

FINAL REPORT – PHASE I

Long-Term Monitoring
For Explosives-Contaminated Groundwater

SERDP Project ER-1298

May 2003

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Nomadics, Inc.

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Groundwater**

Final Technical Report

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Project Background

Military production facilities and other defense installations face enormous challenges in environmental compliance. On some installations, decades of use have resulted in contamination of soil and groundwater with residues of high explosives (HE) and explosive-related compounds (ERCs). For example, there are nearly 17,000 sites on DoD installations that could potentially require environmental cleanup.

While more than 75 percent of the earth's surface is covered by water, less than one percent of all surface water is fresh water that is available for use by the world's population. The vast majority of all fresh water—approximately 96 percent of the world's available reserve—is underground. The United States Geological Survey reported in 1990 that groundwater supplied 51 percent of our country's overall population with drinking water. In some rural areas, as much as 95 percent of the population depended on groundwater sources for their drinking water.

In 1996, the Environmental Protection Agency (EPA) asked states and other agencies to conduct surveys of water quality. The results show that approximately 40 percent of the nation's surveyed rivers, lakes, and estuaries are too polluted for basic uses, such as fishing and swimming. The report, entitled *The Quality of Our Nation's Water: 1996*, concludes:

All levels of government and public and private entities need to work together closely to improve our understanding of the environment and our ability to protect and enhance it. *A critical part of that process is improving the collection and assessment of data.* As the indicators are improved, we should be able to more precisely track changes, both positive and negative, in water quality. The status and trends indicator data will be invaluable for targeting resources and for managing and improving key water quality programs that protect and enhance public health and the environment. *(Emphasis added.)*

Clearly, the quality of our water is a national concern. Furthermore, specific problems may exist at sites that have been exposed to known contaminants. For example, long-term use of energetic materials at defense installations could lead to contamination of groundwater on and near these installations. Because of the large number of DoD sites that are potentially contaminated with HE, and because of the nature of the activities that are (or have been) routinely conducted, monitoring these sites for contamination poses significant challenges. In addition to significant logistical challenges encountered in monitoring some sites, currently used methods for monitoring contamination of

groundwater by energetic materials, such as EPA Method 8330, can be expensive and time-consuming. The monitoring methods employed must also be robust in order to deal with potential interferences from a multitude of sources. Hence, new methods for monitoring contamination of groundwater near sites of use (or manufacture) of energetic materials are needed to enable cost-effective determination of the extent of contamination at these sites. The system described here could facilitate long-term, unattended monitoring of groundwater for contamination by HE and ERCs, resulting in a significant reduction in the costs of monitoring.

Objective

Nomadics was awarded SERDP project CU-1298 to build a prototype TNT groundwater monitoring probe and perform proof-of-concept testing in the laboratory to demonstrate its ability to detect trace amounts of TNT and ERCs in groundwater. Successful implementation of the probe will enable long-term monitoring of groundwater for TNT contamination. The goal is to produce a system that would enable rapid, on-site analysis of HE in groundwater with minimal intervention by users. The data obtained will provide site managers with a cost-effective alternative for monitoring of the extent of energetic material contamination on live fire ranges and formerly used defense sites.

Technical Approach

Explosive residues are introduced into the environment by a variety of activities that occur on DoD training and test ranges. Dud rounds and munitions that undergo both high and low-order detonations all generate some level of environmental contamination. Propellants can also contribute to the contamination problem. When HE and ERCs are released into the environment, these materials partition between soil, air, and aqueous phases. Results from a number of studies on the fate and transport of HE and ERCs in soil have been published in recent years¹⁻³. From these and other studies it has been shown that HE and ERCs in soil can be transported into groundwater through the movement of soil water. These studies suggest that the severity of contamination in groundwater depends on a number of factors including the frequency and duration of use of a range, the type of munitions used, soil type and other environmental factors, and the environmental stability of the explosives in question.

Traditionally, groundwater monitoring has been accomplished by collecting water samples and transporting them to laboratory facilities for analysis. Our approach is to configure a sensitive and selective sensor that detects HE and ERCs into a downhole probe, and to deploy this probe in groundwater monitoring wells. Successful deployment of this system will enable long-term in-situ monitoring for HE and ERCs in groundwater, reducing the need for collection of water samples for analysis in the laboratory.

The sensor platform deployed in the groundwater probe is an adaptation of the Nomadics Fido TNT vapor sensor, originally developed for use as a landmine detector⁴. This sensor was the first trace chemical vapor sensor to demonstrate direct detection of landmine explosive chemical vapor signatures under field conditions. The concentration of TNT in the boundary layer of air near the ground over a landmine is rarely higher than the low to mid parts-per-trillion by volume range, and is often orders of magnitude lower

than this. Hence, sensors with excellent sensitivity are required to detect landmines. The Fido vapor sensor is extremely sensitive, having demonstrated detection of low femtogram masses of TNT in real time without sample preconcentration. Fido achieves this extreme sensitivity through the use of amplifying fluorescent polymers (AFPs) originally developed by our research partners at the Massachusetts Institute of Technology (MIT). Nomadics is the exclusive licensee of these materials for explosive detection applications. A detailed description of the AFP technology is described in Appendix A.

Nomadics developed a version of the AFP-based sensor for use in marine environments. Known as the SeaDog, field tests have shown this sensor to be very promising. The SeaDog, mounted on an autonomous underwater vehicle, was able to detect a plume of TNT in the marine environment at a distance of approximately 50 meters from a source of TNT positioned on the ocean floor. To our knowledge, this is the first time that a chemical sensor has demonstrated detection of a plume of TNT in seawater at significant standoff distance from the source without use of a sample preconcentrator. The sensor used in the groundwater probe is a miniaturized version of this sensor.

The aqueous phase sensor package retains many of the components utilized in the vapor sensor, which is now in its seventh iteration. The electronics package is essentially the same as used in the vapor sensor, with most of the modifications being to the optical and sample handling components of the system. For proof-of-concept testing, a scaled down laboratory prototype of the Nomadics SeaDog was constructed, consisting of all the major components that would be present in a downhole probe. While less than half the size of the SeaDog sensor, the laboratory prototype is not yet miniaturized to the point that it can be inserted into a 2 inch groundwater probe. Rather than focus efforts on miniaturization, more effort was devoted to testing the prototype in the laboratory. With further development, the sensor components can be incorporated into a probe that can be lowered into a 2-inch monitoring well where it can be left for long-term monitoring.

Once the probe is positioned in a monitoring well, samples of groundwater are pumped into a sample analysis chamber. This chamber houses a substrate coated with AFP, enabling rapid detection of TNT and ERCs in water as the water is pumped past the substrate. Binding of target analytes is reversible, so the AFP film is reusable. The response of the sensor is proportional to the concentration of target analytes in the water.

In future implementations of the probe, it is envisioned that response data will be stored in a data logging subsystem consisting of flash memory and a field-programmable gate array (FPGA). When the probe returns to the surface, it remains within the confines of the well, nestled in a specially designed wellhead. Embedded in the wellhead are two induction rings. One is used to recharge the battery in the probe, while the other downloads data from the flash memory. In this way, the probe does not have to be removed from the well, reducing the risk of exposure of personnel to harmful substances that may be present in the well. Because the sensor directly measures the presence of explosives, no reagents or other consumables (other than periodic replacement of AFP-coated substrates and a sorbent cartridge that will be replaced during routine

maintenance) are required and the analysis can be performed on site within minutes of collecting the sample. Data analysis can be completed in the field, reducing the need to ship samples to a lab for analysis. This would likely result in substantial savings of money and time.

Data from future implementations of the probe could be recovered in a number of ways. A person on-site can download it directly from the wellhead. However, further savings can be realized by remotely monitoring the wellhead, either by connecting the wellhead to phone lines, to a local area network, or to the Internet. Such connections can be made with landlines or via wireless links. Thus, data from the probes can be collected without anyone visiting the site. With the addition of a programmable controller for the winch system, the proposed approach offers long-term unattended monitoring. The probe is automatically lowered to a desired depth, where data is collected and stored. During any given sampling cycle, the probe may take readings at several depths. When the sampling is complete, the probe returns to the surface where the batteries are recharged and the data is downloaded for later on-site recovery or remote transmission. Battery life will support years of daily sampling. For sites where electrical power is not available, solar panels can be used to recharge system batteries. The only required scheduled maintenance would be periodic replacement of the probe sorbent traps and AFP-coated substrates. The longevity of these items will depend on the frequency of sampling and environmental conditions, but several weeks of sampling should be easily achievable even with daily sampling.

Hence, the prototype system supports a sampling concept that could greatly reduce the life cycle costs of groundwater monitoring. And, with additional development it is likely possible to develop probes capable of monitoring multiple analytes, including other explosives such as RDX and HMX.

