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Novel Technology for Wide-Area Screening of ERC-Contaminated Soils

Final Technical Report

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Final Report

Novel Technology for Wide-Area Screening of ERC-Contaminated Soils

Introduction

Long-term use of high explosives (HE) on DoD training ranges and other defense installations has in some cases resulted in contamination of soil and groundwater with residues of HE and explosive-related compounds (ERCs). The vast majority of the millions of acres of DoD lands are likely free of contamination, or are contaminated at levels that cause little concern. Nevertheless, virtually all lands on all defense sites have become subject to more rigorous environmental monitoring and regulation. There is an urgent need for technologies that can rapidly detect, quantify, and delineate soils that contain contaminants associated with the use of energetic compounds. These technologies will give site managers the ability to perform cost-effective screening of large areas for possible contamination and to pinpoint specific areas of high contamination.

Current survey methods such as EPA Method 8330 are based primarily on laboratory analytical methods and are both time-consuming (take hours to perform) and expensive (several hundred dollars per analysis). Further, studies relating to the fate and transport of energetic compounds in the environment have shown the spatial distribution of HE and ERCs is often highly heterogeneous. The heterogeneity of the distribution of contamination within an area places unusual requirements on sampling protocols to ensure that samples collected accurately represent the area sampled. Within a large area, there may be only a few small 'islands' of contamination that require remediation. The challenge is to rapidly and accurately identify specific areas requiring cleanup in a cost-effective manner and to avoid the large cost of unnecessary remediation.

Under SERDP project CU-1228, Nomadics developed equipment and methods to cost-effectively address this problem. At the heart of the system is the company's Fido sensor, which is an extremely sensitive detector for TNT and other nitroaromatic compounds. By coupling the sensor with a novel air and soil particle sampling system, it was shown that it is possible to differentiate areas of high contamination within areas of little or no contamination.

During tests conducted at Yuma Proving Grounds, it was possible to differentiate areas with bulk TNT contamination (as from a low-order detonation of a munition) from areas contaminated at trace levels. Areas that were not contaminated with explosives gave little to no response. The test data supported the concept that heavily contaminated land could be isolated from clean areas quickly and with relatively little effort compared to other screening methods. Remediation efforts could then focus on the most heavily contaminated areas.

Technology Description

Nomadics' Fido detection system utilizes novel fluorescent polymers developed by collaborators at the Massachusetts Institute of Technology. Amplifying fluorescent polymers (AFPs), enable detection of TNT and related substances at levels three orders of magnitude below that of the most sensitive commercially available laboratory instruments. The

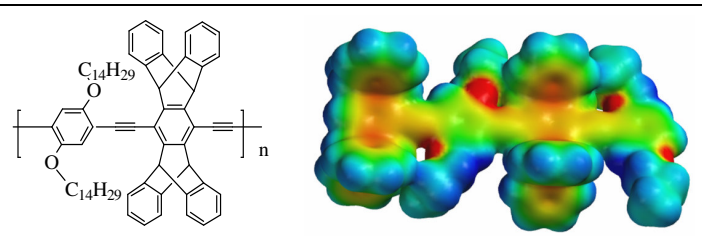

***Figure 1**. Chemical structure of a repeat unit of an AFP and the electrostatic surface of two repeat units of the same AFP (with alkoxy side chains shortened).*

polymer depicted in Figure 1 is one of more than twenty AFPs that have been synthesized for TNT detection, each with slightly different responses to target analytes. Work is underway to develop new AFPs for detection of nitramine explosives including RDX and HMX.

These materials amplify the magnitude of fluorescence quenching that occurs upon binding of target analytes to the polymers. Binding of a single TNT molecule quenches the fluorescence of many polymer repeat units, thereby amplifying the effect of a single TNT binding event. The resulting amplification is a key factor in achieving the exceptional sensitivity of the detector, which has been demonstrated in lab tests to have a minimum detection limit for TNT of approximately 1 femtogram (1×10^{-15} grams). In addition, the polymers are engineered to interact preferentially with target analytes, resulting in excellent selectivity for nitroaromatic compounds. This greatly reduces the probability of sensor false alarms.

The Fido sensor is small, portable, and uses little power. The sensor is easy to operate and personnel can be trained to use it in a few hours. Ambient air is drawn through the sensor and over a thin film of AFP. If vapors of nitroaromatic compounds are present in the sample, the AFP quenches. A photodetector monitors the intensity of fluorescence of the AFP, and a graphical display outputs intensity data to the operator in real time. Response of the sensor to target compounds is almost instantaneous, and binding of analyte to the AFP films is reversible. The magnitude of fluorescence quenching is proportional to the concentration of target analytes contained in a sample.

To prove the wide area screening concept, two sampling strategies were employed. The first method of sampling involved collecting samples encompassing large areas by using a high-volume sampler shown in Figure 2. In this approach, air and soil particles that may be contaminated with HE are collected from the surface of the ground by drawing the air and any entrained particulates through inexpensive, disposable sampling cartridges. This method collects a sample from a large area in a short period of time, making it possible to sample large areas quickly and with relatively few samples compared to other sampling methods. Samples are then analyzed for explosives in the field with the Fido sensor. If a sample from a given area exhibits high levels of contamination, the associated area can be divided into smaller sectors and resampled, enabling localization of the position of the contamination.

***Figure 2**. High volume sampler used during Ft. Sill field tests, June 2002.*

The second method is direct sensing of explosive vapor signatures with the Fido sensor, using the sensor much like a metal detector. The operator slowly sweeps the inlet of the sensor over the ground. In this mode of operation, areas of high contamination can be pinpointed as the sensor is swept across the ground. Contaminated soils will produce vapors of target analytes in the boundary layer of air near the surface of the ground, which can be sampled and quantified with the sensor. In this mode of operation, data can be collected that will enable accurate mapping of contamination levels in a very localized area.

Test Results

Some difficulty was encountered in locating sites suitable for testing the technology. However, during the course of the contract, tests were performed in the Nomadics laboratory, as well as at Ft. Sill, Oklahoma (home of the US Army Field Artillery School). Most recently, the method was tested at the US Army Yuma Proving Ground (YPG) during March of 2004.

