Final Report

Detection and Measurement of Explosives in Groundwater Using In Situ Electrochemical Sensors

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Summary

The results of this study demonstrate that remotely-deployable submersible sensors are capable of monitoring explosive compounds both temporally and spatially in groundwater and can be more cost effective than conventional sampling and analysis. Such new remote-sensing capability can bring significant changes to the way in which nitro-based explosives are monitored. At this time, this technology can be deployed in standard groundwater monitoring wells that are 1.5 inches or greater in diameter. Future modification of the sensor probe could decrease the probe size to less than 3/4 inch to accommodate installation with minimally invasive direct-push technologies, such as cone penetrometer or GeoProbe™ system. Furthermore, the sensor measurement frequency can be easily changed from a remote location, enabling the investigator to tailor the measurement cycle to the speed at which the parameter in question is or may be changing.

During the course of this Strategic Environmental Research and Development Program (SERDP) SERDP Exploratory Development (SEED) project, various working electrode materials and voltammetric waveforms were compared, and relevant experimental parameters were optimized. Based on initial testing we developed a submersible electrochemical probe, using a carbon-fiber electrode assembly, connected to a 50-foot-long shielded cable, for the real-time monitoring of nitro-organic explosives in natural water. The facile reduction of the nitro moiety group allowed convenient and rapid square-wave voltammetric measurements of trace levels of nitroaromatic explosives (TNT, TNB, and Tetryl) down to levels of 50 to 100 ppb. A newly developed background subtraction algorithm was used to minimize background contributions. A highly stable response (with relative standard deviations of 1.0% to 1.5%) was observed for prolonged (10 hour) operations in natural water samples, indicating no apparent surface fouling. Detection limits for nitroamine explosives (HMX and RDX) and nitrocellulose were in the range of 1 to 2 ppm. The peak potential for nitroamine explosives are directly superimposed onto the oxygen peak in the voltammogram resulting in significant increase in detection limits. This interference, caused by the presence of oxygen, complicates the procedures required to measure nitroamine explosives in groundwater. To successfully measure nitroamine compounds, oxygen removal will be required. With oxygen removal, detection limits for nitroamine explosives should approach those of the nitroaromatic explosives. Several potential interferences were investigated including mono- and di-nitrotoluene, 4-amino-2,6-dinitrotoluene, trichloroethylene (TCE), nitrates, chromate (Cr^{+6}), and perchlorate. Laboratory studies determined only degradation products of nitroaromatic explosives, which still contain a nitro group, interfere with the measurement of the nitroaromatic parent explosive. Other common co-contaminates did not interfere with the measurements.

Acronyms and Abbreviations

DNB	1,3-Dinitrobenzene
DNT	2,6 Dinitrotoluene
EPA	U.S. Environmental Protection Agency
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
Hz	hertz
mV	millivolts
μA	microamps
ηA	nanoamps
NMSU	New Mexico State University
PNNL	Pacific Northwest National Laboratory
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
RSD	Relative Standard Deviation
SBIR	Small Business Innovative Research
SCAPS	Site Characterization and Analysis Penetrometer System
SEED	SERDP Exploratory Development
SERDP	Strategic Environmental Research and Development Program
SON	Statement of Need
TCE	Trichloroethylene
TNT	2,4,6 Trinitrotoluene
TNB	1,3,5 Trinitrobenzene
bkg	background
ppb	parts per billion
ppm	parts per million
V	volts

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1 Summary of Detection Limits and Performance Characteristics for Selected Explosives and Explosive Degradation Products Measured by Remote Electrochemical Sensor..... 9

1.0 Introduction

Since World War I, munitions have been manufactured in the United States using a variety of materials, including propellants, explosives, and pyrotechnic materials. Many of these manufacturing sites contain soil contaminated with explosives, which have contaminated the groundwater. A recent study by the Army estimated 1,300 installations worldwide contain approximately 5,500 individual sites contaminated with various compounds that require some form of remedial actions (Pennington et al. 1999). A significant portion of this contamination is caused by the manner in which explosives were handled and disposed of in the past. Congress has mandated that the Army and other services comply with all applicable environmental laws and regulations at these contaminated sites to ensure protection of human health and the environment. The cost of the Army's Restoration Program is currently estimated to range between 7 and 10 billion dollars[1]. The cost of long-term monitoring at contaminated sites is a significant and growing portion of the Department of Defense clean-up budget.

Because of concerns with escalating cost of remedial and restoration programs, SERDP issued a request for proposal (RFP) for technologies that could significantly decrease the cost of long-term monitoring (SEEDSON-01-06 Long-Term Monitoring through SERDP's Cleanup Thrust Area) at contaminated facilities. This project is in response to this RFP and is based on electrochemical detection of explosive detection of explosive compounds in groundwater.

Electrochemical devices offer unique opportunities to address the challenges of environmental analytical chemistry and in-situ monitoring in particular (Buffle and Horvai 2001). The advantages of electrochemical systems include high sensitivity and selectivity, a wide linear range, minimal space and power requirements, and low-cost instrumentation. Submersible devices based on potentiometry (e.g., pH), conductivity, and amperometry (e.g., oxygen) have all been used in the field for many years (Wang 2000; Brett and Brett 1993). The past two decades have seen enormous advances in electroanalytical chemistry, including the development of ultramicroelectrodes, the design of tailored interfaces, the coupling of biological components with electrical transducers, the microfabrication of molecular devices and the introduction of 'smart' sensors and sensor arrays. Advances in controlled-potential techniques have greatly increased the ratio between the analytical and background currents to allow quantitation down to the ppt range (Wang 2000; Brett and Brett 1993). Similarly, recent developments in polymer membrane ion-selective electrodes have enhanced the detection limits of these potentiometric devices to a similar level (Bakker et al. 1999).

The coupling of modern electrochemical detection principles with recent advances in microelectronics and microfabrication has led to powerful and compact analytical devices for real-time, in process monitoring. These developments have led to a substantial increase in the popularity of electroanalysis and to its expansion into new phases and environments. Recent advances in electrochemical sensor technology have expanded the scope of electrochemical devices toward a wide range of organic and inorganic contaminants. Electrochemical devices are extremely suitable for continuous in situ monitoring

[1]Environmental Quality Technology Program. 1998. *Environmental Restoration Technology Program Plan for the 21st Century*. Unpublished internal document, Department of Army, Washington, D.C.

of such pollutants (Wang 1997). The inherent redox activity of nitroaromatic and nitroamine explosive compounds (Wang et al. 1998), i.e., the facile reduction of their nitro group ($-NO_2$), make them ideal candidates for remote electrochemical detection.