Project Accomplishments

Modification of AFP Films for Enhanced Downhole Operation

To date, 25 different AFPs have been synthesized for use in explosives detection applications. These polymers were synthesized either by our collaborators at MIT, or in our Cambridge, Massachusetts polymer laboratory. As previously mentioned, some of the polymers contain binding sites that are engineered to be the electrostatic mirror image of target analytes. This increases the strength of electrostatic interactions between the polymer and target analytes, increasing the value of the analyte binding constant (K_b). The detection limit of the AFP-based vapor sensor is approximately three orders of magnitude lower than for the aqueous phase sensor, primarily due to differences in the partition coefficients for TNT to the polymer from the two different phases. In order to increase the sensitivity of the sensor for aqueous phase sensing, work is ongoing to increase the affinity of the polymer films for TNT. Two approaches are being investigated. The first approach is to modify the chemical structure of the AFP to increase the affinity of the polymer for TNT. Polymer synthesis can be expensive, and is outside the scope of this effort. However, polymer development for underwater sensing applications is ongoing with funding from other sources, and any progress towards

development of new polymers with enhanced sensitivity for aqueous phase sensing will be leveraged for the groundwater sensor.

An approach to increase the affinity of AFP films for TNT is that of blending other materials into the AFP films to increase the retention of TNT. Other polymers such as polyisobutylene and polystyrene have been mixed into AFP films. These polymer blends exhibit significantly enhanced retention of TNT in the Fido vapor phase sensor. Preliminary results indicate that the retention of TNT by these polymer blends in water does not appear to be as pronounced as in the vapor phase. Marginal improvements in aqueous phase sensor response have been observed with polyisobutylene blends. Work in this area is ongoing.

One significant problem encountered with the use of AFP for sensing of TNT in water is that of delamination of the polymer films from the optical substrates onto which they are coated. Early experiments were adversely affected by film delamination from substrates shortly after immersion into water. This problem has been overcome using chemically modified AFPs that covalently link to the substrates. The alkoxy side chains of the polymer have been functionalized with organosilanes that covalently link to the substrate, resulting in polymer films that do not delaminate when placed in water. The polymer chains also cross-link, resulting in films that are much more robust than films made from unmodified AFPs. A significant decrease in sensor sensitivity (a factor of 10) was observed during initial testing of these films. Optimization of the films has improved the loss in sensitivity to a factor of two, which is a five-fold improvement over the response of the first silanized films prepared and tested. The enhanced stability of the films may be an acceptable tradeoff for long-term monitoring applications in which the polymer films remain immersed in water for long periods of time. Optimization of the silanized films is ongoing in an effort to further reduce the loss in sensitivity of the silanized films relative to non-silanized films.

Design Of The Sensor Head And Sample Handling System

Because the sensor measures a change in emission intensity from the polymer films upon binding of TNT, a stable baseline emission intensity reading must be obtained prior to introduction of sample possibly contaminated with TNT or ERCs. This would normally be accomplished in the laboratory by flowing a blank sample of water through the sensor to obtain a baseline emission reading. The sample to be analyzed would then be introduced into the sensor, and any change in polymer emission due to binding of a target analyte measured. This approach is not feasible in a groundwater probe for several reasons. First, the need to store clean water in the probe for use in establishing a baseline reading is simply not feasible due to the large volume of water that would have to be stored in the probe to enable long-term monitoring. The water could be pumped to the sensor from a reservoir outside the well, but possible contamination of the sample as it passes through the supply tubing connecting the probe to the reservoir could be an issue. In addition, the baseline reading should ideally be established using water that contains all constituents found in the groundwater being analyzed (except for HE or ERCs).

A schematic of the system is shown in Figure 1, while the sensor laboratory prototype is shown in Figure 2. The approach taken to obtain a blank sample is to strip molecules of HE and ERCs from a sample of groundwater by passing the sample through a sorbent trap (activated charcoal) that strongly binds (irreversibly) target analytes. This is achieved by opening the intake and exhaust valves to allow the system to fill with groundwater from the well. The valves are then closed, and the water in the system is recirculated through the trap until target analytes are stripped from the sample. Once the blank is stripped of target analytes, the baseline response is recorded. After the baseline is recorded, the valves are then reopened, expelling the blank sample while replacing it with fresh sample from the well. During sample analysis, water is not recirculated as during blank generation. Rather, sample is drawn through the system and expelled back into the well after passing through the trap (filter). Upon introduction of sample into the sensor volume, a reduction in emission intensity from the polymer signals the possible presence of TNT or an ERC. The reduction in emission intensity is proportional to the concentration of target analyte in the sample. The cycle is then repeated as required.

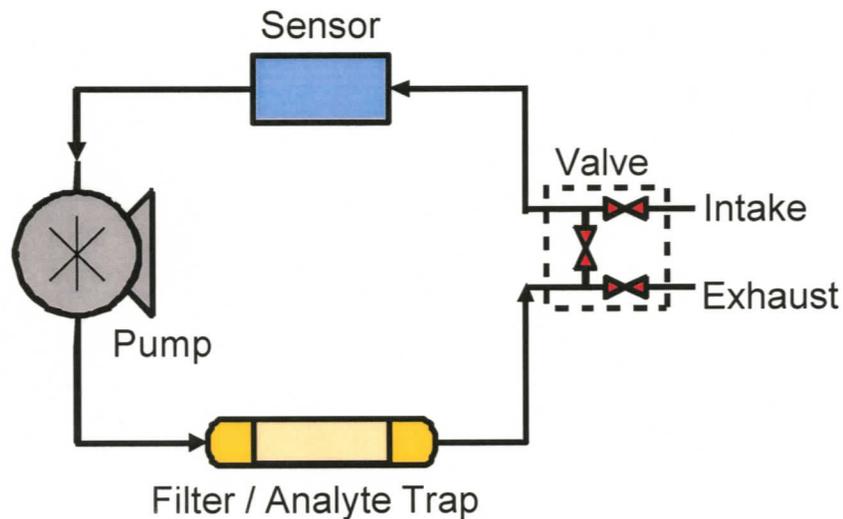


Figure 1. Schematic of the Flow System

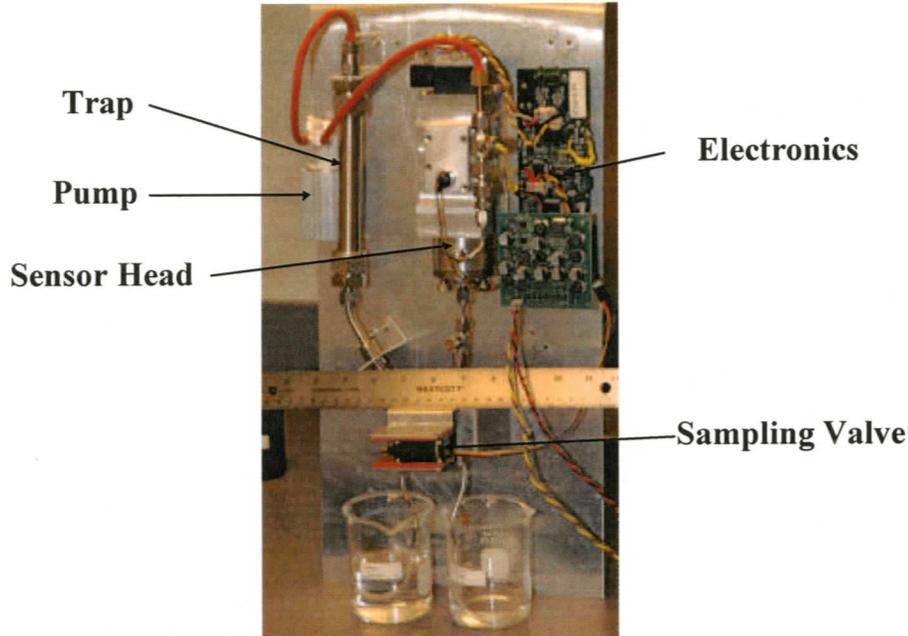


Figure 2. Laboratory Prototype Groundwater Sensor

The charcoal filter is a consumable item that will be replaced during routine maintenance of the system. Although not measured, the traps have a relatively large breakthrough volume, enabling the traps to be used for many analysis cycles.

In order for the AFP films to respond, TNT must bind to the films. When a fluid flows past the AFP film in the sensor, a laminar boundary layer of fluid is established at the surface of the polymer-coated substrate. Molecules of target analytes must diffuse through this boundary layer in order to be detected. If the fluid is air, molecular diffusion in the air is rapid, resulting in efficient mass transport of TNT to the AFP films.

However, in water the molecular diffusion rate of TNT is in excess of three orders of magnitude slower than in air. Hence, as water containing target analytes flows past the AFP film, most of the analyte in the sample does not have time to diffuse from the bulk of the sample and through the boundary layer to the AFP film where it can be detected before being swept out of the sensing volume. Efficient mass transport of target analyte molecules from the bulk flow across the boundary layer to the AFP results in a sharper, more intense response upon introduction of analyte.