The March 2004 tests at YPG demonstrated at the proof-of-concept level the utility of the method. Leveraging access to explosive assets at the site during testing of landmine detection equipment, a field test of the method was completed. Three separate test areas, described in Figure 3, were laid out for the test. The size of each area was 20×20 meters, laid out in a 5×5, 10×10, 15×15, and 20×20 meter boxes that each shared a common corner (refer to Figure 3). A one-square meter area at the center of the 5×5 area was marked in each of the three test areas. The explosives were placed within the 1×1 area in each test area. Prior to placing explosives in each of the three test areas, blank (background) samples were collected using the high-volume sampling method. A blank sample was collected from each of the four boxes making up each test area.

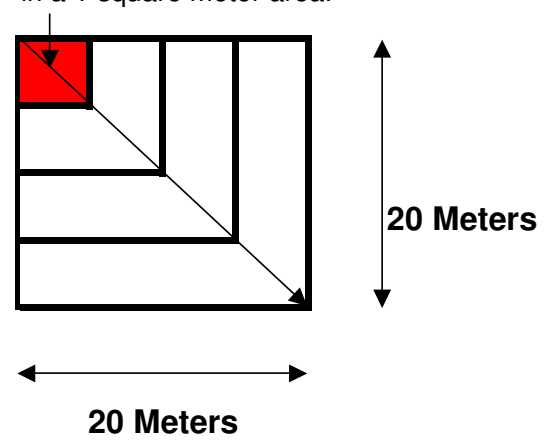

***Figure 3**. Layout of test area. Three areas of this type were utilized.*

After blanks were collected, explosives were placed in each 1×1 meter box within the designated test areas. In Area 1, two pounds of TNT broken into dime- to quarter-sized chunks were spread on the ground over the 1×1 meter area (see Figure 4). In Area Two, five grams of microcrystalline TNT suspended in water were spread over the designated 1×1 area (Figure 5), while 500 mL of a saturated aqueous TNT solution (150 ppm) was poured over Area Three (Figure 6). Explosives were placed in the test areas for approximately four hours prior to sampling. In this way a test area contaminated with chunks of TNT, small crystals (particles) of TNT, and trace-contaminated soil were available for testing. The areas were sampled again after the explosives were placed using the high-volume sampling method.

***Figure 4**. Chunk TNT contamination in Area 1.*

Figure 5. *TNT-crystal contamination in Area 2.*

Figure 6. *Trace contamination in Area 3.*

For each test area, a sample covering the 1×1 meter area was collected by waving the sampling wand of the sampler near the ground, sweeping the wand over the area while sampling air at a rate of one liter per second (Figure 7). Following completion of sampling of the 1×1 meter box, the entire 5×5 meter box (which contained the 1×1 meter box) was sampled by sweeping the entire area with the sampler while walking slowly over the area. The process was repeated for the larger sample areas, first sampling the 1x1 area within the 10x10 meter area (which also contained the 5x5 area previously sampled), and so on. Hence, progressively larger samples, each containing the 1×1-contaminated area, were collected. Sampling was conducted so that the contaminated area was sampled for approximately five seconds near the beginning of the collection of a given sample. The total sampling time required for each box increased as the size of the box increased. Approximately ten minutes were required to sample the 20x20 meter area. Care was taken to prevent walking through the contaminated areas to limit spread of contamination.

Figure 7. *High-volume backpack sampler in use at YPG.*

Figure 8 illustrates the response of Fido to samples collected from the 1×1 meter area contaminated with chunks of TNT. The response is large and easily detectable. The sample for the 20×20 area (containing the contaminated 1x1 meter area) is also shown for comparison. The response, while weaker, is still very strong. It should be noted that the dwell time near the explosive for the 20×20 meter sample was approximately five seconds. This illustrates the ability to sample large areas and still detect the presence of contamination in a smaller area within the sample area. As can be seen from the Figure 8, the response to the blank sample taken prior to placing explosives in the area was negligible.

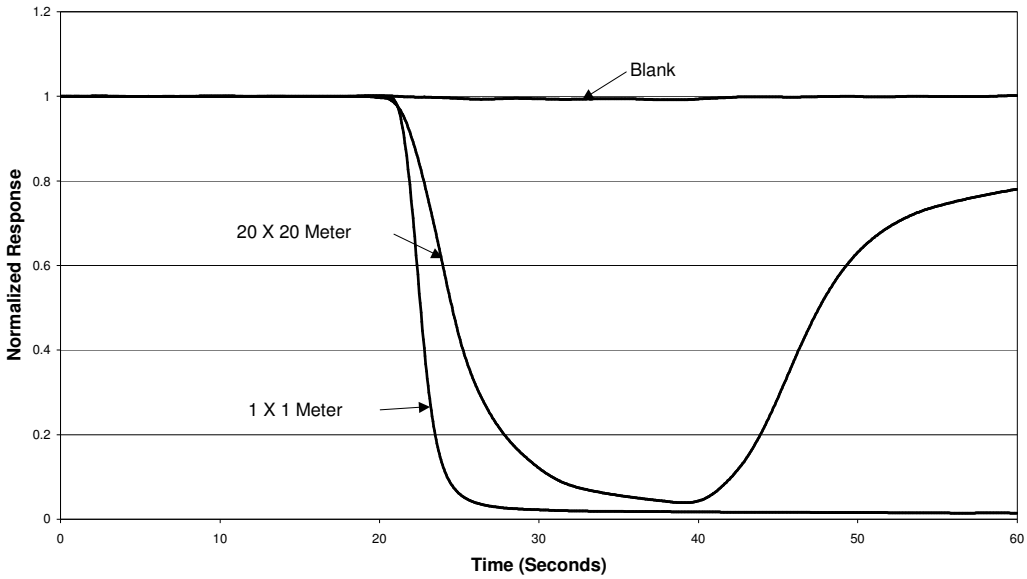

Figure 8. *Results for TNT chunks, showing response prior to explosive contamination, and the response for the sample collected from the 20×20 and 1×1 meter boxes.*

Figure 9 compares the relative response of the trace contaminated, crystal-contaminated, and chunk-contaminated 1×1 meter areas. The trace contaminated area gives a much weaker response than is obtained from the areas contaminated with crystalline or bulk (chunk) TNT. This is presumably due to the fact that the trace source is composed of soil particulates with adsorbed TNT (TNT-soil interactions primarily determine headspace concentration of TNT), while the two other sources behave as bulk TNT (TNT sublimation rate determines headspace TNT concentration). Soil conditions were dry at the time of sampling, which tends to reduce the headspace concentration of TNT over soils. Under these conditions, it was straightforward to differentiate bulk TNT contamination from trace contamination that would have a lesser environmental impact than from bulk TNT contamination.