Thus, based on the potential advantages of electrochemical detection, the objective of this research was to develop in situ sensors capable of replacing conventional methods (sample collection and analysis) to measure the concentrations of TNT, RDX, HMX, Tetryl, (Figure 1) and nitrocellulose in groundwater at 20 to 50 ppb levels with long-term stability. The use of in situ sensor technology can significantly reduce the cost of long-term monitoring because it can be used in existing groundwater monitoring wells and may be installed in explosive-contaminated groundwater using direct-push technology, such as a cone penetrometer or GeoProbe™ system.

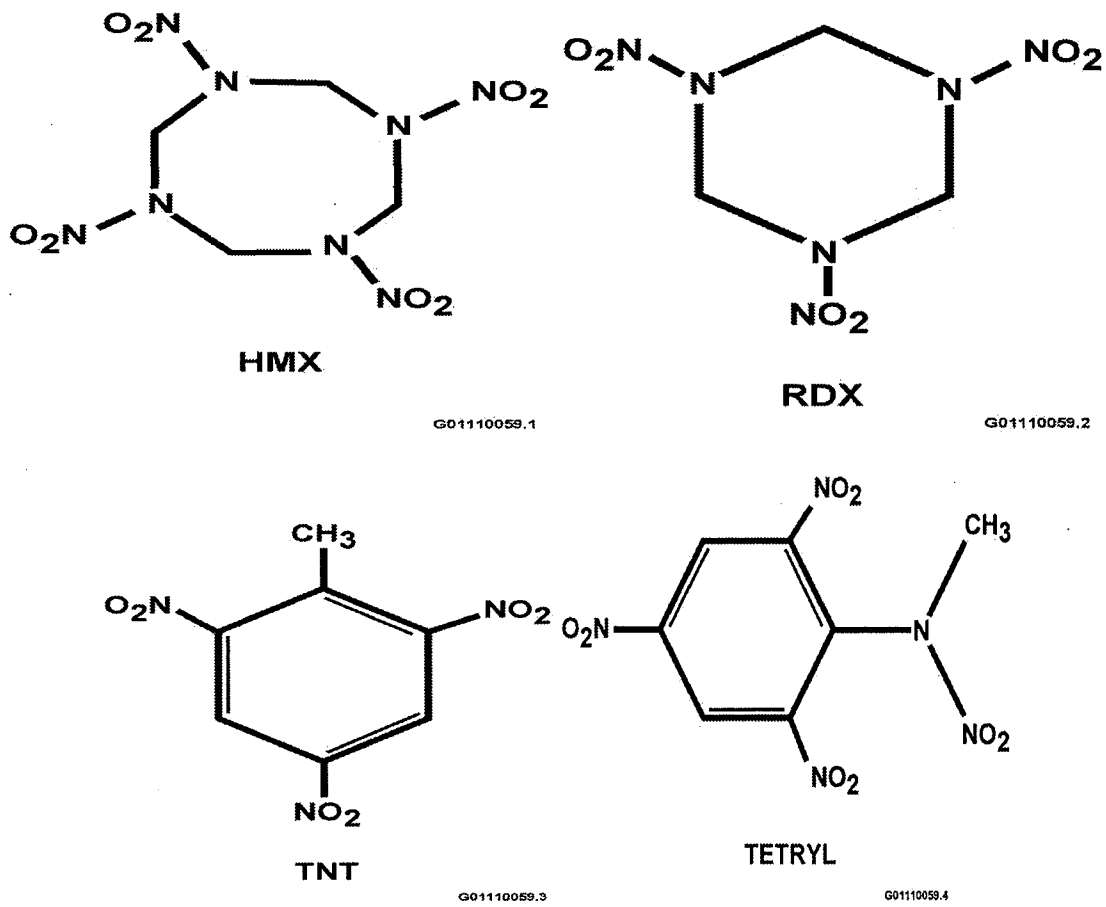

Figure 1. Structure of HMX, RDX, TNT, and Tetryl

The use of in situ sensors to measure groundwater constituents has significant technical benefits over the standard approach of sampling and analyzing groundwater. For example, measurements taken in situ leave little opportunity for the parameter values to change, as is the case for a sample removed from the aquifer. With traditional sampling and analysis, the sample must be treated carefully after collection to prevent erroneous results. Precautions such as filtering the sample to remove particulates, acidification, and cooling of the sample to prevent unwanted chemical changes in the sample are all necessary after a sample has been removed from the aquifer. All of these precautions are unnecessary when analyzing the groundwater in situ with downhole sensors. Normally, a sampling program is conducted on a quarterly basis or even monthly in extreme cases. As a result, it is assumed that natural changes in the groundwater occur on a longer timeframe than the sampling frequency. When using sensors, the best sampling frequency can be determined and implemented at no additional cost. The frequency of the sensor measurement is limited only by the time required for a measurement to stabilize. In addition, the sensor measurement frequency can be easily changed from a remote location, enabling the investigator to tailor the measurement cycle to the speed at which the parameter in question is changing. In this way, the sensors allow the investigator to better understand the dynamics of the system and, in turn, better understand the cause for changes and ultimately what mitigating effects are necessary.

The use of in situ sensors to measure important groundwater properties has the potential for significant cost saving over the standard approach of sampling and analysis of groundwater. For example, standard sampling requires preparation before each sampling event in which the equipment and chain-of-custody paperwork must be prepared. Considering all of the preparation, equipment, and lab costs before each standard sampling event for 10 wells, it is estimated that each quarterly sampling and analysis cycle would cost approximately $1,500, plus $1,100 for delivery of the samples to the lab and $400 for lab analysis including blanks and matrix spikes. Therefore the annual cost for traditional quarterly sampling is estimated at $12,000 for the 40 total number of samples collected.

In contrast, an in situ sensor system involves an initial cost to install the equipment, but has only minor costs associated with maintenance. The initial capital cost of the equipment is estimated to be ~$15,000 for 10 sensors, and installation and calibration labor costs are estimated to be ~$4,000. Annual maintenance costs are estimated to be ~$1,000. Because of the initial capital cost of the sensors, the in situ system would be more costly than standard sampling for a two to three year period, after which, the lower annual costs of the sensors would result in significant long-term cost saving. Once the remote system is operating, the only costs incurred are for data collection from a computer data logging system and the cost ($3,000) of an annual sampling event to verify concentrations of explosives in groundwater. The added value of the in situ sensor system is the near infinite number of sample events per year verses 40 for the traditional method of sampling and analysis.

