

Microchemical Sensors for In-Situ Monitoring and Characterization of Volatile Contaminants

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Abstract—Traditional methods for monitoring sites that may be contaminated with toxic chemicals can be expensive, time consuming, and misrepresentative of in-situ conditions. A few in-situ chemical monitoring systems exist, but they do not attempt to quantify or characterize the contaminant (e.g., location, composition, etc.). This paper presents the development of a microsensor monitoring system that can be used to monitor *and* characterize volatile organic contaminants in the subsurface. A microchemical sensor that employs an array of chemiresistors is packaged in a unique, waterproof housing that is designed to protect the sensor from harsh subsurface environments, including completely water-saturated conditions. The array of sensors is calibrated to provide “training sets” for pattern recognition of various chemicals and chemical mixtures. The sensors and packaging have been tested in laboratory environments, and unique characterization methods are being developed that utilize contaminant transport models and time-dependent, in-situ sensor data to identify the location of the contaminant source. Additional characterization methods that can be employed during soil remediation methods such as soil venting are also being tested to determine the extent and composition of the contamination.

Introduction—Tens of thousands of sites containing toxic chemical spills, leaking underground storage tanks, and chemical waste dumps require characterization and long-term monitoring to reduce health and environmental risks. Current methods are costly and time-intensive, and limitations in sampling and analytical techniques exist. Looney and Falta (2000, Ch. 4) report that the Department of Energy (DOE) Savannah River Site requires manual collection of nearly 40,000 groundwater samples per year, which can cost between \$100 to \$1,000 per sample for off-site analysis. In addition, the integrity of off-site analyses can be compromised during sample collection, transport, and storage. This paper presents the development of microchemical sensors that can be used to provide real-time monitoring and characterization of volatile organic compounds (VOCs) *in situ*, which can provide cheaper and more reliable information.

Microchemical Sensor and Packaging—Ho et al. (2001) performed a review of chemical sensors that are potentially applicable to long-term in-situ monitoring applications. Polymer-absorption sensors (chemiresistors), as described in this paper, were found to be one of the most viable candidates for in-situ applications because of their simplicity and robustness. The chemiresistor consists of a chemically sensitive absorbent mixed with conductive particles that is deposited onto a solid phase, which acts as an electrode. When chemical vapors come into contact with the absorbent, the chemicals absorb into the polymers, causing them to swell. The swelling changes the resistance of the electrode, which can be measured and recorded. The amount of swelling corresponds to the concentration of the chemical vapor in contact with the absorbent. The process is reversible, but some hysteresis can occur when exposed to high concentrations. Chemiresistors have been developed in the past for applications in the

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subsurface (EPA, 1995), but the ability to use these sensors to characterize the contaminant *in situ* has not been addressed.

Two unique features exist regarding the chemiresistors being developed by Sandia National Laboratories. First, rather than using a single electrode and conductive polymer, the chips developed at Sandia can house an array of chemiresistors (Figure 1). The array of differing sensors can be used to identify different VOCs by comparing the resulting chemical signatures with calibration (or training) sets (Hughes et al., 2000). The chemiresistor array has been shown to detect a variety of VOCs including aromatic hydrocarbons (e.g., benzene), chlorinated solvents (e.g., TCE), and aliphatic hydrocarbons (e.g., iso-octane). A second unique feature is that a robust package has been designed and fabricated to house the chemiresistor array (Figure 2). This package is small (< 3 cm diameter) and is constructed of PEEK, a unique semi-crystalline, high-temperature engineering thermoplastic with excellent chemical and fatigue resistance. PEEK is inert to all common solvents and resists a wide range of organic and inorganic liquids. The package is waterproof, but allows gas to diffuse through a GORE-TEX® membrane. Mechanical protection is also provided via a perforated metal plate that covers the chemiresistors. The chemiresistors are situated on a 16-pin dual in-line package that is connected to a weatherproof cable, which can be connected to any data logger.

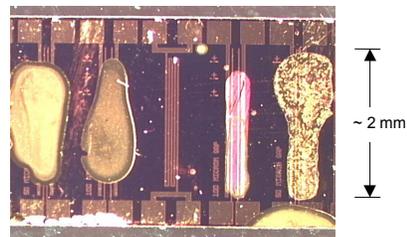


Figure 1. Chemiresistor array developed at Sandia National Laboratories with four different conductive polymer films deposited on different electrodes.

