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Fiber-Optic Sensors for Rapid, Inexpensive Characterization
of Soil and Ground Water Contamination

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1. Abstract

The extent and complexity of worldwide environmental contamination are great enough that characterization, remediation, and performance monitoring will be extremely costly and lengthy. Characterization techniques that are rapid, inexpensive, and simple and that do not generate waste are urgently needed. Towards this end LLNL is developing a fiber-optic chemical sensor technology for use in groundwater and vadose-zone monitoring. We use a colorimetric detection technique, based on an irreversible chemical reaction between a specific reagent and the target compound. The accuracy and sensitivity of the sensor (<5 ppb by weight in water, determined by comparison with gas chromatographic standard measurements) are sufficient for environmental monitoring of trichloroethylene (TCE) and chloroform.

2. Background

The U.S. Department of Energy (DOE) has begun an ambitious program to clean up its weapons complex facilities and to bring all continuing activities into compliance with United States environmental regulations. The physical magnitude of this effort is unprecedented in modern history. Recent estimates¹ indicate that DOE soil and groundwater remediation problems include at least 1.9×10^{11} gallons of contaminated ground water and over 5×10^7 cubic yards of contaminated soils. Over 4800 individual hazardous waste and hazardous substance release sites on DOE properties (not including 24 designated inactive uranium processing sites and 3000 vicinity properties) have been identified to date (DOE, 1993). Contaminants found in soil and ground water on DOE lands include organics (such as solvents and fuels), inorganics (such as salts and metals), radionuclides, and mixed wastes. With the exception of radioactive materials, contaminants on DOE lands are similar to those associated with common industrial practices found throughout industrial nations.

The life cycle of a site restoration project contains several major steps. In sequence, these are characterization; evaluation, selection, and implementation of containment or restoration measures; and performance monitoring during and after remediation.

Characterization technology is used to identify and define soil and ground water contamination problems. Site characterization depends both upon historical records and recollections, if available,

¹Ground water and soil volumes tallied from February 1994 DOE/EM Project Tracking System data sheets excluding Uranium Mill Tailings Remedial Action (UMTRA) projects.

and sampling, testing, and analysis. Generally, state-of-the-practice methods can be effective in characterizing contaminant plumes if the nature of contamination is simple, but heterogeneous subsurface conditions (in either a physical or chemical sense) can make site characterization more difficult and costly. Current practices usually require construction of wells with dedicated pumps, periodic sampling of the wells, and analysis of the samples. This approach requires capital investment for the wells and equipment and creates operational expenses for the skilled labor needed to draw and analyze the samples.

Monitoring schemes are designed to measure soil vapors or ground water for contaminant concentrations to assess the performance of a remedial action or closure. Monitoring data can also be used to check basic assumptions developed site characterization and remediation design. In general, the technical requirements and limitations of monitoring schemes are similar to those for characterization (e.g., dedicated wells, equipment, labor, and sample analysis needs, with concomitant capital and operational costs). Post-closure or performance monitoring, though, is generally performed at intervals over an extended period of time, making it a potentially large ongoing component of site remediation expense.

The ultimate cost of site remediation is strongly influenced by the number and cost of environmental samples needed for the characterization and monitoring steps of the project life cycle. There is, therefore, an urgent need for new analytical techniques that can provide rapid, inexpensive, and credible measurements of contaminant concentrations. A rapid analytical technique could greatly reduce project life cycle costs by significantly reducing sampling and analysis expenses and by facilitating optimum placement of measurement locations (monitoring wells or soil vapor extraction points). Towards this end we are developing and field-testing a fiber-optic sensor technology for monitoring chlorinated organic solvents such as trichloroethylene (TCE) and chloroform. In this paper we describe the sensor technology, emphasizing a design that permits the placement of the sensor into the subsurface solely with hydraulically driven penetrations (hereafter referred to as cone penetrometry).

3. Experimental

The sensor operates on colorimetric principles. In the basic sensor design, optical fibers are used to remotely monitor a quantitative, irreversible chemical reaction that, upon exposure to various target molecules, forms products that absorb visible light. The primary chemical reagent is an outgrowth of the work of Fujiwara (1916), who first demonstrated that basic pyridine, when exposed to certain chlorinated compounds, develops an intense red color. We have shown (Angel et al., 1987) that the absorption of 560-nm light by these colored products is directly related to the vapor-phase concentration of the contaminant and that some selectivity of target molecules is possible through modifications of the reagents and of their relative proportions. We have evaluated the sensor against gas-chromatographic standards; its accuracy and sensitivity (<5 ppb by weight) are sufficient (Colston et al., 1992) for the monitoring of the environmental contaminants trichloroethylene (TCE) and chloroform.

