CHARACTERIZATION USING LASER INDUCED FLUORESCENCE AND NUTRIENT INJECTION VIA BAROMETRIC PUMPING

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ABSTRACT: A laser induced fluorescence probe (LIF) coupled with cone penetrometer technology (CPT) was used to characterize diesel contamination. The LIF system gave real time assessment of the stratigraphy, rapidly defined the plume location, located hot spots, and minimized the number of soil samples taken. TPH analysis of soil plugs confirmed that the LIF probe accurately located hot spots and the horizontal and vertical migration of the contaminate at one diesel contaminated site. A bioventing system was constructed at a second site using horizontal extraction and passive injection wells. Initial in-situ respiration rates with air addition only suggested that hydrocarbon degradation may be nutrient limited. The rate of TPH degradation was maximum between 10-15 ft, but dropped to essentially zero 30 ft below ground surface within the contaminated zone (even though previous analysis at this depth indicated a TPH concentration of 3800 ppm). Soil analysis indicated that nutrient levels may be rate limiting. Viable cells increased from 3×10^6 cfu/g at 3 ft to 1×10^7 cfu/g at 10 ft and remained relatively constant down to 17 ft, compared to 4.5×10^3 in the control area. Barometric pumping has been established at the site and is being used to passively inject the gas phase nutrient, triethlyphosphate (TEP), to increase the hydrocarbon degradation rate.

INTRODUCTION

Since the 1950's, emergency power required for operation of Savannah River Site (SRS) reactors has been met by diesel generator operations. These diesel engines were fueled via a system of above ground storage tanks (AST) in each reactor area (the 108-3 facilities K, L, and C). Past operating practices at these AST facilities resulted in the accumulation of diesel spillage for over 30 years. Efforts to mechanically remove petroleum contaminated soils (PCS) found at the 108-3C AST site began in 1994. Following excavation down to 20 feet, in which approximately 500 cubic yards of contaminated soils were removed, several hand augured samples were taken at the bottom of the excavation pit. Extensive hydrocarbon contamination down to > 40 ft was found. The operating history of the 108-3K and 108-3L AST sites, which were typical to 108-3C, suggested similar contamination at these sites. Based on literature, site characterization, and biosparging data at the SRS (Hazen, 1994), bioventing was proposed as an economical clean-up method. Here we describe technologies used in conjunction with bioventing systems to remediate diesel contaminated soils.

Objective. The primary objective of this work was to determine if laser induced fluorescence (LIF) probing could be used to characterize a diesel contaminated site and optimize injection/vacuum well locations. A second objective was to determine if injection of gaseous nutrients could be performed in a passive mode via barometric pumping with a Baro-Ball (US patent pending).

MATERIALS AND METHODS

Site Characterization using LIF. Cone penetrometer technology (CPT; Fugro Geosciences, Inc., Houston, TX) was used at two sites (108-3 K and L) to rapidly evaluate lithography based on tip resistance and sleeve friction (Figure 1). A cone was continuously advanced into the subsurface at a rate of 2 centimeters per second with a twenty ton driving force. Tip resistance and sleeve friction data were used to determine the underground lithography. An LIF probe was coupled to the CPT to obtain a real-time qualitative assessment of aromatic hydrocarbon contamination (ROST™, Unisys Corp., Eagan, MN).

