts searchable by keyword or by special needs area.

Eighteen topics in 10 needs areas have been recognized that reflect evolving requirements across all waste programs. The topics include air emissions and trace contaminant fence-line monitoring, indoor air vapor intrusion detection, sediment characterization, field determination methods for metals, *in situ* contaminant monitoring, remedy performance monitoring, noninvasive subsurface chemical detection, and characterization and monitoring of mining sites. The needs areas are the focus of quarterly literature searches that provide the abstracts to update the database.

Information needs in special topics sometimes generate focused literature searches The most recent focused literature searches have addressed analytical methods for emerging contaminants (NDMA, PFOS, PFOA, PBDEs, perchlorate, 1,4-dioxane); nanotubes, nanopores, nanoclusters and other foundations for nanosensors; and geophysical methods for locating and/or monitoring DNAPLs.

Adam said that results of completed 21M^2 projects are described in reports available on the website (clu-in.org/programs/21m2/projects/). Some recently completed projects include:

- Mercury speciation analysis scheme using SW-846 Method 7473;
- Open-path FTIR/TDL surveys of fugitive emissions at Region 1/Region 8 landfills;
- Push-point sampling for defining spatial and temporal variations in sediment pore water (resulting in a USGS report); and
- Field tests of nylon screen diffusion samplers and push-point samplers for detection of metals in sediment pore water (another USGS Report).

Projects funded in 2005 include:
- Development of a user's guide for tree coring to examine subsurface volatile organic compounds (Region 1/USGS);
- Demonstration of electrical resistivity tomography and induced polarization tomography methods for characterization of fractured bedrock DNAPL sites (Region 1); and
- Demonstration of an innovative fence-line metal emissions monitor at hazardous waste sites (RTP-ORD).

Application of Ground-Based Optical Remote Sensing to Characterize Area Source Emissions

Susan Thorneloe (EPA/ORD) presented an overview of a project sponsored by EPA's $21M^2$ initiative. This project addressed the need for emissions monitoring and identification of potential “hot spots” on landfills, i.e., for characterizing large-area sources being investigated for future land use options. Redevelopment of landfills in the United States shows a trend toward large-scale recreational use, such as the construction of soccer fields, parks, gyms, and even schools on the landfill cover. And as urban areas expand, it is not uncommon to see newer neighborhoods adjacent to landfills.

This project considered two solutions to the problem of fugitive emission measurement. Optical remote sensing can be used to measure path-integrated gas concentration via the following open-path optical techniques: Fourier transform infrared (FTIR), tunable diode laser (TDL), and ultraviolet spectroscopy (UV-DOAS). Path-integrated optical remote sensing generates a path-average concentration that is ideal for non-homogeneous, large-area sources, and has been used in the project to date. A report, *Evaluation of Fugitive Emissions Using Ground-Based Optical Remote Sensing Technology,* is currently in review. This report will summarize the data from the sites studied so far and provide a comparison of commercially available technologies.

Radial plume mapping (RPM) determines spatially resolved emission profiles using multi-path calculation algorithms: vertical RPM for emission flux and horizontal RPM for leak detection. In the near future, EPA and ARCADIS will conduct a plume capture study using the RPM method. Controlled gas releases will be used to evaluate the effectiveness of the method in capturing plumes originating from sources located a great distance upwind of the configuration.

Several reports on this topic have been issued recently or will be available soon:
- *Measurements of Fugitive Emissions at Region I Landfill* (EPA 600-R-04-001, Jan 2004)
- *Evaluation of a Former Landfill Site in Fort Collins, Colorado, Using Ground-Based Optical Remote Sensing Technology* (EPA 600-R-05-042, April 2005)
- *Evaluation of a Former Landfill Site in Colorado Springs, Colorado, Using Ground-Based Optical Remote Sensing Technology* (EPA 600-R-05-041, April 2005)

- *Guidance for Evaluating Landfill Gas Emissions from Closed or Abandoned Facilities* (EPA 600-R-05-123, October 2005)
- *A Case Study Demonstrating U.S. EPA Guidance for Evaluating Landfill Gas Emissions from Closed or Abandoned Facilities: Somersworth Sanitary Landfill, Somersworth, New Hampshire* (EPA 600-R-05-142, October 2005)