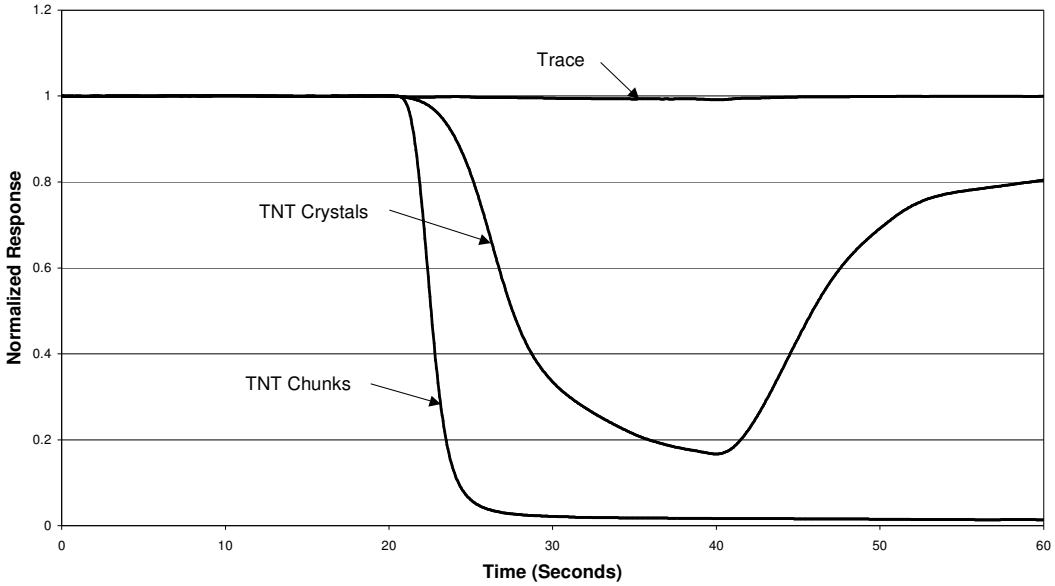

Figure 9. *Comparison of the trace contaminated soil area, TNT crystal-contaminated area, and the TNT-chunk contaminated 1×1 meter areas.*

Direct analysis with Fido gave large responses near the crystalline and chunk TNT, while responses were minimal a short distance away (generally a few centimeters upwind of the material). Over time, the contamination may spread in areal coverage, but this was not possible to determine because of the short time elapsed since the explosives were placed in the test site. It should also be noted that visible degradation of the TNT-chunks and crystals occurred during testing. A reddish residue (presumably due to photodecomposition of TNT (yellowish white) to trinitrobenzene (red)) was observed four hours after the explosives were placed (hot, dry and sunny conditions). This is especially evident upon inspection of Figure 5, where the reddish-brown outline of the area where the crystalline TNT contaminaton was spread is easily visible. Trinitrobenzene is detectable with Fido, with sensitivity similar to that of TNT.

These test results suggest that high-volume sampling can be used to locate high levels of contamination within a relatively large area. In addition, the Fido sensor may have utility in pinpointing the location of the contamination via direct sampling once the areas of contamination has been localized by high volume sampling and Fido analysis.

In June 2002, Nomadics was able to conduct a field test at Ft. Sill, Oklahoma. Ft. Sill is home of the US Army Field Artillery School, and live fire exercises are conducted at the facility on a regular basis. We were allowed on several ranges under the close supervision of EOD personnel. This is our only test conducted on a live fire range, and was a valuable learning experience.

The following sites were sampled:

1) A 105 mm and 155 mm Howitzer firing point.
2) An impact area that had been heavily used in the past. There were no sign of recent use. Tall grass had completely covered the area, obscuring dud munitions that were widely distributed over the area. Impact craters were evident, but they were overgrown with grass.
3) Blanks were gathered from an area close to the range, but off-site where there was little chance of contamination.
4) A grenade range was sampled.

Soil samples and HVV samples were collected at each site. Samples were stored on ice after collection, and were refrigerated once transported to the lab. These samples were analyzed in the Nomadics lab after completion of the field exercise. Analysis methods included headspace analysis of soil 'grab' samples in vials using Fido. After the headspace analysis was completed, the soil 'grab' samples were extracted into acetonitrile, and the extracts were then analyzed by GC- ECD and GC-Fido. Analytes included in the analysis were 2,6-DNT, 2,4-DNT, 1,3-DNB, 1,3,5-TNB, TNT, 2-ADNT, and 4-ADNT.

Figure 10 depicts the results of the analysis of soil samples collected around a dud 105 mm Howitzer dud round located in the impact area. Soil sample extracts were analyzed using an HP-5890 GC with an electron capture detector (ECD), and with a SRI Model 8610 portable GC equipped with a Fido detector. No significant contamination was indicated except in sample I14, which was collected more than two meters away from the round. TNT concentrations near 10 ppm were detected in this sample. Low levels of contamination were detected in several samples. Note that for samples containing high enough concentrations of TNT so that it could be detected by GC-ECD, the concentration measured by GC-ECD and GC-Fido were in good agreement. Fido was able to detect TNT in 9 out of 16 samples, while the ECD detected TNT in 3 out of 16 samples. It is not known whether the contamination found in sample I14 came from the dud round or from another source. The entire area was strewn with range debris and UXO, so the contamination could have been from another source.

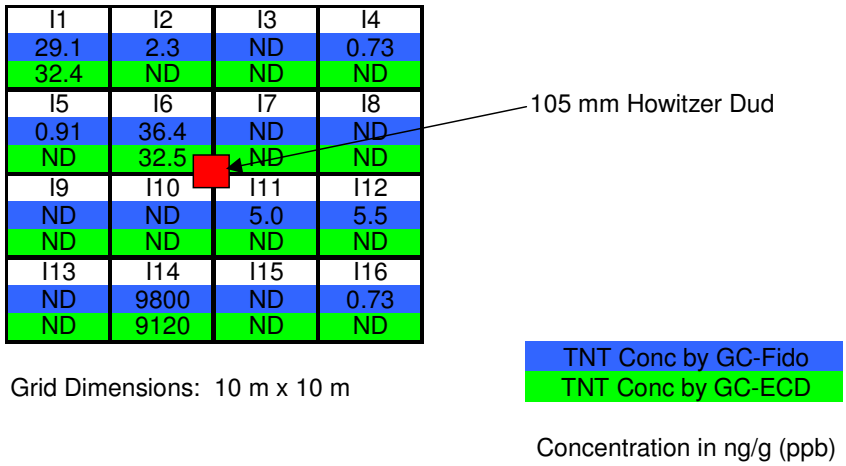

***Figure 10**. Results of analysis of soils near dud 105 mm Howitzer round by GC-Fido and GC-ECD.*

Vapor detection, both high-volume and direct sensing with Fido, failed to detect HE or ERCs in these samples, which were very dry. The importance of soil moisture was indicated as sample I14 could be detected after water was added to it.

