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In Situ Biodegradation of High Explosives in Soils: Field Demonstration

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ABSTRACT: The first field pilot-scale demonstration of a technology for *in situ* remediation of vadose zone soils contaminated with high explosives (HEs) has been performed at the Department of Energy's Pantex Plant. The HEs of concern at the demonstration site were hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and the 2,4,6-trinitrotoluene (TNT) metabolite 1,3,5-trinitrobenzene (TNB). Concentrations ranged from 70 ppm, above the (prior to 1999) risk reduction clean-up criteria of 2.6 and 0.51 ppm, respectively. The shallow (<10 m depth) soils at the site could not be excavated due to the presence of buried utilities. Based on previous laboratory studies, it was found that the contaminated soils had indigenous microbial populations that could be stimulated to degrade the RDX and TNB anaerobically. A 5-spot well pattern with injection at the central well and extraction at the four outer wells (each 4.6 m from the injection well) was used to flood the target vadose zone soils with nitrogen gas with the intent of stimulating the activity of the HE degraders. The system was monitored periodically for gas composition as well as HE concentrations and microbial activity in retrievable soil samples. After 295 days of *in situ* treatment, the average target HE concentrations were approximately one-third lower than the initial site averages. Operation of the pilot-scale treatment system continues.

INTRODUCTION

In the last 2 decades, contamination of soil and groundwater by high explosives (HEs) has been found at many government and private facilities. These facilities typically were involved with the missions of the Department of Defense or the Department of Energy (DOE). The HE contaminants are remnants of past or current manufacture, testing, or training with conventional ordnance or nuclear weapons (Ramsey et al., 1995). Under ambient environmental conditions, HEs are highly persistent in soil and groundwater and exhibit a resistance to potential naturally occurring volatilization or biodegradation (Craig et al., 1995). Most HEs exhibit relatively low water solubilities that contribute to both significant residual concentrations in soil and significant (above clean-up standards) concentrations in groundwater. Efficient and cost-effective techniques for remediating the HE contamination problems are now being developed and implemented at the affected sites. Unfortunately, due to the different site conditions and facility missions, no single remedial approach has yet been found appropriate at all locations. Soil contamination is typically dealt with by excavation followed by treatment and/or disposal, making this approach useful only for relatively shallow soils. It should be noted that the inherent heterogeneity in soil conditions and HE contamination distribution greatly complicate both characterization and remediation of contaminated sites (Crockett et al., 1996). Due to erratic contaminant sources, preferential infiltration in the vadose zone, and limited solubility of the HE compounds, measured HE concentrations can vary by a few orders of magnitude over a short distance laterally or vertically. Delivery of any soil amendment *in situ*, whether in liquid form, water solution, or gas phase, is challenged by these forms of heterogeneity, which also can complicate the presence and distribution of the indigenous microbial population. These conditions make it difficult to unequivocally demonstrate the effects of an *in situ* remediation technology. To date no *in situ* treatment method has been demonstrated to allow reduction of HE concentrations in unsaturated soil, yet there are still sites that need such an alternative.

The Pantex facility, located 27 km (17 mi) northeast of Amarillo, Texas, has utilized HEs in the production of weapons since September 17, 1942 (Ramsey et al., 1995; EPD, 1995). The facility began production of conventional munitions shortly after World War II

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started and remains as the DOE's final assembly and disassembly plant for all nuclear weapons in the United States. Today, the 6500-hectare (16,000-acre) facility, composed mostly of farmland, is operated by BWXT Pantex. During World War II, several buildings were used to process and mold HE in the production of munitions. From 1952 to the present, Pantex has performed casting and machining of HEs for use in nuclear weapons in the area known as Zone 12. Spilled or excess HEs were washed into concrete troughs that emptied into unlined ditches and flowed into playa lakes located on the facility. As a result, the HE-contaminated wastewaters have infiltrated and contaminated the vadose zone, as well as a perched aquifer located 82 m (270 ft) below the Pantex facility. Only since the late 1980s have the HE waste streams been reworked to reduce contaminant discharges.

The primary HEs contaminating the soil and groundwater are octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), 2,4,6-trinitrotoluene (TNT), and 1,3,5-trinitrobenzene (TNB) (Ramsey et al., 1995). In 1996, the Texas Natural Resource Conservation Commission (TNRCC) negotiated subsurface cleanup criteria for these compounds and set the Risk Reduction Standard 2 (RRS2) values for HMX, RDX, TNT, and TNB in soil at 511, 2.6, 5.1, and 0.511 mg/ kg (or ppm) of soil, respectively. It should be noted that the TNB RRS2 value was raised to 310 mg/kg in late 1999, after the commencement of the project reported in this article. The RRS2 requires the removal and/or decontamination of HE to levels such that any substantial present or future threat to human health or the environment is eliminated. Concentrations of RDX and TNB above the RRS2 have been found at several locations at depths less than 9.2 m (30 ft) near a former wastewater treatment building in Zone 12 (see Figure 1) and at depths down to 82 m (Rainwater et al., 2001). Figure 1 provides information about RDX and TNB levels at the depth of 5.5 m (18 ft) to represent conditions near the middle of the eventual target treatment zone, which ranged from 1.5 m (5 ft) to 9.2 m (30 ft) below the ground surface.

To achieve the required cleanup criteria set by the TNRCC, two techniques have been explored, *ex situ* and *in situ* remediation of the soil. *Ex situ* remediation can be used to treat shallow soils that can be easily excavated from the facility. However, some areas at the Pantex facility have a large number of buried utility lines or surface structures that prevent the excavation of soil. Such an area was found near Building 12-43, the former process wastewater treatment facility shown in Figure 1, where extensive HE contamination has been reported in surface soils and subsurface soils caused by HE-contaminated wastewater discharged onto the soil and ditches. The presence of many buried utilities at this location precludes excavation of the contaminated soils. *In situ* bioremediation can offer a feasible approach to treating the HE-contaminated soil without impacting any buried utility lines and surface structures.

The purpose of this project was to develop an *in situ* method to degrade high explosives in the vadose zone. The project involved the construction of an experimental field site to force an anaerobic treatment zone and thus stimulate indigenous microorganisms to degrade the HE. The desired level of treatment was to reduce the HE concentrations to below the RRS2 values, so the work was focused on RDX and TNB. The specific objectives in developing the *in situ* treatment method included (1) location of a site with high levels (greater than 20 mg HE/kg soil) of HEs to remediate, (2) determination of distributions of HE contamination and microbial activity present within the soil, (3) design, construct, and operate the field site and control buildings, and (4) evaluate the effectiveness of the process. More complete reporting of project details is available from Brown (1999) and Rainwater et al. (2001).

BACKGROUND

Previous research at the Texas Tech University Water Resources Center (TTUWRC), the University of Texas, and Idaho National Engineering and Environmental Laboratory (INEEL) demonstrated the potential for *in situ* degradation of the target HE in Pantex soils. Medlock (1998) examined the relationships among HE concentration, metabolic activity within the soil, and microbial population. The soil samples were collected from the first 10 m below ground surface in the Building 12-43 vicinity. Medlock used USEPA (1994) Method 8330 to determine the concentrations of HE in the soil. Microbial activity was determined using the Rapid Automated Biological Impedance Technique (RABIT®) method described in the subsequent section, and microbial populations were quantified with a spiral plate method. He demostrated that aerobic and anaerobic microbial activity was present in all samples taken from the field site and that metabolic activity levels were similar at all soil depths below 1.5 m. HE concentrations did not affect the amount of anaerobic metabolic activity present within the soil, thus showing the anaerobic organisms remained viable in the presence of HEs. Shaheed (1998) conducted multiple tests on soil samples containing HMX and RDX to evaluate the ability of indigenous anaerobic microorganisms to respond to various carbon, nitrogen, and

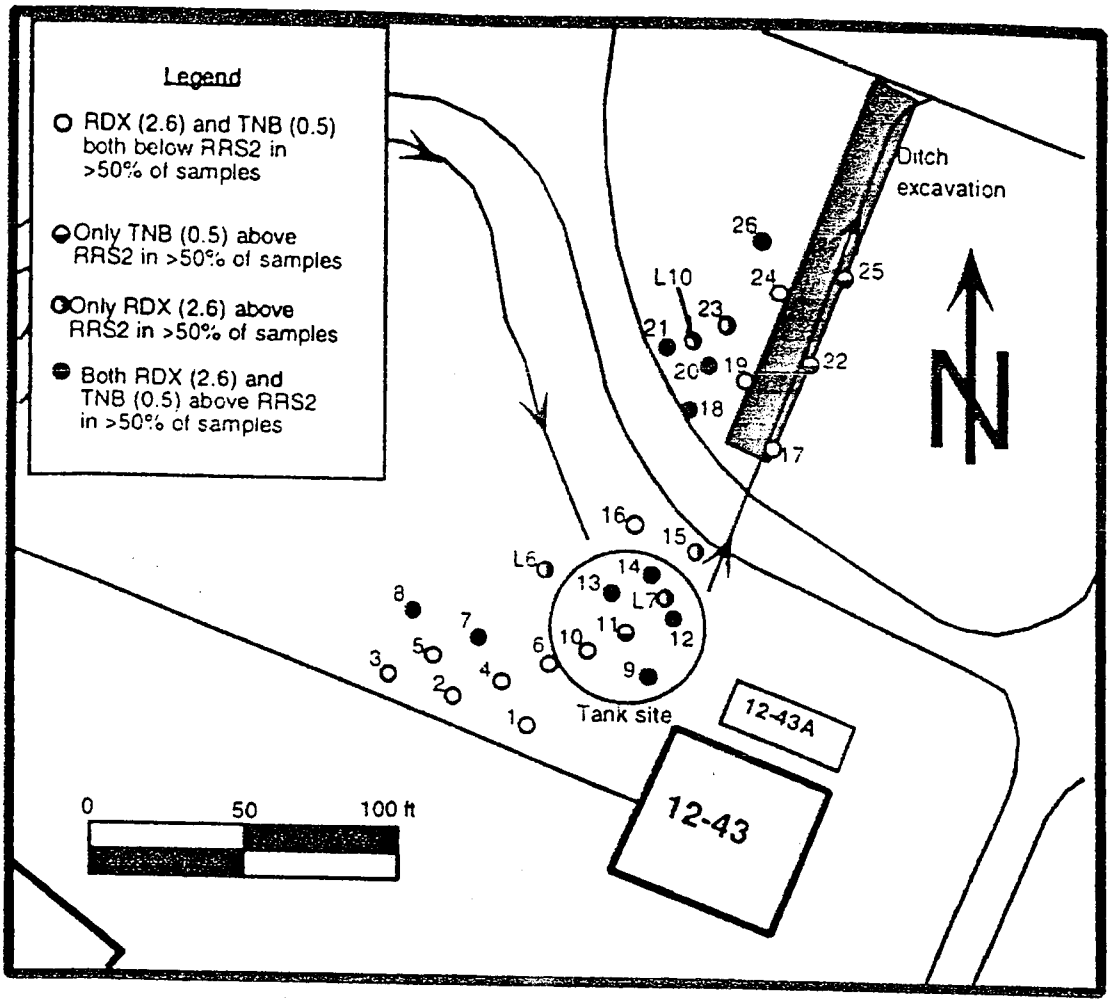

Figure 1. Distribution of RDX (ppm) and TNB (ppm) at 5.5-m (18-ft) in study area within zone 12.

phosphorus amendments in water solutions. The RABIT® method was used to evaluate the response of microorganisms to the nutrients present in the RABIT® test cells. Solutions with relatively high (over 1%) concentrations of nutrients did produce positive metabolic responses when used individually or in combinations.