Hence, efforts to enhance the mass transport of analyte to the AFP films were undertaken. Flow simulations for several candidate flow cell geometries were investigated. The design that was eventually constructed consisted of an AFP film coated on a 10-mm diameter glass substrate positioned inside the flow cell. Opposite the AFP-coated substrate is a metal plate held in close proximity (a gap of 0.010 inches) to the AFP film. Water is introduced at the center of the plate through an inlet hole oriented perpendicular to the AFP-coated substrate. Water flows through the hole in the center of the cell, striking the AFP film and then flowing radially outward toward the edges of the cell,

exiting through a flow channel at the edges of the substrate. The small gap between the plate and the AFP coated substrate minimizes the diffusion distance for molecules of target analyte entrained in the flow of water through the cell. This increases the probability that a given molecule of target analyte will impinge on the AFP film, increasing the mass transfer efficiency and sensor response. This geometry resulted in an enhancement in response kinetics and reduced the amount of time required for the sensor to achieve maximum (i.e., equilibrium) response to a sample.

Figure 3 describes the optical design of the sensor head. Light from a blue light emitting diode (LED) passes through a 10 nm bandpass filter centered at 410 nm, and the light exiting the filter is focused by a lens onto an AFP-coated glass substrate. Light emitted from the polymer passes back through the same lens and is focused onto a 50 nm bandpass filter with a center frequency of 475 nm. This filter blocks stray light from the excitation source. Light passing through the second bandpass filter is then refocused by a second lens onto a photodetector (a small photomultiplier tube).

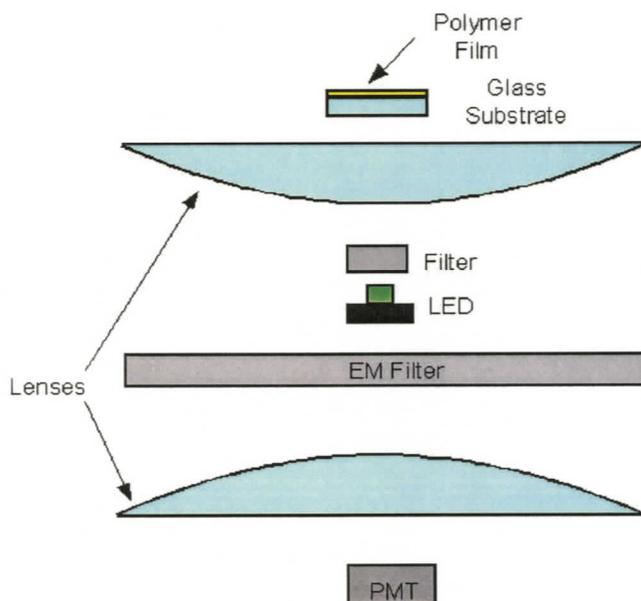


Figure 3. Optical Design of Sensor Head

Design And Integration Of The Signal Processing Circuitry

The prototype sensor used off-the-shelf and existing designs which allowed rapid prototyping. The processing circuitry measures the fluorescence of the sensor prior to and after presentation of the sample to the sensor. These readings are compared. The sensor and processor are electronically and mechanically integrated into a single, small package. The software displays the photon counts from the PMT at a data rate of 20 points per second. The processor displays a real-time graphic representation of the data that allows quick interpretation of the occurrence of a detection event. In future designs,

rather than displaying the data graphically, the data will be logged for post-analysis when required.

Configuration Of The Sensor For Deployment In A Downhole Probe

As can be seen from Figure 2, the system has not yet been configured for deployment in a downhole probe. Rather than focusing on miniaturizing the system for insertion into a probe, most of the effort in this project was focused on designing the sample handling system and sensor flow cell. The remainder of the effort was to perform proof-of-concept testing of the system in the laboratory. Nevertheless, the sensor components are approximately half the size of the SeaDog sensor from which the groundwater sensor was largely derived. In the next project phase, circuitry for the sample collection subsystem, sample chamber, filter / trap, and processor interface will be miniaturized to allow deployment in a downhole probe. Nomadics has experience in deploying downhole sensors in probes that fit in standard 2-inch monitoring wells, having previously developed volatile organic compound and general water quality probes for other government and industrial customers. Figure 4 is a conceptual drawing illustrating the system components deployed in a probe configuration.

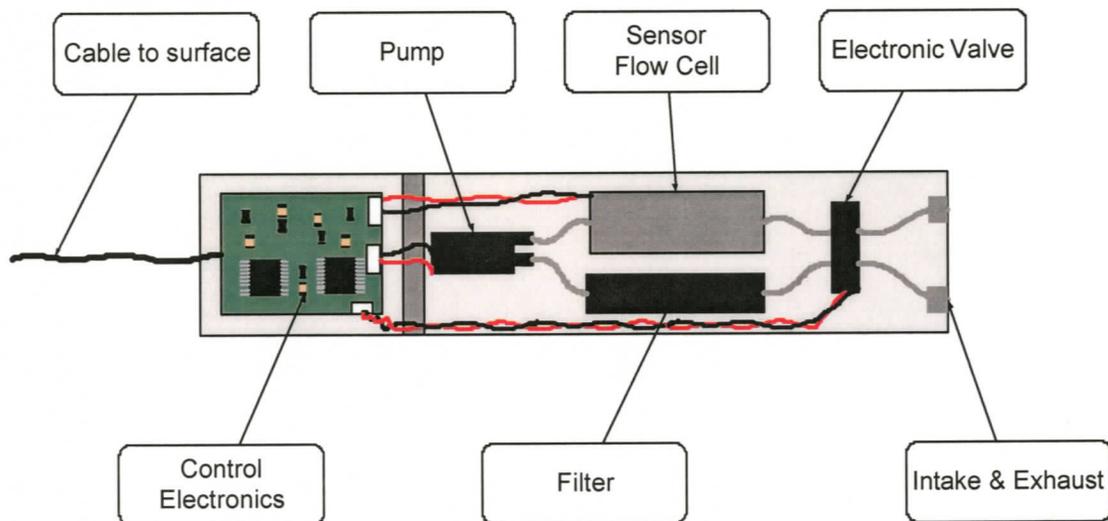


Figure 4. Layout of the Downhole Probe

Laboratory Proof-of-Concept Testing

Using the laboratory prototype shown in Figure 2, tests have been conducted to evaluate the performance of the sensor. To ensure reproducible sample introduction, a syringe pump was used to inject samples into the system. Use of the syringe pump enabled injections of precise quantities of TNT solutions at reproducible sample injection rates. The sensor inlet line was fitted with a Swagelok tee fitting equipped with a septum to allow injection of TNT solutions via the syringe pump. The other leg of the tee was fitted with a short stainless steel inlet tube that was immersed in a beaker of water. This line was used to deliver bulk quantities of water to the sensor. When TNT solutions were

injected, the pulse of TNT solution was quickly dispersed into the bulk flow of water passing through the tee. By carefully monitoring the bulk flow rate of water through the inlet tube and knowing the injection rate of TNT standard solution via the syringe pump, it was possible to estimate the concentration of TNT delivered to the sensor. Waste was discharged from the system into a separate disposal vessel.

TNT solutions were prepared in either deionized or tap water by serial dilution of a standard aqueous TNT solution. In order to limit degradation of the solutions, they were stored in amber glass bottles in a refrigerator, and were freshly prepared twice weekly. All TNT solutions were analyzed by gas chromatography (GC) with an electron capture detector (ECD) prior to use in order to validate the concentration of the solutions. Because direct injections of water into the chromatograph cannot be performed, the TNT was extracted from the solution into toluene prior to injection into the chromatograph. The extraction was accomplished by vigorous mixing of 1 mL of TNT solution with 1 mL of toluene in a 4 mL glass vial. Samples were mixed for one minute using a vortex mixer. After the water and toluene were allowed to phase separate, the toluene layer was decanted from the extraction vial and filtered through a syringe filter into an autosampler vial. The toluene extracts were then analyzed using an HP 5890 GC/ECD system.

Sensor Calibration / Sensitivity Testing

Sensor calibrations were performed by injecting pulses of aqueous TNT at known concentrations and volumetric flow rates. Because the pulse of aqueous TNT was injected into a stream of clean water, the injection pulse was diluted by mixing with the stream of clean water. By varying the concentration of the TNT solution, and the volumetric flow rates of the syringe pump and the pump in the sensor, pulses of aqueous TNT spanning a range of concentrations were introduced into the sensor and were analyzed. For convenience, the flow rates of the syringe pump and system pump were always maintained at the same value. In this way, dilution of the pulse of TNT injected from the syringe pump was minimized. Since the pulse of TNT was injected into a tee in the flow line, when the syringe pump delivered a pulse of aqueous TNT into the system the flow of clean water through the other leg of the tee effectively dropped to zero as the syringe pump was activated. When injection of the TNT pulse was completed, clean water was again drawn through the inlet leg of the tee at a flow rate equal to that established by the system pump. Hence, a constant volumetric flow rate of liquid was cycled through the system at all times. Various flow rates and syringe pump pulse times were used to determine optimum system response values. The system pump functioned over a flow range of 5 to 15 mL per minute. As the pulse duration of the syringe pump was increased, the magnitude of the sensor response increased as the response of the system approached equilibrium. For pulses of sufficient duration, the sensor quenching response would essentially plateau a constant value as the system reached equilibrium.