All blank samples collected were found to contain no HE or ERC residues.

A compilation of the results of the GC/ECD analysis of extracts of soils collected from the grenade range is listed in Figure 11. The results are listed only for 2,4-DNT and TNT, but 1,3-DNB, 1,3,5-TNB, 2-ADNT and 4-ADNT were also detected in some samples. The TNT microbial degradation products 2-

ADNT and 4-ADNT were detected in many samples, but the concentrations were low. While most samples contained TNT, the distribution of TNT concentrations was heterogeneous. The soil samples were composites of several smaller samples collected into a single vial using a spatula. Each composited sample was collected over an area of approximately 1 square meter centered at the positions indicated in Figure 11. The concentrations of TNT and 2,4-DNT are listed, reported in units of ng/g (ppb).

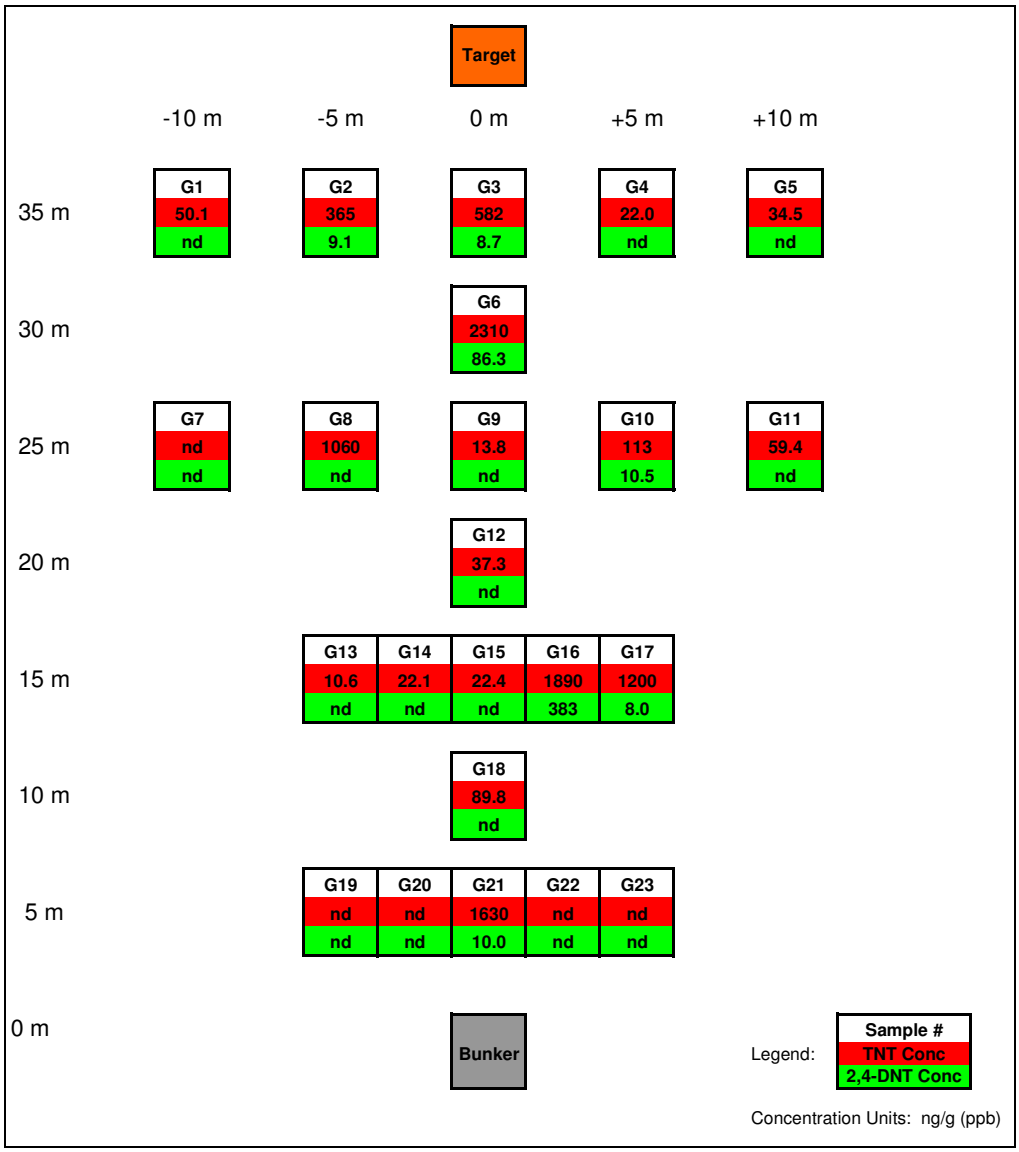

Figure 11. *Results of GC-ECD analysis of soils collected from the Ft. Sill grenade range.*

Headspace analysis with Fido was performed post-test in the laboratory by direct sampling of the headspace in the vials containing the soil samples collected from the grenade range. No response to vapors of explosive-related compounds (ERCs) or explosives was noted for the soils as sampled. The samples consisted of very dry, fine-grained sand. Using a vapor concentration estimation tool provided to us by Jim Phelan of Sandia National Labs, the estimated headspace vapor concentrations for sample G6 at a 1% soil moisture content was in the sub parts-per-quadrillion range. This is below the detection limit of Fido. Sample G6 contained the highest concentration of TNT of any sample in the set, containing 2.3 ppm of TNT by mass. At 4% soil moisture content, the tool estimated the headspace concentration of TNT in this sample at 14 parts-per-trillion, barely detectable by Fido. When water was added to the

sample to increase the soil moisture content to 4% by mass, Fido responded weakly to the sample. This points out the importance of soil moisture content when attempting to detect vapor phase HE and ERCs over contaminated soils.

