Principles and Practices for Diesel Contaminated Soils

Volume VII

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Principles and Practices for Diesel Contaminated Soils, *Volume VII*

Preface

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Sponsored by the Association of American Railroads

In 1985 the Association of American Railroads (AAR) was among the original co-
sponsors of the first conference on the Environmental and Public Health Effects of
Petroleum-Contaminated Soils that was organized by the University of Massachusetts
in Amherst. Since that time, the conference has become an annual event and much in
the field has changed. A decade and half ago, remediation of contaminated soil still
involved many new and unproven techniques. Most railroad environmental staff were
generalists and typically came with background in waste water treatment and/or civil
engineering. There was a great deal to be learned by all parties, including railroads,
about how to remediate petroleum-contaminated soil. In the ensuing years, railroads
have become much more sophisticated regarding the nature of the contamination typi-
cally found on their properties, the risk it poses to human and environmental health
and the technologies available for cleanup. Some of the credit for the industry's ad-
vances can be attributed to the annual University of Massachusetts conference. This
meeting has become the yearly gathering of railroad environmental professionals in
North America and provides an opportunity for them to exchange views, ideas and
findings. The papers presented, the ensuing dialogue, and the publications that have
resulted, have all contributed to the collective knowledge base of the industry and ad-
vanced the scientific and engineering sophistication of the railroad environmental com-
munity.

A major factor motivating the railroad industry's interest in the topic is economic;
remediation is the largest cost item in the railroads' environmental budget. Developing
a well-trained, professional staff to manage remediation activities is a prudent step for
railroads to assure that the their resources are used in a cost-effective manner. As a
consequence, the environmental departments at most large railroads today include a
specialized group of individuals whose sole responsibility is remediation. In concert
with this process the AAR has completed a number of research projects to provide
railroads with information of particular significance to railroad remediation issues and,
since 1991, hosted a special symposium at the University of Massachusetts conference.

This symposium has focused on railroad remediation issues, with particular emphasis on cleanup of diesel fuel spillage and related topics.

As a result, there are now many more options than "dig and haul," and railroad remediation staff have grown well beyond questions of "Will it work"? Currently there are a variety of technologies available, each with their own criteria for successful application. Appropriate use of these options requires more scientific and engineering training on the part of the remediation specialist. Furthermore, the increasing acceptance of risk-based approaches to setting cleanup levels has added a new layer of complexity, while at the same time reducing cost. This is a benefit to railroads because, like all industries, they are striving to improve efficiency in all aspects of their operations. The railroad remediation specialist is under more pressure than ever to cost-effectively manage contaminated property, consequently he or she needs to stay abreast of the latest developments. The AAR's co-sponsorship of the University of Massachusetts conference and the special diesel symposium are responses to the industry's need for the latest information, and both have been a part of the evolution of the railroad industry's increased understanding of remediation technology. This volume is the seventh in a series of books whose purpose is to document and disseminate the information presented at the AAR sponsored symposium on remediation of sites contaminated with diesel fuel, and other topics of interest to the railroad remediation professional.

Although the majority of railroad remediation issues involve diesel fuel, and similar petroleum products, railroads sometimes must deal with other contaminants. This is reflected in Chapters 1 and 2 which discuss new technology for detection of lead in soil and the natural attenuation of chlorinated hydrocarbons in association with petroleum, respectively. Chapters 3 through 7 all discuss aspects of petroleum contamination including: a description of the successful closure of a sludge impoundment lagoon, the cleanup and operational cost implications of diesel fuel spillage in a variety of railroad circumstances, the successful use of on-site bioremediation at a refinery, a cooperative approach that facilitated a real estate transaction involving a contaminated site and its constructive reuse under the Brownfield paradigm, and a useful summary of the steps involved with a landfill capping project on a former rail yard. Chapters 8 and 9 describe the use of phytoremediation, a relatively new technique that uses vegetation to help accelerate the biodegradation of soil contaminants. Finally, Chapter 10 describes recent work by the AAR applying new, more sophisticated analytical methods to the detailed measurement of weathered petroleum hydrocarbon compounds at four railroad sites around the United States. The method was developed under the umbrella of the Total Petroleum Hydrocarbon Working Group specifically for use in Risk-Based Corrective Action (RBCA) assessments.

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Acknowledgements

Contents

CHAPTER 1

INVESTIGATION OF LEAD IMPACTED SOIL AT A RAILROAD FACILITY USING XRF TECHNOLOGY

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INTRODUCTION

As part of a voluntary remediation project at an active railroad facility in Lincoln, Nebraska, an innovative application of X-Ray Fluorescence (XRF) technology was employed to identify the extent of *in-situ* lead contamination in soil and fill material. Conducted under the State of Nebraska's Remedial Action Plan Monitoring Act (RAPMA), the XRF investigation demonstrated success in screening for lead and set the groundwork for "next generation" sample handling and modeling methodology.

SITE DESCRIPTION

The investigation was conducted at an active railroad site that had been contaminated by historical painting operations, including the sand-blasting of lead paint from locomotives and rail cars. Over the years, this sand-blast material, construction debris, concrete, excavated soil, wood, coal, crushed rock and scrap metal debris had been used as fill for a low-lying area of the yard.

Regionally, the site surface slopes to the north and east at an approximate gradient of 0.0025 ft/ft toward Salt Creek (USGS, 1964). Naturally occurring soil in the area is of the Crete series (a deep, moderately well-drained silty-clay soil formed on uplands and stream terraces), with low permeability. The upper two feet of a typical Crete soil is a silty clay loam with slight-to-medium acidity, while the bottom two feet typically

combines mildly alkaline, silty clay with carbonate concentrations (USDA, 1980). At the time of the investigation, the site contained approximately 15,000 cubic yards of above-grade piles and 20,000 cubic yards of below-grade fill.

The subsurface geology of the site shows the aforementioned fill material at depths of up to five feet below-grade level (bgl). Underlying the fill material is a brown-to-yellowish, silty-clay extending from approximately three feet to 15 ft bgl in depth. A sand with silt or poorly graded sand extends from approximately 15 feet to 29 ft bgl. Four geologic samples collected in the vadose zone and from the silty (lean) clay layer beneath the fill material on the site were analyzed for moisture density and permeability. These samples, obtained from borings at depths of approximately 2.0-2.5 ft and 4.5-5.0 ft bgl, showed a vertical coefficient of permeability value ranging from 6.0×10^{-8} cm/sec to 4.9×10^{-6} cm/sec.

For the purposes of the investigation, the site was divided into a north unit and a south unit, based on the distinct topography of the two areas. The north unit generally is flat, with a gentle slope to the east. The south area includes several large piles of soil, concrete and rubble, ranging from two to four feet to more than ten feet in height. Visual characterization of samples taken from both areas suggests that the physical composition of the piles and subgrade material can be classified into five main material types: silty clay with concrete and rock debris; sand-blast sands; concrete rubble; coal; and reddish-brown silt with iron debris.

XRF THEORY AND BACKGROUND

Although available commercially for a number of years for evaluating lead in paint, XRF applications have been limited for soil, in part because the correlation between XRF values and analytical values has not always been good. This drawback can be traced to several factors, including the way in which XRF instruments read and convert lead values in a three-dimensional setting (soil) compared to a two-dimensional setting (such as a paint layer) and improperly prepared soil samples. In this application, these traditional issues were overcome through use of the newest available technology and the development of standard operating procedures for sample handling and preparation.

XRF technology is based on the fluorescence, or electromagnetic energy given off by atoms that have been excited. Since the fluorescence of each element is unique, the characteristic x-rays given off by any excited atom can identify the element. For this investigation, the NITON® Lead in Soil Analyzer was used to field-screen for lead concentrations in the soil. The instrument employs a Cadmium-109 source to produce the required fluorescence and uses preprogrammed algorithms to calculate the concentration of the element based on its characteristic fluorescence from electrons in the L and K shells. By providing these two measurement methods—L and K x-rays—to identify the energy given off from the different shells surrounding the lead atoms nucleus, the NITON instrument is able to correct for factors such as depth and interference from other elements. Although the instrument is capable of analyzing for numerous inorganic compounds, it was calibrated specifically for lead in this application (NITON Training Manual). Based on the incoming data, the NITON instrument displays concentrations of lead in parts per million, averages those concentrations in successive measurements, indicates the precision of the measurement, stores the measurement data, and downloads the data directly into a computer.

Quality control is a critical factor in any XRF application. Even though the instrument self-calibrates by means of an internal tungsten shield, a standards check using high and low National Institute of Standards and Technology (NIST) soil standards performed by the instrument operator to evaluate instrument drift. Since the self-calibration is activated when the instrument is turned on, the standards check was performed after the instrument had warmed up, every 60 minutes during operation, and shortly before its shut-down at the end of the day. If the instrument standard measurements were not within the reported range for the NIST soil standard, the instrument was turned off, turned back on, and allowed to recalibrate before the standards were checked again. During the investigation, the instrument performed well and calibration/standard checks were within the manufacturer's operational requirements.

FIELD ACTIVITIES

Field investigations were conducted at the site in July 1995 (north unit) and March 1996 (south unit). From the north unit, 138 soil samples (72 surface samples and 66 subsurface samples) were collected, while the south unit produced 78 soil samples for a total of 216 samples. Seven sample grids were established in the north unit and nine sample grids were established in the south unit.