15 Years of Environmental Sensors Development by DOE: Changing Strategies, Technologies, and Programs

Dr. David Roelant (Florida International University) reviewed the U.S. Department of Energy Office of Environmental Management's (DOE/EM) history of environmental sensor development under its Characterization, Monitoring, and Sensor Technology (CMST) program. In 1991, site characterization consisted of multiple sampling campaigns and analyses in analytical laboratories. It was an inefficient and extremely expensive process. In 1992, experts from across many disciplines were engaged to bring dozens of available technologies for other applications (e.g., surface and borehole geophysical techniques from the oil and mineral exploration field) into use for environmental characterization and monitoring.

Most technologies needed to be adapted specifically for environmental applications (e.g., characterization of subsurface soils 0-50 ft deep instead of areas covering cubic miles). A five-year research and development plan was prepared for CMST development. Scientists from academia and across agencies were invited to attend a variety of environmental management conferences sponsored by DOE, thus generating wider interest and awareness of CMST development.

By 1995, many soil and groundwater technologies had been developed, but few of them were deployed. Contractors had no incentive to use them, and their application was not yet associated with realistic solutions to characterization and monitoring problems. Other barriers to technology deployment included the inability of DOE and other management and/or regulatory entities to grasp new ideas, such as the concept of data quality objectives. The structure was not yet in place to promote the use of the new technologies. Finding solutions to environmental problems required the development of new ways of thinking as much as development of new technologies. Deployment of the new technologies also was hampered by a lack of defined baseline environmental operations and component costs to allow even rough cost/benefit analyses. Many of the new technologies could not be marketed easily, because their use was not generic; they were suitable only at certain types of sites or required tailoring to work at each particular site. DOE discovered that it needed a champion at each site who was willing to deploy a new technology, and interaction with individual site managers was necessary to achieve the deployment.

The annual CMST was funded at more than $20M in 1995. DOE/EM labored to have expedited site characterization deployed at key DOE sites and accepted as an ASTM standard. When DOE/EM produced its *Baseline Environmental Management Report* (BEMR, 1996) and then 10-Year Plans for every DOE site, post-closure monitoring and its potentially enormous costs became a new focus. DOE formed five Focus Areas for EM-related R&D and began working directly with DOE site restoration managers to develop technologies that were suitable for their deployment.

By 1999, the CMST budget had dwindled to $8M. Eleven soil and groundwater projects were completing development or deployment of technologies/solutions, and critical needs in the area of soil and groundwater had diminished. The Technical Information Exchange (TIE) conferences were effectively transferring technology deployment information and lessons learned across DOE. Industry had become fully engaged in soil and groundwater technology development, with and without DOE funding, and was driving new developments. Regulatory acceptance of innovative technologies was increasing.

Over 20 chemical analysis instruments and methods had been successfully deployed in the field. Limited success with down-hole chemical sensors (e.g., acoustic wave) led to the realization that such sensors had limited longevity and provided no cost savings. This led to the development of the Flow Probe and then to Burge sampling and analysis, as well as improvements to several laboratory chemical analysis instruments (e.g., ICP-MS). Post-closure monitoring became the big soil and groundwater focus.

Today, a new, enormous need exists for soil and groundwater R&D in several important areas: landfill cover performance; long-term assessment of the results of technology deployment; long-term performance assessments of landfill liners, caps, and engineered disposal facilities; and transfer of knowledge and periodic review of changes in site conditions, such as increased contaminant transport.

Boise State University Ion Mobility Spectrometer (IMS) Sensor Project

Molly M. Gribb (Boise State University) provided an overview of the IMS sensor project. Boise State University is collaborating with Washington State University to design, construct, and evaluate a miniature gas-phase IMS system for use in the subsurface. This miniature IMS will perform cost-effective, real-time analysis of gaseous organic contaminants in the subsurface. The system will not require being attended. Sensor data will be monitored via wireless or satellite transmission. The sensors can be used individually or in arrays for long-term monitoring of contaminated sites. The next phase will incorporate monitoring of liquids. IMS probably is the most sensitive method currently used for rapid analysis of chemical warfare agents. The technology is also applicable to the detection of narcotics, explosives, amino acids, and pesticides.