Figure 5 is a series of sensor response curves generated at a flow of 10mL/min while varying syringe pump pulse times. Because mass transport of TNT due to molecular diffusion across the boundary layer is relatively slow, in order for equilibrium between sorbed TNT and bulk aqueous phase TNT to be reached, injection pulses with durations

in excess of 30 seconds were required. Depending on the size of the syringe and the injection rate selected, the syringe volume was not adequate to maintain injection pulses of sufficient duration for the system to reach equilibrium quench values. At concentrations of TNT lower than approximately 50 parts-per-billion by mass (ppbm), the response of the system became erratic due to reasons that have not been positively identified. Hence, the lower limit of detection of the system was near 50 ppbm for TNT. As expected, the response of the sensor increased with increasing pulse times.

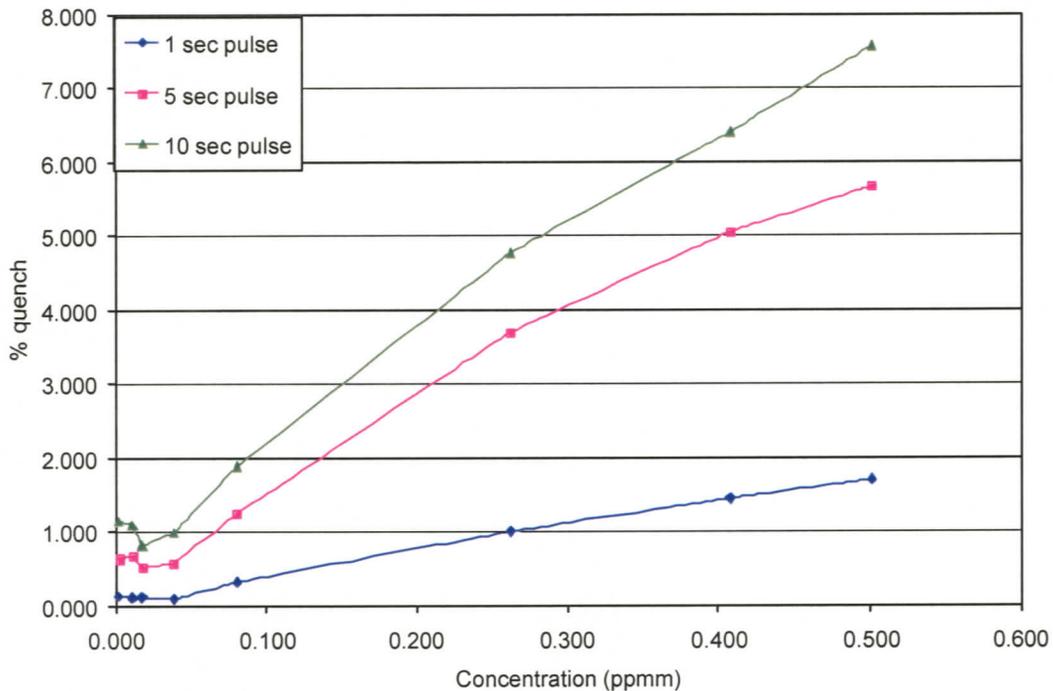


Figure 5. Calibration Curve at 10mL/minute for Various Pulse Times

The sensor response to varying flow rates is shown in Figure 6. While not shown, the calibration curves for the 1-second and 10-second pulse times are similar in trend, again with longer pulse times resulting in larger sensor responses. Due to the design of the sensor sensing volume, as the flow rate of water through the sensor increases, the thickness of the boundary layer of water that TNT must diffuse across becomes thinner, reducing the time required for TNT to diffuse across the boundary layer in order to be sensed. This accelerates the response rate of the sensor, resulting in greater response per unit time for higher flow rates.

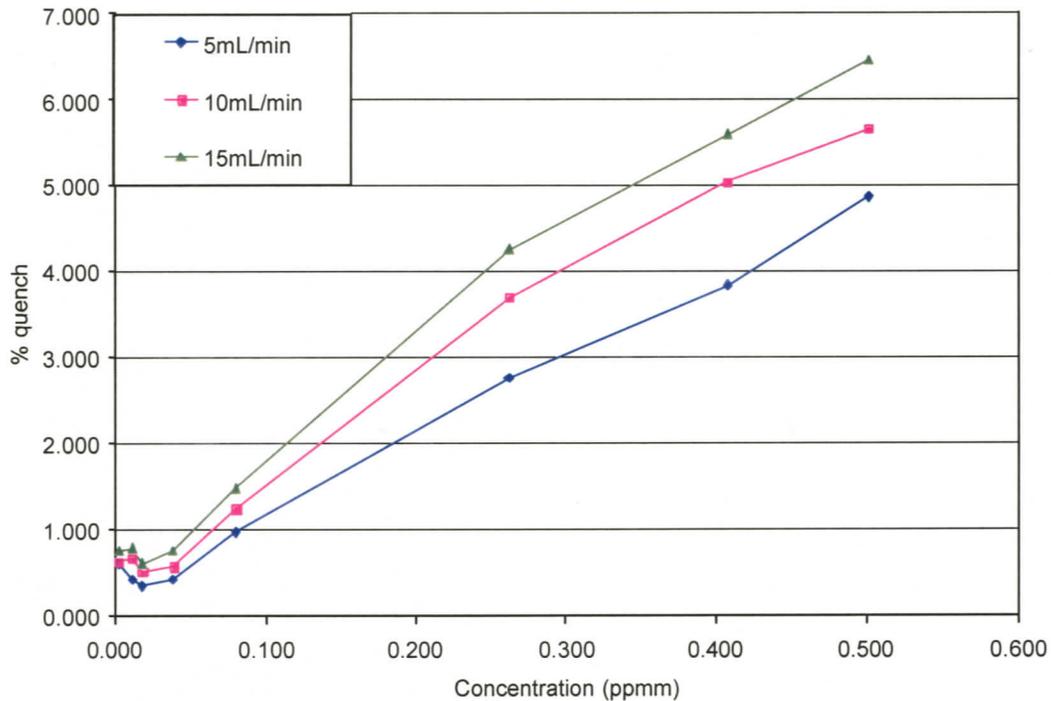


Figure 6. Calibration Curve for a Five-Second Pulse Time and Varying Flow Rates

Figure 7 illustrates the sensor response as a function of flow rate for varying pulse times of a 250 ppbm solution of TNT. While both flow rate and pulse times affect sensor response, increasing the duration of the pulse has a greater effect on sensor response than increasing the flow rate. Figure 8 illustrates sensor response as a function of pulse time for varying flow rates of a 250 ppbm TNT solution. As can be seen in Figure 8, the response as a function of pulse time is not linear as the response approaches equilibrium. For longer injection pulses, the response for all three curves would eventually become constant with time as the response reach equilibrium.

Figure 9 is a plot of sensor response (% Quench) as a function of aqueous TNT concentration. The sample flow rate was 10 mL/min, with an injection pulse time of 10 seconds. The data points represent the average response to three injections at each concentration. The range of responses is also plotted for each concentration. While the noise of the sensor (0.05% typical) should be adequate to resolve responses as low as 0.1% quench (at a 2:1 signal-to-noise ratio), the erratic nature of the response at low concentrations (as evidenced by the data shown in Figure 6) currently limits sensor minimum detection limits to about 20 to 50 ppbm. Once this issue is resolved, the limits of detection of the sensor should be in the single ppbm to upper parts-per-trillion range.

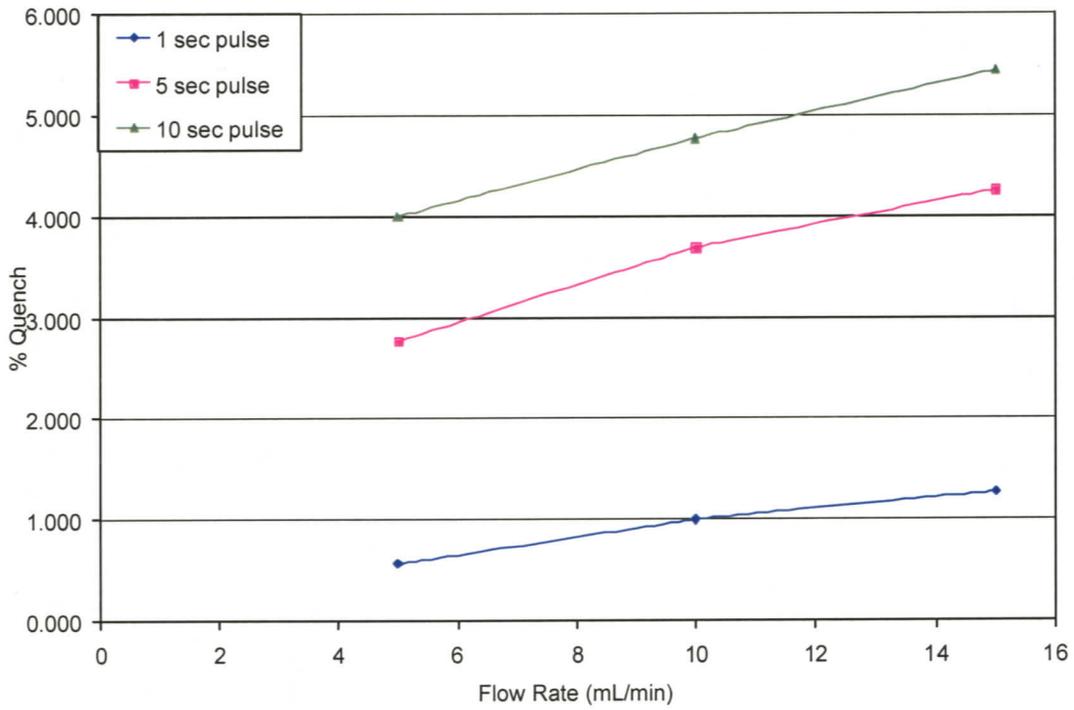


Figure 7. % Quench as a Function of Flow Rate for Varying Pulse Times of a 250 ppm TNT Solution