A random, stratified sampling technique was employed to collect samples from the surface and from selected depths, with a discrete number determined for each sample and location. Samples taken from depths of less than one foot were collected with a stainless steel trowel. A truck-mounted drill rig, backhoe or shovels were used to collect deeper samples. Once target depths had been reached, samples were collected and placed in clear sealable one-gallon plastic bags, with the date, time, sample identification number, and sample depth recorded on each bag. Soil samples were composited in a decontaminated stainless steel bowl, with each sample dried in the sun, in an oven, or over a burner. The soils were then sieved through Number 10 and Number 60 sieves. Soil that did not pass through the Number 60 sieve was ground and re-sieved until enough material passed through to form a 30-gram sample of fine material.

From each sample, three grams of material was placed in a sample canister for XRF analysis. After each use, the NITON instrument was wiped with damp paper towels and sampling equipment was cleaned using distilled water and brushes.

COMPARISON OF XRF AND LABORATORY ANALYSIS

From the 216 samples subjected to XRF analysis, 26 (including two duplicates) also were analyzed by laboratory methods using SW846 method 6010. Whereas the XRF measures total lead in a sample, the SW846 method 6010 laboratory analysis measures extractable lead, which typically is less than the total lead in a sample. In addition, soil type may affect the relationship between total and extractable lead, since clay soil will tend to attenuate metals and yield lower extractable lead, while sandy, fine-grained soil will yield a higher percentage of extractable lead. Finally, heterogeneity also can affect laboratory results due to the bias of the selected sample portion for extraction. The handling and preparation method of sieving and grinding the sample for XRF analysis reduced this bias substantially.

The XRF readout documents results as a number with an uncertainty within which

the actual lead concentration could fall. The uncertainty is defined as precision plus bias, with the precision reported by the instrument and the bias calculated as equal to ten percent of the sample result. The results of the XRF analysis indicate a maximum reported concentration of 25,500 parts per million (ppm) and a minimum reported concentration of 5 ppm for total lead in soil. A breakout of the 216 samples is shown in Table 1.

TABLE 1   Lead Concentrations in Samples

Number of Samples	Range of Lead Concentrations (ppm)
141	< 400
31	400 to 1,000
11	1,000 to 2,000
33	> 2,000

A comparison of the XRF analysis and the laboratory analysis (Table 2) was conducted to determine if there were substantial differences in the quality of the data obtained. Three data points with significant differences between XRF and laboratory results were removed from statistical considerations after determination of operator error in reporting XRF values. Visual comparison of the two test methods (Figure 1) indicates that the XRF consistently demonstrated higher total lead values than did the laboratory analysis. This difference may be attributed to the XRF total-lead measurement compared to the laboratory analysis extractable-lead measurement and to the effects of soil type and sample heterogeneity.

The quality of the data was evaluated on accuracy and precision:

- Accuracy (defined as the ability of the analyses to quantify the actual concentration of lead that exists in the soil) was evaluated by performing a two-tailed T test (Gomez and Gomez, 1984) to compare the mean lead concentration predicted by the XRF analysis with the mean predicted by the laboratory analysis. At the 95% confidence level, the mean predicted by the XRF data (1,865 lead/kg soil) did not differ significantly from the mean predicted by the laboratory analysis (1,516 mg lead/kg soil). The results of comparison indicate that the XRF was able to measure soil lead concentrations in the collected samples as accurately as the analytical laboratory.

- Precision (defined as the ability of the analyses to consistently estimate concentrations of lead in soil) was evaluated by comparing

TABLE 2   Summary of Detected Lead XRF and Laboratory Concentrations in Soil

Sample Designation	LAB mg/kg	XRF ppm
A1XRF011	9330	12143
A1XRF021	5660	348a
A1XRF022	38.5	298
A2XRF011	9110	8414
A2XRF072	19.5	6205a
A2XRF101	10300	13950
A3XRF061	294	302
A4XRF071	501	482
A5XRF053	214	281
A6XRF011	516	453
A6XRF071	553	385
A6XRF101	230	326
ASXRF031	543	621
ASXRF031DUP02	633	621
ASXRF061	337	439
ASXRF071	798	798
ASXRF081	274	366
ASXRF081DUP1	321	366
O1O6	82	113
O5O9	160	796
O6O9	13.4	13
O610	237	491
O614	105	278
O7O3	5810	25500a
O7O6	135	534
O713	147	436

a Differences in XRF results versus laboratory data attributed to operator error in reporting XRF values.

measures of dispersion from the XRF and laboratory data. Sample data generated from the XRF were compared with those from the laboratory to identify any significant correlation. The relative standard deviation (ratio of the standard deviation to the mean) for the XRF data was 210%, a value comparable to the 211% obtained from the laboratory data. Based on these results, the variability within the data sets suggested that neither method analysis demonstrated more precision.

In addition, regression analyses performed for the data set indicated a high correlation between the XRF and laboratory data (Figure 2), suggesting that the accuracy
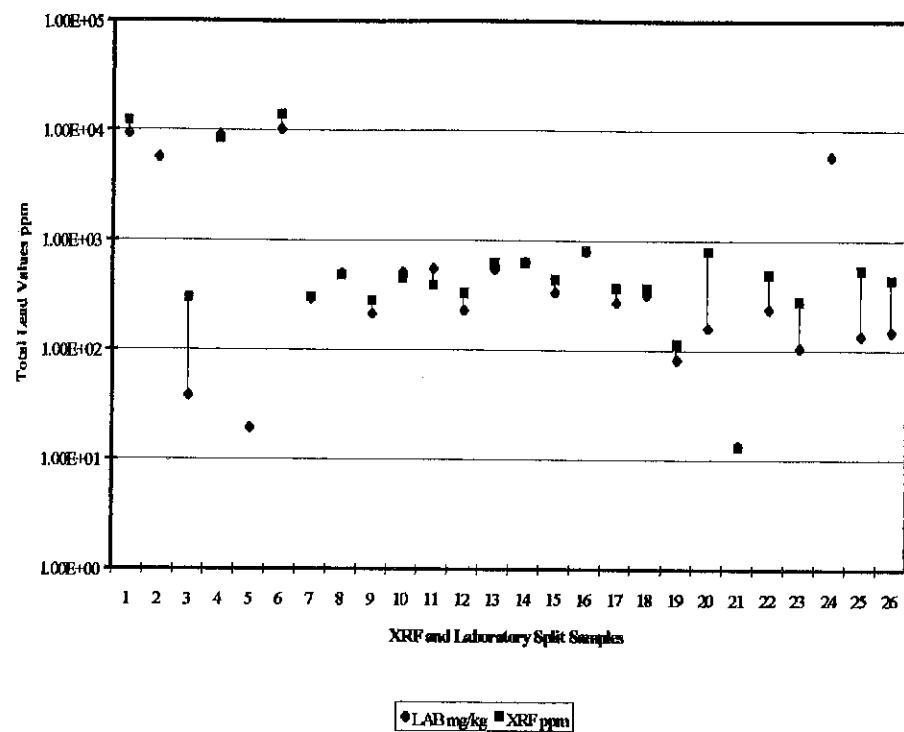
Figure 1   Distribution of XRF versus laboratory data

and precision of the XRF estimates do not differ substantially from the more traditional laboratory methods.

Practical Advantages of XRF Application

Because of the importance of obtaining accurate values and the historic inconsistencies between XRF and analytic values, the practical advantages of XRF application often represented an unacceptable "trade-off." With newer technology, the formulation of effective standard operating procedures for sample handling, and the specialized training of practitioners, substantial advantages are available without any sacrifice of accuracy or defensibility. Among those advantages:

- Worker exposure levels are documented through frequent, nonde-structive monitoring of personal filters, providing immediate knowledge of unexpected increases of exposure and allowing worker protection actions to be adjusted accordingly.

- Hazardous waste sites can be screened quickly to assess the extent and location of contamination. In many cases, XRF technology
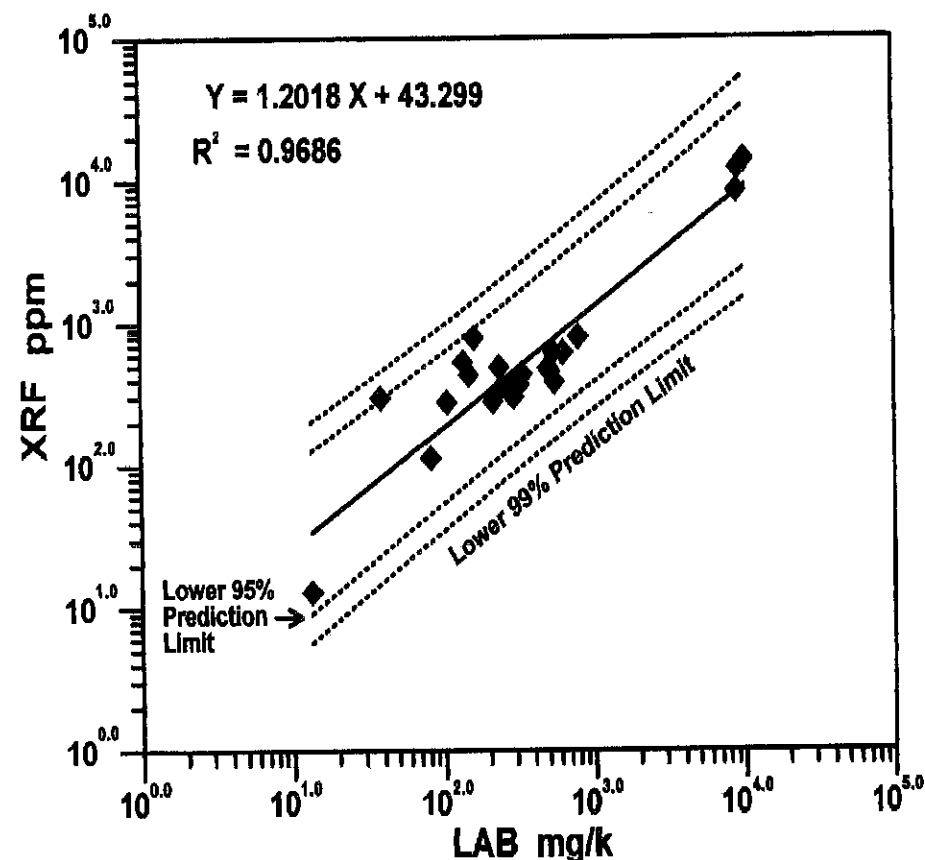
Figure 2   Correlation of lead concentrations in soil estimated with XRF and concentrations quantified using laboratory SW846, method 6010

can localize the source of contamination through three-dimensional analysis of the contamination pattern.