Herbert H. Hill (Washington State University) explained that the miniature IMS is being fabricated from a low temperature co-fired ceramic (LTCC). The LTCC material will allow fabrication of an IMS with superior characteristics (hermetically sealed, higher resolution, smaller size) compared to what is currently possible using conventional fabrication techniques and materials. The IMS system will be packaged in a cone penetrometer housing to allow deployment in the field using direct push techniques. The proposed system is designed for long-term deployment and features wireless transmission of data using cell phone technology.

When a gaseous sample is introduced to the IMS reaction region, it is ionized. The ion gate is activated to allow the ionized species into a drift tube. In the presence of an electric field and a counter-flowing drift gas, the ionized species travel through the drift tube toward the detector.

The various ionized species separate due to differing collision cross-sectional areas, arriving at the detector at different times. As each ion discharges on the detector, a small current is generated. The measurement of this current over time yields a spectrum, which is then used to identify and quantify the analytes in the sample.

The sensor research team recently completed a prototype for the IMS sensor. The device is placed in a cylindrical housing that can be pushed into the subsurface using a truck-mounted hydraulic jacking system. Data collected by the sensor are converted from an analog to a digital signal and then transmitted via satellite to an Internet site, providing researchers with live information about the identity, concentration, and location of the vapors, and a means to continue to monitor them.

In spring 2006, the probe will be tested in the field at the site of a local PCE plume. The team has also received an invitation to field-test the system in a demonstration at the Savannah River Site on that PCE plume in summer 2006.

Monitoring the Air for Toxic and Genotoxic Compounds

Kim Rogers (EPA/ORD) discussed the increasing interest in air monitoring for toxic compounds. This type of monitoring has been a concern in the past in large part because of accidents leading to industrial contamination. Now, however, awareness of the possibility of toxic contamination resulting from deliberate, malicious acts is fueling greater interest, particularly within EPA's Homeland Security Research Center. Compounds of interest include chemical warfare agents, non-traditional agents, and toxic industrial chemicals in gaseous or volatile form. Simple, rapid, and sensitive toxicity monitoring can be achieved using equipment adaptable from the commercial sector.

Wastewater screening assays are being developed for air monitoring using products such as Microtox® and IQ-Tox Test™ with *Daphnia magna* (recently commercially available) for compounds of acute toxicity. The bacterial luminescence of the Microtox® system is expected to be a sensitive indicator of toxic vapors. Also, DNA melting/annealing analysis for assessing genotoxicity provides a rapid and simple fluorescence screening assay for UV-radiation-, chemical-, and enzyme-induced DNA damage.

Rogers' work involves developing chemical agent detection systems that will provide broad toxicological screening information to first responders and building decontamination personnel. The primary goal for this technology is to detect the presence of airborne chemical agents that will damage metabolic or neurological function.

One of the unique features of the technology is that the proposed techniques will be used to characterize a broad range of compounds and agent simulants that are toxic but not expected to be detected by currently available chemical sensor technologies. The ability to detect toxic chemicals on the basis of their potential biological/biochemical function is expected to provide the basis of a rapid-response chemical hazard detection system. The proposed sampling technology also will provide a time-integrated chemical exposure record for numerous locations throughout the building.

Continuous and time-integrated sampling of indoor air will be accomplished using semipermeable membrane devices (SPMDs) consisting of polyethylene tubing containing a thin film of high-molecular-weight neutral lipid, such as triolein. The accumulation of semivolatile organics through the approximately 10 angstrom pores and into the organic phase appears to be similar to transport of organic vapors through biomembranes during respiration. SPMD sampling devices will be interfaced to two types of biochemical detection systems: an enzyme system for detection of organophosphate insecticides and the “nerve agent” class of chemical warfare agents, and a general toxicity assay based on luminescent bacteria for the detection of metabolic inhibitors and membrane-disrupting toxins. Studies will be conducted to compare the proposed toxicity screening system to an ion mobility spectroscopy (IMS)-based technology.

