IN-SITU MICROCHEMICAL SENSORS FOR LONG-TERM MONITORING OF SUBSURFACE CONTAMINANTS

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ABSTRACT

An in-situ chemiresistor sensor has been developed that can continuously monitor volatile organic compounds in a variety of media including air, soil, and water. The chemiresistor consists of a conductive polymer deposited onto a microfabricated circuit that changes its electrical resistance in the presence of volatile organic compounds. The change in resistance can be calibrated to known concentrations of analytes, and arrays of chemiresistors can be used on a single chip to aid in discrimination. A rugged, waterproof housing was constructed to allow the chemiresistor to be emplaced in monitoring wells or immersed in water, and a cable connects the sensor to a surface-based solar-powered data logger employing wireless telemetry. This system has been deployed at Sandia's Chemical Waste Landfill, where in-situ sensor data are posted continuously to a web site (www.sandia.gov/sensor/cwl). The monitoring system at the Chemical Waste Landfill includes two chemiresistors to detect trichloroethylene (TCE) and other sensors to monitor environmental changes at the site. This system has been operating continuously since March of 2003.

INTRODUCTION

Background

Numerous sites across the nation have been contaminated by volatile organic compounds (VOCs) from chemical spills, leaking underground storage tanks, and chemical waste dumps. These sites require characterization and long-term monitoring to reduce health risks and protect the environment. However, current methods that employ manual sampling of soil and groundwater are costly and time-consuming, and the integrity of the samples can be compromised during collection, transport, and storage. Although a number of chemical sensors are commercially available for field measurements of chemical species (e.g., portable gas chromatographs, chemistry kits, etc.), few have been adapted for continuous use in geologic environments for long-term monitoring or remediation applications.

Objectives

The purpose of this work is to develop simple, rugged, in-situ microchemical sensors and systems for unattended real-time monitoring and characterization of VOCs in soil and groundwater. The intent is to reduce the costs associated with monitoring sites contaminated with VOCs while improving public and stakeholder confidence in long-term stewardship activities.

The focus of this paper is on the deployment of these in-situ sensors at the Chemical Waste Landfill in Albuquerque, New Mexico. The Chemical Waste Landfill is a 1.9-acre site that was used for disposal of chemical wastes generated by Sandia National Laboratories' research laboratories from 1962 until 1985. The groundwater at the Chemical Waste Landfill is approximately 500 feet below the surface and flows northwest. The groundwater travel time from the Chemical Waste Landfill to the nearest receptor well 4 miles downgradient is on the order of hundreds of years.

Prior to remediation of the site, which included soil vapor extraction in the vadose zone and subsequent excavation of 52,000 cubic yards of contaminated soil, a vapor plume of trichloroethylene TCE was determined to be the source of elevated TCE concentrations in the groundwater. After remediation, TCE concentrations in the groundwater have been below the maximum contaminant level of 5 parts per billion (ppb) since completion of the vapor extraction in July 1998, with the exception of 12.5 ppb TCE measured in one well in June 2003. In addition, a Corrective Measure Study, Remedial Action Proposal, and Post-Closure Care Plan were submitted following the remediation [1]. The Post Closure Care Plan calls for the long-term monitoring of one upgradient and three down-gradient wells to start in Fiscal Year 2004. Groundwater samples will be collected annually and analyzed for VOCs.

The purpose of this study is to evaluate the use of an in-situ sensor system to provide continuous groundwater monitoring at the Chemical Waste Landfill. A description of the sensors used in the continuous monitoring system is presented in the next section, followed by a description of the field test. Results of the first eight months of the field test (which began in March 2003) are then provided, followed by a discussion of the potential benefits and limitations of the continuous monitoring system.

DESCRIPTION OF SENSORS

Chemiresistor Sensor

The chemiresistor sensor is a chemically sensitive resistor comprised of a conductive polymer film deposited on a micro-fabricated circuit. The chemically-sensitive insulating polymer is dissolved in a solvent and mixed with conductive carbon particles. The resulting ink is then deposited and dried onto thin-film, parallel, non-intersecting platinum traces on a solid substrate (chip). When chemical vapors come into contact with the polymers, the chemicals absorb into the polymers, causing them to swell. The swelling changes the physical configuration of the conductive particles in the polymer film, thereby changing the electrical resistance across the platinum-trace electrodes. The change in resistance can be measured and recorded using a data logger or an ohmmeter[2]. The swelling is reversible if the chemical vapors are removed, but some hysteresis can occur at high concentration exposures. The amount of swelling corresponds to the concentration of the chemical vapor in contact with the chemiresistor, so these devices can be calibrated by exposing the chemiresistors to known concentrations of target analytes.