- Results of sample analysis at industrial sites are available within minutes, allowing quick and thorough assessment of contaminant-removal efforts and providing opportunity to fine-tune cleanup efforts responsibly and cost-effectively.

- Samples can be re-run immediately if any questions arise concerning the results.

- Delivery of real-time data that can be plotted in the field, eliminating the need to wait up to two weeks for analytical results.

- Although the actual costs of using XRF technology or analytical laboratories are similar, considerable cost savings may occur through avoidance of re-mobilization costs and down-time for contractors while waiting for analytical results from a lab.

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USGS, 1964. Lincoln Quadrangle 7.5 Minute Topographic Map. Photo revised 1972 and 1980.

QUESTIONS AND ANSWERS

Q. What is the cost of the unit and would you estimate a cost per sample for the analysis?

I would talk to NITON about the current cost. The cost per sample, that is hard to say. Of course it depends, we can do hundreds of level 1 screenings in a day. That takes about twenty source seconds, which is how long it takes the machine to read the soil. For the level 3 data, we run the machine for 60 source seconds once the sample is prepared. It depends on how many people you have preparing the sample, but you could probably run sixty to seventy level 3 samples per day.

Q. With other XRF instruments is there trouble with interference from other metals?

That is true with any XRF.

Q. With this unit it seems true since you're unable to look at many different metals, that interference would be less. I'm wondering if you had any problems with that?

When we began we had some interferences that generated unrealistic arsenic values that did not show up in the laboratory results. We talked to the manufacturer and found that it was due to some interference. I can't remember the two elements that created the interference. But yes, I think that any XRF that you use you would have to be careful of interference effects.

Q. Do you have interference effects with zinc or copper or nickel?

Copper and nickel did not cause a problem at this site.

Q. So you could get reliable results from copper and nickel.

We were looking into that. The copper and nickel results weren't high enough to cause any interference problems.

Q. Do you know if the instrument would work for zinc?

I believe it will, yes, you just have to go through a recalibration process specifically for zinc.

Q. Two questions. First, did your state agency accept the XRF results as conclusive or are you going to have to go back for verification sampling with traditional lab testing?

During the investigation phase they accepted the XRF data. During the remediation phase which is ongoing, we'll submit the data. I assume that we'll probably have to do some final verifications to the lab report results to convince them. But we'll present the XRF data and we are confident with that.

Q. Did you do any correlation analysis on level 1 and level 2 data to verify.

Well, we did some. I can't remember exactly what the correlation was on the level 1. But during the current remediation phase we're using a 50 percent safety factor. We negotiated a 2,000 part per million cleanup level - the risk-based cleanup level - with the state. So any level 1 reading which approaches or exceeds 1,000 parts per million we then go to level 2 or level 3 screening to confirm.

CHAPTER 2

NATURAL ATTENUATION OF CHLORINATED HYDROCARBONS IN ASSOCIATION WITH PETROLEUM AT A RAILYARD

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INTRODUCTION

Chlorinated solvents are common groundwater contaminants and have been shown to be very persistent in the environment and difficult to remediate. Chlorinated ethenes as solvents were widely used for degreasing in industrial applications. This widespread occurrence of chlorinated solvents in groundwater has received considerable attention and based on the physical characteristics of these chemicals (high density, low viscosity and solubility, and high toxicity) it is generally understood that it is technically impractical to restore impacted aquifers (EPA, 1993). One strategy that is gaining wider acceptance for the management of risks to groundwater is natural attenuation. Natural attenuation has been demonstrated to be effective in reducing risks at petroleum hydrocarbon sites (Weidemeier et al, 1993). This strategy relies on the understanding of the natural processes of biodegradation, dispersion, dilution, sorption, volatilization and/or chemical stabilization that attenuate or reduce the toxicity, mobility or volume of contaminants.

For chlorinated solvents, natural attenuation has been shown to occur under certain circumstances via biodegradation. Tetrachloroethene (PCE) can be degraded by various processes, the most important of which in the groundwater environment appears to be reductive dehalogenation (McCarty, 1996). Under anaerobic conditions,

the degradation products of PCE are trichloroethene (TCE), dichloroethene (DCE), and vinyl chloride (VC). The general sequence of reductive dehalogenation (PCE → TCE → DCE → VC) is observed under increasing reducing conditions. The daughter products DCE and VC have also been shown to be degradable under aerobic conditions.

Changes in the chemical composition of groundwater plumes have been noted at several sites in association with petroleum hydrocarbons. Natural attenuation where the chlorinated hydrocarbons are anaerobically biodegraded has been supported by several lines of indirect evidence, and a protocol for demonstration of this phenomenon is in development by the Air Force (Wiedemeier, 1996). The role of petroleum hydrocarbons in causing reducing conditions to exist in the aquifer as measured by dissolved oxygen levels and several other inorganic parameters are indicators of biological activity used to support natural attenuation. This chapter was prepared to broaden the base of understanding of natural attenuation.

BACKGROUND

This site is a locomotive maintenance facility with associated diesel fueling operations as shown in Figure 1. PCE was used until about 1980 for degreasing. PCE releases are related to two source areas at the site: a PCE storage tank and wastewater sediments in a filled lagoon. A line leak from the 20,000 gallon PCE storage tank was discovered in 1978. Wastewater containing spent solvents (and associated oils and greases) from the maintenance operations was discharged to the former lagoon system. The primary lagoon was filled in 1971 when new tracks and a wastewater treatment system were constructed. Since 1980, an industrial soap has been stored in the PCE storage tank and used for cleaning. Due to a failure of a transfer pump seal, releases of this surfactant have occurred in this area. In addition to PCE releases, petroleum hydrocarbon releases present at the site are related to a diesel fuel storage tank and a locomotive fueling area. Areas of measurable light non-aqueous phase liquid (LNAPL) are shown on Figure 1.