Microfluidic Lead Sensor Incorporating Catalytic DNA

Dr. Donald Cropek (ERDC-CERL) discussed work to develop a field sensor for lead in groundwater or drinking water. A miniaturized lead sensor has been devised that combines a lead-specific DNAzyme with a microfabricated device containing a network of microfluidic channels coupled via a nanocapillary array interconnect. The DNAzyme construct forms a molecular beacon that is used as the recognition element. The nanocapillary array membrane interconnect is used to manipulate fluid flows and deliver the small-volume sample to the beacon in a spatially confined detection window where the DNAzyme is interrogated using laser-induced fluorescence detection. The sensor has been applied to the determination of lead in an electroplating sludge reference material. The quantitative measurement of lead in this complex material demonstrates the selectivity of this sensor scheme and points favorably to the application of such technologies to analyze environmental samples. The unique combination of a DNAzyme with a microfluidic-nanofluidic hybrid device makes it possible to change the DNAzyme to select for other compounds of interest and to incorporate multiple sensing systems within a single device for greater flexibility. Several papers that illustrate the development of this sensor are available on line at http://montypython.scs.uiuc.edu/paper.htm.

Dr. Cropek also is working on the development of perchlorate sensors. Perchlorate is a human health concern, because it interferes with the uptake of iodide in the thyroid, potentially leading to mental health deficiencies. Cropek's approach exploits the same physiological mechanism that elicits perchlorate toxicity in humans to create the chemicophysical structure for detection. The ability to establish physiological conditions *ex vivo* for exploitation on a sensor device may lead to the incorporation of other chemistries onto silicon supports that can detect analytes, predict toxicities, or model chemical interactions.

Environmental Sensor Development at SSD-SD: Past and Present

Pamela Boss (Navy, SPAWAR) provided an overview of sensors developed under the sponsorship of Space and Naval Warfare Systems Center San Diego.

The Site Characterization and Analysis Penetrometer System (SCAPS) is a rapid in-field soil and groundwater analysis system that provides cost-effective characterization of soil conditions to depths of up to a hundred feet or more. SCAPS uses a truck-mounted cone penetrometer system to directly push an instrumented probe into the ground for rapidly characterizing soil types and detecting and delineating the presence and extent of subsurface contamination. A variety of sensors can be attached to the probe to detect different compounds. Sensors using laser-induced fluorescence to detect petroleum compounds, laser-induced breakdown spectroscopy (LIBS) to detect metals, and surface-enhanced Raman spectroscopy (SERS) to detect BTEX, chlorinated solvents, and MTBE have been demonstrated.

The GeoVIS probe is used with SCAPS to obtain detailed information about subsurface soil characteristics on very small spatial scales. The GeoVIS device illuminates the surrounding soil through a sapphire window on the side of the probe. Video signals from the camera are returned to the surface, where they can be viewed in real time on a video monitor and documented on a video recorder. The standard GeoVIS optics system provides a viewing field of approximately 2 by 3 millimeters, and a magnification factor of 100 when viewed on a standard 13-inch monitor. GeoVIS has been used several times to characterize nonaqueous phase liquid contaminants at the former Alameda Naval Air Station and Naval Air Station North Island.

The TEC-SERS (thermoelectric-cooled SERS) probe, which comprises a membrane interface probe and a TEC-SERS sensor module that responds to a library of volatile organic compounds, such as chlorinated solvents, for subsurface VOC detection. While SPAWAR has demonstrated feasibility of detecting VOCs using the TEC-SERS approach, the probe has not been pushed into the ground to date.

The TRIDENT Probe is a multi-sensor water sampling device for screening and mapping groundwater plumes at the surface water interface. For analysis of conductivity, it detects contrast in salinity and/or clay content in unconsolidated sediments, and its sensitivity to temperature allows detection of groundwater by thermal contrast with surface water. The porewater sampler component allows contaminant characterization and detection of other groundwater-specific tracers.

The Total Copper Analyzer can measure the total concentration of copper in the effluent in real-time, right at the effluent location, allowing for the rapid separation of the effluent requiring treatment. The analyzer consists of two processes, an inline ultrasonic digestor for the acidification and digestion of the effluent, coupled with an ion-selective electrode for detection and reporting.