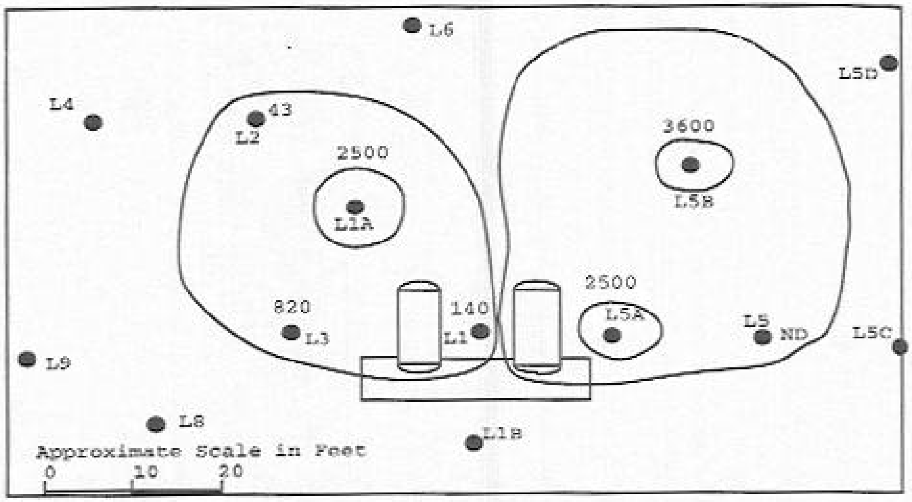

FIGURE 1. LIF/CPT push locations (●) and estimated TPH contours (—, ppm) at 108-3L. Wells outside the contour lines were clean based on LIF readings and/or soil analysis (ND: not detected).

Site Characterization and Bioventing Design at 108-3C site. Petroleum contaminated soil (500 yd^3) was removed from 108-3C (20' deep) which ranged in total petroleum hydrocarbon (TPH) concentrations from 56 to 3000 ppm (n=19, mean=1122 ppm). Petroleum contamination was also found another 11 ft below the pit (3800 ppm), but diminished significantly at 21 ft below the pit (11 ppm). Additionally, lateral soil borings indicated contamination ranging from 90 to 900 ppm TPH. Because of the extensive contamination below the bottom of the pit, further excavation was not performed. It was decided to back-fill the pit with the contaminated soil and use bioventing to degrade the TPH.

Eight passive injection wells were installed using CPT (2" ID and 45' deep with 10' of well screen) and were positioned around the pit. Discrete zone piezometers (4 -1" ID), with multiple sampling ports, were positioned within the pit before back filling. CPT technology was used to install three vadose piezometers outside the zone of contamination (10', 20', and 45'). Once the piezometers were in place, the pit was back-filled. At certain points during back filling, a layer of corrugated ABS pipe with slots was positioned in the pit and connected by a tee. Straight PVC riser was connected at the tee and taken to the top of the pit. The corrugated pipe was positioned at three layers 10', 15', and 20' down. Each PVC riser (4") was connected to a tee and reduced to one inch pipe. One inch pipe from each riser was connected to a globe valve, elbowed to a flow meter, and teed into a manifold. The manifolded system was connected to a vacuum pump (Roots/Dresser, Rotary Lobe Blower, 14" Hg). The top of each tee was capped and threads added for a sampling port and addition of a pressure reading device. Each injection well was connected to a 3 gallon diffusion chamber at the air/gas outlet, and the inlet was connected to a Baro-Ball constructed of PVC. The Baro-Ball is essentially a check valve to allow air flow through the tank, but preventing any backflow should in-situ pressure become greater than atmospheric. The diffusion chamber can be filled with volatile nutrients (e.g., triethylphosphate - TEP) and transported by air flow through the chamber into the injection well.

Analytical and Microbial Methods. Soil samples were analyzed for TPH by Weston Analytics (Lionville, PA) using EPA method 8015M. Groundwater samples were analyzed for TPH and BTEX (EPA 8240). Viable counts were determined using 1% PTYG plates (Balkwill et al., 1989). Total nitrates (NO^-_2, NO^-_3) and total extractable phosphates (PO^-_4) were quantified using ion chromatography. Soil gas samples were extracted from discrete zone sampling ports for using instrument pumps or a twin-headed diaphragm vacuum pump (KNF Neuberger, Inc., Trenton, NJ) to determine O_2 and CO_2 concentrations. O_2 was measured using an Model 320P-4 O_2 analyzer (Teledyne Analytical Instruments, City of Industry, CA) and a GEM 500 (LandTec, Commerce, CA). The GEM was also used to measure CO_2, and static and differential pressure.