2.0 Investigation

All experiments were conducted with a Bioanalytical Systems, Inc. (BAS) CV-50W Voltammetric Analyzer. Based on an evaluation of numerous working electrode materials, the most suitable was

determined to be a carbon fiber. The remote sensor consisted of a three-electrode housing that includes a carbon fiber working electrode, a silver/silver chloride reference electrode, and a platinum counter electrode connected through environmentally-sealed connectors to a long shielded cable (Figure 2). Square-wave voltammograms were recorded over the 0.0 to -0.8V range, using an amplitude of 25 mV, and frequency of 15 Hz. All experiments were conducted at room temperature and with an addition of an ionic strength buffer consisting of 0.25 m sodium chloride.

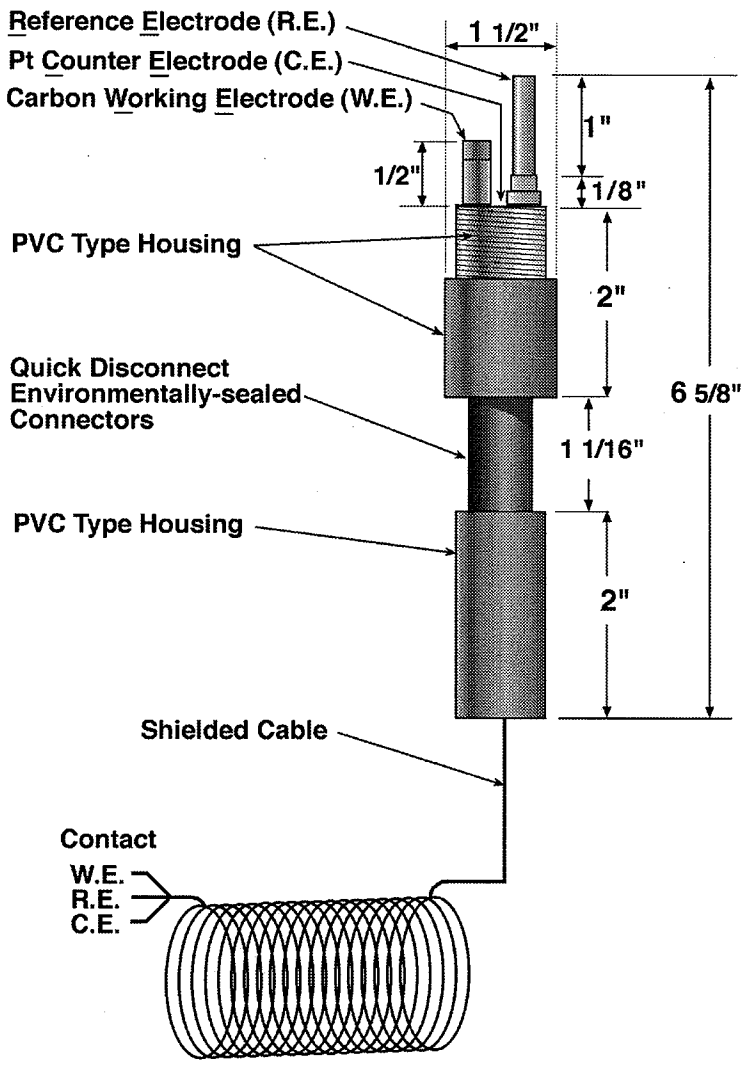

Figure 2. Diagram of the In Situ Probe Used to Measure Explosives in Natural Water

2.1 Electrodes Materials Evaluation

The choice of the working-electrode transducer is crucial to attain reliable monitoring of organic-based nitro explosives. Therefore, various electrode materials were examined and compared for their voltammetric signal, background current, and overall signal-to-background characteristics. These

characteristics included gold, gold-mercury amalgam, ruthenium, iridium dispersed carbon electrode, screen-printed carbon, a Goodfellow carbon fiber, glassy-carbon, and a Aesar™ carbon fiber. The Aesar carbon fiber offered the most attractive performance in terms of signal to noise characteristics and was selected for all subsequent work.

2.2 Voltammetric Waveform

Various voltammetric waveforms can be used to generate the current-potential voltammetric profiles. These differ mainly in the excitation waveform and, hence, yield different signal-to-noise characteristics. We compared the response of the carbon fiber sensor for TNT using linear sweep voltammetry, differential pulse voltammetry, and square-wave voltammetry. The later yielded the most favorable performance characteristics with detection limits down to 50 ppb TNT. Square-wave scanning also can be performed very rapidly (over a 5-second period), thus allowing 12 runs per minute. No improvements were observed when the square-scan was preceded by a delay time indicating no accumulation of TNT onto the working electrode. Most favorable conditions were observed using a square-wave amplitude of 25 mV and a frequency of 15 Hz. Further improvements were obtained using the baseline-subtracted square-wave operation.

This effective computer-controlled background-subtraction protocol was developed to correct for high baseline contributions surrounding the explosive reduction signal, and allows convenient quantitation of ppb concentration levels. For example, Figure 3A and B displays the square-wave voltammetric for a 500 ppb tetryl solution. In Figure 3A, the square-wave voltammogram for tetryl "s" and the background "b" signal without tetryl is recorded in the conventional mode, and in Figure 3B it is in the subtractive mode. Such large baseline contribution obscures the tetryl signal and prevents convenient quantitation of parts per billion concentrations of tetryl. In contrast, the subtractive mode effectively compensates the background signal and leads to a well-defined response signal, with three reduction peaks.

Dramatic improvements, associated with the baseline correction approach, are illustrated also in Figure 4 for analogous remote measurements of 0.25 ppm TNT. Once again, the effective compensation of the rising background allows convenient monitoring of low parts per billion of TNT levels (curves b versus c). An extremely low detection limit of around 50 ppb can, thus, be estimated.

2.3 Detection Limits and Performance Characteristics

Table 1 contains performance characteristics for several explosives and explosive degradation products studied under this project. These data indicate good reproducibility (Relative Standard Deviation [RSD] 1 to 2%), high sensitivity, and low detection limits (of 50 to 100 ppb nitroaromatic explosives and 1 to 2 ppm for nitroamine explosives).