Fig. 1 shows the architecture of the microsensor, which integrates an array of chemiresistors with a temperature sensor and heating elements [3]. The polymers used to comprise the chemiresistor array include poly(epichlorohydrin) (PECH), poly(N-vinyl pyrollidone) (PNVP), poly(isobutylene) (PIB), poly(vinyl tetradecanal) (PVTD), and poly(ethylene-vinyl acetate)

(PEVA). The chemiresistor array has been shown to detect a variety of VOCs including aromatic hydrocarbons (e.g., benzene), chlorinated solvents (e.g., trichloroethylene (TCE), carbon tetrachloride), aliphatic hydrocarbons (e.g., hexane, iso-octane), alcohols, and ketones (e.g., acetone). Because each polymer has a different affinity to different compounds, statistical methods can be used to provide discrimination capabilities.

The on-board temperature sensor comprised of a thin-film platinum trace can be used to not only monitor the in-situ temperature, but it can also be used in a temperature control system. A feedback control system between the temperature sensor and on-board heating elements can allow the chemiresistors to be maintained at a fairly constant temperature, which can aid in the processing of data when comparing the responses to calibrated training sets. In addition, the chemiresistors can be maintained at a temperature above the ambient to prevent condensation of water, which may be detrimental to the wires and surfaces of the chemiresistor.
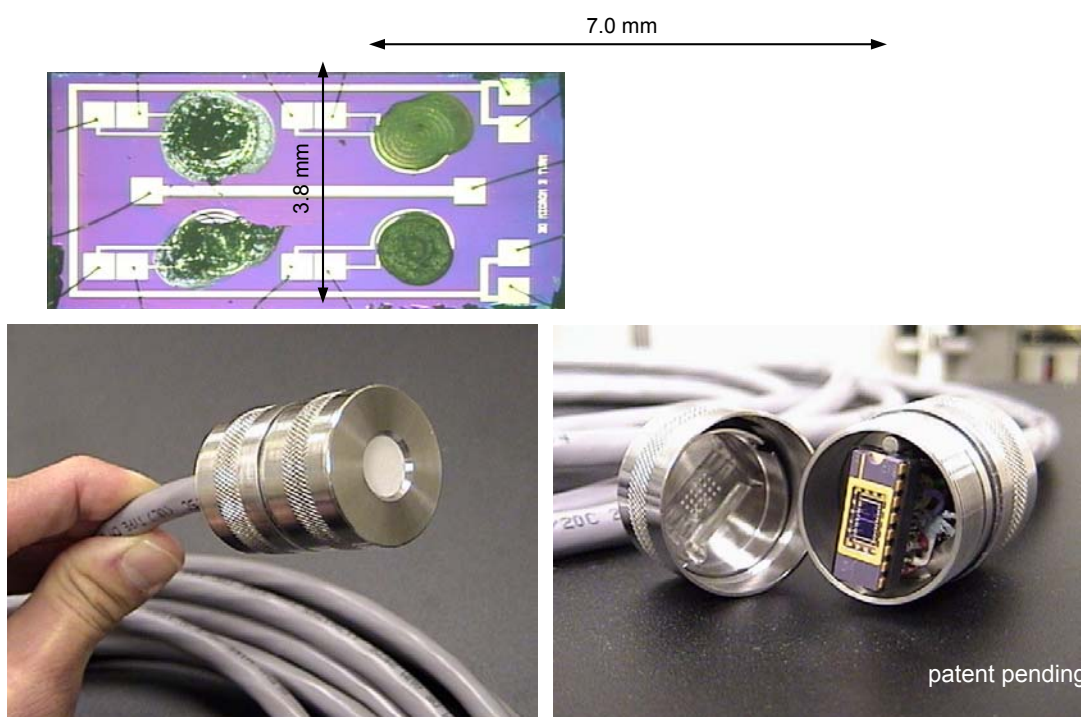

Fig. 1   Top: Chemiresistor arrays developed at Sandia with four conductive polymer films (black spots) deposited onto platinum wire traces on a silicon wafer substrate. A platinum resistance temperature detector (rtd) is on the perimeter of the chip and a platinum heating element is in the middle. bottom left: Stainless-Steel waterproof package that houses the chemiresistor array. Bottom Right: Disassembled package exposing the chemiresistor-array chip inside of the 16-pin DIP.