RESULTS AND DISCUSSION

The LIF probe, combined with the CPT quickly located the contaminant plume, minimized the number of soil samples taken, and estimated the stratigraphy of the subsurface. In general the stratigraphy consisted of three clay layers separated by sand or sand and slit. In many cases, hot zones were noted at the interface between sand or sand and silt and a clay layer. Site L was found to have significant TPH contamination in the soil (up to 3600 mg/kg), but relatively low levels of TPH and BTEX in the groundwater (TPH = 6.6 mg/L and xylene = 120 ug/L; benzene was not detected). However, the maximum TPH concentration in the soil at 108-3K was 11 mg/kg and 1.2 mg/kg in the water, while BTEX was not detected in the groundwater at site K.

A quantitative correlation between the LIF peak intensity and TPH concentration was not observed (Figure 2 and 3). For example, a peak intensity of 85% at 3' to 6' for well L3 was correlated to a TPH concentration of approximately 750 ppm, compared to a peak intensity of approximately 20% at well L1A which correlated to 2500 ppm. This may have been due to the heterogeneity of the soil and the fact that LIF and soil borings were not performed in the same hole (the holes were within 1-2' of each other). An alternate approach for TPH quantification involves probing with LIF technology after soil sampling with the CPT. However, with the exception of one LIF reading the results indicated that when the LIF peak intensity was greater than 5%, diesel fuel contamination was identified in the soil sample (Figure 3). Moreover, within each bore hole the LIF reading was proportional to the TPH concentration; e.g., a flat LIF baseline gave a TPH concentration of zero (Figure 2). Another advantage observed using the LIF, was the ability to delineate smear zones, areas which could not be measured using discrete zone sampling.

The LIF and TPH data indicated that the contamination was centralized within two areas underneath each tank previously located at the site (around well clusters, L2-L1A-L3 and L5B-L5A) at 3'-15' and at 20'-24', with the highest concentrations found between 3' and 10'. Both the LIF and TPH soil analysis indicated that wells along three axes (L4-L9-L8, L6-L1-L1B, and L5D-L5C) were either clean or had very low levels of contamination (Figure 1 and 3).

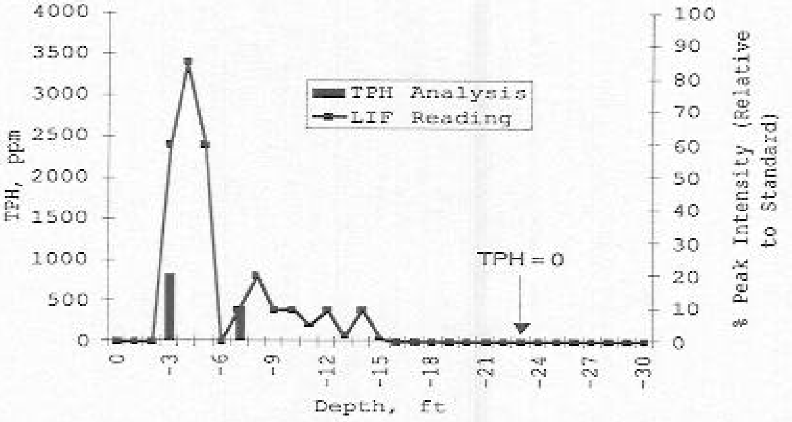

Figure 2: Direct Comparison of LIF and TPH Concentrations in Well L3.

In-situ Respiration at 108-3C. Initial soil gas analysis showed that certain areas within the backfill were metabolically active, since oxygen concentrations had dropped to 6 to 10% relative to the control piezometers, but increased to near atmospheric levels once the extraction was initiated. Shut-down in-situ respiration studies, showed that oxygen consumption rates ranged between 0.8 and 1.7% per day across the site and varied as a function of depth. TPH degradation rates were estimated from the oxygen consumption data using a batch reactor design equation, assuming zero order with respect to hydrocarbon concentration, and using the stochiometry of hydrocarbon oxidation (Hinchee and Ong, 1992).