Soil samples collected at the firing point were found to contain primarily 2,4-DNT, with traces of 2,6-DNT detected (see Figure 12) when analyzed by GC/ECD. No TNT was detected at the site. The levels of DNT found in the soils produced headspace concentrations below the direct vapor sensing detection limit of Fido at the soil moisture content present at the time of sampling. No 2,4-DNT was detected on the HV vapor cartridges by direct vapor analysis with Fido. The propellant used in 105 mm rounds contains DNT, which accounts for its presence at the site. The levels of 2,4-DNT are heterogeneous as on the grenade range, but are highest near the gun. 11 of the 15 samples collected within 25 meters of the muzzle of the gun contained 2,4-DNT at detectable levels.

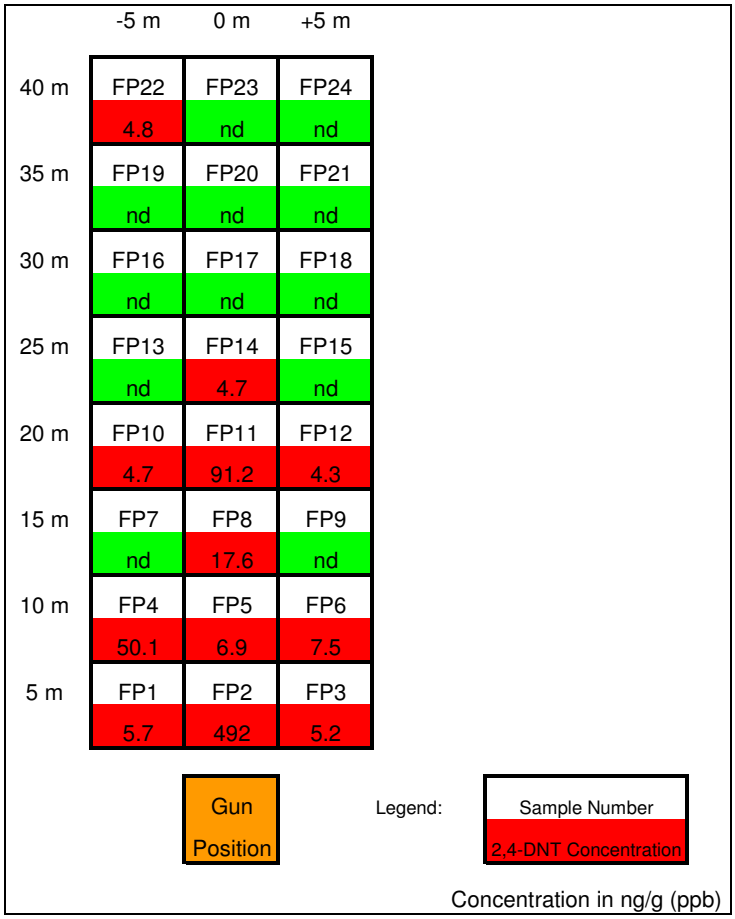

Figure 12. *Results of GC-ECD analysis of 2,4-DNT in soils at 105 mm Howitzer firing point.*

At first glance the results of this test seemed disappointing because vapor-phase detection of HE and ERCs with Fido was not widely observed. However, after laboratory analysis of the samples was completed, many samples were found to contain contamination at low levels. The low levels of contamination on the range coupled with dry soil conditions decreased the vapor phase concentrations of these materials to very low levels. Addition of water to the soils made vapor phase detection of target analytes possible in some cases. While not demonstrated here, detection of slightly higher concentrations of contamination approaching maximum permissible limits of contamination should be routinely detectable by vapor sensing provided environmental conditions are favorable.

Estimation of Soil HE Concentrations Based on Vapor-Phase HE Concentrations

One of the goals of this work was to demonstrate the relationship between headspace vapor concentrations of HE and their concentration in the soil. The goal was to measure the concentration of target analyte vapors in the boundary layer of air over a contaminated area, and from this measurement determine the concentration of HE in the soil. The relationship between soil HE concentrations and the concentration of HE in the vapor phase that is generated by contaminated soil is a complex one. Parameters including but not limited to soil type, temperature, soil moisture content, and the partition coefficients for HE into the various soil constituents all affect the concentration of HE in the vapor phase over a contaminated soil. Hence, to estimate soil HE concentrations from vapor phase headspace measurements requires measurement or estimation of these and other parameters. When measurements are made in the laboratory, a contaminated soil sample is usually confined in a sealed container where chemical equilibrium between vapor phase and condensed phase HE can be achieved prior to measurement of concentrations of target analytes. In a field setting this is not the case, as equilibrium between vapor and condensed phase analytes will not likely be achievable due to the dynamic nature of the environment where dispersion of the vapor into a reservoir of infinite volume (rather than into a small volume of air in a vial containing soil) occurs.

Perhaps a pseudo-equilibrium can be achieved in the soil-air boundary layer, or in subsurface soils, but it is difficult to collect samples from either of these locations. Soils could be collected and transferred to vials and allowed to reach equilibrium prior to analysis, but to do so would render the high-volume sampling method utilized here much more expensive and time consuming. Hence, models for soil-air partitioning of HE developed in a laboratory under equilibrium conditions will not likely be adequate for estimating soil concentrations of HE under non-equilibrium conditions in the field. At best, it may be possible to supply rough order-of-magnitude estimates for soil HE concentrations by measurement of vapor-phase concentrations, provided a few critical parameters can also be measured or estimated. Field test data suggests that it may be possible to differentiate heavily contaminated areas from trace or non-contaminated areas, but assignment of accurate, quantitative soil HE and ERC concentrations will be very difficult in all but the best of circumstances.

The fact that determination of soil HE concentrations from vapor-phase measurements would be difficult became clear early-on during a laboratory investigation of the critical factors that establish soil headspace vapor concentrations of HE over contaminated soils. This task involved analysis of soils and soil headspaces using standard laboratory analytical methods and the Fido sensor. Soil headspace concentrations of TNT were measured by GC/ECD analysis of samples collected using solid-phase microextraction (SPME). The same measurements were also made using Fido to directly analyze the headspace from vials containing soils contaminated with TNT. The concentration of TNT in the soil was measured by extracting the TNT into solvent (acetonitrile), followed by GC/ECD analysis of the extract. The role of temperature, soil type, and soil moisture content on vapor-phase concentrations of TNT were selected for evaluation.