A robust package has been designed and fabricated to house the chemiresistor array [2]. This cylindrical package is small (~ 3 cm diameter) and is constructed of rugged, chemically-resistant material. Early designs have used PEEK (PolyEtherEtherKetone), a semi-crystalline, thermoplastic with excellent resistance to chemicals and fatigue. Newer package designs have been fabricated from stainless steel. The package design is modular and can be easily taken apart (unscrewed like a flashlight) to replace the chemiresistor sensor if desired. Fitted with

Viton O-rings, the package is completely waterproof, but gas is allowed to diffuse through a GORE-TEX® membrane that covers a small window to the sensor (see Fig. 1). Like clothing made of GORE-TEX®, the membrane prevents liquid water from passing through it, but the membrane "breathes," allowing vapors to diffuse through. Even in water, dissolved VOCs can partition across the membrane into the gas-phase headspace next to the chemiresistors to allow detection of aqueous-phase contaminants. The aqueous concentrations can be determined from the measured gas-phase concentrations using Henry's Law. Mechanical protection is also provided via a perforated metal plate that covers the chemiresistors. The chemiresistor chip is epoxied and wire-bonded to a 16-pin dual-inline package (DIP), which is connected to a weatherproof cable. The cable can be connected to a hand-held multimeter for manual single-channel readings, or it can be connected to a multi-channel data logger for long-term, remote operation.

The sensitivity of these devices depends on the type of polymer used in the chemiresistor, thickness of the polymer film, the amount of carbon particles added to polymer, separation distance between the electrodes, and the type of analyte. A general observation for the chemiresistors developed at Sandia is that the best chemiresistors for a particular vapor can detect vapor concentrations on the order of $1/1000^{th}$ (or 0.1%) of the saturated vapor pressure of the analyte being detected. For some VOCs, this detection limit is below the maximum concentration limits set forth by the United States Environmental Protection Agency (U.S. EPA) for air and drinking water. For example, m-xylene was reliably detected at $1/100^{th}$ its saturated vapor pressure, or approximately 100 parts per million (ppm) by volume in the gas phase. According to Henry's Law, this corresponds to ~2 ppm by mass in the aqueous phase, which is less than the 10 ppm maximum contaminant level imposed by the U.S. EPA. However, for TCE, the chemiresistors can detect gas-phase concentrations as low as 100-1000 ppm, which corresponds to an aqueous TCE concentration of ~1-10 ppm. The U.S. EPA maximum contaminant level for TCE in drinking water is 0.005 ppm, well below the current detection limits. Nevertheless, many applications such as pre-screening and remediation monitoring do not require the capability to provide such low detection limits. In addition, efforts are ongoing to develop integrated preconcentrators that can increase the apparent sensitivity of the chemiresistor sensors.

Thermocouples

T-type thermocouples from Omega Engineering, Inc. were used to monitor the in-situ temperatures in both a vadose-zone well and a saturated-zone well at the Chemical Waste Landfill. A Teflon insulated T-Type thermocouple (part #5TC-TT-T-24-36) was used in the vadose-zone well, and a PVC-coated-tip T-Type thermocouple (part #5TC-PVC-T-24-180) was used in the saturated-zone well. The depths of the sensors in the vadose-zone well and in the saturated-zone well were approximately 60 feet and 500 feet, respectively.

Pressure Transducers

Pressure transducers were used to monitor the atmospheric pressure changes in the vadose-zone well and the water level in the saturated-zone well. An Omega PX215 pressure transducer (0-30 psia) was deployed in the vadose-zone well, and a Campbell Scientific CS400 submersible

pressure transducer was deployed in the saturated-zone well, approximately 18 feet below the water table, which is located about 493 feet below ground surface.

Relative Humidity Sensor

An Omega HX92AC relative-humidity sensor was deployed in the vadose-zone well to monitor changes in the relative humidity. Although one might intuitively expect that the relative humidity would be close to 100% in the subsurface, the vadose-zone well "breathed" as a result of atmospheric pressure changes. When the atmospheric pressure was high, air from the surface (which was typically dry), flowed into the well, causing the relative humidity to decrease. When the atmospheric pressure was low, air would be sucked up from the screened portion at the bottom of the well, causing the relative humidity to increase. Because changes in water-vapor concentration affect the response of the chemiresistor sensors, the relative humidity and temperature were recorded for use in the chemiresistor predictive models (see Calibration of Chemiresistor Sensors).