The attractive behavior of the submersible voltammetric probe is illustrated in Figure 5 and displays calibration data for TNT over the 0.5 ppm to 5.0 ppm range (without the background correction). The remote sensor responds favorably to these 0.5 ppm increments. Such well-defined signals resulted in a linear calibration plot (not shown), with a slope of 140 nA/ppm and a correlation coefficient of 0.988). The background-correction capability, illustrated in Figure 4, offers a lower detection limit for TNT.

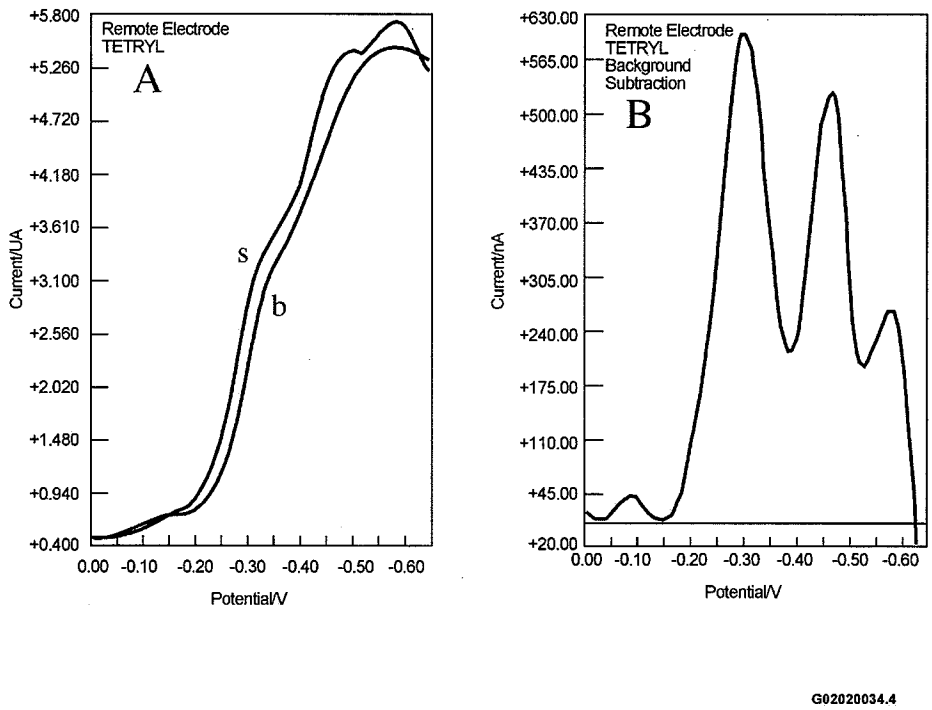

Figure 3. Response of the Remote Probe. Conventional response "s" in 3A and background-corrected response in 3B voltammograms for 500 ppb tetryl, along with the corresponding baseline signal "b" in Figure 3A.

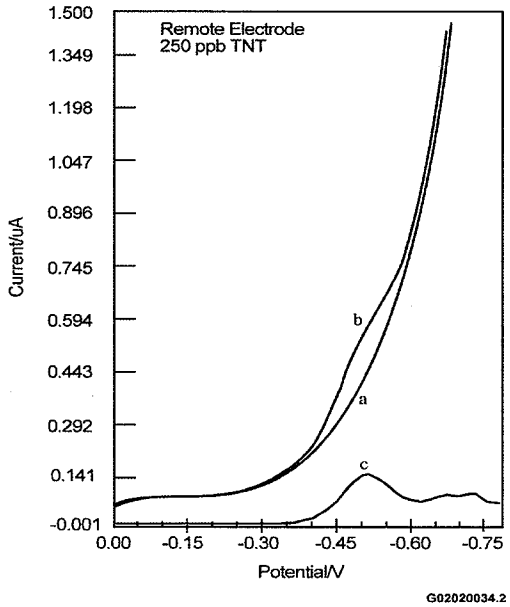

Figure 4. Response of the Remote Probe to 250 ppb TNT. Conventional (b) and background-corrected (c) voltammograms, along with the corresponding baseline signal (a).

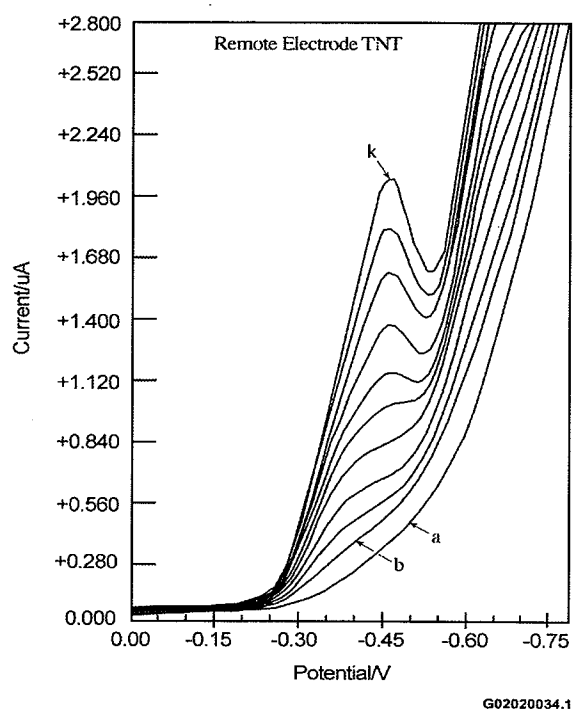

Figure 5. Response of Submersible Electrochemical Sensor to Successive 0.5 ppm Increments in TNT Concentration (b-k), and Corresponding Background Signal (a)

Figures 6 and 7 depict voltammograms generated with varying concentrations of nitrocellulose and HMX in laboratory water, respectively. The maximum signal for both nitrocellulose and HMX are directly superimposed onto the oxygen background peak (Bkg). These results demonstrate small changes in current response relative to large change in nitrocellulose concentration and results in significantly higher detection limits for the nitroamine explosives versus the nitroaromatic explosives listed in Table 1. To improve detection limits and specificity for the nitroamine explosives, one option would be to remove oxygen through purging with an inert gas (e.g., nitrogen or helium) or with the addition of a reducing agent (e.g., sodium dithionite) to the test solution. Figure 8 shows the drastic decrease in the oxygen background signal in the voltammogram by simple purging the sample with nitrogen. Based on these results, we anticipate detection limits for the nitroamine compounds to approach those of the nitro-aromatic compounds.