Four soil types (sandy loam, loamy sand, clay, and sand) were obtained for analysis. The soil was contaminated by adding four parts aqueous TNT (by mass) to one part soil. The mixtures were then allowed equilibrate for 24 hours with mild mixing. The concentration of TNT in the aqueous solutions was varied to produce soils with different levels of condensed-phase contamination spanning the parts-per-million concentration range. For each soil type, five concentrations of aqueous TNT were used to prepare soil spikes. These dilutions (20, 40, 75, 100, and 150 ppm) were prepared from a saturated aqueous TNT solution (150 ppm m/m). After 24 hours, the soil / aqueous TNT mixtures were filtered and dried in a laboratory fume hood. When the soils were almost dry, they were transferred to an oven and baked at 105°C for a short time to reduce the soil moisture content to near 0%. After drying, the soils were thoroughly mixed and quickly transferred to amber glass bottles for storage. When the soil was not

in use, it was kept frozen to minimize degradation. The soil was tested at 20°C, 25°C, 30°C, and 40°C and at soil moisture concentrations of 0%, 2%, 5%, and 8%. The soils at the various moisture contents were prepared by addition of deionized water to the soil prior to analysis. After addition of water to the soil, the soil was maintained at a given temperature for at least two hours prior to analysis. The soils were not analyzed at higher temperatures and moisture content because of problems encountered with rapid degradation of the samples at higher temperatues and moisture contents.

Aliquots of the contaminated soil were then analyzed. Extracts of the soil in acetonitrile were analyzed by GC/ECD to determine the soil TNT concentration. Aliquots of these soils were also transferred to 200 mL amber, wide-mouth glass bottles for analysis of headspace by Fido, and also to 40 mL amber glass vials with septa closures to facilitate collection of headspace samples by SPME for analysis by GC/ECD. Three replicate measurements for each soil type and concentration at the specified temperatures and soil moisture content were completed for the GC/ECD analysis, and seven replicates for each set of test conditions were completed for Fido analysis. Temperature of samples was maintained by placing the samples in a temperature-controlled a water bath.

Figures 13 and 14 illustrate the Fido response (% quench) to headspace vapors as a function of soil moisture content and temperature, respectively, for sandy loam soil contaminated at five TNT concentrations. The average value of the % quench for seven replicates is plotted, with error bars representing +/- 1 standard deviation in the responses. Figure 13 illustrates the effect of soil moisture content on headspace vapor concentrations. As demonstrated previously, and during field testing, extremely dry soils liberate very low (undetectable) levels of TNT vapor, but when water content is increased, the headspace concentrations of TNT rise by orders of magnitude.

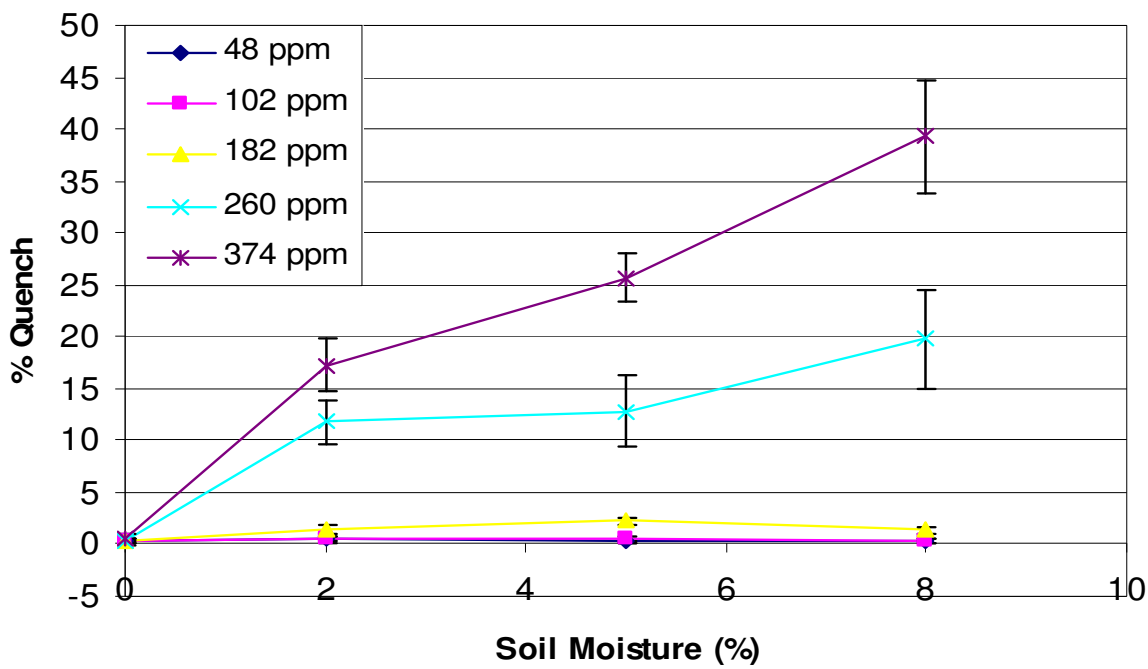

***Figure 13**. Fido % quench as a function of soil moisture content at 30°C.*

From Figure 14 it can be seen that the soil temperature also affects headspace concentration, with the levels of HE increasing as the temperature increases (as would be expected). The results for the other soil types are similar in trend, but different in magnitude.