FIELD TEST PREPARATION

The sensors described in the previous section were deployed in two wells downgradient of the Chemical Waste Landfill. Fig. 2 shows a map of the site and the location of the two wells. In preparation for the deployment, the chemiresistor sensors were calibrated in the laboratory. The other sensors were calibrated by the manufacturers. Chemiresistor array E19 was used in the vadose-zone well and contained four chemiresistors comprised of PIB, PVTD, PNVP, and PEVA polymers. Chemiresistor array E25 was used in the saturated-zone well and contained four chemiresistor sensors comprised of PECH, PNVP, PIB, and PEVA. The polymers were chosen based on their responsiveness to TCE (and water vapor) in various environmental conditions.
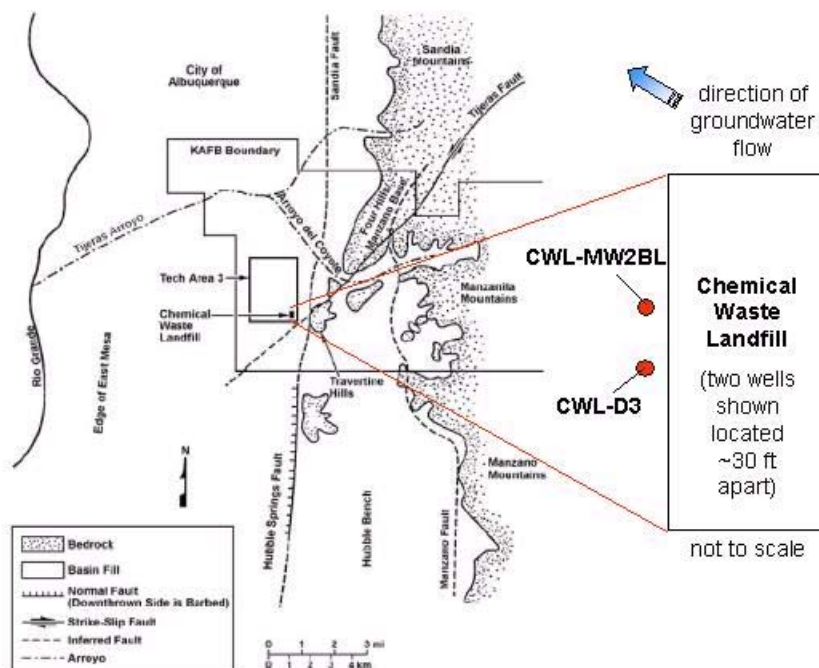
Fig. 2 The Chemical Waste Landfill at Sandia National Laboratories, New Mexico and the Two Wells Instrumented with the Remote Sensor System (from http://www.sandia.gov/sensor/cwl/).

Calibration of Chemiresistor Sensors

Each chemiresistor is individually calibrated to known concentrations of the target analyte. For the Chemical Waste Landfill, TCE is the analyte of interest. The calibration procedure begins by establishing a baseline resistance for each chemiresistor sensor. For the chemiresistor sensor array (chip E19) that was deployed in the unsaturated zone (where the relative humidity can be less than 100%), dry air was passed across the sensor in order to remove the ambient water vapor and provide a baseline. For the chemiresistor sensor array (chip E25) that was deployed in the saturated-zone well, clean humidified air (100% relative humidity) was passed across the sensor to establish a humidified baseline. The sensors are allowed to reach equilibrium, which is determined by visually evaluating the stability of the chemiresistor resistances over time. If the measured resistances appear to be stable then a steady baseline is recorded. Then, known

concentrations of TCE are added and the sensors are allowed to stabilize while exposed to known concentrations of TCE. The concentrations of TCE are verified by an MTI 200 micro gas chromatograph. A typical calibration run for the chemiresistor exposed to TCE used 500, 1000, 5000, 10,000-ppm$_v$ TCE.