The analytical utility of the submersible explosive probe is based on the linear dependence between the peak current and the explosive concentration. Such dependence was examined for solutions of 1,3 DNB of increasing concentrations over the 100 to 1,000 ppb range (Figure 9). Despite these extremely low concentrations, the voltammetric sensor offers convenient detection, particularly when used in the subtractive mode. The peaks are proportional to the 1,3 DNB concentration. The resulting calibration plots (also shown on the right) are linear with a correlation coefficient of 0.979.

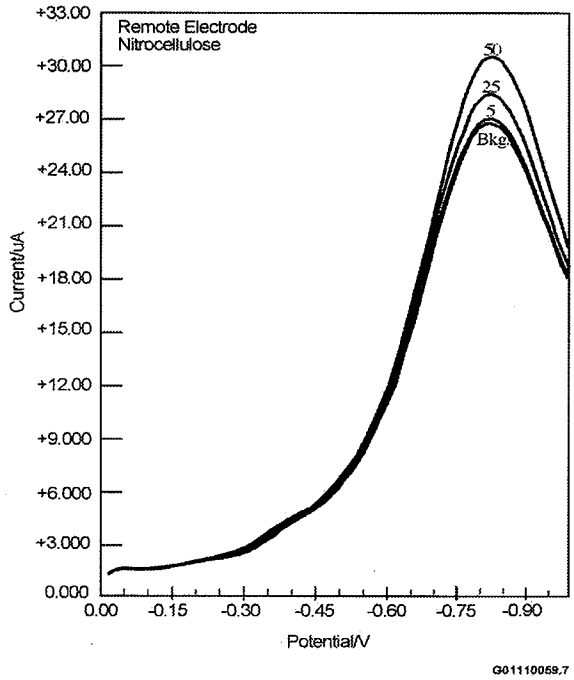

Figure 6. Remote-Electrode Voltammograms for 0, 5, 25, and 50 ppm Nitrocellulose

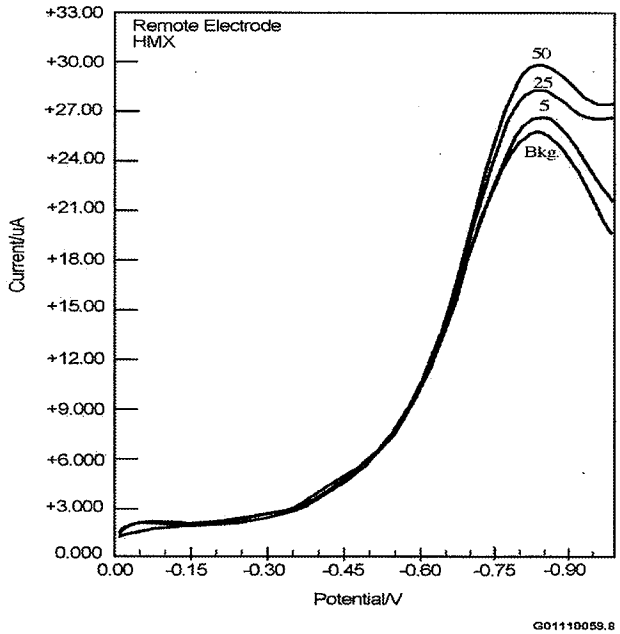

Figure 7. Remote-Electrode Voltammograms for 0, 5, 25, and 50 ppm HMX

Table 1. Summary of Detection Limits and Performance Characteristics for Selected Explosives and Explosive Degradation Products Measured by Remote Electrochemical Sensor

Compound	Sensitivity (μA/ppm)	R^2	Short-Term Precision (RSD,%)	Detection Limits (ppm)
2,4,6 Trinitrotoluene (TNT)	1.51	0.986	1.15	0.05
2,6 Dinitrotoluene (DNT)	2.09	0.972	1.69	0.1
1,3,5 Trinitrobenzene (TNB)	2.00	0.982	1.81	0.1
1,3-Dinitrobenzene (DNB)	2.84	0.979	1.04	0.1
Tetryl	1.09	0.991		0.05
HMX				1-2
Nitrocellulose				1-2
RDX				1-2
Conditions – Differential pulsed voltammetry; initial potential 0.00 V; final potential –1.00V; scan rate 25 mV/s; pulse width 50 ms; pulse period 200 ms.				

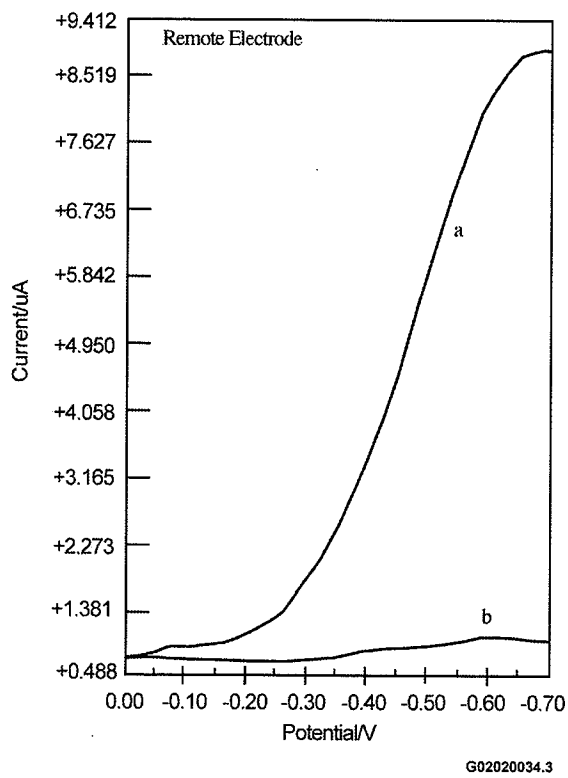

Figure 8. Remote-Electrode Voltammograms Comparing Oxygenated (a) and Deoxygenated (b) Water