Spill Sentry is an automated oil-spill monitor that continuously monitors and notifies personnel programmed into the contact list, within minutes, of a detected petroleum spill. The device uses ultraviolet fluorescence technology to detect a sheen on the surface of the water.

Bioluminescent dinoflagellates are sensitive to metals, organics, and oceanographic processes and could serve as indicators of potential toxicity and developing red tides. The BioBuoy is the first autonomous platform that measures bioluminescence, seawater clarity, and temperature. The sensor package consists of a photomultiplier tube for measuring bioluminescence, a transmissometer for measuring water clarity, and a thermistor for measuring temperature.

The Benthic Flux Chamber can be used as an effective, non-intrusive monitoring and compliance tool for direct quantification of sediments as contaminant sources.

SSD-SD also has developed several bioassay techniques. Qwiklite and QwikSed were developed as bioluminescent field screening tools to detect the presence of toxic metals and organics in sediments and pore-water samples. A single-cell gel/comet assay has been used successfully for assessing pollution-induced DNA damage and repair in organisms in response to sediment contamination. This biochemical toxicity indicator technique provides data on the integrity of DNA in single cells, is sensitive and quantitative, and is applicable to diverse cell populations.

Electrochemical Sensors and Biosensors Based on Functional Nanomaterials for Environmental Monitoring

Yuehe Lin (Pacific Northwest National Laboratory) presented information on nanosensors being developed at PNNL.

Self-Assembled Monolayers on Mesoporous Supports (SAMMS) is a hybrid of two frontiers of materials science: self-assembly techniques and mesoporous materials. SAMMS is created by attaching a monolayer of molecules to mesoporous ceramic supports. One end group of the functionalized monolayers is covalently bonded to the silica surface and the other end group can be used to bind metal ions. The larger pore size offered by the mesoporous materials (20-200 Å) enables attachment of the monolayer as well as access to the binding sites within the pores. The high surface area of the materials (1000 m^2/g) also allows an extremely high density of binding sites. Both the monolayer and the mesoporous support can be tailored for a specific application. For example, the functional group at the free end of the monolayer can be designed to selectively bind targeted molecules, while the pore size, monolayer length, and density can be adjusted to give the material specific diffusive and kinetic properties.

The SAMMS technology was originally developed for DOE to identify the separation and removal of mercury from the environment. SAMMS is being developed in several engineered forms, such as beads, membranes, and membrane cartridges, and can be delivered with a variety of chemically active substances. Electrochemical sensors have been developed by embedding SAMMS particles on carbon paste electrodes or by coating a SAMMS thin-film on a microchip-based gold electrode array. These sensors have demonstrated enhanced sensitivity for monitoring toxic metals and U(VI).

Multi-walled carbon nanotubes (MWCNTs) can be fabricated as nanoelectrode arrays. Such a nanoelectrode array is used to collect electrochemical signals associated with target biomolecules, which are specifically bonded to the molecular probes covalently attached to the end of the MWCNTs. The probe molecules could be designed as specific biomarkers, such as nucleic acids or proteins. In addition, MWCNTs have a wide potential window, well-defined surface functional groups, and good biocompatibility, which are all necessary properties for biosensors.

At PNNL, researchers have successfully fabricated nanoelectrode arrays from millions of low-density aligned carbon nanotubes (CNTs). The technique effectively insulates the side-wall and takes advantages of the high-electron transfer rate of open-ended structure, resulting in a greatly improved signal-to-noise ratio. CNT nanoelectrode arrays (CNT-NEAs) have been devised for chemical and biological sensing. A nanoelectrode array includes a carbon nanotube material comprising an array of substantially linear carbon nanotubes. The proximal end of the carbon nanotubes are grown from a catalyst substrate material so as to form the array with a pre-determined site density in which the carbon nanotubes are aligned with respect to one another within the array. The array assembles with an electrically insulating layer on the surface of the carbon nanotube material, from which the distal ends of the carbon nanotubes extend beyond the electrically insulating layer; the protruding part of the CNTs was mechanically removed by polishing and formed carbon naotube tips nanoelectrode array. CNT-NEAs can be designed variously to detect metal ions or an amount of glucose in a test sample.