Speitel et al. (2001) investigated the feasibility of *in situ* bioremediation by determining the environmental conditions needed for RDX to be degraded by the indigenous microorganisms present in soil samples provided by the TTUWRC from cores taken near Building 12-43. The experiments involved the addition of varying amounts of oxygen, nitrogen, and organic carbon source to the headspace of closed vials containing 2-g portions of soil inoculated with ^{14}C-radiolabeled RDX. The samples were incubated at 20°C, and the radiolabeled RDX and its derivatives were monitored at regular intervals by a liquid scintillation counter. The results showed that anoxic (little or no oxygen) environmental conditions should be present for microorganisms to be able to degrade RDX. In addition, added biodegradable organic carbon increased biodegradation rates.

In support of the remediation work at Pantex, experiments with soils from the Pantex site were performed at INEEL (Radtke, personal communication, 1998; referenced in greater detail in Rainwater et al., 2001). These tests evaluated volatile carbon sources applied to simulated vadose zone soils for their potential to stimulate anaerobic activity resulting in reductive transformation of RDX and TNB. The soil samples were provided by the TTUWRC from samples collected near Building 12-43. The introduction of nitrogen gas to the columns created the anaerobic atmosphere needed by the indigenous microorganisms to

biodegrade HEs. Ethanol, acetone, acetic acid, and isobutyl acetate vapors were selected as possible carbon sources to be introduced with the nitrogen. Three soil column replicates for each organic solvent addition and three nitrogen only soil columns were used in the experimental apparatus. In the soil column setup, solvent-laden nitrogen and humidified nitrogen were combined and injected through the soil column. Each of the 15 soil columns was injected with nitrogen and the four organic vapors for 98 days. At the end of the 98-day test period, the soil columns were sampled and those samples were analyzed for HEs. Average RDX and TNB concentrations were lower after treatment for all five test conditions. With nitrogen alone, RDX and TNB concentrations were 20 and 60% lower, respectively, after treatment. The columns with the added vapors also showed reductions in RDX (all near 20%) and TNB (85 to 95%).

These laboratory studies provided sufficient encouragment for a pilot-scale field demonstration at the Pantex site near Building 12-43. The scope of this initial demonstration included injection of nitrogen only into a target treatment zone extending downward to 9.2 m (30 ft) below the ground surface. Nitrogen only, without added volatile organic carbon sources, was used to avoid additional permit modifications for possible volatile emissions as required by the Pantex Plant air permit. High safety concerns due to current HE operations near Building 12-43 also discouraged use of injected organics in the field test site. The goals for this Phase I treatment study were to demonstrate and evaluate a process for controlling the unsaturated zone atmosphere with nitrogen and hopefully encourage degradation of the target HEs. If Phase I proved successful, later phases would incorporate further refinements and pursuit of organic vapor injection.

MATERIALS AND METHODS

HE Analyses

A modified version of Method 8330 (USEPA 1994) for HEs in soil was developed and validated by Medlock (1998). To bring the HEs and related compound concentrations in the extraction solvent into the working range of the HPLC, a larger soil sample size of 6 g was utilized and the extraction solvent had to be reduced via evaporation. The modified method was rigorously tested for reproducible recoveries from soil samples from the Pantex site, taking into account the mixed nature of clay, silt, and sand that comprised the soil. The first steps of the modified method were the same as the original method in that each sample was homogenized, dried at room temperature, ground with a mortar and pestle, and passed through a 30-mesh sieve. The extraction process involved tumbling a 6-g soil sample with 10 mL of acetonitrile in a plastic centrifuge tube for a period of 4 h. After tumbling, the tubes were centrifuged at 4000 rpm for 5 min, and the supernatant fluid from each tube was decanted and stored in a separate centrifuge tube. To ensure complete HE removal, three separate extractions (total tumbling time of 12 h) were performed on each sample and the supernatants were combined.

To concentrate the HEs in the extraction solvent, the supernatant solvents were placed in a water bath at 55°C and injected with nitrogen gas to facilitate the evaporation of acetonitrile. After the volume of supernatant had been reduced to 3 mL, an equal volume of 5 g/L calcium chloride solution was added to precipitate the suspended and colloidal materials. The resulting mixture was then allowed to settle for at least 15 min. The decanted mixture was filtered with a 0.2-µm Teflon® syringe filter, and a 1.5-mL aliquot was transferred into a sealed glass vial for use in an HPLC autosampler.

HPLC analysis was performed using a Varian 9010/9050 with a Varian autosampler. A Whatman C-18 reverse phase HPLC column (25-cm × 4.6 mm, 5 µm) was utilized as the column. The mobile phase for the Varian HPLC was a 60:40 (v/v) mixture of HPLC-grade methanol/deionized water with a flow rate of 1.3 mL/min and UV wavelength of 254 nm. In addition, the column temperature was maintained at 35°C with a column heater. These HPLC conditions provided optimal peak resolution and separation. The validation of the method found a method detection limit (MDL) of 0.1 mg/kg (or ppm) for the HE compounds of interest in the Pantex soils. Limited project funding allowed only analysis for RDX, TNB, HMX, and TNT without additional breakdown products. It is recognized that analyses for breakdown products could have increased the confidence in the experimental results, if the breakdown products were persistent.

Microbial Activity Analysis

The purpose of the application of the RABIT® method was to monitor the general health of the microbial population before and during treatment, as it was unknown how the injected gas stream would impact the microbes. A general description of the RABIT® procedure is given in this section, because this application was the first demonstration of the impedance technique as a screen for microbial activity in a field environment (Medlock, 1998). Increased microbial metabolism results in an increase in conductance and capacitance while causing a decrease in impedance

and a consequent increase in admittance (Eden and Eden, 1984; Don Whitley Scientific, 1996). The general technique developed by Don Whitley Scientific (1996) measures the changes in admittance (measured in microsiemens, μS) over time. The RABIT® method reported by Medlock (1998) is advantageous due to its short duration, repeatability, and ability to evaluate large numbers of soil samples. Also, by changing the culture medium, it has the potential capability of simultaneously testing for different microbial populations within a soil sample.

There are two different testing methods that can be utilized in the RABIT® system. In the direct method, the test soil and a nutrient broth are placed in a plastic test cell where they are in direct contact with the two system electrodes. Oxygen is not excluded from this test, so aerobic and/or facultative organisms can grow, but strict anaerobes are unlikely to grow. Growth of organisms in the soil sample increases conductance because of charged metabolite production (Don Whitley Scientific, 1996). However, if the microbes do not produce charged end products, growth will not be detected by the direct method. In the indirect method as used in this study, the test soil (0.5 g) and nutrient broth are placed in a glass tube and inserted into a test cell. The two electrodes in the test cell are immersed in a potassium hydroxide (KOH) solution stabilized with agar. Oxygen is limited in this method, thus allowing the growth of facultative and/or anaerobic organisms. Microbial metabolism is monitored via the production of carbon dioxide (Don Whitley Scientific, 1996). Any carbon dioxide produced as a result of normal metabolism is absorbed by the KOH, causing a resultant decrease in conductivity.

In both the direct and indirect methods, the user defines the detection criteria that will be used to establish a time to detection (TTD). TTD is the time required to reach the point of detection, at which the growth rate has met or exceeded the growth detection criteria for three consecutive 6-min intervals. If the growth detection criteria are met, "growth detected" will be recorded along with a TTD. If the growth detection criteria are not met, then "no growth detected" will be reported. The RABIT® system also reports the total change in admittance (TCA) over the entire test period, typically 48 h, for each direct and indirect test. The indirect RABIT® method developed was applied to HE-contaminated soil borings from Zone 12. Medlock (1998) previously showed that TCA corresponded to an increase in microbial activity due to the differences in TCA between test soil samples and sterile (heated at 375°C for 24 hours) controls.

Field Site Establishment

The field site for the demonstration was set up north of Building 12-43 following characterization of the HE distribution in the vicinity. The intent was to identify a site with RDX and TNB concentrations above 20 ppm and large enough to allow construction of a modified 5-spot injection and extraction well system. The potential study area was explored by geoprobe, with soil samples collected continuously to a depth of 9.2 m (30 ft). The vertical limit of the investigation and potential remediation application were those originally set by the Pantex Plant Environmental Restoration staff. The investigative sampling was done with geoprobe rigs, first with one provided by a local contractor, and later with one provided by Sandia National Laboratory through the DOE's Innovative Technology Remediation Demonstration (ITRD) program. Typical samples sizes were 5 cm (2 in) in diameter and up to 1.2 m (4 ft) in length, depending on the amount of recovery. The soil samples were analyzed at 0.6-m (2-ft) intervals using Method 8330 as described in the previous section. In addition, the soils were analyzed at 1.2-m (4-ft) intervals by the RABIT® indirect method to indicate microbial activity. Figure 1 relates geoprobe sample locations with RDX and TNB concentrations above the RRS2 clean-up criteria.

The target treatment depth interval was planned for 1.5 m (5 ft) to 9.2 m (30 ft), as the planned nitrogen injection would be kept far enough below the ground surface to prevent direct loss of the injected gas to the atmosphere. In addition, the conventional wisdom about the site implied that surface concentrations of the HE compounds were often much greater than those at greater depth. For these reasons, reporting of the observed soil concentrations in this article concentrates on the soil samples collected within the 1.5 m to 9.2 m range. This approach provided 65 samples for the initial or pre-Phase I conditions. Typically, RDX and TNB showed up in similar magnitudes in similar sampling locations. In preparation for comparison with posttreatment values, Crockett et al. (1996) recommended examination of the statistical distribution of the collected data values, primarily testing for normality or lognormality. Lognormal distribution is typically suspected when the dataset has many low and few high values. In the statistical analyses, all nondetects were replaced with one-half the MDL, or 0.05 ppm. The analysis showed that the data were neither normally or lognormally distributed. Figure 2 presents a graphical representation of the test result. The 65 (n) measured values were ordered, given a rank (m), and assigned a cumulative probability (P) according to the Weibull formula (Viessman and Lewis, 1995).