Data Interpretation and Characterization—In addition to the unique packaging design of the chemiresistor sensors, novel methods are also being developed that analyze the time-dependent nature of the contaminant transport processes in porous media to characterize contaminants *in situ*. For example, the location of a subsurface contaminant or leak is often unknown, and traditional monitoring methods require that the monitoring device be in the immediate vicinity of the contaminant to detect and identify the contaminant location. Because the chemiresistor detects the vapor phase of the VOC, the sensor does not have to intercept the contaminant plume in the vadose zone. Diffusion of the contaminant vapor from the source region to the chemiresistor sensor produces a time-dependent “breakthrough” curve that can be used to estimate the distance to the source term. Figure 3 shows the results of a one-dimensional column experiment that consisted of the chemiresistor package at one end of the column and a contaminant source term (saturated iso-octane) at the other end. A completely dry, 10-20 mesh sand was placed in the column between the sensor and contaminant boundary condition. The concentration measured by the sensor was normalized to the maximum concentration, and results were plotted as a function of time and compared to predictions of analytical solutions of diffusion transport. The analytical solution requires input parameters for the effective diffusion coefficient and the distance between the source and the sensor location. The diffusion coefficient for iso-octane at 1 bar and 22 °C is $6.5 \times 10^{-6} \text{ m}^2/\text{s}$, and the tortuosity coefficient for dry sand is estimated to be approximately 0.25. The actual distance between the

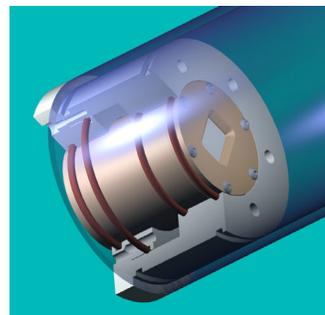


Figure 2. Weatherproof chemiresistor housing that can be emplaced in a monitoring well or cone penetrometer.

contaminant boundary condition and the sensor was 36 cm. The analytical solutions for three assumed distances are plotted in Figure 3 to demonstrate how the location of the contaminant can be estimated. Results indicate that the measured concentrations align most closely with the predicted results that assume a distance of 40 cm. More rigorous statistical methods can be used to better quantify the location based on the analytical predictions, but variations in parameters such as liquid saturation, temperature, and pressure will affect the results in real applications. Methods to compensate for variations in these parameters are being investigated. Similar analyses can also be performed in multiple dimensions.

In-situ sensors can also be used to optimize remediation methods such as soil-vapor extraction in the vadose zone and air sparging in the saturated zone. These methods rely on the advective fluid (air) to volatilize and remove the contaminant from the subsurface. However, heterogeneities in the subsurface can cause mass-transfer limitations when the advective fluid bypasses regions of stagnant contamination (Ho and Udell, 1992). *In-situ* sensors can be used to determine when the effluent concentrations have dropped to levels that are no longer cost-effective for the system to be operated. These sensors could trigger the pumps to shut down, allowing the system to re-equilibrate as the contaminant diffuses to the advective zones. When the concentration reaches a “productive” level, the sensors could trigger the pumps to turn on again. This automatic feedback system can save money by operating the remediation system only when contaminant concentrations are at a significant level. It could also act as a sentinel for sites that are prone to contamination. Finally, chemical signatures in the effluent during the remediation process can also allow additional characterization of the contaminant (Ho, 1998).

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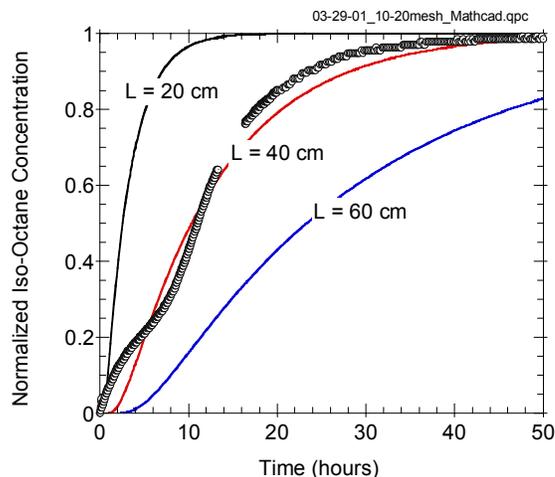


Figure 3. Plot of normalized concentration as a function of time for the 1-D column experiment. The data points are shown as circles, and the results of the analytical solution are shown as solid lines for three assumed distances.