HYDROGEOLOGY

The site is located within the former floodplain of a creek system in eastern Nebraska. Two distinct aquifers underlie the site: an unconfined alluvial aquifer and a bedrock aquifer within the Cretaceous Dakota Formation. Within the alluvial aquifer, units of varying permeability have been identified: the upper clay, upper sand, lower clay, and lower sand units. The bedrock consists of shale and sandstone layers. Site lithology is shown on geologic cross-section included as Figure 2. Based on pump tests, the hydraulic conductivity of the upper clay and upper sand units were determined to be 0.32 ft/day and 34 ft/day, respectively. The groundwater flow in the upper clay and upper sand is generally to the northeast in this area and discharges to a stream east of the site. The groundwater gradient is 0.004 ft/ft. Based on the measured hydraulic conductivity, the estimated groundwater flow velocity is 28 ft/year in the upper clay and 197 feet/year in the upper sand. The soil fraction of organic carbon (f_{oc}) is 0.005 in the upper clay and 0.00013 in the upper sand. The depth to groundwater is typically 10 feet across the site. The groundwater is highly saline in this area and not suitable for drinking water.
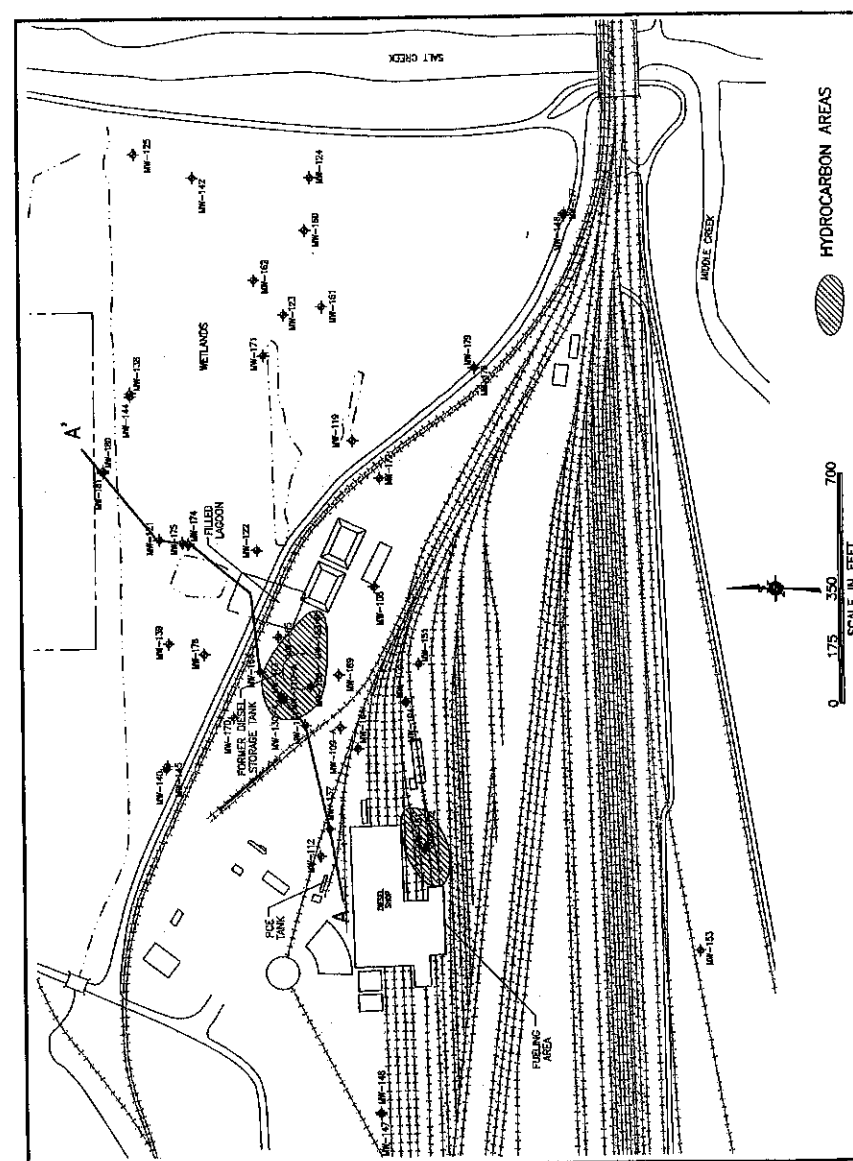
Figure 1   **Site map**
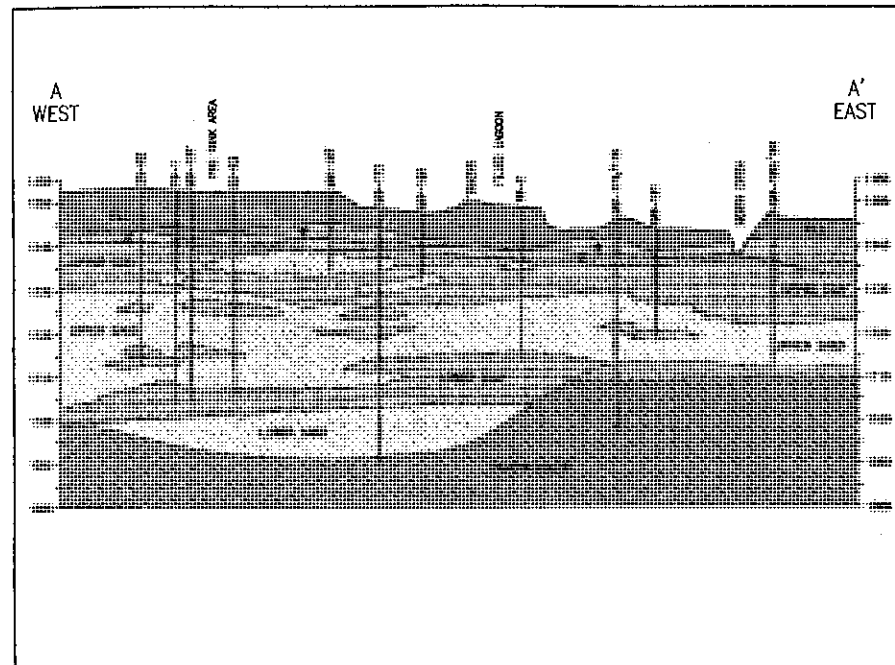
Figure 2   Cross section A to A′

GROUNDWATER GEOCHEMISTRY

The average groundwater concentration of total dissolved solids (TDS) is 4,733 ppm in the upper clay. The TDS concentrations are highly variable in the upper clay due to varying industrial activities across the site. The TDS levels in groundwater increase in the lower units; the average is 5,623 ppm in the upper sand and 8,433 ppm in the lower sand and bedrock. The groundwater is sodium chloride dominated as shown in the Piper diagrams included as Figure 3. The overall groundwater system indicates conditions favorable for reductive dechlorination of the VOCs (Weidemeier et al, 1996). The presence of the petroleum hydrocarbons has resulted in anaerobic groundwater conditions. The dissolved oxygen (DO) is below 1 ppm and the redox potential is less than -10 mV across most of the site. The other inorganic parameters present variable evidence of natural attenuation. The chloride concentrations are naturally high and no significant increase is noted due to reductive dechlorination. The concentration of nitrate is less than 1 ppm and ferrous iron is greater than 1 ppm in the source areas which indicates favorable reductive pathways may exist. The sulfate concentrations are generally greater than 20 ppm, which may compete with reductive pathways.

FATE AND TRANSPORT

The fate and transport of PCE at the site shows strong evidence of biodegradation. PCE was the only chlorinated solvent used at the site. Concentrations of PCE in soils
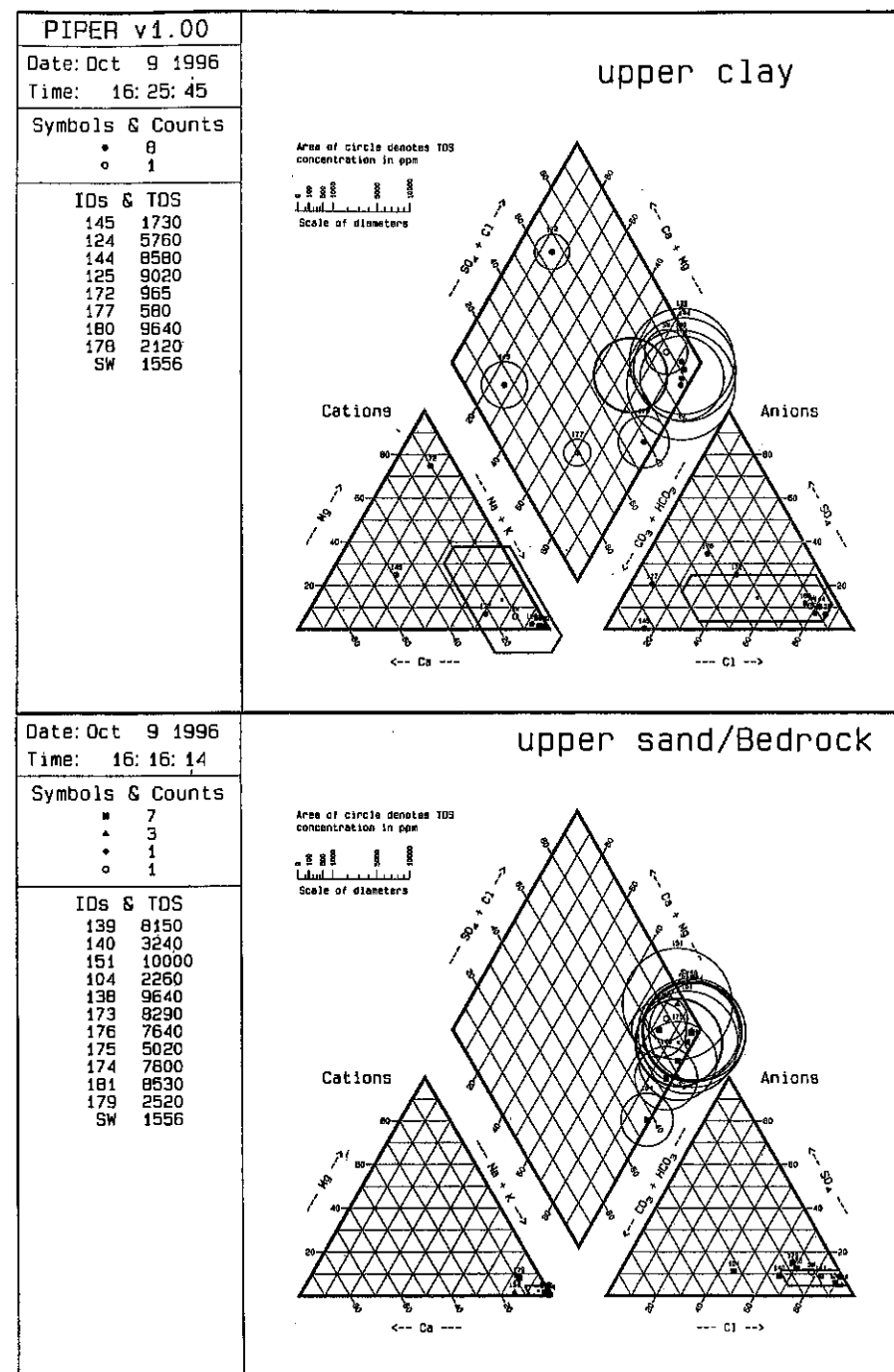
Figure 3   Groundwater Piper diagrams

of the source area are high. Soils contain PCE at up to 640 ppm in the PCE Tank area. In the Filled Lagoon a 1 to 2 foot layer of buried sediment contains PCE at 30,000 ppm. The other chlorinated VOCs (TCE, DCE and VC) in soil are typically an order of magnitude lower than PCE. The PCE concentrations in groundwater are also high in the source areas. Groundwater in the upper clay near the PCE Tank area contains PCE higher than the solubility limit (200 ppm) at 660 ppm. This high concentration is due to the surfactant that was spilled in this area. The upper sand concentrations are 26 ppm in the PCE Tank area. The upper clay groundwater contains PCE at 34 ppm in the Filled Lagoon area. The other chlorinated VOCs are much lower than PCE in the source areas. In groundwater downgradient of the source areas PCE is much reduced or absent, and degradation products increase relative to PCE. Figure 4 shows the concentration of the various chlorinated VOCs over distance from the source areas. The degradation products DCE and VC persist in groundwater in wells downgradient from the source areas. Monitoring wells along the stream, which is over 2,000 feet from the source areas, contain DCE and VC at levels up to 0.050 and 0.025 ppm respectively in both the upper clay and upper sand.