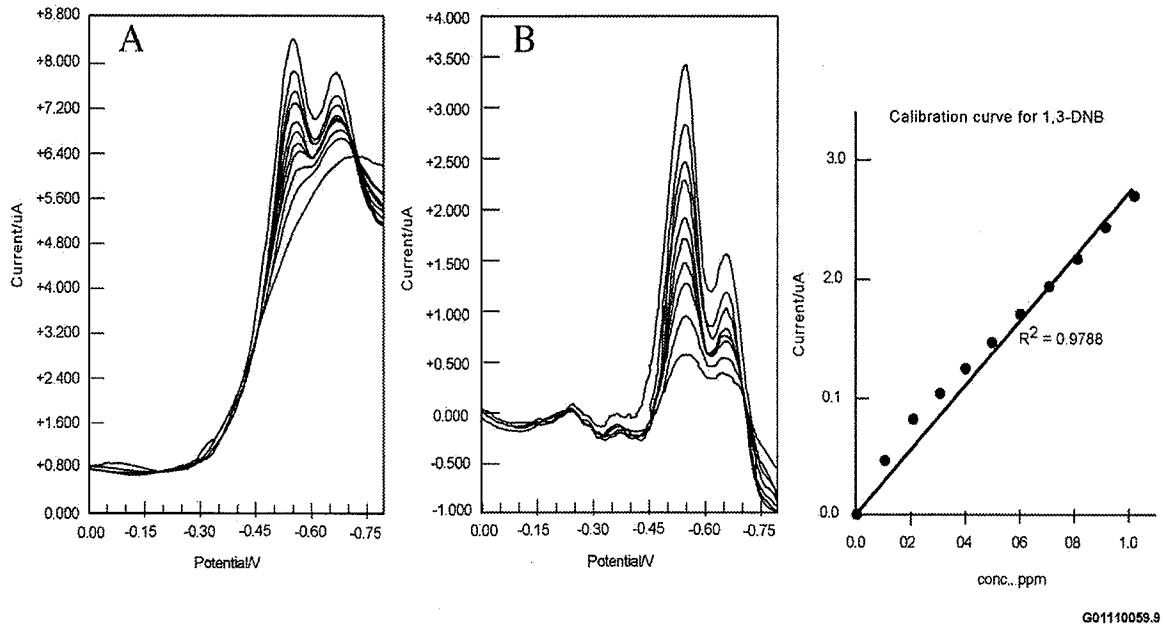

Figure 9. Calibration Data Obtained with Remote Explosive Sensor. Response for increasing levels of 1,3 DNB (100 to1,000 ppb), recorded with the conventional (A) and subtractive (B) voltammetric modes.

2.4 Stability and Carry Over

The stability of the response has an important bearing on the practical utility of the probe. The carbon-fiber transducer behaved normally over prolonged operations (4 to 10 hours), with no apparent surface passivation. The stability was evaluated using a series of 50 repetitive measurements of 2 ppm 1,3 DNB over a prolonged (4 hour) period. As indicated from Figure 10, such series yielded a highly stable response (for both conventional and subtracted operations, left and right, respectively), with a relative standard deviation of 1.04%. No apparent loss in sensitivity was observed for analogous measurements of 7 ppm TNT over a 10-hour period using an untreated river water sample. This series of 31 successive runs yielded a relative standard deviation of 1.2%. This indicates that constituents of the natural water sample do not foul the surface, in the short term.

The device responds favorably and rapidly to sudden changes in the TNT level, with no apparent carry over. The lack of memory effect was assessed upon switching between 3-ppm, 10-ppm, and 3-ppm TNT solutions. The response decays sharply upon placement in the 3-ppm TNT solutions, and rises sharply upon returning to the 10-ppm solution. Such dynamic properties indicate great potential for providing alarm and warning capabilities. Monitoring frequencies as high as 12 runs per minutes are attained in connection to the fast square-wave scanning.