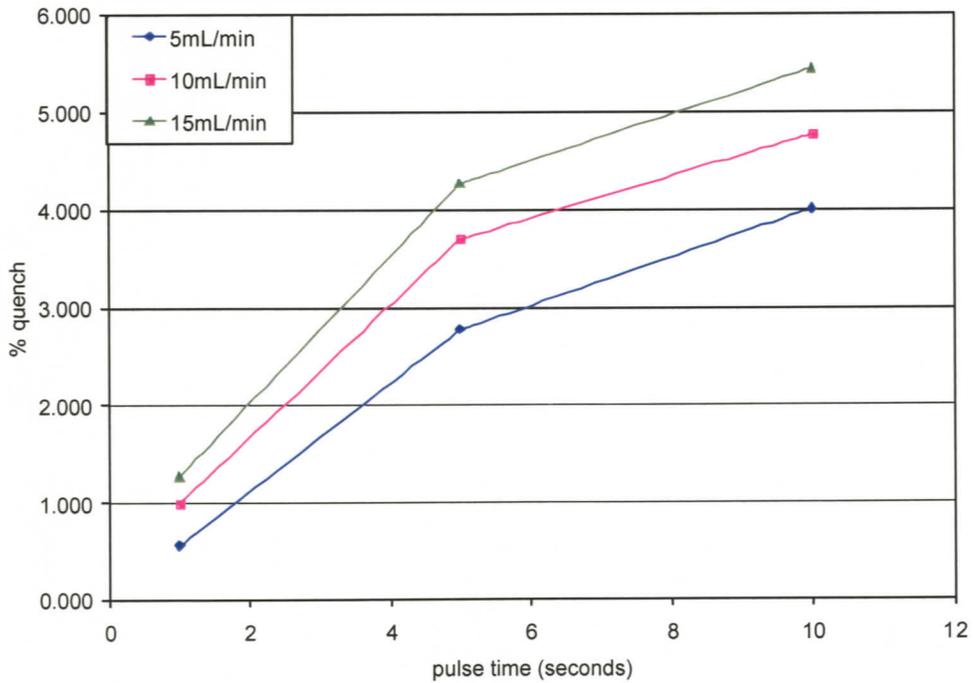


Figure 8. % Quench as a Function of Pulse Time for Varying Flow Rates of a 250 ppm TNT Solution

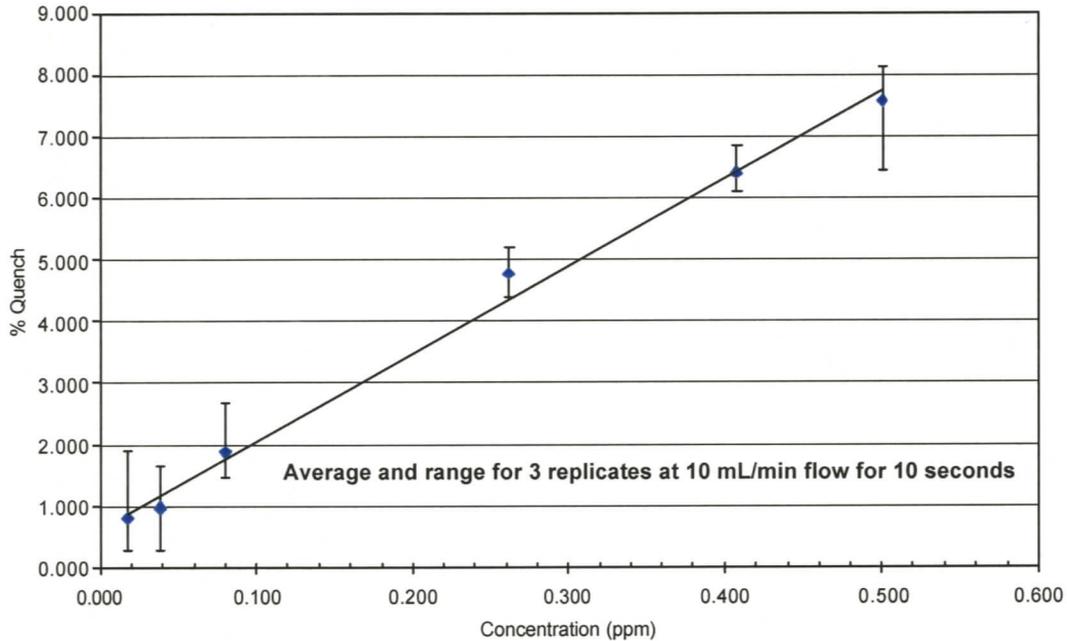


Figure 9. Sensor Response as a Function of Aqueous TNT Concentration

Sensor Response to Fluctuations In Temperature

Since fluorescence is temperature dependent, fluctuations in the temperature of an AFP film will result in shifts in emission intensity. In general, AFP films in air exhibit a 0.1% change in emission intensity per degree change in absolute temperature, with the emission decreasing at higher temperatures. Other AFP-based sensors developed by Nomadics have temperature control capabilities to maintain stable sensor temperatures but since the temperature in a monitoring well should not fluctuate rapidly, the sensor does not at present include temperature control circuitry. Controlling temperature greatly increases sensor power consumption and complexity. Since the temperature of the system deployed in a groundwater monitoring well is not expected to fluctuate rapidly at a given deployment depth, temperature control has been omitted. Care was taken to limit temperature fluctuations during laboratory experiments, but direct temperature control was not attempted. However, TNT solutions and water were allowed to thermally equilibrate to room temperature for several hours prior to experiments being conducted.

Response To Chemical Interferents

While there may be only one principal contaminant at a given site of environmental contamination, there is a possibility that groundwater could be contaminated by a multitude of substances. There is also the possibility that naturally occurring substances in groundwater could induce sensor responses if a sensor does not have adequate selectivity. AFPs are very selective for target analytes, but the potential for chemical

interferents cannot be ruled out. As discussed earlier in this report, the probability of response to interferents is low due to the excellent selectivity of the polymer. Because it is impossible to test a sensor against every potential interferent, two commonly encountered substances in groundwater on DoD sites (perchlorates and trichloroethylene) were selected for testing.

Solutions of trichloroethylene (TCE) and potassium perchlorate were prepared and introduced into the sensor using the syringe pump arrangement previously described. Figure 10 shows the response to a saturated aqueous solution of TCE. It can be seen that the emission intensity of the polymer increases by approximately 3%, rather than decreasing as in the case of a TNT response, as in Figure 11. Figure 11 is the response of the sensor to a 10 second pulse of 100 ppbm TNT solution injected at a flow rate of 10 mL/min. The quench followed by a recovery in emission intensity after the pulse of TNT has passed through the sensor is a typical response to TNT. Note that the response to TCE is much different than that of TNT.

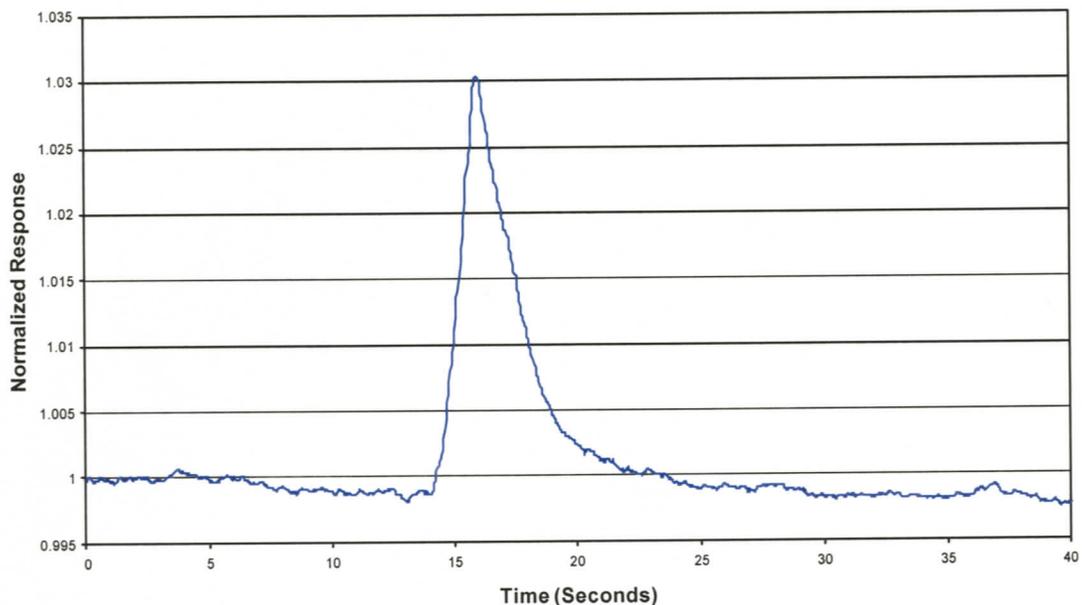


Figure 10. Response to Saturated Aqueous TCE Solution

Figure 12 illustrates the response of the sensor to a mixture of saturated aqueous TCE containing 250 ppbm of TNT. A response indicative of TCE is noted initially, followed by a quench indicative of TNT. This more complex response curve can be explained in terms of the relative affinity of the AFP for the two analytes. Initially, the response to TCE dominates over the response to TNT. However, once the injection pulse ends, the TCE quickly desorbs from the AFP film and the emission intensity quickly drops towards baseline. However, TNT bound to the film has a higher affinity for the AFP, resulting in a longer residence time for TNT on the film relative to TCE. Hence, TCE quickly desorbs while significant TNT remains bound to the film, explaining the initial increase followed by a decrease in emission intensity of the film.