The relative change in resistance for the sensors during an exposure is found by first determining the average stable baseline resistance values, R_b, for two minutes prior to the exposure of TCE. Next the value of the resistance during an exposure to TCE is calculated by taking a two-minute average of the steady resistance values, R, once steady-state conditions had been reached. The relative change in resistance is calculated using Eq. 1.

$$\frac{\Delta R}{R_b} = \frac{R - R_b}{R_b}$$

(Eq. 1)

For the chemiresistor sensor used in the vadose-zone well (chip E19), this process was repeated at different temperatures (in refrigeration units and ovens) to accommodate a lower-than-room temperature in the vadose-zone well of approximately ~17ºC. In addition, the calibrations were repeated at different water vapor pressures (using water bubblers with dilution streams of dry air) to accommodate the fluctuating relative humidity in the vadose-zone well (typically between 50-100% relative humidity as a result of barometric pumping). Additional details of the calibrations can be found in Ho et al. [3]. The temperature, water vapor pressure, and the response of the four chemiresistor polymers (Eq. 1) were used as the predictor variables in a multivariate factor-analysis regression model generated in Statistica™ to predict TCE concentrations. The model that is used for E19 is presented below:

TCE (ppm) = 2.26E+03 –2.19E+02*TempC + 3.82E+05*ΔR/R$_{b\ PNVP}$*ΔR/R$_{b\ PEVA}$
    + 2.40E+03*ΔR/R$_{b\ PVTD}$*TempC + 1.43E+03*ΔR/R$_{b\ PEVA}$*TempC + 2.99E+01*ΔR/R$_{b\ PVTD}$*Vp –
    4.75E+04*ΔR/R$_{b\ PIB}$ *ΔR/R$_{b\ PNVP}$*TempC + 8.07E+03*ΔR/R$_{b\ PIB}$*ΔR/R$_{b\ PVTD}$*ΔR/R$_{b\ PEVA}$*TempC

Where:
   TempC = Temperature of sensor in degrees Celsius
   Vp = Water vapor pressure of water in Pascals

The chemiresistor sensor used in the saturated-zone well (chip E25) was calibrated using an elevated temperature of the chip at 25ºC, which was obtained by applying approximately 3 volts to the heater bar on the chip (see Fig. 1). Because the groundwater temperature is approximately 20ºC, we desired to maintain the sensor at a temperature above the ambient temperature to prevent condensation. Without localized heating, previous tests had shown that condensation caused spurious results to occur [3].   In addition, because the sensor in the saturated-zone is exposed to a constant 100% relative humidity, calibrations were only conducted under conditions that yielded water-vapor concentrations corresponding to 100% relative humidity at approximately 20ºC. The multivariate factor-analysis regression model generated in Statistica™ for chip E25 is shown below:

TCE (ppm) = -3.45E+00 + 1.56E+05*ΔR/R$_{b\ PECH}$ – 3.82E+07*ΔR/R$_{b\ PECH}$*ΔR/R$_{b\ PIB}$ –
    1.88E+06*ΔR/R$_{b\ PECH}$*ΔR/R$_{b\ PEVA}$ + 5.79E+05*ΔR/R$_{b\ PNVP}$ *ΔR/R$_{b\ PEVA}$ +
    4.62E+07*ΔR/R$_{b\ PIB}$*ΔR/R$_{b\ PEVA}$

Data Acquisition System

To collect the data from the deployed sensors at the Chemical Waste Landfill, a Campbell CR23X datalogger was used. Since the site is remote without convenient access to electrical outlets, an 80 amp-hour battery manufactured by Interstate was used to power the CR23X, and a 20-watt solar panel was used to recharge the battery. The datalogger was programmed to collect data once an hour. Once the data are collected, the program turns on a cell phone that is housed inside the datalogger. The CR23X interfaces with web posting software via the cell phone. The CR23X, cell phone, and modem are contained in a Campbell Scientific enclosure that is mounted on a tripod. The solar panel and a Yagi antenna are also mounted on the tripod. Fig. 2 shows the data logging station next to the vadose-zone well.

Web Posting

A web site was created to continuously post the data collected from the Chemical Waste Landfill. The website displays many different aspects of the monitoring station located at the Chemical Waste Landfill, including current subsurface sensor readings, maps of the site and wells, live video of the site (SNL internal use only), and photos of the sensors.

The web posting is accomplished by utilizing two Campbell Scientific, Inc. software packages (LoggerNet Version 2.1, Real Time Data Monitor (RTDM) Version 1.6) and a cellular transceiver with an external RJ11C telephone interface. A computer with LoggerNet software, RTDM software, and a Hayes-compatible phone modem is connected to a standard phone line and used to call the cellular equipped data-logging station every hour. The LoggerNet software application allows the user to set-up, configure, and retrieve data, locally and remotely, from multiple data-loggers. The Edlog feature of LoggerNet allows the user to create unique programs that can collect, process, and store data for future retrieval. The Setup and Connect feature of LoggerNet allows the user to connect to the logger on a specified schedule allowing automated collection of data.