The BIOSCREEN version 1.3 analytical model (Newell et al, 1996) was used to evaluate the fate and transport of PCE in groundwater. A degradation rate half-life for PCE of 1.2 days was used to evaluate first-order biodegradation. This half-life for PCE is an average estimated from numerous field sites (Ellis, 1996). Figure 5 contains the model output for the upper sand from the PCE Tank and Figure 6 is for the upper sand from the Filled Lagoon. The modeled results for the PCE Tank upper sand correlate well with the site data, the results for the Filled Lagoon upper sand indicate that the degradation rate is higher than modeled. The model output for the PCE Tank upper clay is shown in Figure 7. The site data does not correlate with the modeled results. This indicates that the transport in this unit is probably controlled by higher permeability sand stringers with low levels of organic carbon.

CONCLUSIONS

Based on the site data there is adequate evidence for natural attenuation of PCE occurring at this site. The limited data on indicator parameters provide evidence that the groundwater conditions are favorable for anaerobic degradation of the chlorinated VOCs especially with the presence of the petroleum hydrocarbons. The high concentration of petroleum serves as a primary substrate of carbon to drive the reductive dechlorination. The distribution of the chlorinated VOCs in groundwater also supports natural attenuation with PCE being replaced by the degradation products of DCE and VC downgradient from the source areas. The modeled first-order degradation of PCE agrees well with published degradation rates for the sand units. The fate and transport of PCE in the clay units appears to be controlled by preferential flow paths. This site is a good candidate for natural attenuation since the groundwater is not suitable for drinking water and there are no receptors that would be affected based on the modeled results. Further data is needed to demonstrate the effectiveness of natural attenuation at this site.
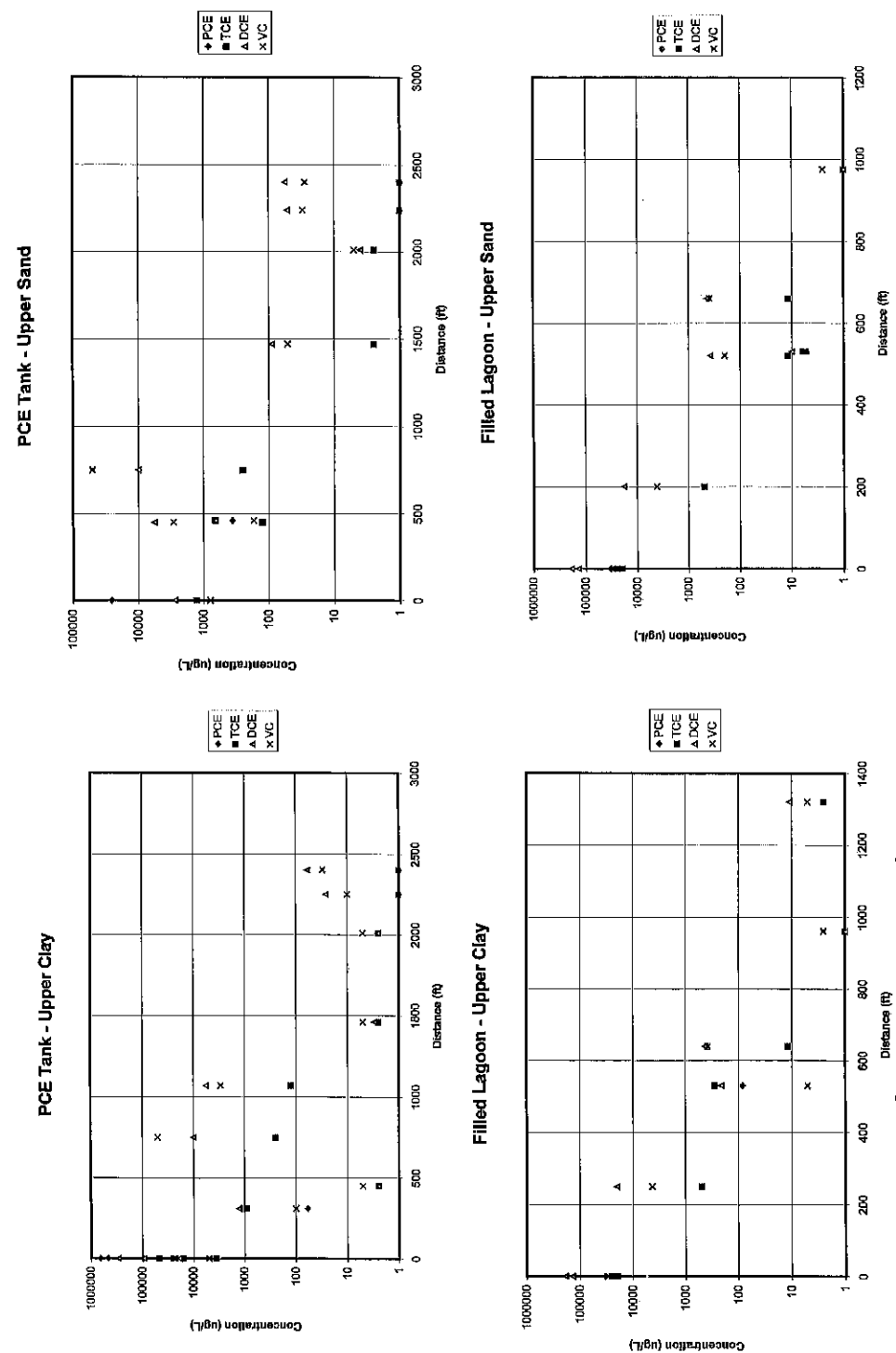
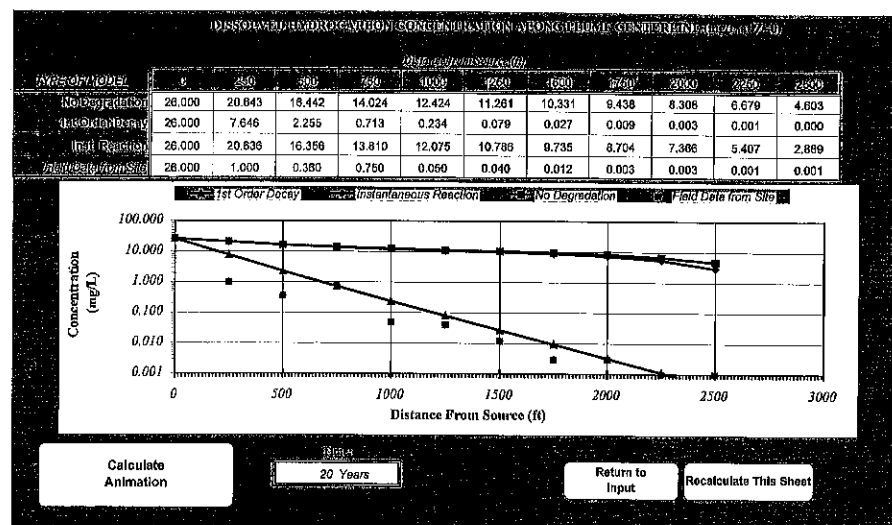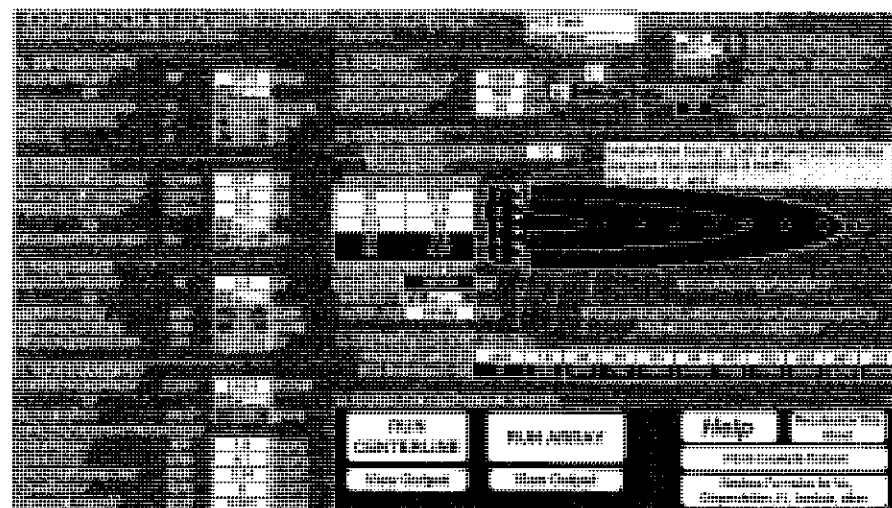**Figure 4   Groundwater VOCs vs. Distance**