The estimated degradation rates appeared to peak between 10' and 15' bgs, with lower rates near the surface and deeper in the pile (Figure 4). These rates correlated with an increase in cell numbers and nutrient levels at these points; total viable counts were higher at 10' and 15', 5 x 10^6 to 2 x 10^7, compared to 3 x 10^5 at 3'. Viable counts for uncontaminated soils adjacent to this site were 4.5 x 10^3. Also, NO_3 levels were higher at these depths, 20-80 ppm compared to non-detect at 2' and 17'. However, phosphate levels ranged from 0-0.3 ppm regardless of the depth (2'-17').

Barometric Pumping at 108-3C. Before the vacuum pump and diffusion chambers were installed, significant inhaling and exhaling were noticed from the injection wells, suggesting that barometric pumping was occurring at the site. Passive bioventing via barometric pumping has been previously noted (Foor, 1995). Pressure and flow rates were periodically measured and indicated that as the atmospheric pressure increased, the vacuum at the well head increased which resulted in air flow through the diffusion chamber and into the well (Figure 5). Air flow was only measured when the vacuum was 1 mbar (0.4 in H_2O) or greater, the reported cracking pressure of the Baro-Ball (Pemberton, 1996). Measured flow rates ranged from 1 to 70 ml/min up to a vacuum of 1.4 in H_2O. The vacuum pump, when in operation, had little effect on the injection wells (measured in terms of vacuum), regardless of the valving on the horizontal wells. This was probably due to the permeable nature of the backfill causing short circuiting of the system.