RTDM is a software application that allows the user to create a unique data display. Through the use of RTDM Designer, the user can create an object-oriented form, which can display data from a data (*.dat) file. Items such as numeric and text displays, charts/graphs, alarms, and diagnostic data can be display and manipulated based on the creators needs. RTDM monitors the source data file and when the source data file is updated, RTDM updates the information contained in a currently running form. After the data are updated, RTDM initiates a Timed Output Image, which creates a Graphics Interchange Format (GIF) or Joint Photographic Experts Group (JPG) file and posts it to a specified path. These GIF or JPG files can then be displayed on a designated web site.

RESULTS AND DISCUSSION

Sensor Data

As detailed in the previous section, data are collected from the subsurface sensors once an hour and posted to a web site (www.sandia.gov/sensor/cwl). Fig. 3 shows a snapshot of a screen image of the web site.
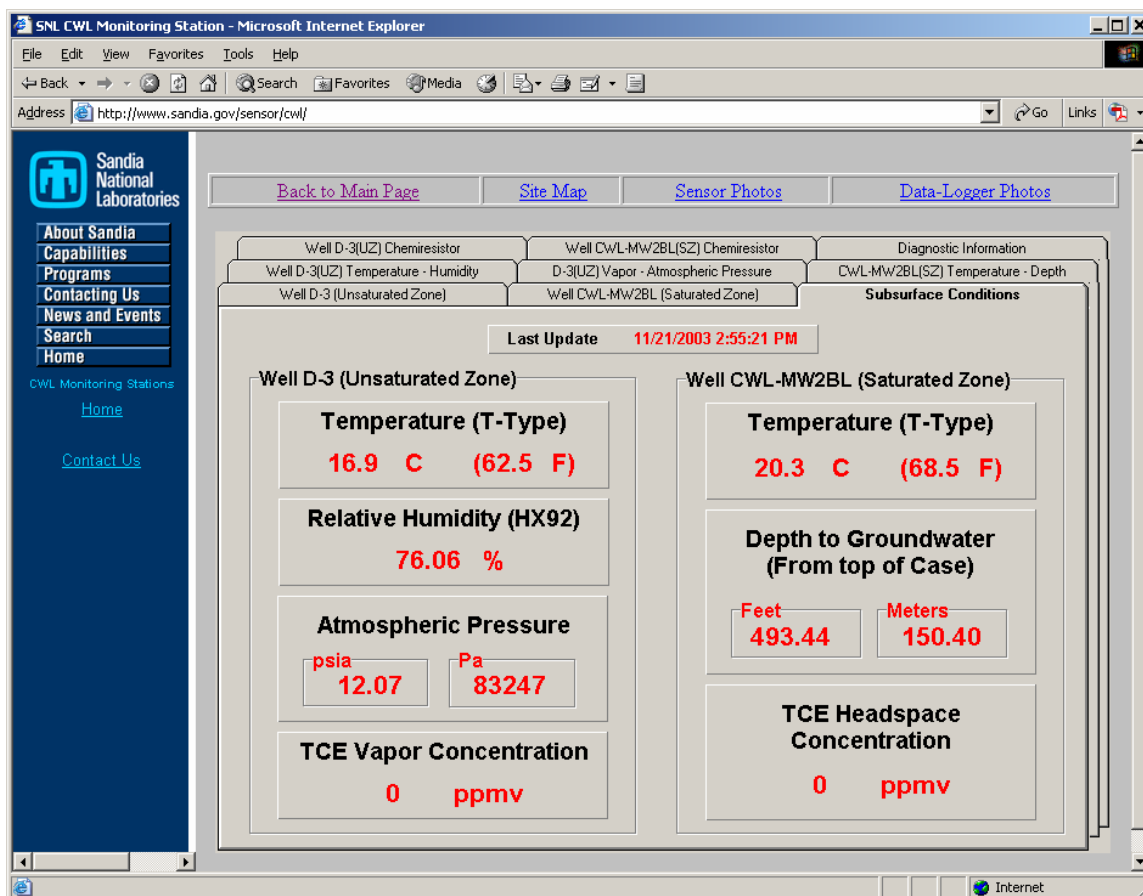

Fig. 3   Screen image of web site containing continuously monitored data at the chemical waste landfill. The chemiresistor sensors monitor for changes in TCE concentrations, which are currently below detectable limits. (from www.sandia.gov/sensor/cwl)