Figure 5   PCE tank upper sand BIOSCREEN output
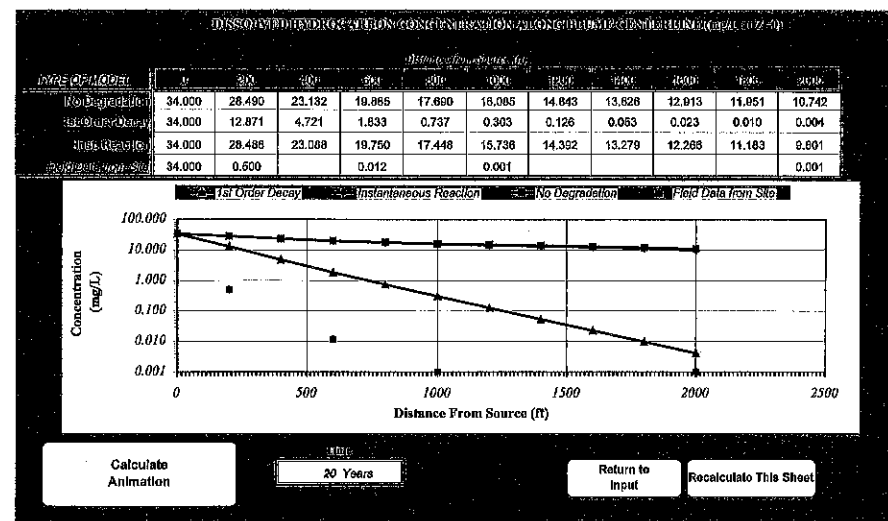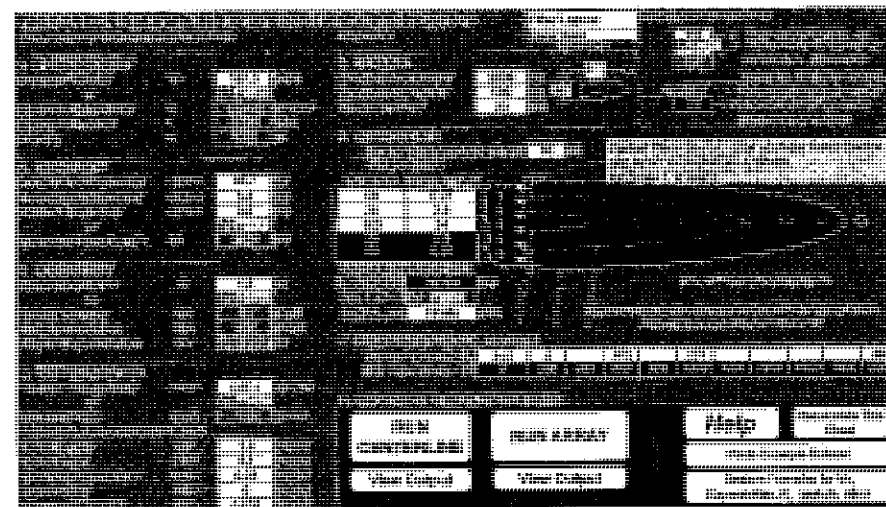
Figure 6   Filled lagoon upper sand BIOSCREEN output

Q. Your data suggests that, at least in part, there is microbial activity there. Do you have any direct evidence along microbial analysis lines that supports that contention?

No, we don't have any direct microbiological data. My conclusion is that the site data is conclusive. I'm not sure the microbiological data would provide any additional evidence that would make that any more conclusive.

Q. You're basing your argument on the culture of the microbes in the subsurface. It would seem that at least you should draw a link between their presence or absence there because indeed there are other forces that could lead to the dechlorination of the PCE that you have in place. Is there any specific iron content in the soil?

We didn't look at the iron content in the soil. The actual mechanisms for the reduction at the site are probably not understood, although it does appear that there is evidence to support degradation. There are typical daughter products being developed that you would see from reductive dechlorinization of PCE. So that is more or less anecdotal evidence there is microbiological activity going on.

Q. The questions are directed along the lines of, okay, you have at least the converted process, or at least a possible process there, is it a winnable process? And it seems to me that you need to draw stronger lines of cause and effect before you rely on the process.

I think we do need to develop some stronger lines. This has been a screening mode we are in right now.

CHAPTER 3

CLOSURE OF PETROLEUM SLUDGE SURFACE IMPOUNDMENTS BY IN-SITU SOLIDIFICATION

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INTRODUCTION

Norfolk and Western Railway Company (Norfolk and Western) operates a railroad car and locomotive switching and maintenance facility (The Shaffers Crossing Railyard) in Roanoke, Virginia. Norfolk and Western previously operated six unlined surface impoundments (the "sludge lagoons") at the Shaffers Crossing Railyard. Radian International LLC (Radian) was retained by Norfolk and Western to perform engineering design of, and to provide subsequent construction oversight for, closure of the sludge lagoons site. Closure activities were conducted from 1996 to 1997. This chapter details the activities performed by Radian and other contractors to complete the closure of the lagoons site.

Site History

It is estimated that the sludge lagoons were operated from the early 1970s until the late 1970s. The lagoons received wastewater treatment solids and sludges that consisted mostly of dissolved air flotation (DAF) unit skimmings, oily water and grit from oil/water separators and oil/water emulsions from the cleaning of pollution abatement systems and equipment. In the early 1980s, two of the lagoons at the west end of the site (Lagoons 1 and 2) were backfilled with soil. Prior to site closure activities, sludge

and groundwater samples were collected during several sampling events conducted at the lagoons site.

Site Status Prior to Closure

At the time site closure activities were initiated, the lagoons site was inactive and was surrounded by a fence with a locked gate. The four remaining lagoons (Lagoons 3,4,5 and 6) contained a mixture of water, emulsified oil and semi-solid sludge. An unimproved site access road extended across the southern edge of the site and ended near several soil mounds. Six monitoring wells were located in the vicinity of the site: three within the perimeter fence and three outside the fence. Figure 1 shows the pre-closure layout of the site.

Sludge Sampling

In 1990, 1991 and 1993, samples of sludge from each of the lagoons were collected for analysis. Sludge samples were analyzed for volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), pesticides, polychlorinated biphenyls (PCBs), total petroleum hydrocarbons (TPH), moisture content, regulated constituents included under the Toxicity Characteristic Leaching Procedure (TCLP) and hazardous waste characteristics (ignitability, corrosivity and reactivity). The maximum total VOC and SVOC concentrations detected in sludge samples were 47 mg/kg and 608 mg/kg, respectively. TPH concentrations in sludge ranged from 110,000 mg/kg (11 percent) to 340,000 mg/kg (34 percent). Results for moisture content in the sludge ranged from 55 percent to 70 percent. TCLP and hazardous waste characteristic results indicated that the sludge was not hazardous according to 40 CFR 261.20 through 261.24.

Groundwater Sampling

In 1990, 1993 and 1994, groundwater samples were collected from monitoring wells located within the vicinity of the site. Groundwater samples were analyzed for VOCs, SVOCs, metals, TPH, PCBs and pesticides. Several VOCs were detected in groundwater samples. Two VOCs were detected above their maximum contaminant levels (MCLs): vinyl chloride at a maximum concentration of 4 ug/L (MCL = 2 ug/L), and chlorobenzene at a maximum concentration of 104 ug/L (MCL = 100 ug/L). It should be noted that chlorobenzene no longer has an MCL. Several metals were detected in groundwater samples, including barium at 519 ug/L, cadmium at 230 ug/L and lead at 200 ug/L.