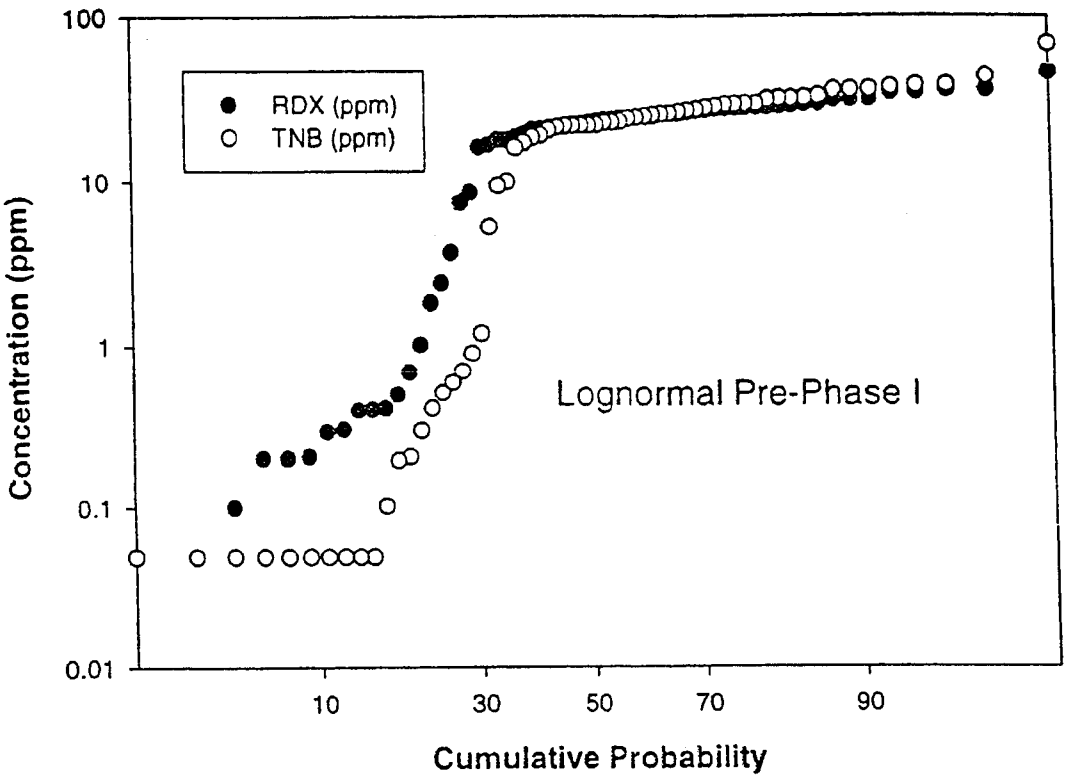

Figure 2. Lognormal plot of RDX and TNB concentrations in pretreatment soil samples.

$$P = \frac{m}{n+1} \qquad [1]$$

The cumulative probability vs. concentration data were plotted with SigmaPlot (SPSS, 1997). Because the data did not form a straight line on the log concentration vs. probability graph. Figure 2 demonstrates visually that these RDX and TNB values were not lognormal. The normality test also failed. These findings indicated that discussion of mean and standard deviation of the datasets was of limited value, and that nonparametric presentation of the data was warranted. Comparison of the parameters of the initial condition data are shown in greater detail later with the posttreatment data in the posttreatment results.

It was possible to demonstrate the distribution of the HEs in the subsurface by making contour plots of HE concentration between the boreholes using Surfer® (Golden Software, 1999). Referring back to Figure 1, a south-north cross-section that could be called A-A' can be formed by connecting boreholes 10, 13, 16, 18, 20, 23, and 26. Figure 3 shows the resulting plot for RDX distribution. A noticeably high concentration area was obvious near borehole 18. The low concentration area at depths less than 4.6 m (15 ft) near borehole 13 represented a location where a sump tank had been removed and replaced with clean backfill soil. Figure 4 shows an east-west cross-section B-B' for RDX through boreholes 19, 20, and 21. The concentrations were lower near borehole 19 as it bordered a stormwater drainage ditch, which allowed more concentrated infiltration of HE-free runoff water. It is interesting to note that these plots indicate persistently significant concentrations along the entire borehole depth at certain locations, while concentrations in some areas changed greatly across distances of as little as 4.6 m (15 ft).

Based on those findings, a 5-spot pattern was established using holes 18, 19, 20, 21, and 23 in Figure 1. Figure 5 describes the final layout of the system, with 18, 19, 20, 21, and 23 later labeled as E4, E3, I, E2, and E1, respectively. The injection (I in Figure 5) and extraction (E1 to E4) wells were bored using a geoprobe rig provided by Sandia National Laboratory (SNL). Each well extended to a depth of 9.2 m (30 ft) and had a diameter of 5.1 cm (2 in). The wells were cased with 2.5-cm (1-in) schedule 80 PVC pipe and were screened from 1.5 to 9.2 m (5 to 30 ft). The slot size of the screen

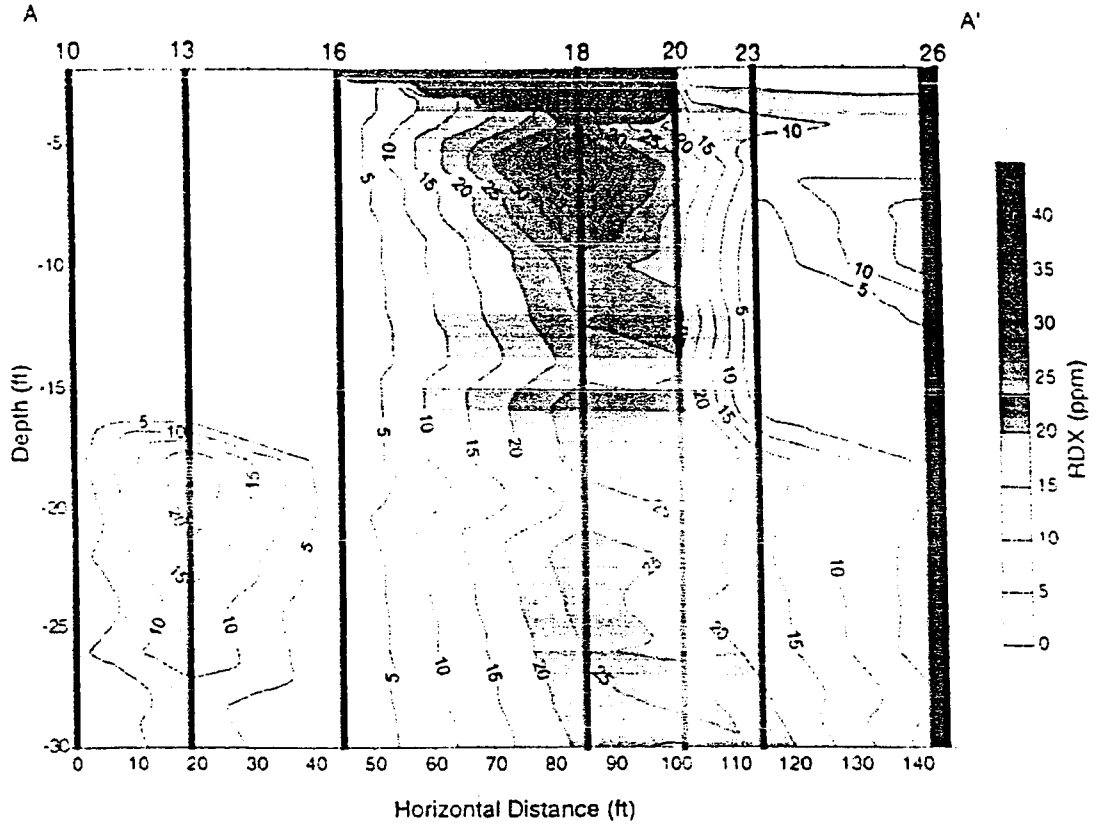

Figure 3. Pretreatment RDX distribution along South-North cross section.

was 0.51 mm (0.020 in). The screened section of each well was sand-packed to allow for adequate gas flow into and out of the wells. Bentonite chips were placed in the annulus of the 0.9 m (3 ft) above the sand pack in each well, then hydrated to prevent water from infiltrating through the annulus down into the well. The surface completion of the well included concrete in the annulus of the last 0.6 m (2 ft) to the ground surface and a steel 25-cm (10-in) diameter manhole to allow access to the connections to the 0.64-cm (0.25-in) copper injection-extraction tubing.

Six gas sampling wells (show as "Gx-x" in Figure 5) were installed to allow monitoring of the gas composition across the field site. Gas sampling ports were placed at three different depths to allow sampling of gas composition in the shallow and deep regions of the treatment zone. These wells were bored to their desired depths using a 7.6-cm (3-in) diameter auger. In each well, the gas sampling ports were set at depths of 2.4, 4.6, and 7.6 m (8, 15, and 25 ft). The gas sampling ports were constructed from a 20-cm (8-in) wire mesh screen (Geoprobe AT-86-17S stainless steel 3/16-in implants) with a geoprobe drive tip placed on the end. A 0.64-cm (0.25-in) O.D. plastic tube carried the sampled gas to the top of the well where it was then joined to a 0.64-cm (0.25-in) O.D. copper tube using a compression fitting. The three gas sampling ports were sand-packed to allow for adequate gas flow into the sampling port. In addition, bentonite chips were placed in between each gas sampling port to prevent gas from moving vertically within each well. The surface completions were the same as the injection and extraction wells.

A set of specially designed, strategically placed *in situ* environmental samplers (SPIES) were used to monitor the amount of HE degradation that was occurring in the treatment zone. This concept was encouraged by the scientific panel of the ITRD program, which contributed services, funding, and advice to this project. The SPIES soil samples were removed from the actual field site using a geoprobe rig, and the initial HE concentrations were determined for each end of the soil sample. Each soil sample was initially 0.6-m (2 ft) long with a diameter of 2.5 cm (1 in). The ITRD panel discouraged homogenization of the soil in the SPIES before reinsertion into the subsurface to minimize any