The sensor data in the unsaturated-zone well is shown in the left column of Fig. 3. The temperature in the vadose-zone well is fairly constant at ~17ºC, and the relative humidity can fluctuate between 50% and 100% because of barometric pumping. The atmospheric pressure recorded by the pressure transducer in the vadose-zone well is inversely correlated to the relative humidity. High-pressure systems tend to push drier air into the well, whereas lower pressure systems tend to draw moist air from the screened portions near the bottom of the well. The TCE vapor concentration has been below the detectable limits of the chemiresistor sensor, which is approximately 1000 ppm in the gas phase (~10 ppm in the aqueous phase). This has also been confirmed by standard laboratory analysis procedures using a gas chromatograph and mass

spectrometry, which showed concentrations of TCE below maximum contaminant levels of 5 ppb in the aqueous phase (~0.5 ppm in the vapor phase). The purpose of the continuous monitoring system is to detect large changes (releases) of TCE concentration.

Because the relative humidity fluctuates in the vadose zone, the chemiresistor sensors also fluctuate significantly (Fig. 4). However, the multivariate regression model allows for these significant changes caused by water vapor, and only unique changes caused by the presence of TCE will indicate a concentration of TCE. A few false positive readings have occurred in the unsaturated zone, primarily when large precipitation events have allowed water to enter the well and contact the sensors. In these cases, the abrupt change in the sensor responses were not correctly interpreted by the model.

The sensor data in the saturated-zone well is shown in the right column of Fig. 3. The temperature of the groundwater is fairly constant at ~20ºC, and the water level has also been fairly constant at about 493 feet below ground surface. Occasional perturbations to the water level have been observed and recorded as a result of nearby drilling.

Because the environmental conditions in the saturated-zone well (500 feet below ground surface) are more stable than the environment in the vadose-zone well, the chemiresistor responses are more stable. Fig. 4 shows the raw resistances from the four chemiresistor polymers during the first eight months of this test, which began in March 2003. The localized heating prevents condensation and yields very stable responses from the chemiresistors. The combined response, as predicted by the Statistica™ model, has not shown any detectable TCE concentrations in the saturated-zone well.
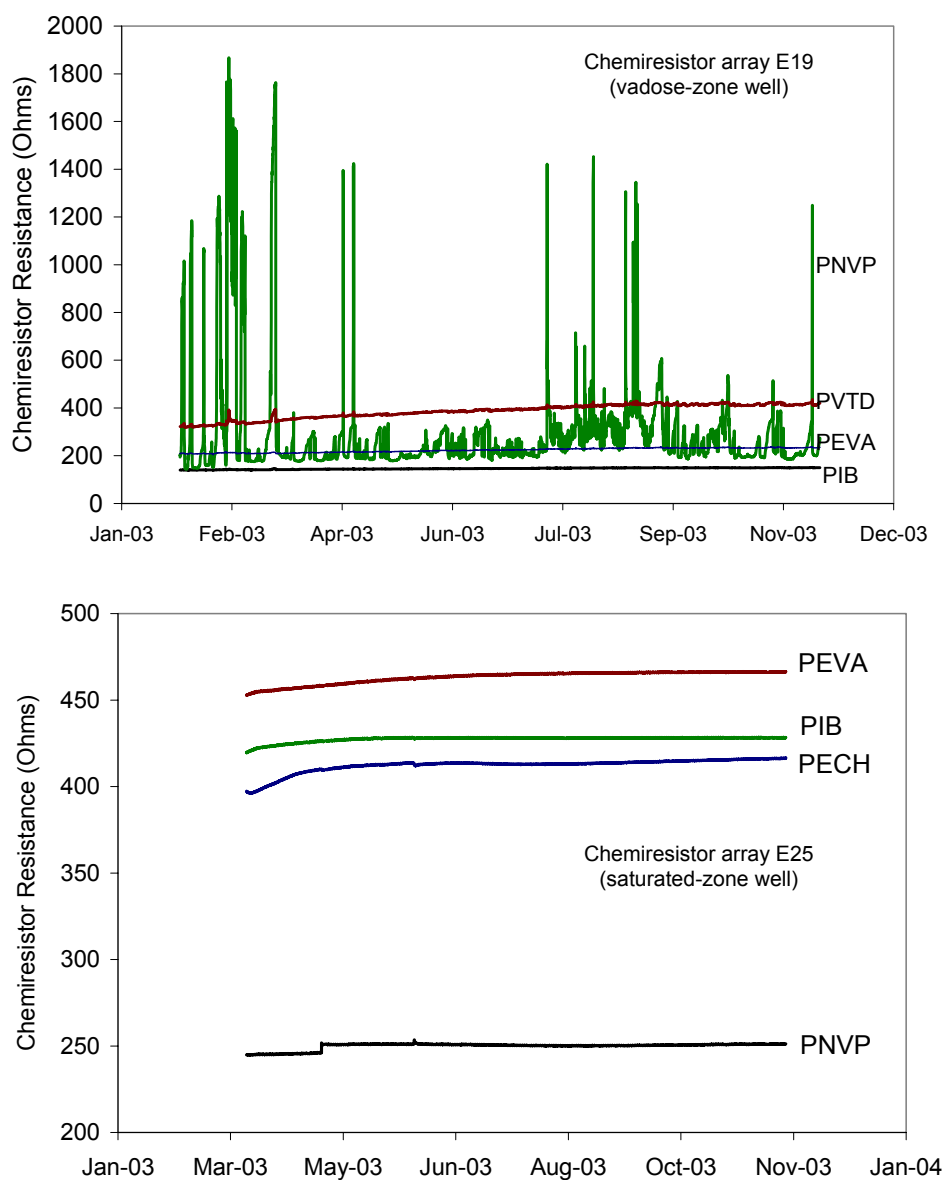
Fig. 4 Measured Resistances of Four Chemiresistors on Chips E19 (Top) and E25 (Bottom). E19 is Deployed in the Vadose-Zone Well, Where Relative Humidity Fluctuates, Causing Large Variability in the Chemiresistor Responses, Especially PNVP (A Polar Polymer). E25 Experiences a Stable Response as a Result of Constant Relative Humidity (100%) and Localized Heating of the Chip to Prevent Condensation. E19 Was Deployed in January, and E25 Was Deployed in March 2003.