A biosensor linked to a hand-held electrochemical detector can identify organophosphates (OPs) in solution with a high degree of sensitivity. OP compounds are known to inhibit the activity of acetylcholinesterase (AChE). The biosensor consists of electrodes coated with carbon nanotubes. The carbon nantotubes hold the enzymes (AChE), which are targeted to the organophosphate chemicals, and electricity is applied. If organophophates are present, there is a decrease in the electrical current that can be correlated to the amount of chemical present. The hand-held biosensor detection system will facilitate the on-site saliva monitoring of exposures to pesticides or OP nerve agents.

Capillary electrophoretic (CE)-microchips have been devised on both glass and polymer substrates and integrated with an electrochemical detector (ECD). Investigators have systematically optimized the separation and detection processes and demonstrated the analytical performance for fast separation and detection of compounds, such as explosive mixtures, in less than two minutes. Electrochemical detectors have proven to be well suited for microchip CE systems. The microchip systems are particularly attractive because of their high sensitivity and selectivity, inherent miniaturization, portability, and low cost. An automated microscale SPE system has been developed and optimized for preconcentration of explosives from well water into acetonitrile. The technical objective of this research is to develop a microanalytical system based on advanced "Lab-on-a-Chip" technology by integrating the CE-microchip with an ECD for the real-time, on-site detection of explosives and their degradation products in groundwater. A microchip CE/ECD is also being developed for detection of organophosphate pesticides, such as paraoxon, methyl parathion, and fenitrothion.

Real-Time Water-Quality Monitoring for Water Security Applications

Ronald Baker (U.S. Geological Survey) is working on a project relevant to the safety of the U.S. water supply. The researchers want to find answers to the following questions:

- Can water-quality monitoring increase security?
- What sensors should be used?
- How reliable are the available sensors?
- What are the maintenance and replacement intervals?

The GAO testimony document, *Drinking Water: Experts' Views on How Federal Funding Can Best Be Spent to Improve Security* (GAO-04-1098T), states, "The need to develop near real-time monitoring technologies which would be particularly useful in quickly detecting contaminants in water that has already left the treatment plant for the consumer, has by far the strongest support." Nearly 100% of experts consider this need a high priority.

The overall objective of the Water Security Research Program is to develop a real-time water-quality monitoring system for drinking water safety and security, evaluate available sensors for use in such a system, and install and test the system in real water distribution systems. Five distribution-system sites have been established at which free chlorine, specific conductance, pH, oxidation-reduction potential, and temperature are being measured. The sensor data are transmitted to a secure USGS webpage using satellite telemetry. Additional sites, based on model results identifying locations optimized for public health protection (e.g., water utilities, pumping stations, government buildings, hospitals), will have monitoring devices installed pending resolution of logistical issues.

Of the devices tested, pH sensors were stable and accurate for the most part, but they require replacement after 1 to 2 years, and "drift" over time means the electrode requires reconditioning every 4 to 5 months. Specific conductance sensors have showed excellent performance. The oxidation-reduction sensors are very accurate after an initial break-in period. A chlorine residual sensor that is still in beta testing needs membrane replacement every 1-2 months and calibration every two weeks.

The investigators have found that the need for sensor maintenance or replacement is not always obvious by data observation alone because data from a non-responsive sensor may appear to represent conditions quite reasonably. Sensors must be maintained properly because calibration drift affects data accuracy and precision. Quality assurance includes assessing and correcting data to reflect drift. Shorter maintenance intervals and more frequent calibrations reduce chances of significant sensor drift and improve data accuracy.

Current work on characterizing water-quality variability in a distribution system is divided among the various participants. EPA conducts controlled laboratory experiments and selects sites based on distribution-system modeling. Sandia National Laboratories develops distribution system and sensor network models. USGS establishes and operate a network of field sites, collects and manages water quality data, and prepares interpretive reports. The cooperating water utility allows access to distribution system sites, provides a distribution system description and model, and supports the field effort by preparing water and electrical connections and drains.