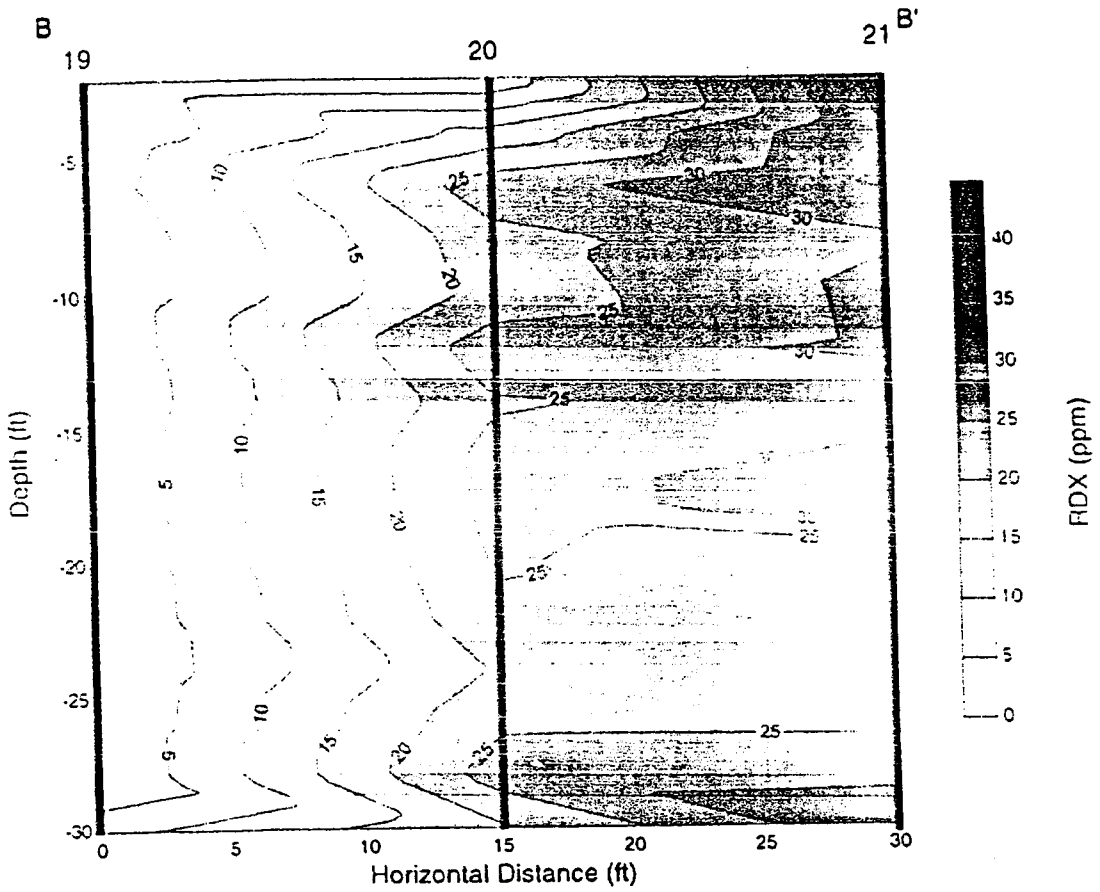

Figure 4. Pretreatment RDX distribution along East-West cross section.

bias from handling. These SPIES soil samples were each housed in a plastic tube with small holes drilled around the circumference to allow adequate movement of gas into the soil sample. The SPIES wells (shown as "Sx-x" in Figure 5) were constructed to have soil sample depths of 2.4, 4.6, or 7.6 m (8, 15, or 25 ft, depth noted on Figure 5). Figure 6 depicts the downhole configuration. The six SPIES wells were cased using 6.4-cm (2.5-in) PVC pipe with screened sections in the bottom 0.76 m (2.5 ft) of the well. The screened section of each well was sand-packed and bentonite chips were used just above the screened section. A 0.64-cm (25-in) copper tube was installed from the middle of the screened section to the manhole to monitor the composition of gasses in the well. The surface completions were the same as the injection and extraction wells. The SPIES soils were retrieved at selected times and analyzed for HE and microbial activity.

The entire site was covered by a 12 m by 12 m (40 ft × 40 ft), 60-mil high-density polyethylene (HDPE) geomembrane to prevent infiltration of water and limit communication with the atmosphere. A soil and gravel cover was placed on top of the HDPE to hold the geomembrane in place. Plumbing work to each well and sampling location in the finished field site was completed using 0.64-cm (0.25-in) O.D. copper tubing, and compression fittings were used to join all copper tubes. The tubing lines were run from the finished field site to the small control buildings located approximately 46 m (150 ft) southwest of the finished site. Each gas sampling position had its own tube that ran all the way back to the control building for sampling access. All gas sampling was done at the control building rather than directly on the treatment site because the treatment site was actually constructed in a higher security zone near another building with ongoing HE operations. TTUWRC staff could access the control buildings with normal security escorts, but access to the treatment site itself required additional permission and scheduling around the HE operations in the nearby building. One control building housed

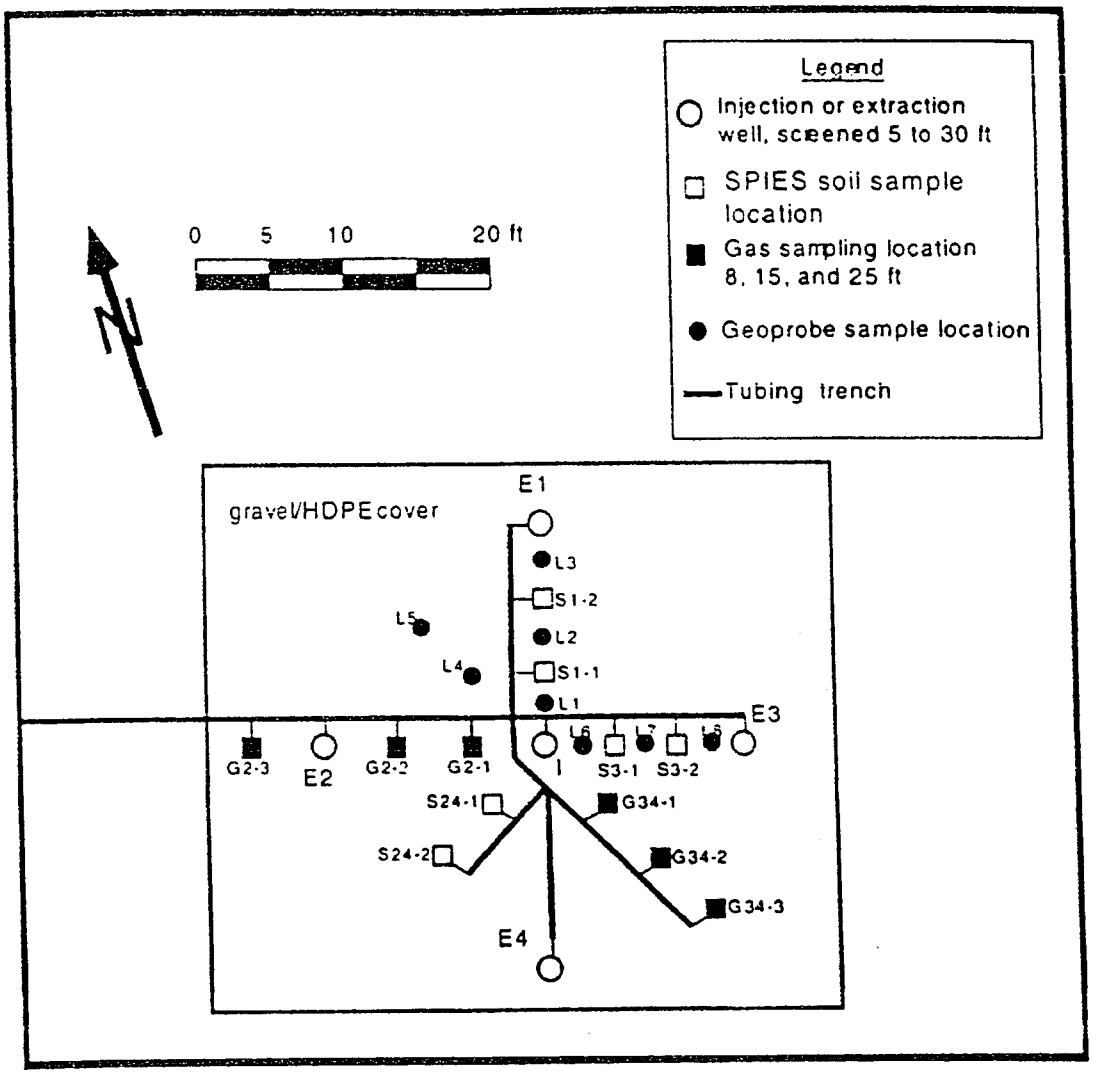

Figure 5. Layout of field treatment site.

most of the plumbing controls, valves, flow meters, and extraction pumps. The other control building housed the liquid nitrogen cylinder, water column, and gas-monitoring devices.

Field Site Operation and Maintenance

The purpose of the nitrogen injection system was to create anaerobic conditions within the soil in the treatment zone. The injection flow rate was 4.8 L/min (nominal 0.17 scfm). The residual pressure in the liquid nitrogen cylinder was used to inject nitrogen gas into the injection well. The nitrogen was bubbled through a water column to maintain a relative humidity of approximately 30% in the nitrogen gas and prevent dehydration of the soil. Each of the 4 1/3-hp extraction vacuum pumps were set with rotameter flow controllers to target flow rates of 4.8 L/min (nominal 0.17 scfm).

A single vacuum pump was used to extract gas from the 18 gas sampling ports and the six soil sampling gas ports. Each of the 24 gas sampling lines was equipped with a two-way valve at the control building so that the lines could be sampled individually. During the sampling process, each sampling line was pumped long enough to purge at least twice the gas volume contained in the tubing and sampling position. The extracted gas sample was collected in a 2-L tedlar gas sampling bag for later analysis.

The gas composition from the extraction wells and gas sampling ports was analyzed with a LANDTEC™ GA-90 landfill gas analyzer. The gas analyzer was used to determine the percent oxygen,

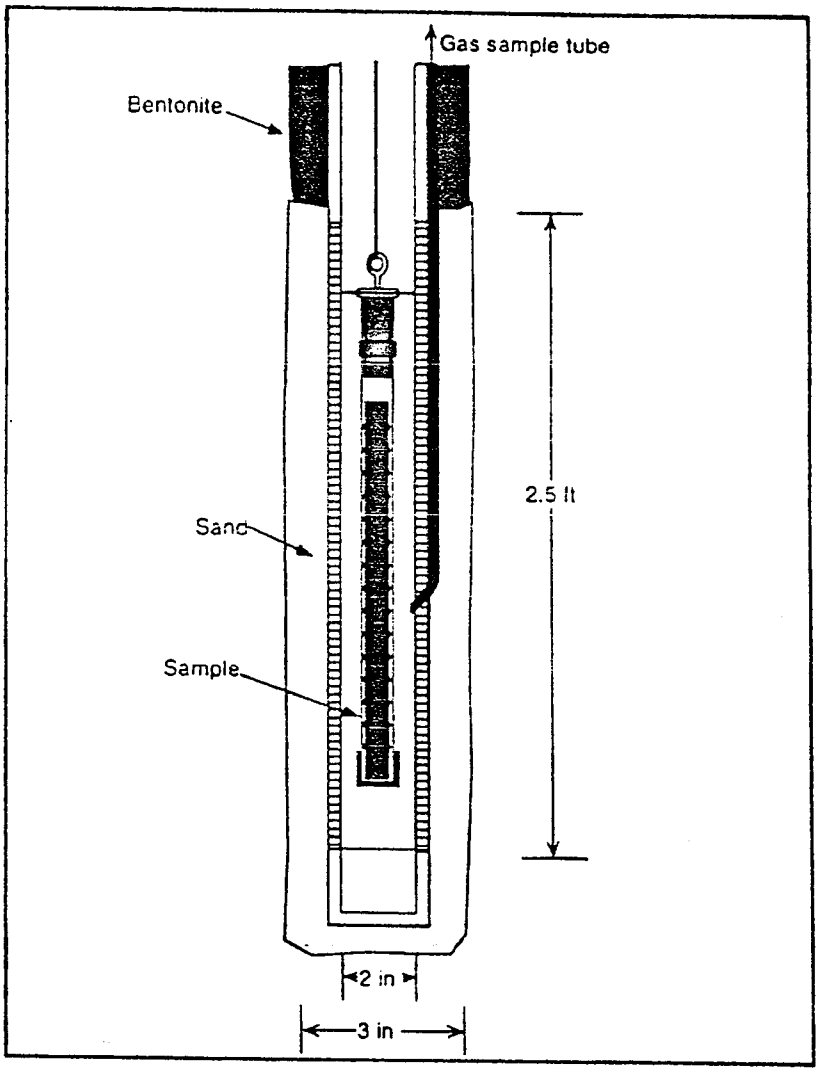

Figure 6. Strategically placed *in situ* environmental samplers (SPIES, not to scale).

methane, and carbon dioxide in the extracted gas. Gas composition monitoring was performed weekly on all extraction wells, gas sampling ports, and gas ports in the soil sampling wells. In addition to the reported gas composition data, the facility permit required weekly monitoring of the VOC content of the granular, activated carbon-treated effluent gas from the system. The effluent gas was analyzed to determine if volatile organic carbon compounds were being generated in the treatment zone. VOC content was measured relative to a 114-ppm methane standard gas with a Foxboro field flame ionization detector (FID).