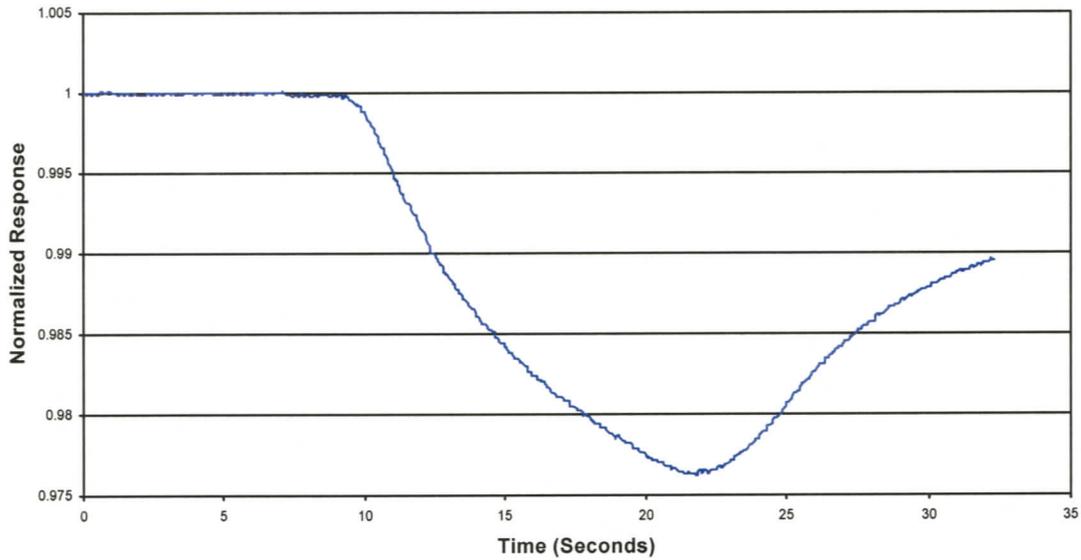


Figure 11. Response to a 10 Second Pulse of 100 ppbm TNT Injected at 10 mL/min

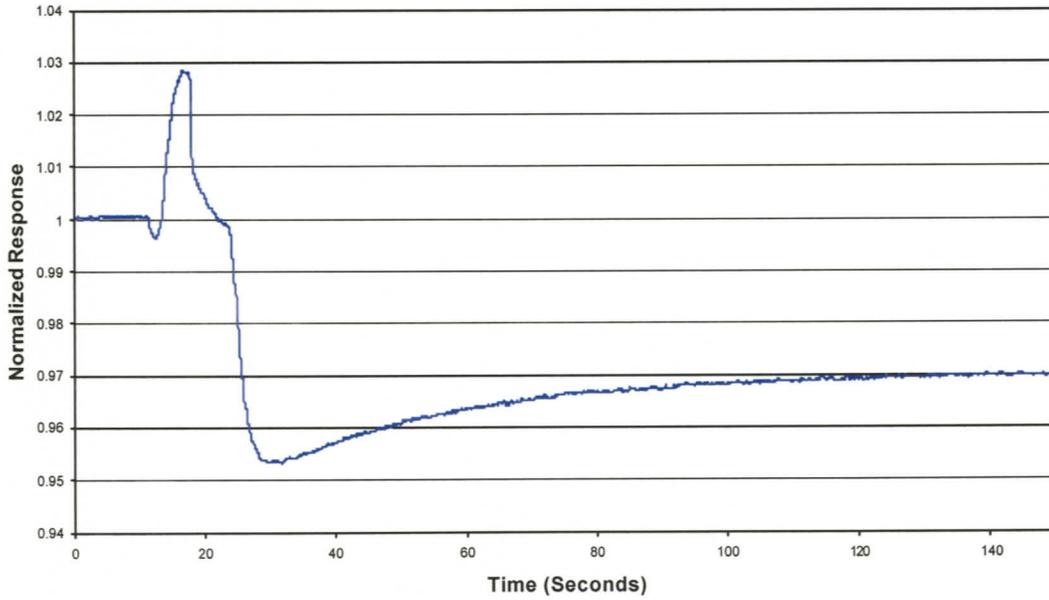


Figure 12. Response to Saturated Aqueous Containing 250 ppbm TNT Solution

It should be noted that the AFP film exposed to TCE still responded to TNT solutions after repeated exposure to TCE, with little evidence of adverse affect.

Similar experiments were conducted using saturated potassium perchlorate solutions. Figure 13 illustrates the sensor response to a pulse of saturated potassium perchlorate solution, with the scale on the y-axis adjusted to match that of Figure 12 for the mixed TCE / TNT solution. As with the response to TCE, a slight increase in emission intensity resulted from injection of potassium perchlorate, but the response was much smaller than that of TCE. Again, polymer films were apparently not adversely affected by exposure to potassium perchlorate, yielding good responses to TNT after exposure to the interferent.

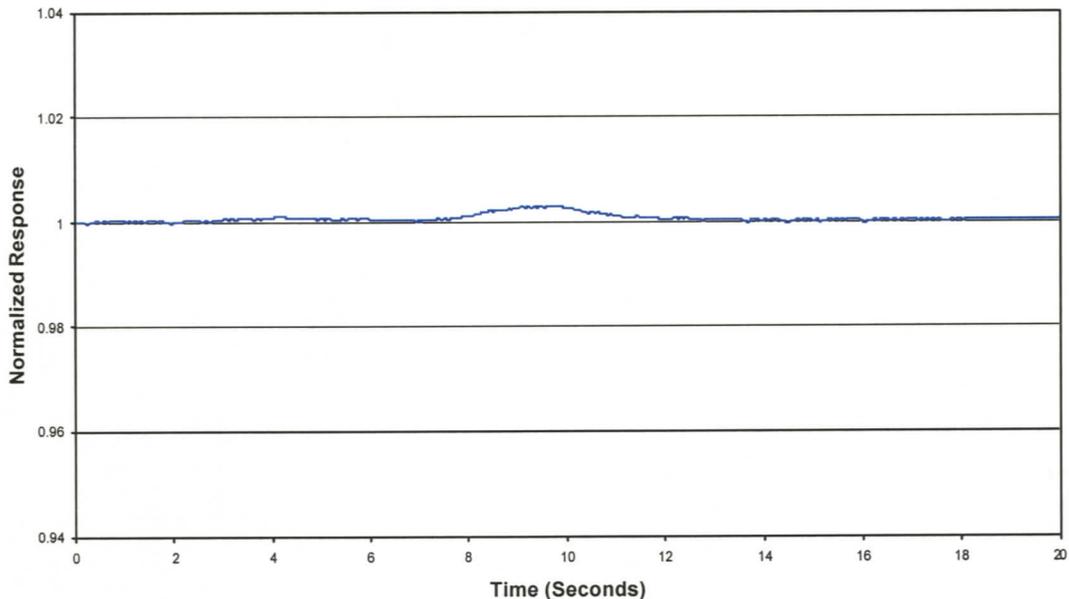


Figure 13. Sensor Response to a Pulse Of Saturated Aqueous Potassium Perchlorate

Polymer Longevity Experiments

The lifetime of an AFP film immersed in water was investigated over time. A film was prepared and installed in the sensor. Initially after the film was installed, the response of the sensor to a 100 ppm TNT solution was recorded. The AFP film was left in the sensor while water was recirculated at 15 mL/min continuously for two weeks. The response of the film to the 100 ppm TNT solution was occasionally every 24 hours over the course of the two-week test period. As can be seen from Figure 14, the brightness of the polymer film dropped by 20% in the first 24 hours, then steadily declined over the period of the test. To generate this chart, the emission intensity over time was normalized to the initial emission intensity. The non-covalently attached AFPs were used for this test. This should represent a worst-case scenario for polymer film delamination, as the spin-cast films used in this test are much less robust than the covalently attached polymer films. It should be noted that the excitation source was not left on continuously during these tests to limit the effects of possible photodecomposition of the film. The excitation source was switched on prior to a measurement being made just long enough for the system to reach a stable baseline (less than five minutes per measurement).