New technologies are being tested at Site DW3. This facility will have the first commercial use of a chlorine probe in a YSI multiparameter water-quality monitoring system. The participants are also installing a total organic and inorganic carbon analyzer and a UV-VIS spectrophotometer with software for estimating water-quality parameter values and detecting unexpected changes in water quality.

Water-quality variability is analyzed spatially with regard to age of water, distance between monitoring sites, and type of water (surface water, groundwater, or mixed). Analyses are scheduled at 15-minute intervals (or more frequently if needed), hourly, daily, weekly, monthly, seasonally, and annually to assess variability over these spans of time.

Over the long term, the distribution system sites will serve as practical test beds for sensors and emergency warning system components in the field. There is potential for a model calibration effort using a tracer in a sub-area of the distribution system. The participants will learn how to use hydrologic and water-quality modeling effectively to select sensor location, study the natural variability of water-quality characteristics in a distribution system, and determine the capabilities, limitations, and maintenance requirements of sensors. But so far, the most important question has yet to be answered: Will the introduction of contaminants of concern cause detectable changes in water quality?

In answer to a participant's question, Baker acknowledged that a month is a long life for any sensor; in groundwater, a longer period is possible. While reducing O&M costs is a strong motivator to develop sensors that can be left in place for long periods of time, even the simplest sensor requires regular maintenance. While automated prevention of fouling may be possible, the need to recalibrate the device periodically is likely to continue.

Field Portable Electrochemical Sensors for Uranium and Other Species in Aqueous Samples

Dale Russell (Boise State University) discussed handheld portable sensors that have been developed at the University for the detection of actinides (uranium, plutonium, thorium), heavy metals (mercury, cesium), and volatiles organics (benzene, toluene). These sensors have two operating modes: field effect transistor (FET) type or potential sweep type using cyclic voltammetry (CV).

The hand-held uranium sensor was developed for detection in the field for possible use in monitoring for non-proliferation treaty compliance. It is robust, sensitive, and portable, and it has the capability for autonomous operation and data logging. The unit also is highly selective (to minimize false signals) and operates in real time. This sensor has remediation applications for uranium detection in water in containers, holding tanks, and process streams. It can also be used for detection at a distance from the source, to monitor run-off and uranium fate and transport in surface and ground waters, and to detect uranium in saturated soil.

To assemble the sensor, a chemical field effect transistor (ChemFET) was fabricated using novel polymers and electrochemical deposition techniques. Several polymers were specifically synthesized for electrochemical deposition. The polymers are derivatized for metals or for polyatomic species. As the target analyte binds to the polymer, the electronic or electrical property of the polymer or target analyte changes, and the changes are concentration-dependent. A nanoliter electrochemical deposition method was developed to deposit the polymers specifically onto the gate electrode of a p-type metal-oxide-semiconductor-field-effect-transistor (pMOSFET). The ChemFET operates in an aqueous environment and so is suitable for deployment in groundwater for the detection of uranium.

The ChemFETs can be fabricated using different approaches to suit different purposes. For uranium sensing, several derivatives of polythiophene polymer films, one of which is sensitive to the uranyl ion, are separately deposited onto the pMOSFET gate electrodes. The films are electrochemically deposited using nanoliter volumes of electrolytic solution (patent pending). The uranyl-sensitive ChemFET is immersed in a uranyl acetate solution and removed after an hour. Optical microscopy, micro-FTIR and electrical measurements are performed before and following electrochemical deposition and uranyl acetate exposure.

This small, simple, robust, inexpensive sensor has no moving parts. It is able to treat uranium and other actinides like any other redox-active metal. Detection is based on redox and complexation chemistries, not radiochemical signature, and is accomplished via direct chemical-to-electronic signal transduction. In conclusion, research and development at Boise State University has produced selective, field-portable sensors capable of rapid sub ppb-detection in water. The sensors show wide dynamic ranges and good selectivity for target analytes. In the FET mode of operation, the sensor exhibits a total change in gate potential, which allows detection of all actinides. In the CV mode of operation, the sensor differentiates species based on redox potential. Mixtures of actinides were differentiated in CV mode with detection limits in the mixture of 0.1 ppb thorium, uranium and plutonium. Boise State University will continue to work on the optimization and sensitivity of these sensors.