The sensor system has three major components: a miniature pumping and delivery system for renewing the chemical reagent, an electro-optic readout device for monitoring the transmission of the sensor, and the sensor itself. The system design allows consecutive measurements to be taken at short intervals in an on-demand basis; control and monitoring are done remotely. The small reaction volume of the sensor allows a large number of measurements to be made before the reagent reservoir must be recharged. This allows the sensor to stay in place for a long time before it must be serviced.

Figure 1 shows the most versatile version of the reagent delivery system, which was designed to fit into a standard cone penetrometer system. The high-aspect-ratio design was achieved by placing the reagent supply into a gas-tight 5-ml syringe that is opposed to an identical, empty syringe. The syringe plungers are fixed with respect to one another and are simultaneously driven by a motor and drive screw. Therefore, as fresh reagent is delivered to the sensor, spent reagent is captured in the empty syringe, making recovery and disposal easy. The motor is encoded to permit monitoring of the remaining reagent volume.

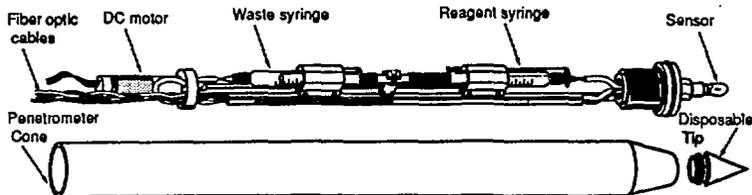


Figure 1. Assembly drawing of the reagent delivery system and penetrometer cone. The reagent is connected to the sensor by means of micro-tubing. The syringe reservoirs are held in place with quick disconnect clamps for easy servicing. The cone is made from corrosion resistant steel tubing with 6.35 mm wall thickness.

A custom penetrometer cone, also shown in Figure 1, was designed by S. Cooper of the U. S. Army Corps of Engineers Waterways Experiment Station (COE/WES) and S. Brown of Lawrence Livermore National Laboratory (LLNL) and constructed at LLNL. The cone (495 mm long, 44.5 mm o.d., 33.75 mm i.d.) is threaded to receive standard 1 m x 33.75 mm COE/WES push rods. The reagent delivery system and sensor are housed in the cone and are isolated from the environment until the measurement depth is reached. The TCE sensor was exposed to soil vapors by means of a removable and disposable ground-penetrating tip. The cone is driven to the desired depth and then retracted by 15 cm, thereby leaving the removable tip at depth while exposing the sensor to soil vapors and creating a void or "probed volume" of approximately 200 cm³. Communication from the ground surface to the sensor and support equipment housed in the cone is accomplished with a custom-built 60 m long umbilical cord containing two optical fibers, a tube for vacuum evacuation of the probed volume, and a six-wire electrical cable for electronic instruction delivery and data acquisition.

4. Field Results

The DOE Office of Technology Development Integrated Demonstration at the Savannah River Site (SRS) was chosen as the initial location for the field demonstration and evaluation of the sensor technology. The objectives of the work reported here were to deliver the sensor, using cone penetrometry, to multiple depths at multiple locations; to expose the sensor to a range of TCE concentrations; and to observe the effect of pumping, as in a vadose zone "grab sample" operation, on the measurement process.

Before the experiments the umbilical cord was threaded through 47 one-meter long push rods, allowing us to reach depths of at least 41 m. Four separate pushes (to depths of 9, 14, 41 and 33 meters) were accomplished over two days. The average push rate was 1 m/min. All "pushes" were carried out by COE/WES participants. Experiments were controlled from the surface by means of a portable optical sensor readout device and portable computer. Measurements were made in both a quiescent ("static") and vacuum extraction ("dynamic") mode. A total of 121 individual TCE concentration measurements were made during the four pushes; measured concentrations ranged from ~2 ppm by volume (static measurement at 9 m depth) to ~120 ppm by volume (dynamic measurement at 14 m). It is of particular note that the time to depth for the 41 m push was only 50 min.