OPERATIONAL AND POST-TREATMENT RESULTS

Operation of the system began on May 24, 1999. Operation continued relatively continuously for 333 days, with occasional maintenance shutdowns. Experience showed that some air and runoff water leaks occurred near some of the manholes, and the leaks were repaired by rebuilding the leaking concrete collars for the manholes. Unfortunately, most of the gas sampling ports did not allow gas flow for sampling, so it was concluded that the plastic tubes from the ports were most

likely blocked by squeezing by the swelled bentonite annular packing. The gas sampling ports in the SPIES were then used as the primary indicators of the target zone oxygen levels, as well as methane and carbon dioxide. The SPIES soils were originally planned to be sampled on a monthly schedule. The initial SPIES retrieval took place after 3 months of operation, a delay hopefully long enough for the oxygen levels to fall to the target level of 5% within the target treatment zone. Samples were taken from the upper and lower ends of the SPIES after 110, 151, 184, 213, 252, 284, and 333 days of exposure in the system. Near the end of the treatment phase, at 295 days, a geoprobe was used to collect core samples from eight locations in the treatment zone (shown as L# in Figure 2).

Gas Composition Results

The gas compositions for the extraction wells and SPIES holes were monitored in the field with the landfill gas analyzer. Based on the theoretical 5-spot flow regime, the oxygen levels in the extraction wells were expected to reach approximately 16% after the injected nitrogen had completely broken through. However, only E1 achieved this lower level, while E2, E3, and E4 leveled out at over 20 % oxygen, similar to atmospheric air. Figure 7 shows the variations in oxygen levels within the treatment zone as measured in the SPIES holes, which indicated that nitrogen was moving throughout the target treatment zone. It was concluded that the same leaks that allowed water into E2, E3, and E4 were also allowing atmospheric air to be introduced into the gas flow produced at these wells, keeping the measured oxygen levels near atmospheric. The manhole at E2 was regrouted in March 2000, and the produced oxygen level immediately fell. Regrouting of the manholes at E3 and E4 was scheduled after the termination of this first field test and prior to future nitrogen injection.

The goal of the nitrogen injection was reduction of the oxygen levels in the target treatment zone to below 5% to achieve conditions conducive for the target HE degraders. As seen in Figure 7, the oxygen levels did not begin to fall significantly in the SPIES until after the leaks within the manholes were stopped with epoxy. Oxygen levels fell below 5 % in S1-1, S1-2, S24-2, and S3-2 for much of the time after the extraction well flow rates were increased. Over the duration of the project, it was learned that the SPIES holes were best sampled with a relatively low flow rate, using a low suction 1/8-hp vacuum pump. With the smaller pump, the oxygen levels were typically several percent lower than samples pulled with the larger 1/3-hp pump. The larger suction capacity pump apparently drew in more atmospheric air through leaks at the SPIES holes, diluting the soil atmosphere in the SPIES themselves. The persistent relative variability in oxygen levels between the SPIES holes, even after over 300 days of operation, indicated preferential flow may have occurred within the injection/extraction flow regime, or that air leakage during sampling was more significant at some holes. The oxygen levels at S24-2 and S3-2 were consistently higher than the other four SPIES. Also shown in Figure 7 is some increase in the oxygen levels at all the SPIES holes near the end of the report period. These increases were likely due to the erratic stoppages in nitrogen gas flow caused by the inconsistent behavior of the liquid nitrogen tanks. These problems should be reduced in the next phase of the project when a nitrogen generator will be installed at the site as a source with continuous flow and pressure.

No methane was ever detected in any extraction well or SPIES hole gas sample. Figure 8 shows the variations in carbon dioxide in the SPIES holes. Carbon dioxide production from HE mineralization would be insignificant compared to natural sources of carbon within the soil matrix. There are numerous potential sources of carbon dioxide in this system, such as normal degradation of naturally occurring organic matter in the soil. VOC content measured relative to a methane standard gas with an FID was typically 1 to 5 ppm, similar to background atmospheric concentrations.

Microbial Activity

The purpose of the indirect RABIT® analyses was to monitor the general microbial activity level within the treatment zone. The initial average activity as indicated by the total change in ± 95 % confidence interval) was 4270 ± 740 µS, calculated from 35 samples from the 5 injection and extraction well holes. The TCA levels measured in 35 sterile controls from the same 5 injection and extraction holes averaged 750 ± 68 µS. Figure 9 shows a typical comparison of the measured oxygen levels and RABIT® TCA levels for SPIES hole S1-1. It did appear that the higher TCA values correlated roughly with the lower oxygen levels at all the SPIES. The average posttreatment TCA measured from the 56 samples from the eight geoprobe locations was approximately 3960 ± 360 µS, similar to the initial site average. These results indicated that indigenous microorganisms in the samples were metabolically active throughout the treatment period. The large TCA changes were known to be microbially based because splits of the same samples after sterilization showed much smaller TCA values. The concern about the nitrogen gas injection causing excessive negative impact on the microbial activity appeared to

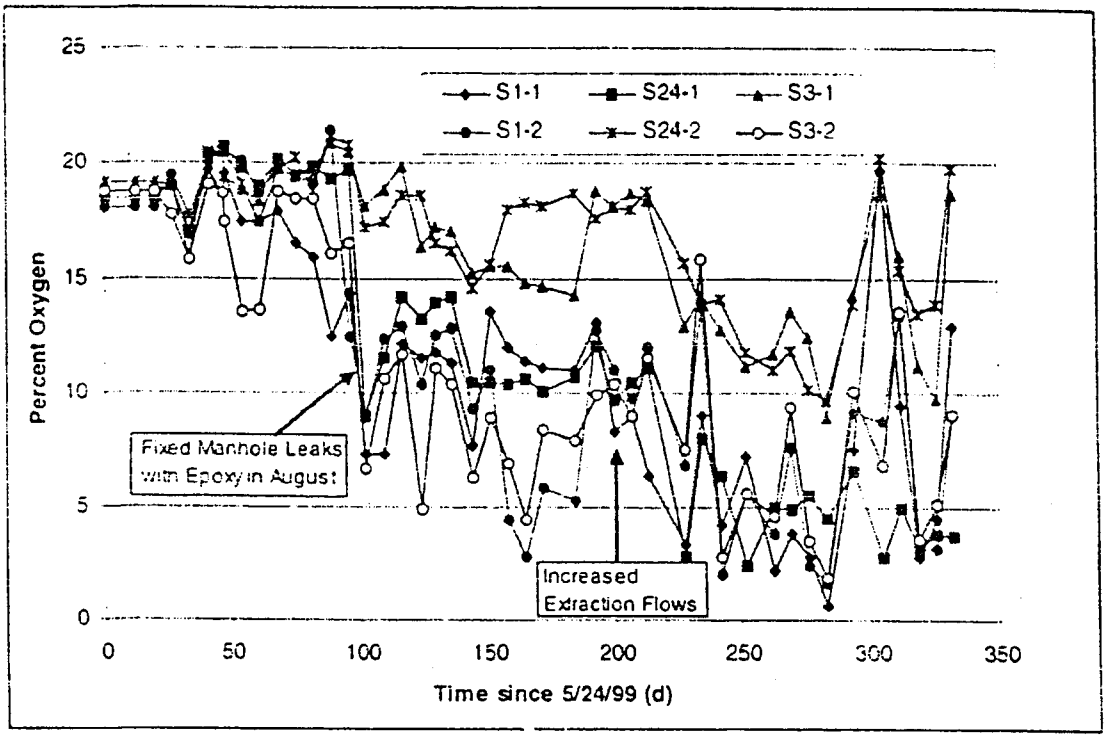

Figure 7. Variations in percent oxygen in SPIES holes.

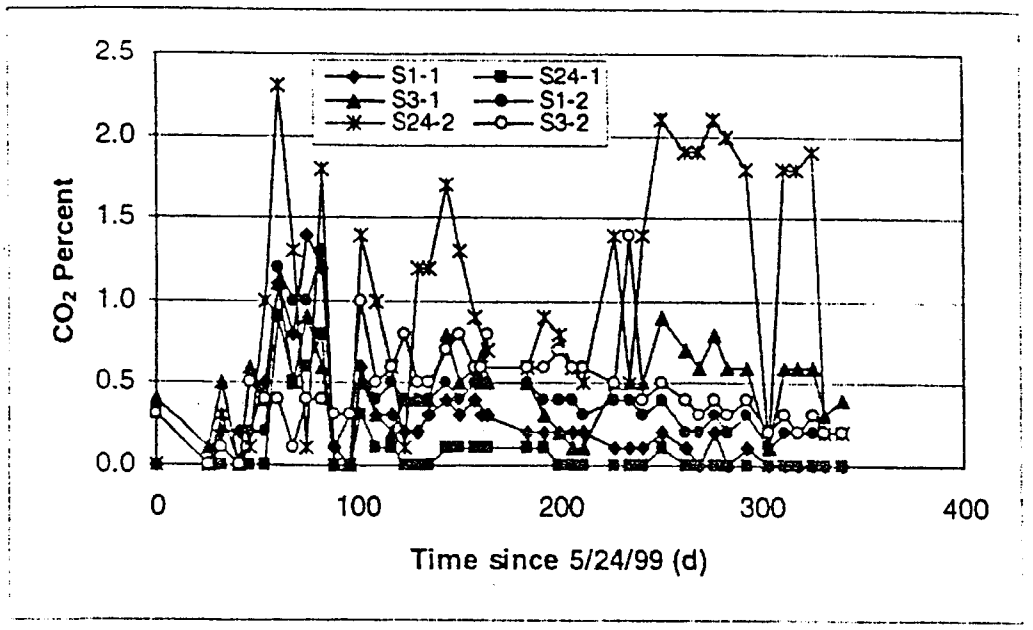

Figure 8. Variations in percent carbon dioxide in SPIES holes.