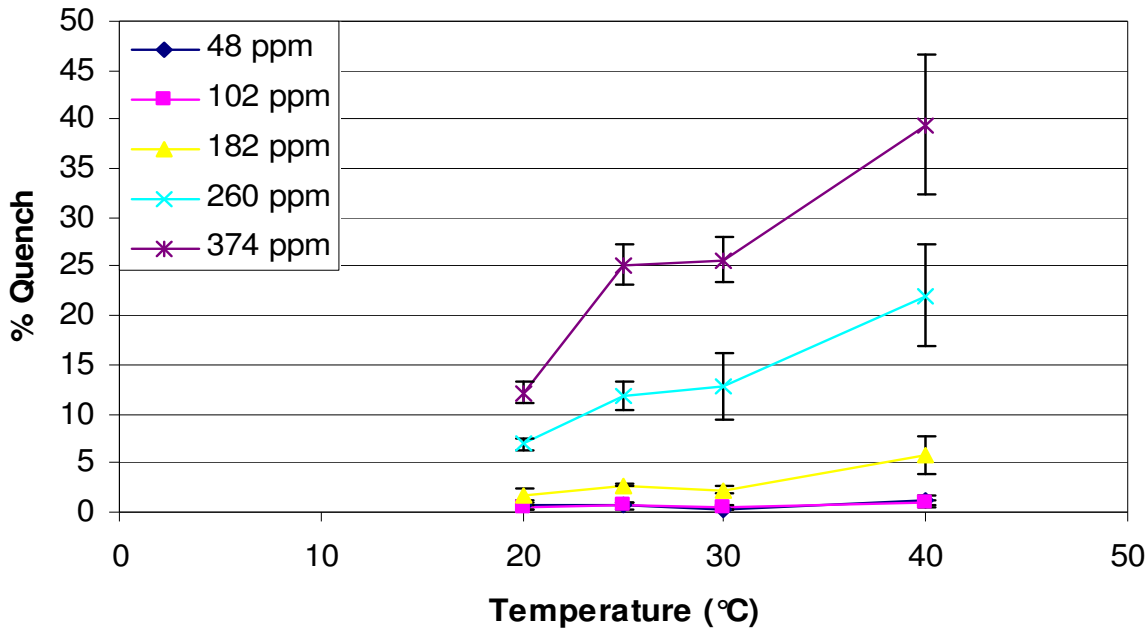

***Figure 14**. Fido % quench as a function of temperature at 5% Soil Moisture.*

Difficulties were encountered in collection of the SPME/GC/ECD data. The responses for the various replicates collected under apparently identical test conditions were found to be very non-reproducible (almost random in some cases), sometimes varying by almost two orders of magnitude. In addition, the results were often counter to what would be expected. For instance, on numerous occasions samples collected at higher temperatures were found to contain less TNT than those collected at lower temperature. This variability made it difficult to interpret much of the data.

The exact reason for the non-reproducibility in results was difficult to ascertain. Degradation of samples was suspected as the primary reason for the non-reproducibility. There was evidence in the GC/ECD data for conversion of TNT into amino-dinitrotoluenes, consistent with microbial degradation of the samples, and the degradation was more severe for the samples analyzed at higher temperatures and moisture contents (again consistent with microbial degradation of the TNT). When samples were analyzed with Fido, the analysis time per replicate was short, enabling seven replicate measurements to be collected for a given set of test conditions in a few minutes. Conversely, to collect and analyze the SPME/GC/ECD samples for a given set of conditions required several hours due to the more lengthy SPME sample collection (15 minutes or more per sample) and ECD analysis times (approximately 45 minutes per sample). The half-life of TNT in some soils under conditions favorable for microbial degradation is on the order of a few hours. Hence, this could explain some of the variability, particularly in the SPME/GC/ECD results.

What could be inferred from the results of the analysis was that the vapor-phase concentration of HE over contaminated soils is highly dependent on factors such as soil moisture content and temperature. There are undoubtedly other parameters that were not evaluated here that play a role as well. Hence, for this approach to be quantitative, other key environmental parameters would have to be measured along with the vapor phase concentration of HE. The values of these parameters are likely as heterogeneously distributed as the HE contamination, making their measurement difficult.

Even though it may not be possible to assign accurate quantitative values to soil contamination levels, the field test data from YPG points out that it may be possible to assign rough order-of-magnitude estimates as to the level of contamination in an area. This type of information could still be useful, providing

insight into which areas on ranges are most heavily contaminated and helping to identify which areas are clean. This information could be used to make decisions as to which areas should receive priority consideration for further monitoring, analysis, or cleanup.

Standoff Detection of Contamination by Energetic Materials

A proof-of-concept demonstration of an alternate method for potentially screening large areas for contamination by HE was completed in the laboratory. The method involves dispersing spherical substrates (in this case glass or styrene-divinylbenzene beads) coated with amplifying fluorescent polymers over an area suspected of being contaminated with energetic materials. The dispersed beads are then interrogated from standoff using an excitation source and a light-gathering apparatus (in this case a telescope fitted with a digital camera). If the area is contaminated, the fluorescence of the polymers will be quenched, while beads dispersed over clean areas will remain fluorescent.

This concept was demonstrated using a cylindrical test cell that was essentially a 1-inch deep container for holding soils. The test cell was divided in half, creating an upper and lower hemisphere. The top half was filled with uncontaminated soil, and the bottom half was filled with dry, TNT-contaminated soil. The concentration of TNT in the soil was approximately 100 ppm m/m. After the soils were loaded into the test cell, AFP-coated styrene-divinylbenzene beads were distributed randomly on the surface of the soil.

Figure 15 is an enhanced false-color image of the fluorescence emission from the beads. The fluorescence of the beads immediately after dispersal is illustrated in the frame labeled 'Initial', and the emission one minute after the soil was sprayed with a small amount of water is shown in the frame labeled '1 minute'. The soil in the lower hemisphere of the cell (the contaminated half) one minute after applying water is quenched relative to the initial emission intensity, while the upper hemisphere (the uncontaminated half) remains essentially unchanged one minute later. It was interesting that the beads did not quench until water was added, again confirming the important role of soil water in the mass transfer of TNT in soils.