Table 1 gives the results of an extended experiment performed after the sensor was pushed to 33 m, which placed it approximately 6 m above the water table. We made three measurements with the cone tip in place to zero the sensor and then removed the tip and made 15 consecutive static measurements. The TCE concentration measured by the sensor was 18.8 ± 5.0 ppm. We then performed

nine consecutive measurements under dynamic conditions. Here the concentration jumped abruptly into the 30-ppm range and remained stable for the duration of pumping, yielding a TCE concentration of 34 ± 1.3 ppm. When we discontinued pumping, the concentration almost immediately dropped back to the previous static values (average concentration 14.4 ± 1.8). This is slightly less than the initial measurements but identical within experimental uncertainty. It is noteworthy that the first three readings after retraction of the tip gave higher concentration values than the next eight measurements. This is probably attributable to the vacuum, and the resulting greater soil extraction, generated upon initial retraction of the cone to form the probed volume. Removing the first three measurements (29.8, 26.9 and 20.0 ppm) from the initial static set yields a mean TCE concentration of 16.1 ± 1.4 ppm, which agrees very well with the mean and uncertainty obtained during the second static set of measurements.

TABLE 1. TCE concentrations measured *in situ* under static (unpumped) and dynamic (vapor extraction) conditions.

Pump	TCE concentration (ppm, by volume)											Mean
Off	29.8	26.9	20.2	18.2	18.0	16.6	16.7	15.8	15.0	14.6	14.6	18.8
On	35.2	33.7	32.1	33.6	33.3	32.5	36.2	35.2	34.3			34.0
Off	23.7	18.4	16.0	15.5	14.2	13.2	14.4	12.9	13.0	13.0	13.2	14.4

5. Discussion

The work described above represents one of a wide range of sensor technologies now being prepared for testing and application. The development, commercialization, and use of automated sensor systems to quickly and inexpensively measure contaminant concentrations *in situ* will benefit site investigation and monitoring by reducing costs and improving the quality and types of data available. A similar revolution in field measurement capabilities occurred in geomechanics several years ago, when automated piezoelectric measurement of hydraulic pore pressure in rock and soil began to replace conventional water level measurements made with tag lines in wells and standpipes. These improved hydrologic measurements were particularly valuable for projects such as dams, tunnels, and engineered slopes. The improved, lower-cost data supported better understanding of project performance and improved operational safety.

Automated systems for *in situ* measurement of contaminant concentration are likely to have a comparable or greater impact in site investigation and remediation system applications for contaminated soil and ground water. These systems could be used in several ways:

- Installation in advance of migrating plume or at site boundaries for contaminant detection or watchdog applications (as illustrated in Figure 2).
- Reduce characterization and monitoring costs associated with conventional well sampling and sample analysis.
- Monitor concentrations during extract-and-treat and other groundwater cleanup operations (including new cleanup technologies) to support optimization of design and operations (also illustrated in Figure 2).
- Investigate changes in spatial distribution of contaminants with time to verify effects of design assumptions on remediation.
- Providing "ground truth" measurements to verify geophysical remote sensing or underground imaging to detect Non-Aqueous Phase Liquids (NAPLs) and delimit plume boundaries.

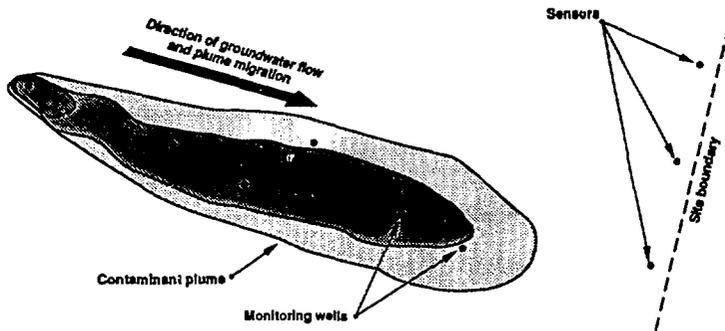


Figure 2. Generalized plan view of ground water contamination plume showing locations of monitoring wells (or penetrometer-installed sensors) to measure contaminant concentration changes with time (within the plume) or to detect contaminant spread (watch dog applications along site boundary).

6. Conclusions

All objectives of the initial penetrometer-mediated sensor-placement demonstration were accomplished. This technology represents the most rapid and cost-effective means to obtain initial survey information on subsurface contamination distribution for a variety of chlorinated solvents. Its impact on optimizing the siting of monitoring wells will significantly reduce remediation costs. With lower sensor costs and lower cost of installation, this approach to measuring contaminant concentrations *in situ* should provide better quality, more complete data, thus improving understanding of *in situ* processes and phenomena during site characterization and remediation.

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