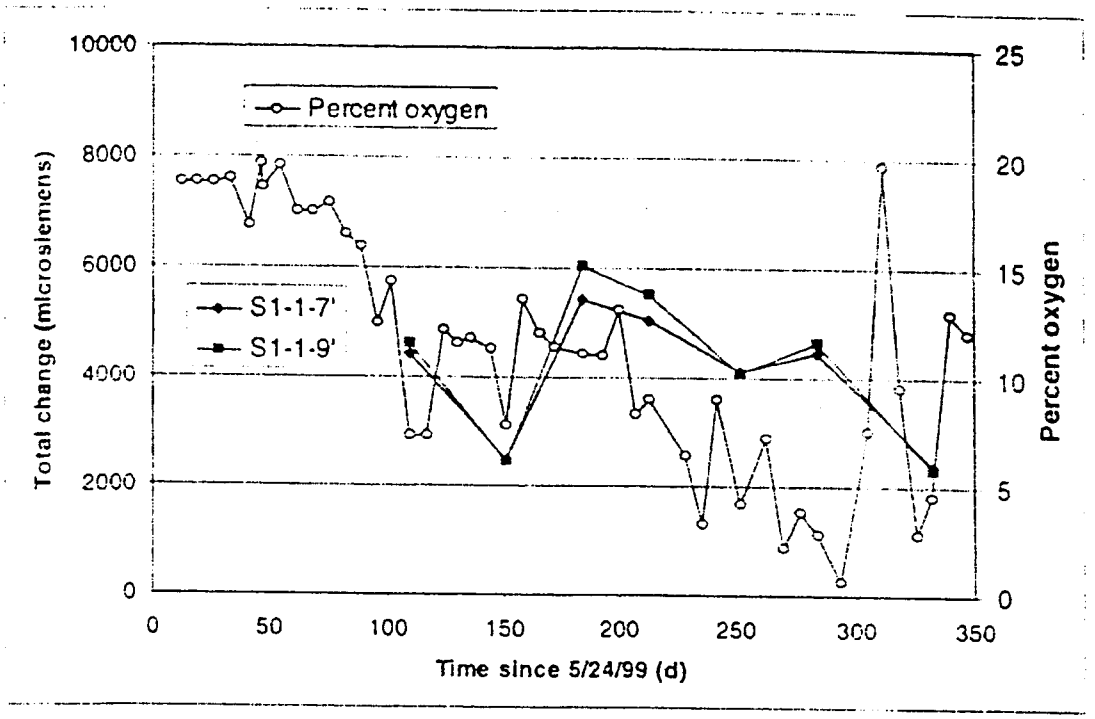

Figure 9. Comparison of TCA and percent oxygen levels at SPIES hole S1-1.

be unfounded. These data did not indicate which microorganisms were active, and the identification of individual organisms was not within the funding level of the project.

Soil HE Concentrations

SPIES Samples — The SPIES soils were retrieved, sampled at both ends, and analyzed seven times during the 333 days of treatment. The initial concentrations of RDX were above the RRS2 value of 2.6 ppm in all SPIES except S1-1. Figures 10 and 11 show the changes in the RDX and TNB concentrations, respectively. RDX concentrations generally decreased over time, with S24-1 as the notable exception. S24-1 had significantly lowered oxygen content displayed in Figure 7. The reason for the consistently high RDX value is unknown. By Day 184, the RDX concentrations were below the RRS2 value of 2.6 ppm at all but S24-1 and S3-2, with little difference in subsequent events. S3-1, S3-2, S24-1, and S24-2 all had significant initial TNB concentrations in the initial sample, but by Day 184 only S3-2 and S24-1 had TNB above the pre-1999 RRS2 value of 0.51 ppm. It is noted that S24-1 and S3-2 ended up with the higher values of both compounds. S24-2 and S3-1 had the widest fluctuations in oxygen percentage as shown in Figure 7, but both SPIES still showed considerable changes in both RDX and TNB over the treatment period. It is possible that the difficulty in sealing the SPIES holes and preventing temporary inward leakage of atmospheric air during vacuum sampling contributed significant uncertainty to the oxygen measurements relative to the actual atmospheric composition achieved by the injection process during sampling. Still, the consistently lower values of RDX and TNB in most of the SPIES samples implied that the treatment was having measureable effects.

Core Samples — After 295 days of treatment, soil cores were collected with a geoprobe unit provided by the Pantex Environmental Restoration group. The cores were 5-cm (2-in) diameter, 1.2-m (4-ft) long, collected continuously to depths of 0 to 9.2 m (30 ft) at the locations L1-L8 shown on Figure 2. These locations were selected to be in the target treatment zone between the injection and extraction wells, to avoid the buried plumbing, and to allow for future sample locations elsewhere. The intent was to get some samples from positions directly between the injection and extraction wells along with other samples (L4 and L5) that did not lie along the shortest flow lines. The core samples were collected as "continuous" core, and subsamples were analyzed every 0.6 m (2 ft) in the

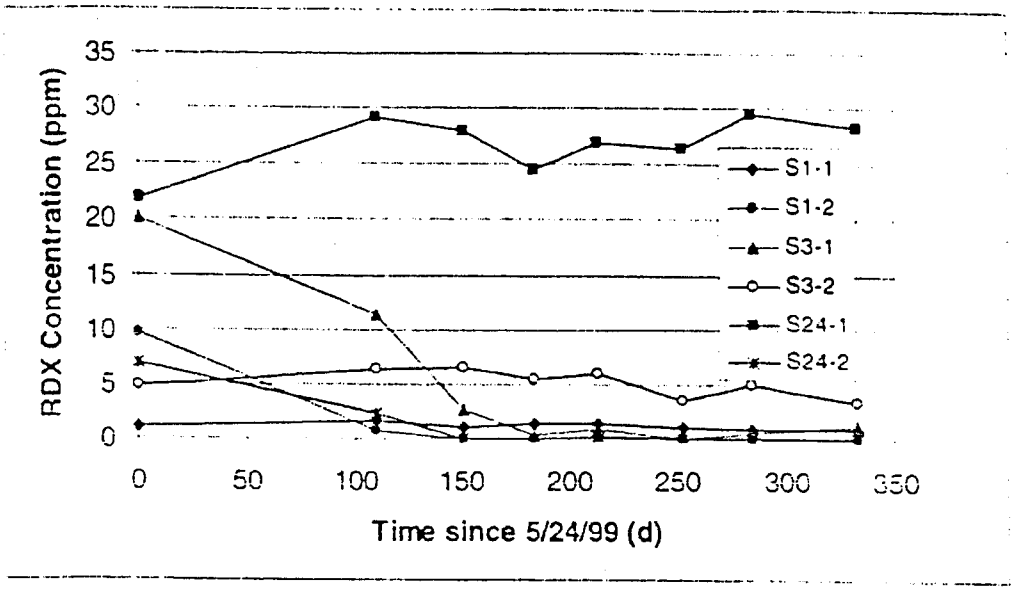

Figure 10. RDX concentrations in SPIES soil samples during treatment.

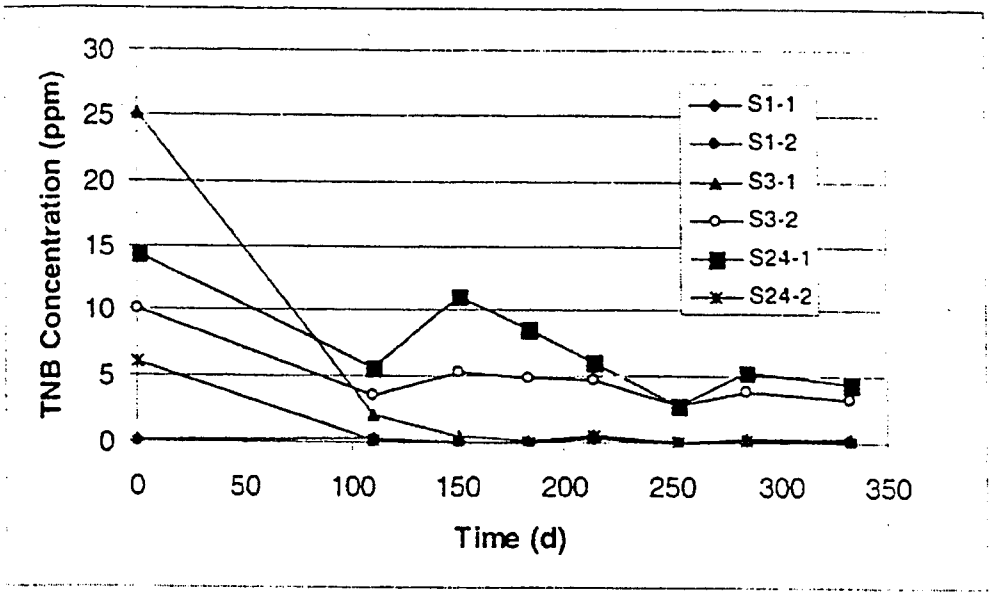

Figure 11. TNB concentrations in SPIES soil samples during treatment.

cores. After removal of the samples, the holes were filled with bentonite chips, which were then hydrated to seal the holes.

Evaluation of the RDX and TNB concentration distributions considered both statistical and spatial aspects. First, similar to the compilation of the pretreatment values, the dataset was tested for normality and lognormality. Using the same graphical approach, the dataset was found to be neither normal nor lognormal. Figure 12 shows the plot of log concentration vs. cumulative probability for both compounds. The lack of linearity was obvious. In addition, it is arguable that describing the data with parameters based on normality is of little value, even though it is conventional. An alternative nonparametric analysis is given later in this section. As is often done by convention, the mean, standard deviation, 95% confidence intervals, standard error, and coefficient of variation in percent were calculated for comparison between the pre- and posttreatment datasets. As the target treatment zone was for depths from 1.5 m (5 ft) to 9.2 m (30 ft), a separate yet similar analysis was done for the soil samples within that depth range. Table 1 shows the results of these calculations. The mean values appeared to be somewhat sensitive to the selected datasets, but the other parameters were relatively similar for both datasets. The coefficients of variation varied from 65 to 112%, within the typical ranges cited by Crockett et al. (1996). When this much variability is present in the datasets, it is difficult to confirm that the treatment process was effective unless the change in concentration after treatment is also large. As there was little information on which to set the original Phase I pilot treatment duration, it was not possible to *a priori* set such a duration within the time and funding limitations of the project. If only the samples from within the target zone are compared, the average (± 95% confidence interval) RDX concentration went from 18.7 ± 3.0 ppm before treatment to 12.4 ± 2.0 ppm after Phase I, while the TNB average went from 18.6 ± 3.6 ppm to 11.9 ± 2.3 ppm. These differences can be expressed as an approximately 34% lower RDX average and a 36% lower TNB average. Figure 15 summarizes the comparison of the datasets in histogram form with averages and 95 % confidence intervals.