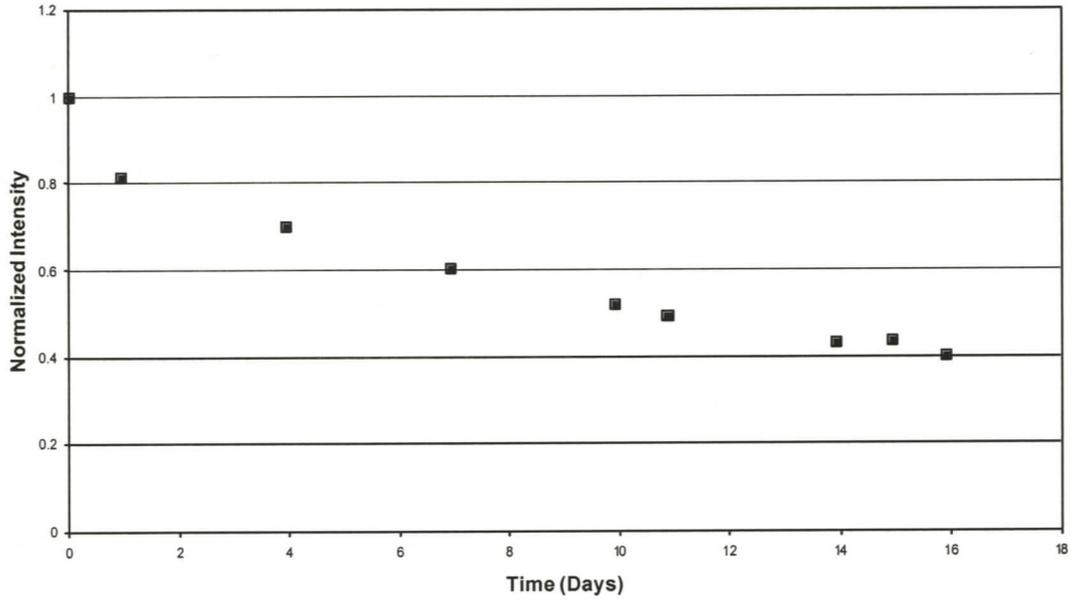


Figure 14. Water-Immersed Polymer Film Brightness Over Time

The response (percent quench) over time behaved erratically (see Figure 15). For the first four days, the response to TNT dropped almost linearly. However, an apparent increase in sensitivity occurred between days 4 and 10, followed by a decrease in sensitivity after 10 days. Over the course of the test, the sensitivity to TNT dropped by approximately a factor of three. The reason for this decrease has not been determined.

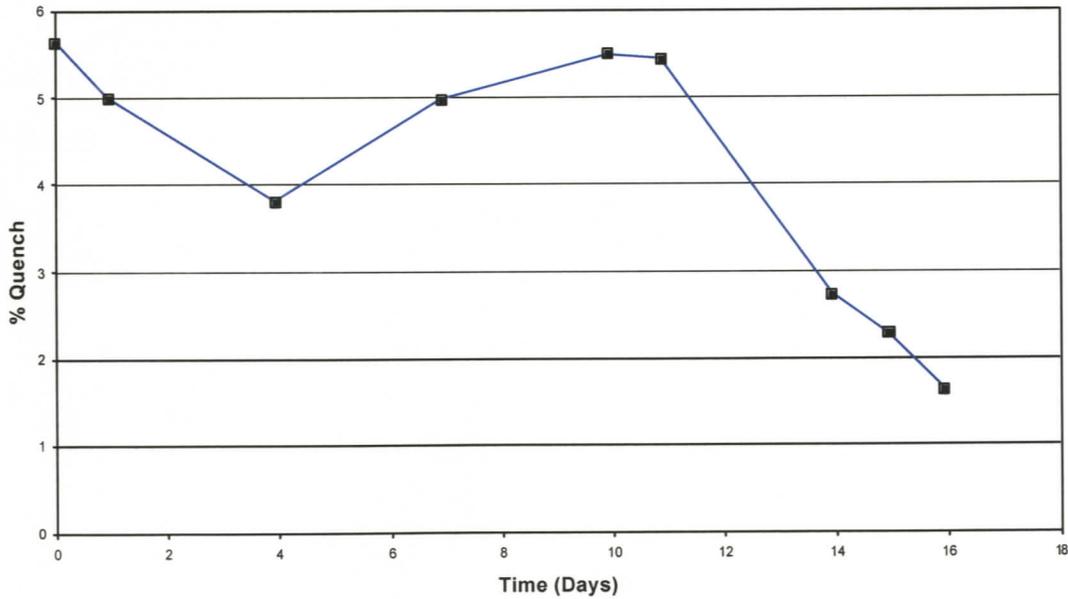


Figure 15. Variation of Sensitivity to TNT Over Time

Summary

The project to date has resulted in the construction of a prototype groundwater sensor that has successfully completed proof-of-concept testing. The probe was able to directly sense TNT in water with lower detection limits of approximately 50 ppbm. Response of the sensor to potential interferents such as saturated aqueous TCE and potassium perchlorate was weak and easily discernable from a TNT response. The sensor was able to detect TNT in the presence of both of these groundwater contaminants often present at DoD sites of interest. The probe was able to operate unattended for two weeks in the laboratory with some degradation in performance, but at the end of the two week period the sensor was still functional and able to sense TNT.

Proposed Future Plans

The prototype groundwater sensor will require some miniaturization in order to fit into a 2-inch groundwater monitoring probe. The integration should proceed smoothly as most of the components used in the prototype will already fit into the probe. Circuit boards will have to be redesigned with a different form factor in order to fit into the probe. The photodetector currently used (a small PMT) is slightly too large, so a smaller photodetector will be required. Alternative sorbent materials should be investigated to improve long-term performance of the analyte trap.

Improvements to the longevity of AFP films should also be pursued. The two week longevity experiments suggest that normal spin cast films of AFP are marginally effective as deployed for long-term monitoring applications. AFP films covalently bonded to the glass substrate are an attractive alternative that should be investigated further and optimized. Other sample introduction methods could possibly be employed to further lengthen the effective useful lifetime of the films. Sampling using solid-phase microextraction (SPME) methods is a possible alternative that would eliminate the need for the AFP film to be immersed in water. Sensing of target analytes upon desorption from the SPME device would occur in the vapor phase rather than directly from the aqueous phase. While more complex, this device could possibly be more sensitive and capable of longer periods between maintenance.

AFPs capable of detecting other substances of interest (RDX, HMX) are being investigated through funding from other sources. If new AFP development efforts produce new AFP materials with sensitivity for these compounds, an effort to incorporate these materials into a probe would be very advantageous. This would require redesign of the sensor sampling volume to accommodate two AFP films (one for nitroaromatics and one for nitramines). Nomadics has already successfully developed a dual channel vapor sensor for nitroaromatics, so this development effort should proceed with minimal risk.

The incorporation of on-board sensor calibration would also be beneficial, enabling performance of the sensor to be verified in-situ.

Once a prototype downhole probe is completed and tested successfully in the lab, field testing of the device would be performed to evaluate the performance of the system under typical conditions. After evaluation of the performance of the device, any necessary improvements warranted by field test data would be pursued.

As previously discussed, probe deployment methods and data logging capabilities could be greatly enhanced in an advanced prototype system. These capabilities will greatly enhance the utility of the probe, making user intervention in the field less frequent. The ability to monitor groundwater contamination remotely without visits to test sites by personnel has many advantages and should result in significant cost savings while providing enhanced monitoring capabilities.

APPENDIX A AMPLIFYING FLUORESCENT POLYMERS

The Nomadics vapor and water-based explosives detection systems utilize a breakthrough technology developed at the Massachusetts Institute of Technology (MIT) by Professor Timothy Swager. Amplifying fluorescent polymer (AFP) technology allows the detection of TNT and related substances at levels below that of the most sensitive commercially-available laboratory instruments. These sensory materials make it possible to detect low levels of TNT and ERCs that may be encountered in groundwater.

The fluorescent polymer materials used in the sensors amplify the fluorescence quenching that occurs upon binding of TNT to films of the materials^{5,6}. In order to achieve this effect, individual fluorescent monomers were linked, forming a polymer with an extended network of conjugated multiple bonds along the polymer backbone. Thin films of AFP materials coated onto a suitable substrate form the sensory element of the Nomadics detection system. These films exhibit high fluorescence and spectroscopic reproducibility.

Structurally, the polymers consist of a conjugated backbone with rigid, three-dimensional pentyptycene groups (see Figure A1). These structural entities minimize undesirable self-quenching that results from overlap of the backbones of the highly conjugated polymer chains (π - stacking). The rigidity and three-dimensional structure of the polymer forms cavities in the films that accommodate small molecules and helps to enhance diffusion of small molecules into the films. The polymer depicted in Figure A1 is only one of over twenty AFPs that have been synthesized for TNT detection, each with slightly different responses to target analytes.