Additional information reported on the web site includes battery voltage, panel temperature, heater voltage, chemiresistor resistances, 3-day plots of various parameters, and diagnostic information about the system. Surface conditions recorded from a nearby meteorological station are also posted to the web site. Links are provided to relevant web sites regarding the Chemical Waste Landfill and the chemiresistor research.

Cost Analysis

The cost of the in-situ chemiresistor-sensor monitoring system was comprised primarily of the initial capital equipment costs and the labor associated with deploying and maintaining the system and web site. The total cost for the first six-month period was just under $50K. Both the materials cost and the labor cost have decreased dramatically since the initial deployment of the system. Only a few hours of labor have been charged each month to maintain the web site and sensors since June 2003. Ongoing maintenance of the monitoring system and web page is estimated to cost approximately $1K-$3K a month.

Compared to traditional sampling of the wells, Collins et al. [4] estimates that the cost of sampling one well at the Chemical Waste Landfill is approximately $22K. Most of that cost is labor. In contrast, a year's worth of continuous, real-time data can be available to the public via an in-situ chemiresistor sensor monitoring system for about the same cost it takes to get the results of a single traditional groundwater sample. The estimated cost of maintaining the sensor system and web page for two wells is about $12K–$36K year (for repairs and hardware/web maintenance). This operating cost is not anticipated to increase significantly if additional wells are added to the monitoring system. However, a significant limitation of the chemiresistor sensor system is its high detection limits (for TCE, ~1-10 ppm in the aqueous phase, ~100-1000 ppm in the gas phase). The maximum contaminant level for TCE in water is 5 ppb, which is much lower than the detection limits of the chemiresistor. Currently, the chemiresistors cannot attain those detection limits, but preconcentrators are being developed to increase the sensitivity of the chemiresistors [3].

CONCLUSION

The purpose of this work was to develop simple, rugged, *in-situ* microchemical sensors and systems for unattended real-time monitoring and characterization of VOCs in soil and groundwater. The intent is to reduce the costs associated with monitoring sites contaminated with VOCs while improving public and stakeholder confidence in long-term stewardship activities. Results of field tests at the Chemical Waste Landfill show that the in-situ chemiresistor sensor shows promise for cost-competitive use in long-term monitoring activities. Data have been automatically collected and posted to a web site every hour for the past eight months (beginning in March 2003). The purpose of this application is to detect large changes in concentration of TCE at the site. Other applications requiring continuous monitoring for large changes in concentration (contaminant leaks or releases) may be suitable for the chemiresistor sensor system. Additional research to increase the sensitivity of the sensor using a preconcentrator to achieve detection limits comparable to maximum contaminant levels in drinking water is currently ongoing.

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