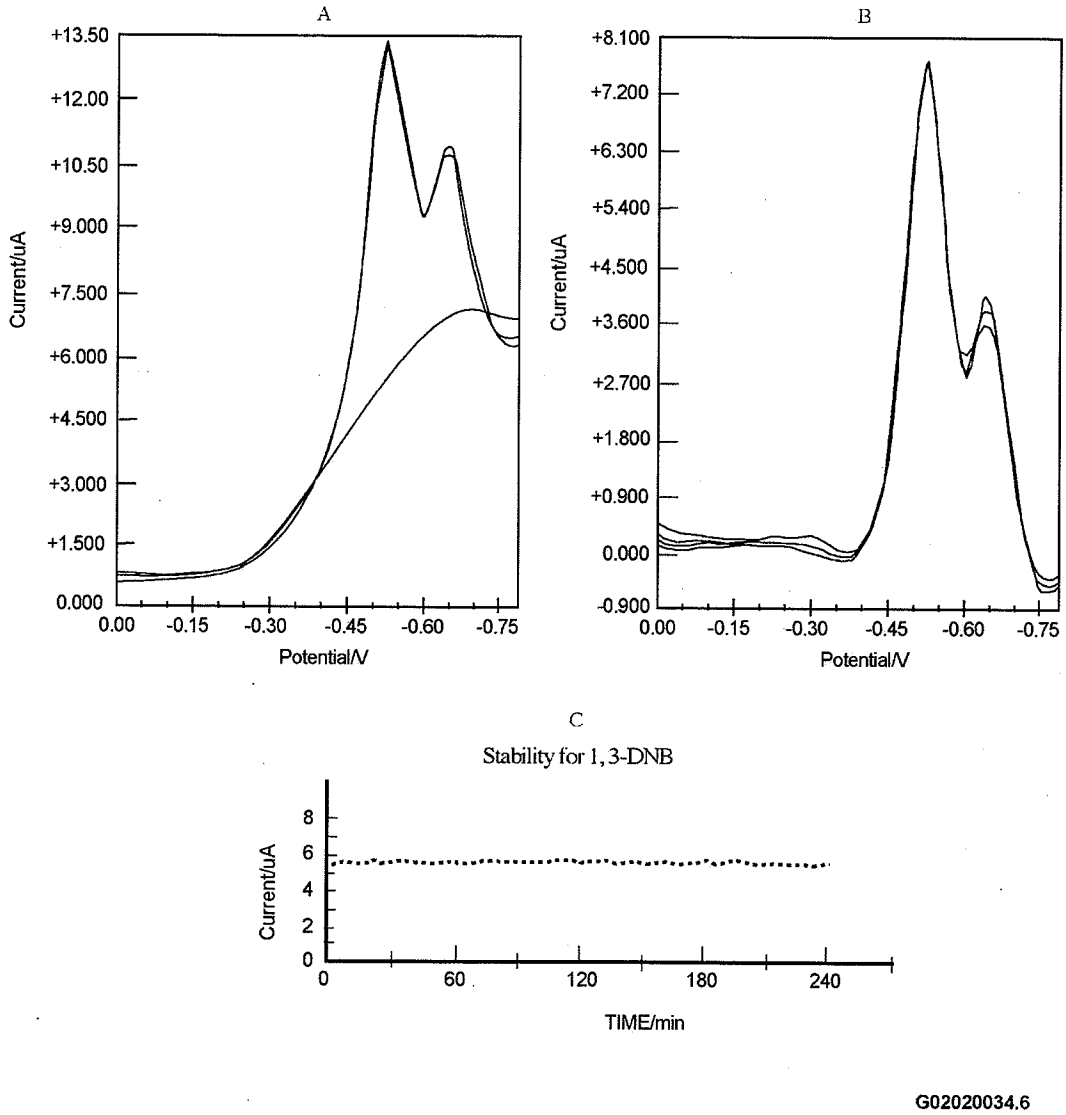

Figure 10. Fifty Repetitive Measurements of 2 ppm 1,3 DNB Using Conventional (A) and Subtractive (B) Modes, with the Resulting Stability Plot (C)

2.5 Deployability

The in situ probe used for this study was specifically designed to be installed directly into existing groundwater monitoring wells with diameters of 1.5 inches or greater. As this technology matures the probe can be miniaturized to less than 3/4 inch. Miniaturizing the probe would allow installation using direct-push technologies, such as a cone penetrometer (e.g., Site Characterization and Analysis Penetrometer System [SCAPS]) or GeoProbe™-type systems. As with any in situ measurement technology, questions arise about the representativeness of the measurement concentration to actual concentrations within the aquifer. During typical well sampling, standard U.S. Environmental Protection Agency (EPA)

protocol requires the removal of three borehole volumes of water or until indicator parameters (pH, specific conductivity, and temperature) stabilize. This approach is reasonable if

- contaminants of concern are redox sensitive, e.g., chromate as chromium(VI)
- unstable due to biological activity, e.g., benzene, nitrates, and phosphates
- volatile, e.g., volatile organic hydrocarbons
- flow conditions within the well are stagnant.

Studies (McCormick et al 1981; Rosen and Dickinson 1969; Spangord et al. 1980; Hale et al. 1979) have demonstrated that explosive compounds in groundwater are extremely stable with respect to biological degradation, and they are not redox sensitive or volatile. Therefore, if sufficient flow exists through a well, the concentration of the explosive compound measured in the well by the in situ sensor should be representative of its concentration in the aquifer, without purging. Sensor placement within a well should be within the screened interval and within a flow field with sufficient flow to be self-purging. Placement of a sensor into an aquifer using direct-push technology is significantly less invasive than installation of a monitoring well. Typically, with direct-push technology, the sensor is installed and the formation is allowed to collapse around the probe. The flow field is minimally perturbed and quickly re-establishes around the sensor. The installation of a sampling point using this approach is clearly favored over installation of a new monitoring well, both from cost perspective and representativeness of the measurement to aquifer conditions.

Although the in situ sensor is easily deployed, there remains the need to characterize (or pre-characterize) groundwater being monitored by the sensor. Regardless of the method used to access the groundwater (monitoring wells or direct-push technologies), characterization of the groundwater will be required at the sampling location. Characterization is critical to identify the specific explosive compounds, nitro degradation products, and their concentrations. Groundwater samples can be collected in any groundwater monitoring well before installation of the sensor and annually to verify results measured by the sensor system. Groundwater samples can be collected with a bailer through the cone rods before installation of the sensor. The cone rod with a screened interval below the water table can be left in place and the sensor can be inserted down the center of the rod into the screened interval. Water samples can routinely be collected by removing the sensor and dropping a bailer below the water level. The sensor can be recalibrated and returned or replaced if necessary. These recommendations for characterization are based on experience with state and federal regulators. Most regulators insist that verification sampling occur initially, and on an annual basis, from the monitored wells or point. Pre-installation sampling and verification sampling at the sampling point should not affect the utility of the sensor, but will result in a longer payback period for return on investment.

3.0 Conclusions

The results of this study demonstrate that remotely-deployable submersible sensors are capable of monitoring explosive compounds both temporally and spatially in groundwater and can be more cost effective than conventional sampling and analysis. Such new remote-sensing capability can bring significant changes to the way in which nitro-based explosives are monitored. At this time, this technology can be deployed in standard groundwater monitoring wells that are 1.5 inches or greater in diameter. Future modification of the sensor probe could decrease the probe size to less than 3/4 inch to accommodate installation with minimally invasive direct-push technologies, such as cone penetrometer or GeoProbe™ system. Furthermore, the sensor measurement frequency can be easily changed from a remote location, enabling the investigator to tailor the measurement cycle to the speed at which the parameter in question is or may be changing.

The measurement of nitroamine explosives will require the removal of oxygen from the samples to provide selectivity and sensitivity similar to that of nitroaromatic explosives. The presence of nitro-degradation products from explosives interferes with estimates of the explosive concentrations measured by the in situ sensor. To deal with this, however, results from pre-characterization of groundwater samples and annual sampling can be used to estimate the bias caused by their presence in the sample and aquifer.

The premise investigated in the proposal for this SEED SERDP project holds true. The use of sensors to remotely monitor organic explosives has significant technical and potential cost savings over the traditional sampling and analysis approach. Coupling of modern electrochemical detection principles with recent advances in remote sensing has led to powerful and compact analytical devices for real-time monitoring. The new remote sensing capability should bring significant changes to the way in which organic explosives are monitored, and to pollution control and prevention, in general.

4.0 Recommendations

Based on the results of this SERDP SEED project, we recommend future work should use our patented renewable-reagent remote in situ sensor probe (US Patent # 5,942,103), based on microdialysis sampling and in-situ manipulation of the collected sample. The renewable-reagent electrode was not used during this project. The benefits of the renewable-reagent electrode include the ability to internally remove oxygen from the sample cell, deliver an optimal (ionic strength, pH) internal buffer solution, and protect the electrodes from biofouling. The probe also has built-in calibration capabilities.

Measurement of nitroamine-based explosives requires removal of oxygen. The addition of an ionic buffer normalizes the sample matrix to improve precision of the measurement. Also, the use of a membrane-enclosed cell allows for the addition of biocide material to prevent fouling of the electrodes.