Site Regulatory History

In 1994, the Virginia Department of Environmental Quality (VaDEQ) issued a letter classifying the sludge contained in the lagoons as non-hazardous. This decision was based on the analytical results discussed previously, and on historical information provided by Norfolk and Western regarding the operation of the lagoons. In 1995 VaDEQ approved Norfolk and Western's closure plan for the site. The plan proposed treatment of free liquids in the lagoons, followed by in-situ solidification of lagoon sludges and capping of the site using compacted clay.
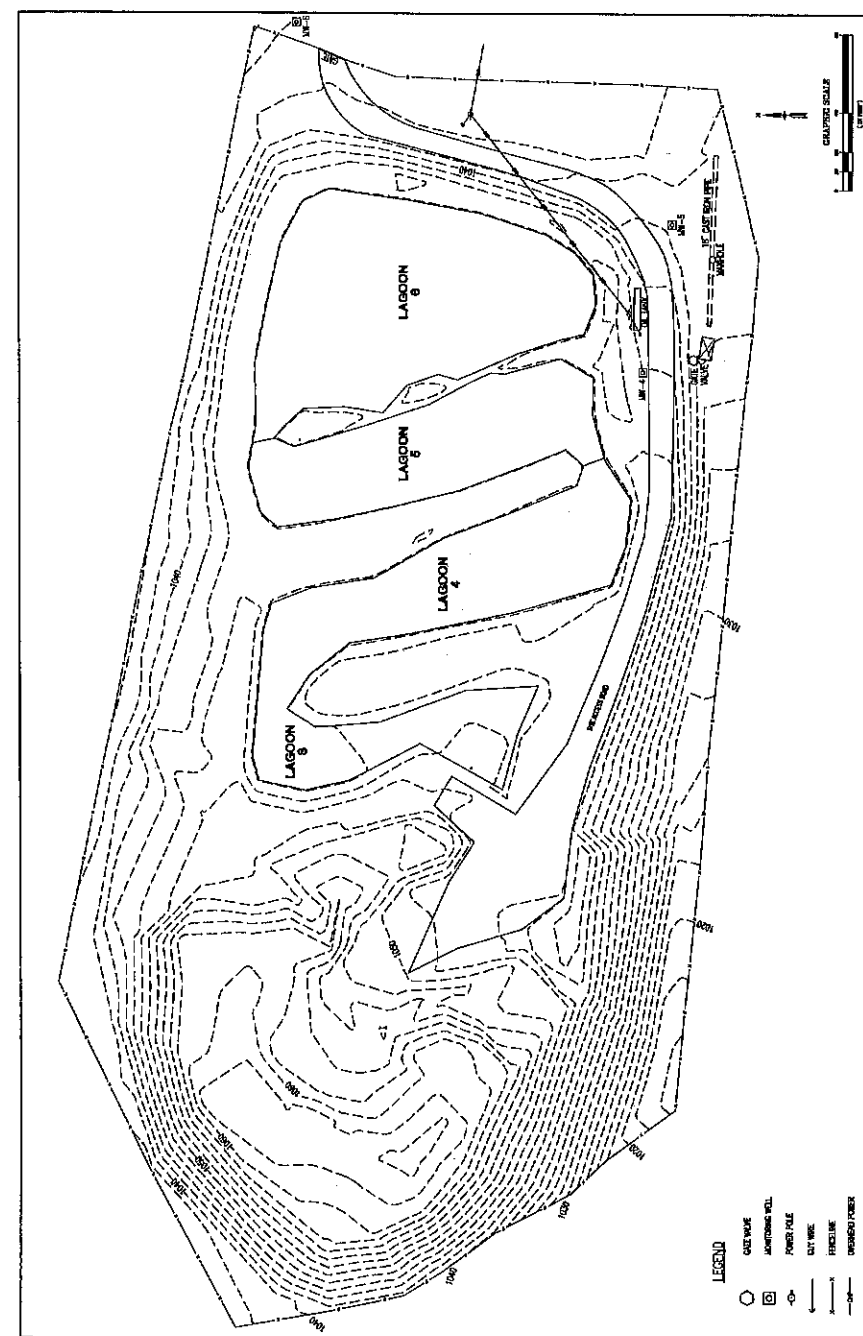
Figure 1   Initial site conditions

Significant requirements outlined in the site closure plan included:

- Any sludge encountered at the site, either within Lagoons 3,4,5 and 6, or above former lagoons 1 and 2 would be solidified;
- Solidified sludge would pass TCLP concentration requirements, as listed in 40 CFR 261.24;
- The site would be covered with an engiueered cap with a permeability lower than the permeability of the underlying soils, or with a maximum permeability of 1×10^{-5} cm/sec;
- Post-closure care of the site would be conducted, iucluding groundwater monitoring and maintenance of the low permeability cap and site fencing.

TREATABILITY STUDIES

In 1995 and 1996, sludge samples were collected from the lagoons during three sampling events so that sludge treatability studies could be performed. The purpose of the treatability studies was to select the most appropriate solidification agent or agents for this project, and to determine the proper mixing ratios. During each sampling event, sludge was collected from each of the four lagoons at varying locations and depths. A composite sample was created for each sampling event by combining aliquots from all of the grab samples. Free liquids were decanted from the sludge samples during collection to simulate site conditions which would be expected following the initial task of collection and treatment of lagoon liquids.

The following agents were tested as part of the treatability studies:

- Portland cement;
- Boiler fly ash (from a Norfolk and Western boiler);
- Boiler fly ash (from an independent supplier);
- Crushed limestone (from Norfolk and Western);
- Granular lime;
- Cement kiln dust;
- Kaolin (aluminum silicate).

Treatability Study Considerations

Various solidification agents and combinations of agents were evaluated for the treatability studies. During evaluation of each agent or agents, consideration was given to the following parameters:

- Ultimate compressive strength of the solidified matrix;
- How quickly the solidified matrix gained compressive strength;
- Ability of the solidified matrix to meet TCLP requirements; and
- Cost to purchase and deliver the agent or ageuts.

Ultimate Compressive Strength

The ultimate achievable compressive strength of the solidified matrix was considered an important factor. This parameter indicates how well the solidified matrix would support a low-permeability cap or any other surface loads applied to the site. Based on calculations performed by Radian, and approved by VaDEQ, it was determined that a compressive strength of 15 psi would be adequate to support the low-permeability cap system at the site without subsidence.

Short-Term Compressive Strength

Short-term compressive strength of the solidified matrix was considered an important parameter for this project because of the expected difficulty associated with handling and staging extremely low strength material at the site. Because the site had limited available open space, it would have been difficult to store significant quantities of material that was not sufficiently cohesive to be stockpiled. It was derermined that the solidified matrix must gain significant compressive strength in the first 24 hours, and obtain the bulk of its ultimate compressive strength within tbe first seven days.

Ability to Meet TCLP Requirements

Whereas this parameter was considered important for ultimate approval of the closure, it was not used for selection of the solidification agent. Because all previous sludge samples bad passed TCLP tests without solidification, it was considered likely that any of the agents evaluated would generate a matrix that would also pass the TCLP test. As expected, the selected solidification agents were tested and did pass the TCLP test.

Cost to Purchase and Deliver the Solidification Agent

The purchase cost of the agent was an important parameter. Lower-cost agents can sometimes be substituted for higher-cost agents and still allow the solidified matrix to meet all other requirements. Delivery cost was also a significant factor. Therefore, to minimize project costs, local sources of the various ageuts were used for treatability testing whenever available.

Results of Treatability Studies

For each proposed solidification agent or combination of agents evaluated, benchscale laboratory tests were conducted. All samples were mixed and compacted in the laboratory to simulate conditions expected at the site during full-scale solidification activities. Table 1 includes each of the solidification agents (or combinations) that were considered for this project, and presents pertinent information for each test. The table also includes the rationale for selecting or rejecting various agents or combinations. Because of concerns regarding the comparability of the results from tests performed on samples collected in 1995 versus samples collected in 1996, the sampling date is also included for each agent or combination of agents listed in Table 1.

For the treatability studies, two types of compressive strength testing was conducted: 7-day compressive strength tests were performed using a penetrometer; and 28-day unconfined compressive strengths were calculated using ASTM Method

TABLE 1   Treatability Study Results

Agent(s)	Source	Approximate Purchase Cost (per ton)	Optimum Mixing Ratio (by weight) - (sludge:agent:agent)	7-Day Strength	28-Day Strength	Sampling Round(s)	Comments
Class F Boiler Fly Ash; Type I/II Portland Cement	JTM Ind; Roanoke Cement	$10; $80	1.0:1.0 (fly ash): 0.25 (cement)	> 60 psi	17.7 psi	1996	This combination was selected because it met the compressive strength and workability requirements, and because the purchase cost for agents was considered reasonable. An attempt to substitute Norfolk and Western fly ash yielded 12.5 psi at 28 days.
Cement Kiln Dust	Roanoke Cement	$13	1.0:1.0	> 50 psi	16.3 psi	1995	Not selected because material consistency was dry and cracking at 28 days. Material did not appear to be easily compactable.
Type I/II Portland Cement	Roanoke Cement Corporation	$80	1.0:1.0	> 50 psi	428 psi	1995/1996	Not selected because of high cost. The agents that were ultimately selected did include portland cement at a lower addition rate than that required for use of cement as the only agent. 1996 sludge sample yielded >120 psi at 28 days.
Lime (granular)	Rockydale Quarries	$9	4.0:1.0	38.2 psi	Not performed	1995	Not selected because of the high addition rate required to achieve compressive strength and failure to meet short-term workability requirements.
Boiler Fly Ash	Norfolk and Western	$0	1.0:1.0	20.8 psi	< 5 psi	1995/1996	Not selected because it did not meet the 28-day strength requirement. In addition, there was a question regarding the ability of the Norfolk and Western boiler to produce sufficient quantities of the agent for this project. 1995 sample yielded 20 psi at 7 days and was not tested at 28 days.
Class F Boiler Fly Ash	JTM Industries	$10	1.0:1.0	20.8 psi	< 5 psi	1995/1996	Not selected because it did not meet the 28-day strength requirement.
Lime (crushed stone); Type I/II Portland Cement	Norfolk and Western (local); Roanoke Cement Corporation (local)	$0; $80	1.0: 0.5(lime); 0.5(cement)	14 psi	Not performed	1995	Not selected because of difficulty and cost associated with pulverizing lime into a granular form.
Lime (granular); Cement Kiln Dust	Rockydale Quarries (local); Roanoke Cement Corporation (local)	$9; $13	1.0: 0.15(lime); 1.3(kiln dust)	Not performed	97 psi	1995	Not selected because of low workability in the first few days after mixing. These agents were not tested for the 1996 sludge sample.
Kaolin; Portland Cement	Dry Branch Kaolin (New Jersey); Roanoke Cement Corporation (local)	$300; $80	1.0: 0.15(kaolin); 0.95(cement)	Not performed	433 psi	1995	Not selected because of high cost of agents.