Figures 13 and 14 are contour plots that represent cross-sections that could be formed based on the positions of the samples. Both compounds had somewhat

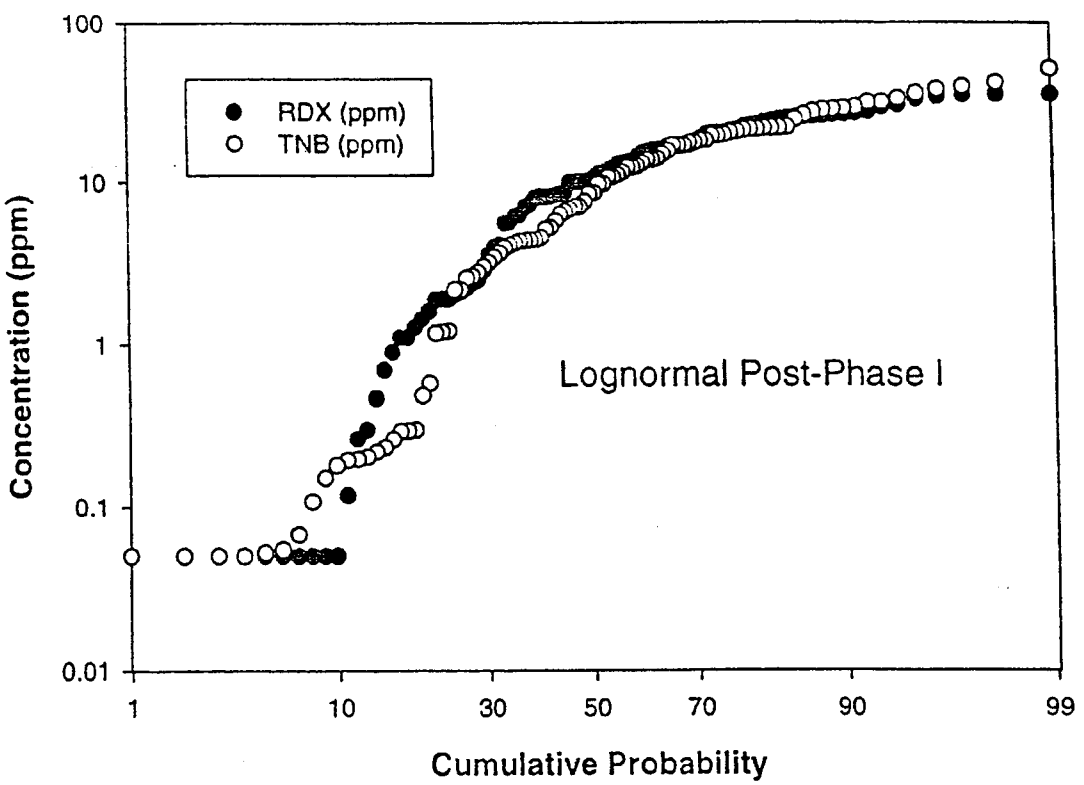

Figure 12. Lognormal Plot of RDX and TNB Concentrations in Post-Treatment Soil Samples.

Table 1. Comparison of sample set means (ppm) and related statistics.

	With All Sample Values				Samples Deeper than 1.2 m			
	Initial Conditions		After Phase I		Initial Conditions		After Phase I	
Statistical Parameter	RDX	TNB	RDX	TNB	RDX	TNB	RDX	TNB
Number	74	74	117	117	65	65	101	101
Average (ppm)	18.2	17.1	10.9	10.3	18.7	18.6	12.4	11.9
Standard Deviation	12.6	14.9	10.4	11.5	12.2	14.9	10.4	11.6
95% Confidence Interval	2.9	3.4	1.9	2.1	3.0	3.6	2.0	2.3
Standard Error	1.5	1.7	1.0	1.1	1.5	1.8	1.0	1.2
Coefficient of Variation (%)	69	87	96	112	65	80	84	98

similar distributions, so only RDX is shown here. Figure 13 shows a cross-section that lies between the injection well I and extraction well E1. This distribution shows the larger concentrations near the south, and the much lower concentrations to the north. This cross-section would lie between holes 20 and 23 on Figure 3, the much larger south-north cross section based on the pretreatment values. The greater differences appeared to be in the shallower soils, from 1.5 m (5 ft) to 7.6 m (25 ft) and toward the north. Figure 14 shows a cross-section selected to include the remaining posttreatment sampling positions, even though they did not lie in a straight line. Higher concentrations were seen toward the northwest, off the lines between the injection and extraction wells. The L6-L8 boreholes lay between the boreholes numbered 19 and 20 on Figure 4, with L8 closest to borehole 19. Due to the more complex RDX distribution in Figure 14, where concentrations varied by over a factor of 2 over distances of less that 1.5 m (5 ft), it is difficult to identify areas of significant change between pre- and posttreatment conditions. Additional plots and complete tabulation of the soil HE data were included in Rainwater et al. (2001).

In recognition of the lack of a simple statistical distribution for the soil concentration values, the data were ranked and analyzed for presentation as box-and-whisker plots to more properly demonstrate the nature of the datasets (Berthouex and Brown, 2002). The plots were generated with SigmaPlot 4.0® (SPSS, 1997). The plots show the median value as a line in the middle of a box that has the 25th and 50th percentile values as the ends of the box, with whiskers that show the position of the 10th and 90th percentile values. Any outliers beyond the 10th and 90th percentiles are shown as individual data points. Figure 16 shows the resulting box plot for the initial and post-treatment RDX and TNB values in the target depth range. For reference, a dotted line on each box shows the mean values previously reported in Table 1. Table 2 provides the numerical values for the median and other percentile values. The pretreatment medians were 22.5 and 21.8 for RDX and TNB, respectively, while the posttreatment values were 10.2 and 8.4, respectively. The percent differences in pre- and posttreatment median values were 54 and 61%, respectively. While this approach may represent the results more positively, it is certain that the process has not yet brought much of the *in situ* soil down to concentrations below the RRS2 levels.

CONCLUSIONS

Based on these encouraging results, the treatment process appears to be successful in reducing the RDX and TNB concentrations at the site. However, the challenges posed by heterogeneity of soil and HE distribution prevent the direct conclusion that the nitrogen injection was absolutely responsible for the different concentrations found before and after treatment. The status of the technology can be discussed using a "lines of evidence" approach such as that used in risk assessment and risk-based corrective action (see USEPA 1996; TNRCC guidance for HE in soil is still under development). Primary lines of evidence are based on actual data collected from the site under characterization or remediation that directly show the changes in concentrations for contaminants of concern over time and space and are used primarily for plume stability description. Data from the site indicate it satisfies the primary line of evidence requirement. Secondary lines of evidence consider observed data for indirect indicators of the chemical or biological processes that are known to encourage decreases in the concentrations of the contaminants of concern. The qualitative identification of increased carbon dioxide production in the zone of interest indicates presence of biological activity. Tertiary lines of evidence include the findings of field or microcosm studies that employ actual

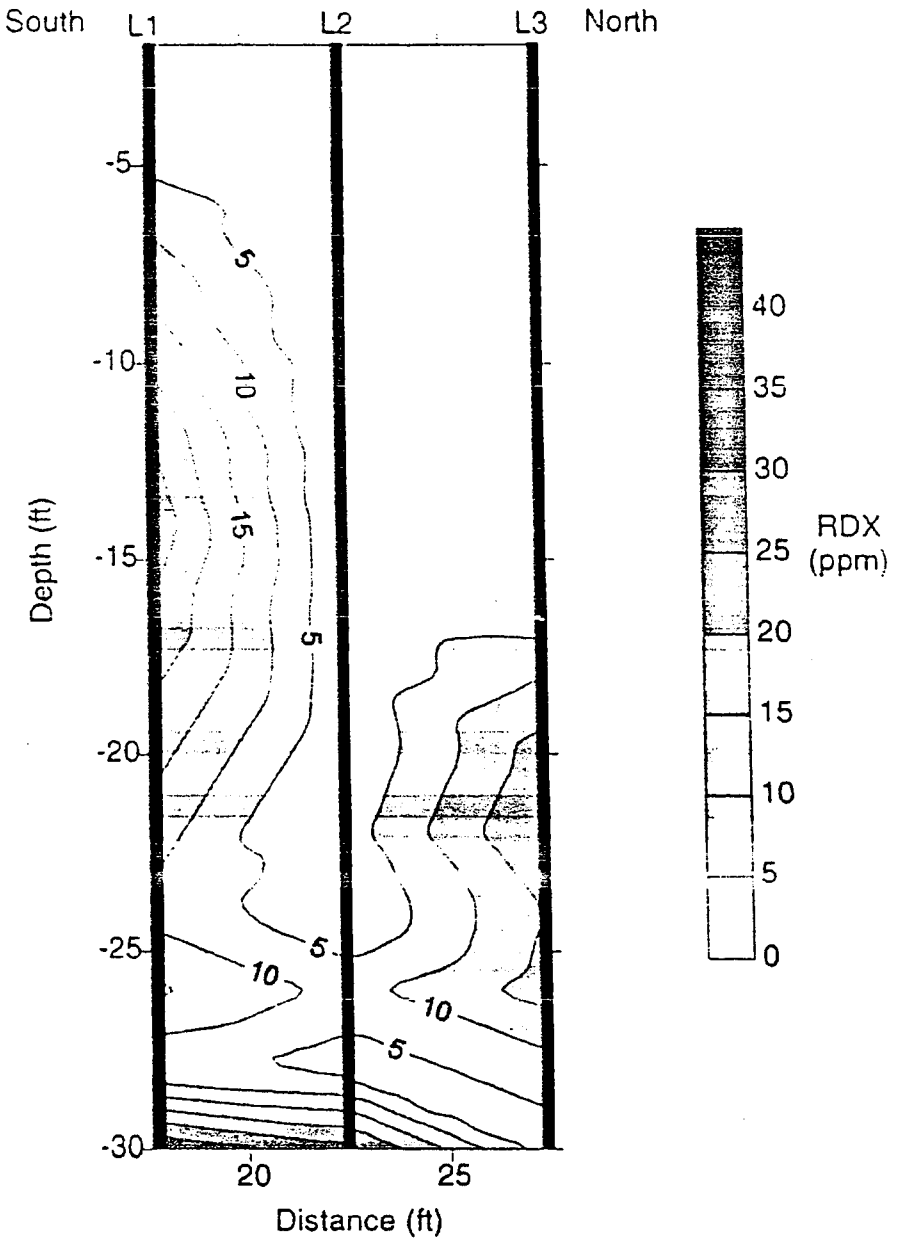

Figure 13. Posttreatment RDX distribution along small South-North cross section.