Future system improvements include further miniaturization and integration, a built-in microprocessor-controlled electronic control assembly for automatic unattended operation, 'smart' data processing, and signal transmission with warning capabilities. However, longer term studies will be necessary to fully explore the capabilities/limitations of the in situ sensor for long term monitoring of explosives in groundwater.

A continuation of this program to a full SERDP project requires a multifaceted approach. Pacific Northwest National Laboratory (PNNL) and New Mexico State University (NMSU) would again team to refine the renewable-reagent electrode sensor probe assembly. We would begin working with an industrial partner to manufacture prototype sensor probe assemblies. Presently, PNNL is working with two small businesses through the U.S. Department of Energy's Small Business Innovative Research (SBIR) Program. Both of these firms are working toward commercialization of in situ electrochemical-based sensors. These businesses may be interested in a teaming relationship with PNNL and NMSU. These companies have the capability to improve the sensor design, further miniaturize the sensor to fit into small wells, and have been experimenting with improving long-term sensor stability. They also have the capability to incorporate system improvements, such as electronic control assembly, for automated unattended operations, smart data processing, and remote communication for data transfer from the field to an office.

The overall goal of a continued SERDP project would be to develop a prototype sensor system that can be field tested for extended periods of time. Two potential field test sites have been identified. PNNL previously obtained groundwater samples containing explosives from Umatilla Army Depot located in north-central Oregon 30 miles from PNNL. Another option would be to conduct a field test at White Sands Missile Range near Los Cruces, New Mexico (i.e., close to the NMSU location). White Sands has several wells contaminated with explosives.

5.0 References

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Appendix

Project Review Responses

Appendix

Project Review Responses

The project review conducted in November identified several questions to be addressed in the final report. These questions are answered within this report. However, these specific questions and their answers are also presented below.

1. Describe how the sensor would be deployed in the field. Please include a discussion of the type of wells that can be used, well purging, and placement of the sensors.

   Response. The in situ probe used for this study was specifically designed to be installed directly into existing groundwater monitoring wells with diameters exceeding 1.5 inches. As this technology matures the probe will be miniaturized (3/4 inch). The objective is to have the ability to install the in situ probes using direct-push technologies, such as a cone penetrometer (SCAPS) or GeoProbe™ system.

   As with any in situ measurement technology, questions arise about the representativeness of the measurement concentration to actual concentrations within the aquifer. During typical well sampling, standard EPA protocol requires the removal of three borehole volumes of water until indicator parameters (pH, specific conductivity, and temperature) stabilize. This approach is reasonable if contaminants of concern are redox sensitive (e.g., chromate as chromium [VI]), unstable due to biological activity e.g., benzene, nitrates, and phosphates, or volatile organic hydrocarbons), or if flow conditions within the well are stagnant. Explosive compounds in groundwater have been demonstrated to be extremely stable to breakdown by biological activity; they are not redox sensitive, or volatile. Therefore, if sufficient flow exists through a well, the concentration of the explosive compound measured in the well by the in situ sensor should be representative of its concentration in the aquifer, without purging. Sensor placement within a well should be within the screened interval and within a flow field with sufficient flow to be self-purging. Placement of a sensor into an aquifer using direct-push technology is significantly less invasive than installation of a monitoring well. Typically, with direct-push technology, the sensor is installed and the formation is allowed to collapse around the probe. The groundwater flow field is minimally pertabated and quickly re-establishes around the sensor. The installation of a sampling point using this approach is clearly favored over installation of a new monitoring well, both from cost and representativeness of the measurement to aquifer conditions.

2. Discuss the sensitivity and selectivity of the sensor and the goals for further refinement of the sensor.

   Response. The sensitivity (detection limits) of the in situ sensor to nitroaromatic explosives (TNT, TNB, and Tetryl) range from 50 to 100 ppb. Detection limits for nitroamine explosives (HMX and RDX) and nitrocellulose ranged from of 1 to 2 ppm. The peak potential for nitroamine explosives are directly superimposed onto the oxygen peak in the voltammogram resulting in a significant increase in detection limits. The in situ sensor is selective for explosives and explosive degradation products, which contain a nitro moiety on the molecule. The in situ sensor was insensitive to other common co-contaminates such as chromate (Cr^{+6}), nitrates, perchlorate, and trichloroethylene (TCE).

   Based on the results of this SERDP SEED project, for future work we recommend using our patented, renewable-reagent remote in situ sensor probe (US Patent # 5,942,103), based on microdialysis sampling and in-situ manipulation of the collected sample. The renewable-reagent electrode was not utilized during this project. The benefits of the renewable-reagent electrode include the ability to internally remove oxygen from the sample cell, deliver an optimal (ionic strength, pH) internal buffer solution, and protect the electrodes from biofouling. The probe also is very versatile and has a built-in calibration feature. As discussed, measurement of nitroamine-based explosives requires removal of oxygen. The addition of an ionic buffer normalizes the sample matrix to improve precision of the measurement, and the use of a membrane-enclosed cell would allow for the addition of biocide material to prevent fouling of the electrodes. Future system improvements include further miniaturization and integration, a built-in microprocessor-controlled electronic control for automatic unattended operation, 'smart' data processing, and signal transmission with warning capabilities. However, longer-term studies will be necessary to fully explore the capabilities/limitations of the in situ sensor for long term monitoring of explosives in groundwater.

3. Discuss the need for pre-analysis of the samples and how this will impact the utility of the sensor.

   Response. Although the in situ sensor is easily deployed, there remains the need to characterize (or pre-characterize) groundwater being monitored by the sensor. Regardless of the method used to access the groundwater (monitoring wells or direct-push technologies), characterization of the groundwater will be required at the sampling location. Characterization is critical to identify the specific explosive compounds, nitro-degradation products, and their concentrations. Groundwater samples can be collected in any groundwater monitoring well before installation of the sensor, and annually to verify results measured by the sensor system. Groundwater samples can be collected with a bailer through the cone rods before installation of the sensor. The cone/ Geoprobe rod with a screened interval below the water table can be left in place, and the sensor can be inserted down the center of the rod into the screened interval. Water samples can routinely be collected by removing the sensor and dropping a bailer below the water table. The sensor can be recalibrated and returned or replaced as necessary. These recommendations for characterization are based on experience with state and federal regulators. Most regulators insist that verification sampling occur initially, and on an annual basis from the monitored wells or point. Pre-installation sampling and verification sampling at the sampling point should not affect the utility of the sensor, but will result in a longer payback period for return on investment.