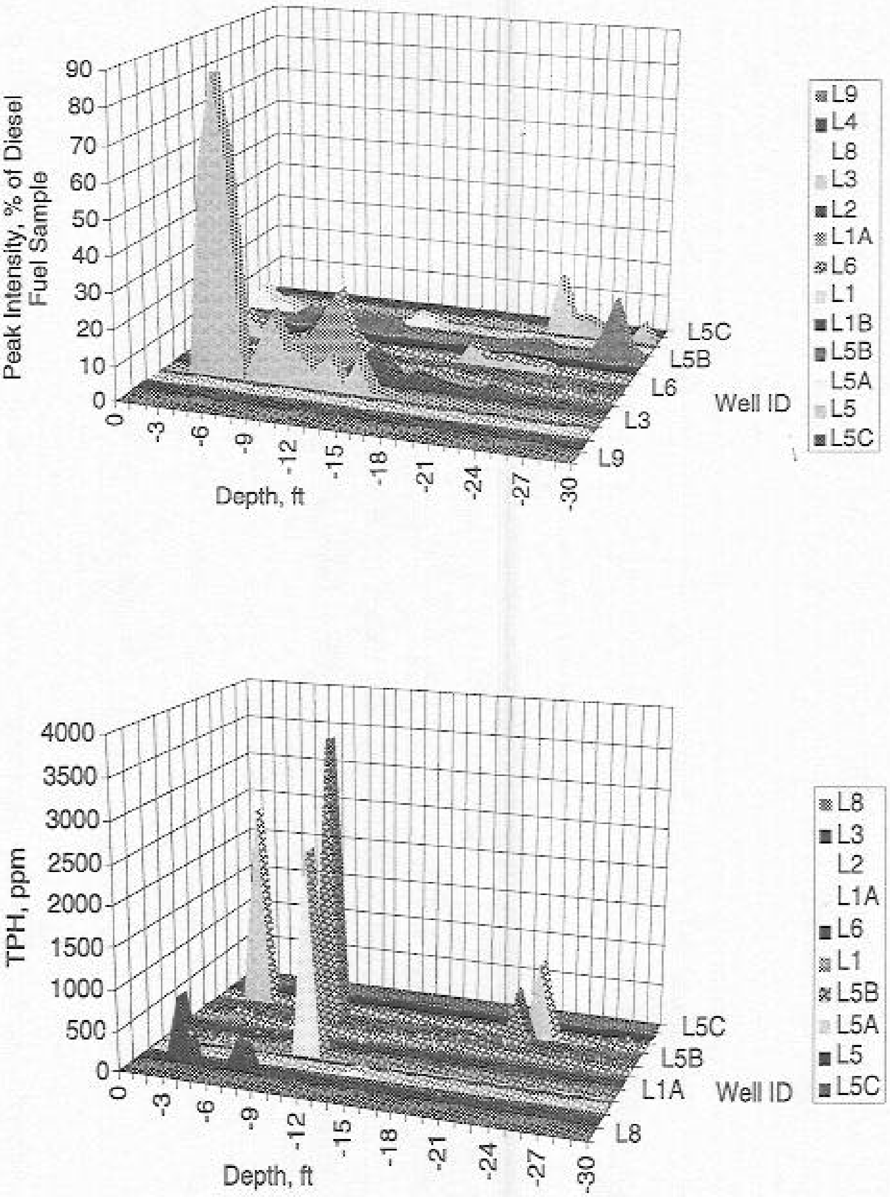

FIGURE 3. Three Dimensional View of LIF Readings (Top) and TPH Concentrations (Bottom).

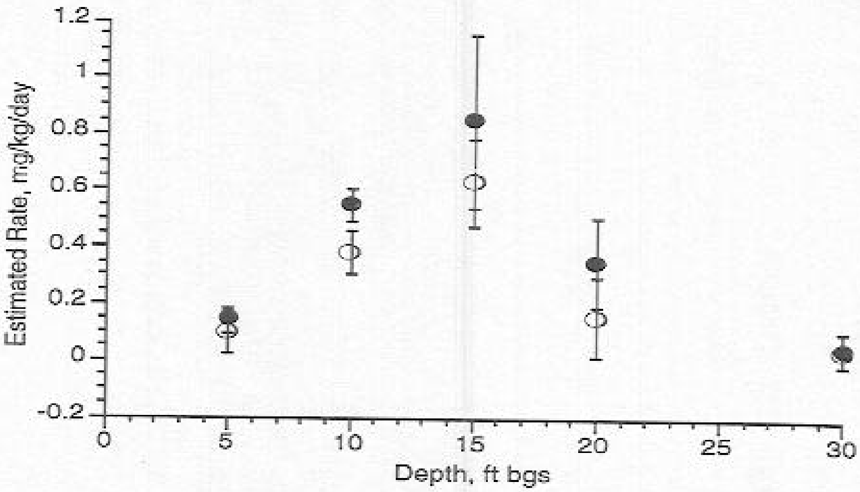

FIGURE 4: Change in the Estimated TPH Degradation Rate as a Function of Depth Within the Contaminated Zone: 6/96 and 8/96 (●) and 10/96 (○).