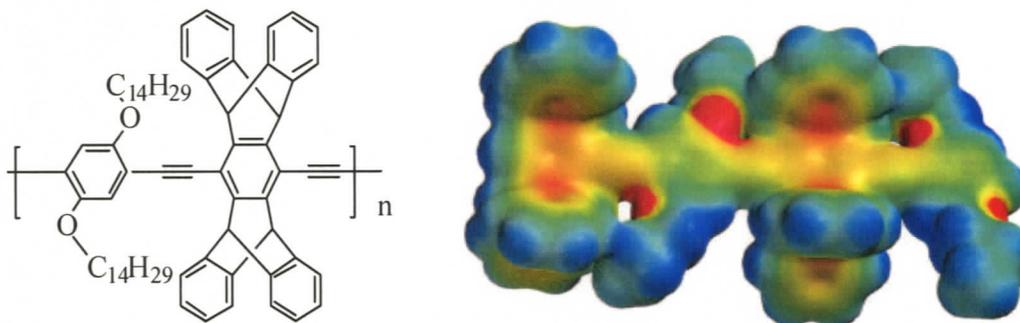


Figure A1. Chemical Structure of a Repeat Unit of an AFP and the Electrostatic Surface of Two Repeat Units of the Same AFP (with Alkoxy Side Chains Shortened)

The electrons in this system are extremely delocalized, enabling the polymer backbone to function as a 'molecular wire'. These polymers exhibit very efficient energy transfer. When thin films of the polymers absorb photons of light, the excitons (i.e., excited state electrons) that are formed efficiently propagate along the polymer backbones and between adjacent polymer chains. Because of the efficiency of exciton migration, a single exciton propagates through many polymer repeat units during its excited state lifetime. The migration rate of the exciton and the lifetime of the excited state determine

how far the exciton may propagate. If either the rate of migration of the exciton or its excited state lifetime is large, the exciton may sample many receptor sites during its lifetime. Eventually, the exciton may transition back to the ground state, resulting in fluorescence. The number of excitation events resulting in fluorescence is given by the expression

$$n = I_a \phi_f,$$

where n is the number of adsorption events that result in fluorescence, I_a is the number of light quanta absorbed, and ϕ_f is the fluorescence quantum efficiency.

When an electron-deficient (i.e., electron accepting) molecule such as TNT binds to the polymer film, a low-energy 'trap' is formed. If the exciton migrates to the site of the bound electron-deficient molecule before transitioning back to the ground state, the exciton will be trapped (a non-radiative process), and no fluorescence will be observed from the excitation event. In effect, since the exciton samples many receptor sites, the probability that the exciton will sample an occupied receptor site is greatly increased. Hence, the probability that a photon absorption event will result in fluorescence is greatly reduced when TNT molecules are present, resulting in an amplification of the quenching response (refer to lower frame of Figure A2).

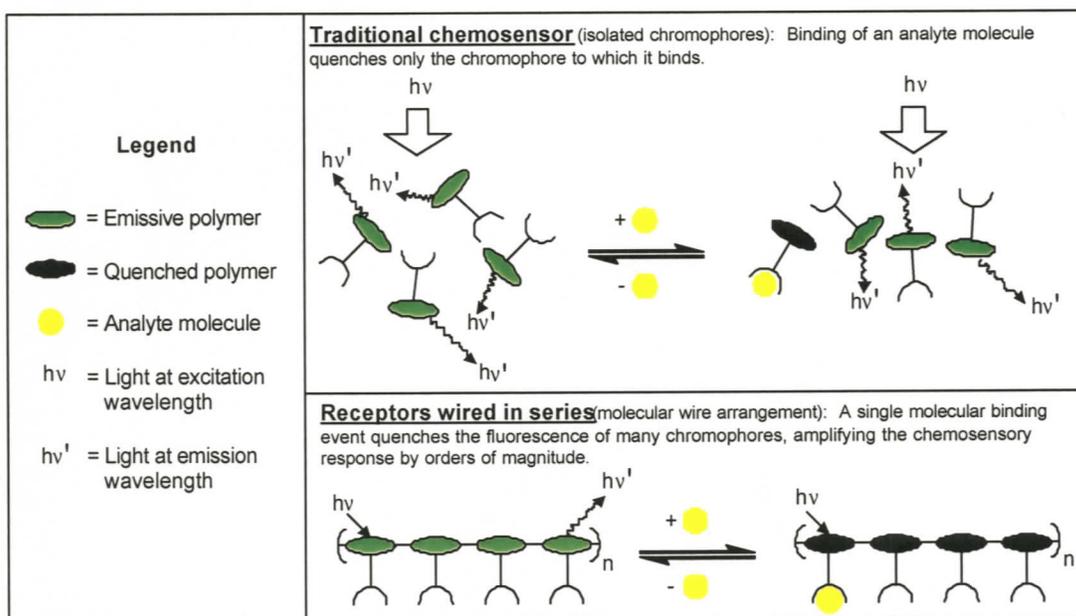


Figure A2. Comparison of Monomeric and Polymeric (Amplifying) Quenching Mechanisms

Individual excitons are not confined to the polymer chain upon which the original photon absorption event occurred. In addition, the excitons follow a 'random walk' trajectory, implying that an exciton can pass through the same polymer repeat unit more than once. However, the amplification effect can be better understood if it is assumed that the migration of the exciton is confined to a single polymer chain, and that the exciton samples every receptor site in the entire polymer chain at least once before transitioning

back to the ground state. If the polymer chain consists of N repeat units, binding of a single analyte molecule to the chain will then result in quenching of N polymer repeat units (i.e., all the repeat units in the chain). By comparison, if the entire polymer chain consisting of N repeat units were broken into N monomeric units, one binding event would quench the fluorescence of only the monomer to which the analyte molecule was bound, resulting in a reduction in emission of only $1/N$. The amplification effect described here is the mechanism responsible for the exceptional sensitivity of the sensor. In practice, the polymers exhibit an effective amplification in response of between 100 and 1000 as compared to conventional (monomeric) quenching mechanisms. The sensitivity of the AFP has enabled development of the Fido series of sensors capable of detecting 10 femtograms of TNT in the vapor phase, and the SeaDog, capable of detecting TNT in the aqueous phase in the low parts-per-billion by mass range.

These polymers are engineered to be preferentially responsive to specific target analytes via three factors that influence the magnitude of fluorescence quenching (FQ)⁵. The first factor is steric constraints. The mechanism for fluorescence quenching is electron transfer from the electronically excited polymer to the quencher. The rate of energy transfer (Forster energy transfer) is greatly influenced by the distance between the electron donor (the polymer backbone) and acceptor (quencher), with the rate varying as the distance between the donor and acceptor to the inverse sixth power. Small molecules such as the target ERCs fit into the cavities in the films and have good access to the polymer backbone. Larger molecules are excluded, greatly reducing their ability to quench the polymer.

The second mechanism providing selectivity is electrostatic complementarity between the polymer and target analytes. It is postulated that the polymers, which are electron-rich, bind reversibly to electron-deficient nitroaromatics through an electrostatic-type interaction. Compounds that have a strong affinity for the polymer (i.e., those that have a large binding constant K_b) are more likely to bind strongly with the polymer. To enhance binding of target compounds, receptor sites that are electrostatic mirror images of the target molecule have been specifically synthesized into the polymer backbone. This further enhances selectivity.

Finally, for electron transfer to the bound molecule to occur spontaneously, the overall free energy change (ΔG^0) for this process must be negative. In order for this requirement to be satisfied, a bound molecule must have a standard reduction potential large enough to cause ΔG^0 to be negative. In equation form, the magnitude of FQ can be approximated as

$$FQ \propto (C) \left[\exp(-\Delta G^0) \right] (K_b),$$

where (C) is the concentration of quencher in the sample. Hence, for significant quenching to occur an analyte must bind strongly to the film and have the appropriate reduction potential. Compounds that bind weakly to the film and/or have weakly favorable reduction potentials will result in significant quenches only when these compounds are present in very high concentrations.

The combination of factors discussed in the previous paragraphs appears to be sufficiently restrictive to prevent most compounds from being strong quenchers of AFP. In practice, except for nitroaromatic compounds derived from TNT, few compounds that quench the polymer have been encountered in actual field tests. The selectivity of the AFP is a definite advantage for groundwater monitoring applications. Because the sensor appears to exceptionally differentiate target analytes from chemical interferents, it should be particularly useful at DoD sites contaminated with a range of substances.

APPENDIX B REFERENCES

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**APPENDIX C
PAPERS, PUBLICATIONS, AND PRESENTATIONS**

Sensing explosives in aqueous solutions was discussed at the following conferences.

- Mark Fisher, 2002. “Long-Term Monitoring for Explosives-Contaminated Groundwater”, SERDP and ESTCP 2002 Partners in Environmental Technology Technical Symposium & Workshop, December 2002, Washington, DC.
- Matthew Dock, Mark Fisher, Colin Cumming, 2002. “Sensor for Real-Time Detection of Underwater Unexploded Ordnance”, in Proceedings of UXO/Countermines Forum 2002, September 2002, Orlando, Florida.