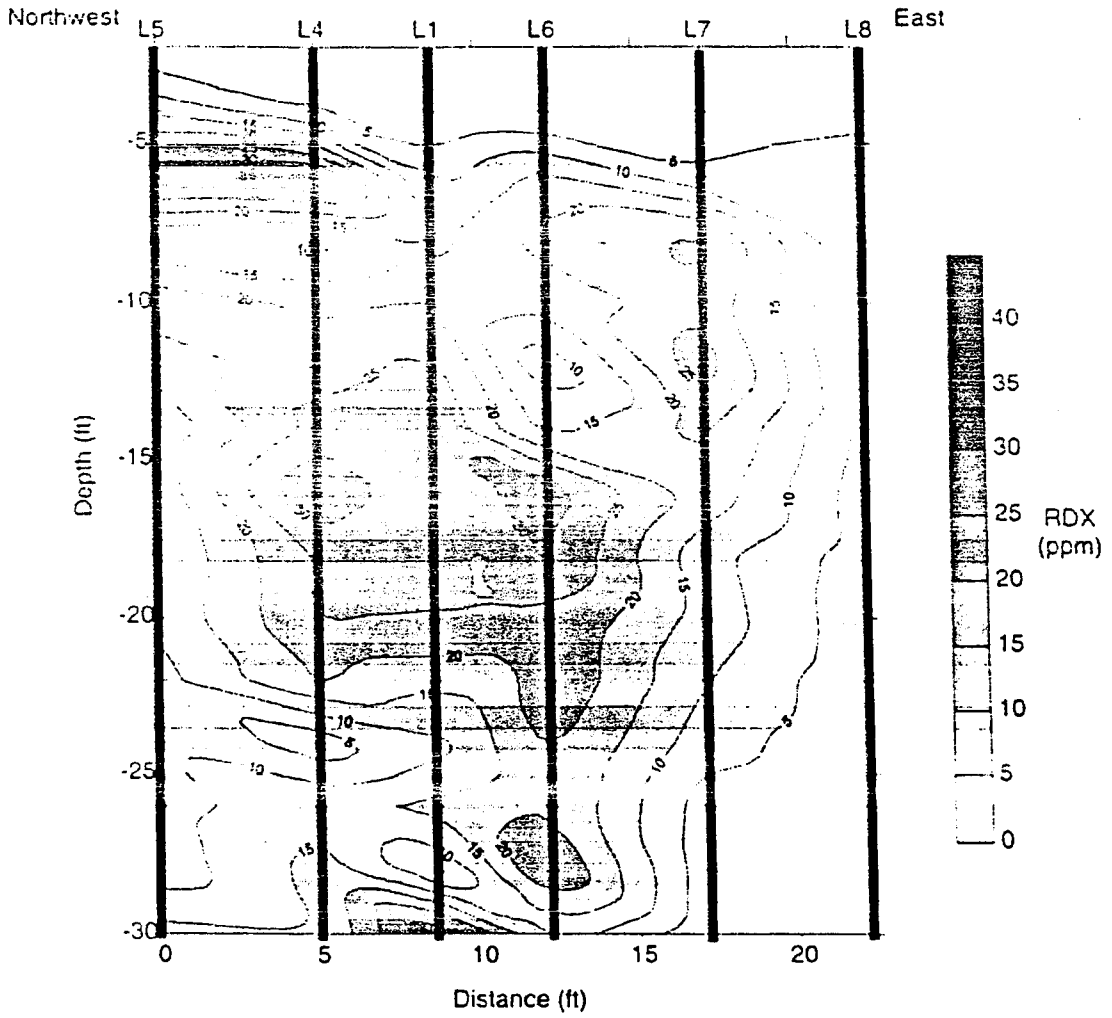

Figure 14. Posttreatment RDX distribution along Northwest-East cross section.

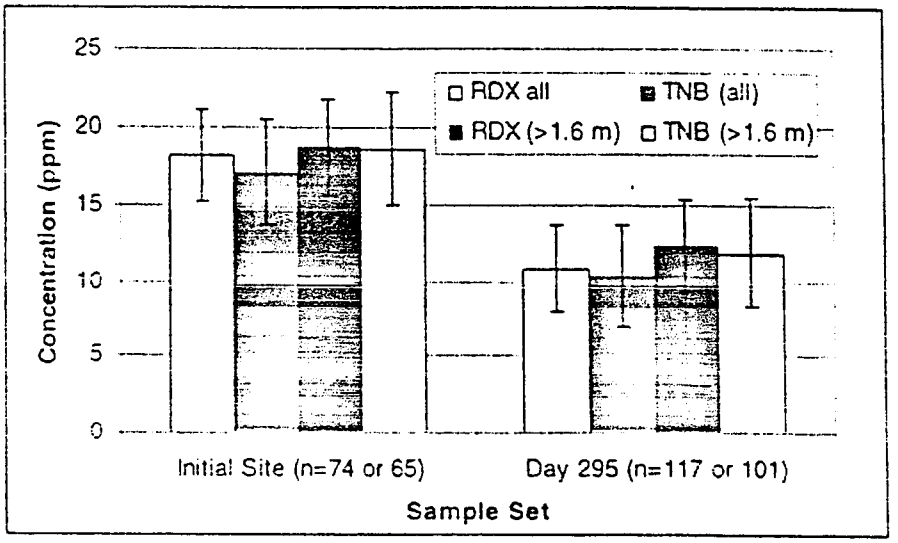

Figure 15. Comparison of mean (±95% confidence intervals) RDX and TNB concentrations before and after treatment.

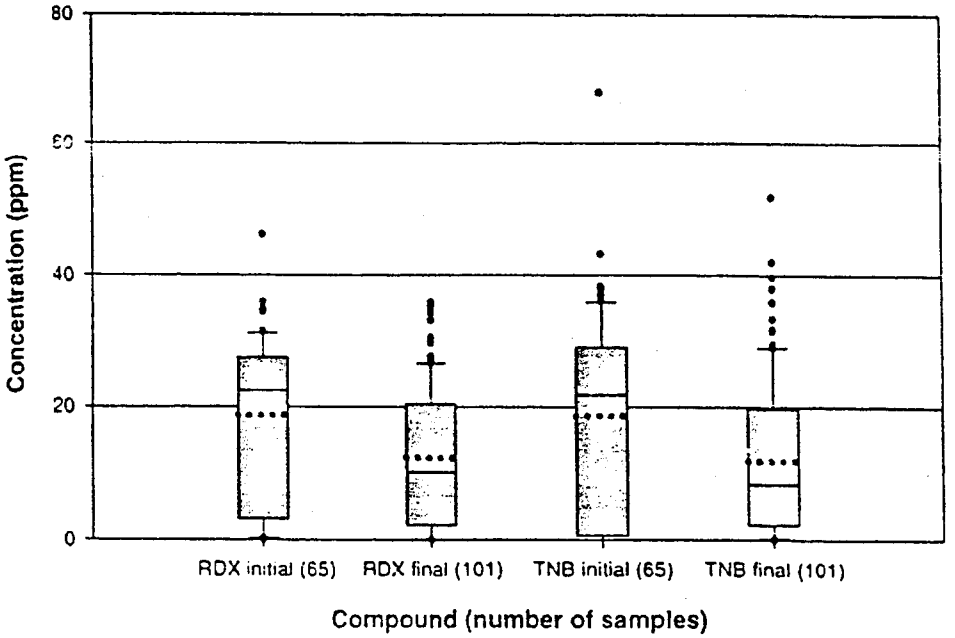

Figure 16. Box and whisker plots for pre- and posttreatment RDX and TNB concentrations in target treatment zone.

Table 2. Comparison of treatment zone sample set medians (ppm) and other percentiles.

Statistical Parameter	Initial Conditions		After Phase I	
	RDX	TNB	RDX	TNB
Number	65	65	101	101
10th percentile	0.26	0.05	0.06	0.18
25th percentile	3.1	0.6	2.1	2.2
Median	22.5	21.8	10.2	8.4
75th percentile	27.5	29.1	20.5	19.8
90th percentile	31.2	35.9	26.5	29.0

contaminated soil from the site. The impedance data gained from supporting laboratory experiments indirectly supports and strengthens both primary and secondary lines of evidence data. Therefore, the findings of this pilot-scale field study, and the laboratory studies that preceded it, can be seen as relevant evidence that this treatment process is effective in reducing the concentrations of the target contaminants, RDX and TNB.

It is recognized that the challenges of *in situ* remediation of heterogeneous distributions of RDX and TNB in heterogeneous soils are great. The work reported in this project was meant to provide hard lessons learned from the field application as well as to encourage further scientific efforts in this topic. For example, it is much more difficult to inject and control the flow of a nitrogen gas stream in the subsurface soils than to move air in the subsurface as in soil vapor extraction. Attempts to prevent oxygen leakage and diffusion into the target zone must include careful construction practice. In hindsight, the manholes used to connect the wells and sampling positions were all potential leak sites, so future applications should consider alternative installations. Heterogeneous soil and HE conditions cannot be avoided at all sites, but when the contaminated soil is a known continuing source for groundwater contamination, *in situ* treatment deserves consideration. Active sites such as the Pantex Plant may not be allowed to excavate large volumes of soil without replacing or rerouting underground utilities, the cost of which should be compared to remediation alternatives. Another alternative is to grade and cap the contaminated soil locations to prevent future infiltration. This and any alternative must be accepted by both the site owners and the regulatory agencies. The final decisions ultimately will be found through the evolving process of risk assessment.

Further research is necessary to determine the complete potential for this approach to reduce HEs in soil *in situ*. First, while this pilot study focused on decreases in RDX and TNB concentrations in soil, it is known that the reductive transformation of these compounds can produce multiple intermediates prior to complete mineralization. Future work at this site will include analyses for known breakdown products of RDX and TNB. Second, this first phase of the pilot study employed only nitrogen injection, without the use of volatile carbon sources such as those demonstrated in the soil column studies. After the completion of this Phase I field project, additional microcosm and soil column tests were planned to further refine the selection of type and concentration of organic vapor to encourage the RDX and TNB transformation. Third, the duration of the pilot test reported here was likely not long enough for complete bioremediation of the target compounds. Finally, a strategy for developing relative toxicity assessment parameters, techniques, and models must be developed for incorporation into existing risk-based cleanup and closure paradigms.

The *in situ* demonstration continued at this field site after Phase I. The system has been modified in two ways. First, the liquid nitrogen tank source was replaced with a membrane nitrogen generator for continuous, dependable nitrogen supply with much higher flow rates than previously available. Second, the flow regime was reversed, with injection at the four outer wells (known in this report at E1, E2, E3, and E4) and extraction at the central well (I). This scheme should lead to more uniform reductions in oxygen content within the treatment system. Based on the findings of the INEEL lab studies, an organic carbon source will be added to the nitrogen stream in 2002. Future publications will present later findings.

ACKNOWLEDGMENTS

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