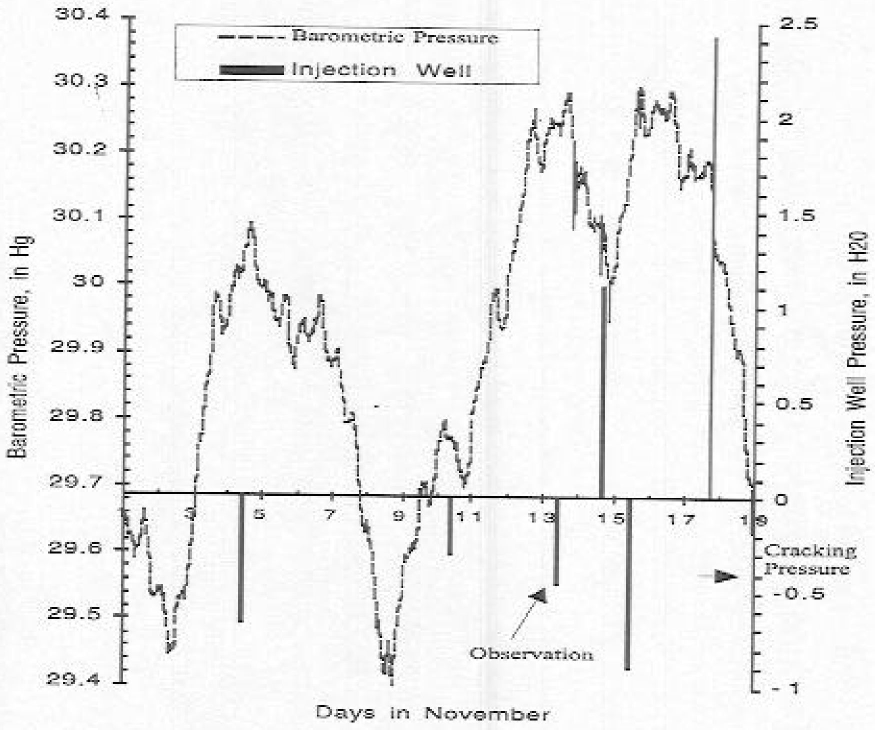

FIGURE 5. Effect of Barometric Pressure on Injection Well Pressure

CONCLUSIONS

Conventional characterization of diesel contmainated soils typically involves collecting samples at regualr intervals or when a change in lithography is noted (SCLUFTF, 1989). Soil samples must be taken down to 50 ft or below the water table to ensure that the depth of contamination is verified (SCLUFTF, 1989). Representative samples are then sent for analysis using laborious and time consuming methods. In most instances hot spots can not be located due to the soil heterogeneity and randomness of sampling, which prevents optimal location of injection or extraction wells. This study showed that LIF probe coupled to CPT allows real-time assessment of lithography and rapid plume definition (able to evaluate 300-400 ft per day), while minimizing the number of soil samples required to accurately locate hot spots and to delineate smear zones. This information is in turn necessary to optimize well location and screening intervals. Although further research is required to use the LIF probe to measure the rate of hydrocarbon degradation, the LIF probe could prove valuable in assessing bioventing performance and determining site closure points.

The estimated maximum degradation rate was relatively lower than rates reported for other diesel bioventing sites, 1-2 mg/kg/day compared to 6-30 mg/kg/day. The low rates could be due to many factors, such as low TPH concentration and low nutrient concentrations. A significant amount of degradation could have occurred in the excavated soil during storage and the backfilling process when fertilizer was added to the soil, since in-situ respiration studies were performed 8 months after backfilling and installation of the biosystem. Recently, soil samples taken at 10' and 15' show that the TPH levels have declined from 1100 ppm to 100-180 ppm. Moreover, barometric pumping during the in-situ respiration studies could have underestimated the rate of oxygen consumption.

Also, the lower respiration rates at the deeper depths (20' to 30') could be due to nutrient limitation and not low TPH levels. This is supported by the fact that the TPH degradation rate was maximum between 10-15 ft (bgs), but declined to essentially zero 30 ft (bgs) within the contaminated zone, even though previous analysis at this depth showed a TPH concentration of 3800 ppm and that nitrate and phosphate concentrations were below detection limits (0.5 ppm). For this reason the gaseous nutrient, triethylphosphate (TEP), will be injected into the pile. In-situ respiration rates will be periodically monitored to see if TEP will increase the respiration rate and hence the hydrocarbon degradation rate. Finally, preliminary data indicated that barometric pumping, coupled with the Baro-Ball, can be used to passively inject gaseous nutrients. Passive bioventing can be integrated into a strategy that includes intrinsic bioremediation, thereby further reducing the over all costs of the remediation.

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