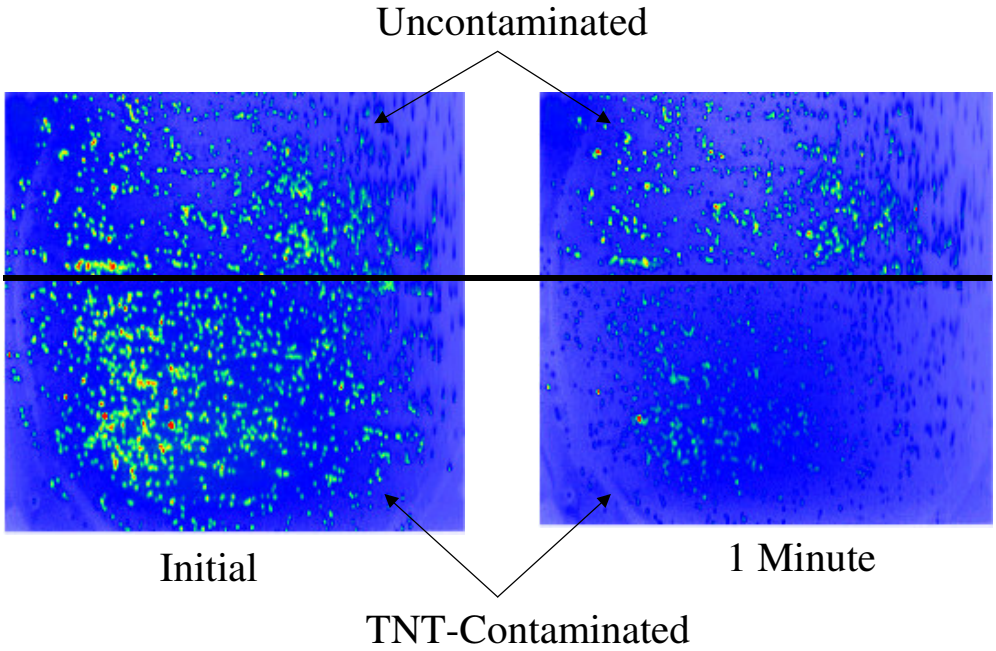

***Figure 15**. Laboratory demonstration of standoff detection of TNT in soil using AFP- coated beads.*

While the laboratory demonstration was successful, there were numerous technical challenges that prevented demonstrating the method outdoors. There were concerns related to potentially adverse environmental impact that may occur when the AFP-coated beads were dispersed in the environment. It was shown that the polymer photodegrades in a few hours upon exposure to sunlight, but the impact of the bead material and the photodecomposition products of the AFP are unknown. Since the polymer photodegrades in sunlight, outdoor testing would have to be conducted at night. Finally, the hardware used in the lab for the proof-of-concept demonstration was not particularly amenable to use in the field, so the approach was not demonstrated outdoors.

Cost/Benefit of the Technology

Substantial cost savings could be realized with the wide area sampling approaches demonstrated here, while providing an unprecedented level of monitoring. The cost reduction is due primarily to the fact that it will be possible to survey large areas for contamination by collecting and analyzing a greatly reduced number of samples compared to more traditional screening methodologies. The cost of analysis per sample will be much less (a total cost of approximately $10 per sample) than for currently accepted laboratory methods ($250-1000 per sample). Since samples will be analyzed in the field, the turnaround time for results will be minimized, thereby providing range managers with data from which to make informed, on-site decisions enabling more efficient and cost-effective range management.

Figure 16 illustrates the concept. Assume an area of 10,000 square meters (a 100 x 100 meter area) is free of explosives in all areas except for a single 1 square meter area. If the 10,000 square meter plot were divided into 1 square meter grid sectors for sampling, 10,000 samples would be collected from the plot if each sector were sampled. Obviously, 10,000 samples are far too many samples to analyze. If the cost to analyze a sample by Method 8330 were $100, the cost to analyze the set of samples would be $1,000,000. However, if a single soil sample composite were collected from the 10,000 square meter area and analyzed, the costs incurred to screen the area would be dramatically reduced.

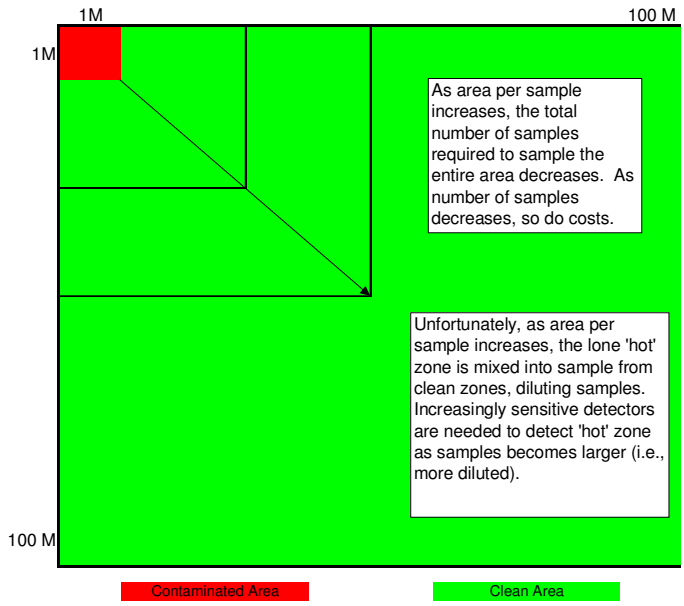

***Figure 16**. Wide area sampling could reduce costs but requires an extremely sensitive detector such as Fido.*

The problem with this approach using traditional spot-sampling methods is that unless the resolution of the sample collection is on the order of a sample every meter, the contaminated area in our example case may not be sampled and go undetected. In addition, if soil from the contaminated area is actually sampled during formation of the sample composite, when the contaminated soil is mixed with mostly uncontaminated soil from the other spot samples the concentration of HE in the mixed sample composite will likely be diluted below the detection limit of traditional laboratory methods. On the other hand, high-volume vapor sampling (with a single filter costing a few dollars) followed by analysis of the sample with the highly sensitive Fido detector (cost per analysis estimated to be less than $2 per sample) could

confirm that the area is contaminated. Not counting labor costs, the total cost of analysis per sample will be on the order of $5. Analysis of the filter can be completed on-site in seconds, giving the range manager immediate feedback as to the extent of contamination. The 100×100 meter area could then be subdivided into smaller sectors and re-sampled in order to locate the source of the contamination. Once the point of contamination is isolated, the smaller area could be screened directly with the Fido sensor to estimate the level of explosive contamination in a localized area.

In the above example, as the one square meter contaminated area is included into an increasingly larger "clean" sample area, the concentration of TNT in the sample will be reduced by dilution with clean sample. Hence, as the area per sample increases, the sensitivity of the detector becomes increasingly important. Detector sensitivity will likely determine the upper limit to the maximum area interrogated per sample, and hence will ultimately determine cost savings.

Conclusions and Recommendations

Based on the results of field testing performed during the project, we believe that the basic wide area sampling methodology is sound. The method could be beneficial as an area reduction tool, enabling differentiation of uncontaminated areas from areas that are sufficiently contaminated to create an adverse environmental impact. The method may not provide the same level of accuracy as laboratory analytical methods for quantitative analysis of contamination levels of HE in soils, but it may provide order-of-magnitude estimates as to the contamination level at a given site. This information could be useful for making decisions as to which areas on DoD facilities should receive priority consideration for evaluation of possible adverse environmental impacts.

We are well aware that the potential for adverse environmental impact caused by explosives such as RDX and HMX is greater than for TNT, and the inability of Fido to detect these explosives is a limitation of the system. However, Nomadics is currently developing sensing materials that will enable detection of RDX and HMX with Fido. We recently demonstrated detection of RDX and PETN at the 1 nanogram level, which is only slightly less than the sensitivity of commercially-available IMS systems for these explosives. The polymer development work is being funded under other contracts, and it is expected that materials with greatly enhanced sensitivity to RDX and HMX will be available for testing within 12 to 18 months. Once the ongoing polymer development effort is complete, the technology will be very compelling for use as an environmental screening tool. The technology should at that point be considered a candidate for transition into the ESTCP program.