Sensor Technology Supported by EPA Small Business Innovation Research (SBIR) Program

April Richards (EPA/ORD) began her presentation with a brief overview of the federal SBIR program. SBIR is a set-aside program that promotes commercialization of new products by encouraging small businesses to engage in federal research and development.
Small businesses are defined as for-profit entities located in the U.S. with fewer than 200 employees. The SBIR program comprises approximately 2.5% of the federal R&D budget and had over $2 billion in funding in 2004. Eleven federal agencies, including EPA, participate in the SBIR program.

In supporting its mission to protect human health and the environment, EPA uses the SBIR program to develop and commercialize innovative environmental technologies needed by EPA regions, program offices, and states. Grants are awarded in two phases. Phase I is expected to produce a proof of concept, with an award of up to $70,000 in a six-month period of performance. Phase II focuses on commercialization, with an award of up to $225,000 over a two-year period. EPA's FY 2006 SBIR budget is $6.5 million.

Richards provided examples of technologies funded in the last few years:

- A field instrument for the measurement of metals in soil using spark-induced breakdown spectroscopy; Physical Sciences, Inc., Phase II completed 2002.
- A 3-in-1, continuous, automated, ambient/fenceline/fugitive emissions instrument using pneumatic focusing gas chromatography for analysis of VOCs and HAPs; VOC Technologies, Inc., Ongoing Phase II project, patent pending.
- Robust, tunable diode lasers for environmental monitoring using TDL spectroscopy to detect mobile emissions and fenceline trace gases in the part-per-trillion range; Vescent Photonics, Inc., Phase II completed 2005.
- Electrochemical sensor for Cr(VI) in water using self-assembled monolayer (SAM)-modified microelectrode arrays for remote monitoring of groundwater and surface water; Eltron Research, Inc., Phase II completed 2004.
- Nanocrystalline zero-valent iron (Z-Loy™) for *in situ* remediation of contaminated soils and aquifers; OnMaterials, Inc., Phase II completed in 2005, patent pending on manufacturing process. [Richards noted that this example is not sensor-related, but she chose to include it because of the high level of interest in uses of nanoscale ZVI.]

She urged the attendees to forward any needs for solicitation topics right away to meet the upcoming solicitation cycles. In 2006, EPA's Phase I solicitation will open March 23 - May 24, and Phase I contracts will be awarded in February 2007. The Phase II solicitation will open in July 2007, and Phase II contracts will be awarded in April 2008. More information on the upcoming SBIR cycle is available on the Web (www.epa.gov/ncer/sbir), along with previous research solicitations, abstracts and final reports from awardees, EPA success stories, and links to other agencies.

In answer to participant questions, Richards acknowledged that, while SBIR personnel in different agencies interact via the federal SBIR managers' meetings, coordination of what is funded by the various agencies could be improved. Because SBIR programs differ greatly from agency to agency, each agency prepares its own solicitations, rather than collaborate on them. However, agencies do sometime work together on specific topics; EPA and DOE are currently exploring joint efforts.

MEETING WRAP-UP

John Koutsandreas (DOE) announced that *Barrier Systems for Environmental Contaminant Containment and Treatment* has just been issued by CRC Press. The book addresses the materials used in barriers, defines their properties, and explores how they perform in the field. The text also contains two case studies that demonstrate the value of validating field performance.

One participant remarked that some of the presentations delivered at the meeting had been of particular interest, because they are linked to subsurface monitoring. Gaining knowledge of the water flux in the vadose zone is required to understand risk and contaminant transport. This is an area in which the unknowns are so large that they could well drive future development of sensors for use in the long term. Another participant said that understanding the flow of fluids also is important in determining whether contaminant containment (as in landfills) is failing. Even conservative modeling is not always effective. He suggested that moisture movement through the vadose zone and how well models are predicting it—i.e., where contaminant monitoring begins to dovetail with performance monitoring in geologic systems—could be a topic for a future Roundtable meeting.

Kovalick reminded attendees to be alert for material for cost and performance case studies. He also suggested that they visit the $21M^2$ website, consider the needs areas, and ponder the possibilities of partnering with one of the Regions to acquire project funding.