D-2166. The unconfined compressive strength results were typically lower than the penetrometer readings. This relationship was expected because the 7-day tests were performed under confined conditions (within the sample mold), while the 28-day tests were performed under unconfined conditions. Unconfined compressive strength by ASTM Method D-2166 is considered a conservative indicator of field compressive strength, because material compacted in the field will be somewhat confined by the surrounding soil and other solidified material placed at the site. This confining pressure will cause the solidified matrix to display a higher compressive strength in the field than in the laboratory.

Treatability results indicated that the inclusion of portland cement as a solidification agent greatly increased the ultimate compressive strength of most of the mixtures. A combination of Class F boiler fly ash and Type I/II portland cement was proven to be the best solidification alternative, based on performance and cost.

SITE CLOSURE ACTIVITIES

Closure activities were conducted at the lagoons site in 1996 and 1997. Closure activities included:

- Clearing and grubbing the site in the vicinity of the lagoons;
- Regrading portions of the site to allow staging of equipment and materials;
- Treatment of water and emulsified oil using a plate-and-frame filter press;
- Collection and disposal of contaminated and non-contaminated debris at the site, including an oil skimmer, a telephone pole and two steel tanks;
- Solidification of sludge with boiler fly ash and portland cement;
- Placement of solidified sludge back into each of the lagoons and above the former level of the lagoons;
- Grading of the site to promote surface drainage away from the former lagoons area;
- Application of a winter cover to the site to prevent erosion;
- Installation of a low-permeability geosynthetic clay liner (GCL) on top of the solidified sludge;
- Placement of 12 inches of clean soil fill and 6 inches of clean topsoil above the GCL and solidified sludge; and,
- Establishment of a grass cover at the site.

Site Preparation

Several modifications were made to the site prior to the commencement of closure activities. The site access road was widened and covered with crushed stone to prevent soil erosion and to minimize the formation of ruts or other deterioration that might inhibit the passage of vehicles or heavy equipment. Areas at the east and west ends of the site, including the area above former Lagoons 1 and 2, were cleared, grubbed and

graded to facilitate placement of materials and equipment. Site trailers were staged at the east end of the site immediately inside the fence.

Treatment of Free Liquids in the Lagoons

Collection and treatment of free liquids, including free-phase emulsified oil, was necessary because large volumes of this material, if left in place, would inhibit solidification of lagoon sludge.

Treatment Methodology

Prior to closure, liquid samples were collected from the lagoons for treatability testing. Based on the results of this testing, it was determined that treatment using a plate-and-frame filter press would be adequate to meet expected requirements for discharge to the local publicly-owned treatment works (POTW). It was also concluded that diatomaceous earth would be added to each treatment batch to enhance removal of emulsified oil by the filter press.

Discharge Permits

Prior to discharge of treated water from the lagoons site, it was necessary to obtain a permit from the local water treatment authority. Discharge of treated water from the site to the city sanitary sewer was allowed based on meeting limitations for several metals, oil and grease, TPH and benzene, toluene, ethylbenzene and xylene (BTEX).

Treatment System Description

The water treatment system consisted of the following elements:

- A collection pump to remove liquids from the lagoons;
- A shaker screen to remove coarse (greater than 1 inch diameter) solids from the water;
- A mixing tank;
- A primary storage tank to hold liquids prior to treatment;
- A chemical addition tank (for diatomaceous earth);
- A plate-and-frame filter press unit;
- An oil/water separator;
- A tank for storage of removed oil; and
- Two parallel banks of treated water storage tanks.

Figure 2 shows a schematic diagram of the system.

Operation of the Treatment System

During closure operations, twenty batches were treated, eighteen of which were discharged to the city sanitary sewer system. The first two treatment batches were not discharged because concentrations of several metals were above the discharge standards. The water from these first two batches was pumped back into the lagoons and was

ultimately retreated. Discharge of treated water was conducted after testing indicated that all parameters were within acceptable concentrations.

A total of 1,186,800 gallons of water was discharged from the treatment system to the city sanitary sewer. Treatment of lagoon liquids was discontinued when the oil and grease concentrations in the treated effluent could no longer be kept under the discharge limitation of 200 mg/L. All remaining liquids in the lagoons were solidified along with the lagoon sludge. In addition, spent diatomaceous earth collected on the filter press screens and a small volume of separated oil were returned to the lagoons to be solidified.

Sludge Solidification

Sludge contained in each of the four lagoons was solidified using boiler fly ash and portland cement. Sludge solidification was conducted at the site from August 1996 to January 1997. Solidified sludge was placed back into each of the four lagoons and
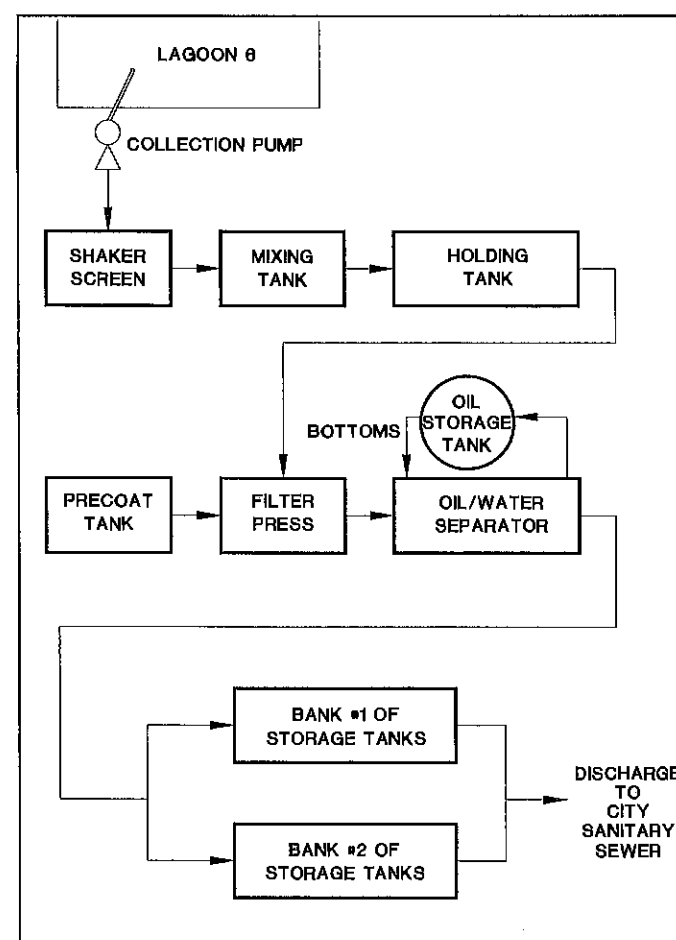
Figure 2   Water treatment system schematic

compacted. Because the volume of solidified sludge exceeded the volume of the lagoons, some solidified sludge was stockpiled in the area of the lagoons. Solidified sludge that was not placed into the lagoons was ultimately spread out across the site and compacted.

According to the treatability studies discussed previously in this report, sludge solidification was performed in batches using the following mixing ratios (by weight):

Sludge	1 part
Boiler Fly Ash	1 part
Portland Cement	0.25 parts

For solidification and stockpiling activities, the following equipment was used: two tracked excavators, two tracked excavators with extended-length booms, and one low ground pressure (wide track) D-6 bulldozer. A rubber-tired backhoe was also used at the site to perform various functions that supported solidification activities, however, this unit was not used to handle solidified sludge.

The proposed methodology for conducting solidification operations consisted of progressing from west to east across the site (from Lagoon 3 to Lagoon 6), solidifying and replacing sludge in each lagoon as the project proceeded. It was planned that sections in each lagoon would be cleared so that solidification and replacement of solidified material could then be performed in each section. Sludge weights for each batch were calculated using a sludge density of 73 pounds per cubic foot. This density was determined during the initial treatability studies, described previously. Fly ash weights were measured prior to delivery of the material, and portland cement weights were measured on-site with a scale.

Soil Sampling in each Lagoon

As required by VaDEQ, soil sampling was performed in each lagoon during site closure operations. One sample was collected from the soil underlying each lagoon and analyzed for permeability. Soil samples were collected using Shelby tubes. The purpose of this sampling was to determine whether the liner proposed for covering the site had a lower permeability than the underlying soil. Table 2 lists the permeability results for soil samples collected at the lagoons site.

TABLE 2   Native Soil and GCL Permeabilities at the Lagoons Site

Lagoon	Permeability
3	8.0×10^{-9} cm/sec
4	2.0×10^{-8} cm/sec
5	1.4×10^{-8} cm/sec
6	2.1×10^{-7} cm/sec
Average Permeability -	6.3×10^{-8} cm/sec
Liner (GCL) Permeability -	5.0×10^{-9} cm/sec

As can be seen from these results, the permeability of the GCL is lower than any of the samples collected from the soil underlying the four lagoons.

Description of Solidification and Placement Activities

As discussed above, sludge was collected and solidified starting in Lagoon 3 and continued progressively through Lagoons 4, 5 and 6. As each lagoon was cleared of sludge, solidified material was placed back into the lagoon and compacted. When possible, sludge was transferred from the lagoon currently being cleared to the adjacent lagoon for temporary storage. As sections in each lagoon were cleared of sludge down to the underlying soil, surveys were performed to determine the lagoon bottom elevations.

For most of the solidification batches processed at Lagoon 3, mixing of sludge and solidification agents was performed in the bottom of the lagoon. Solidified material was initially stockpiled within the lagoon prior to placement and compaction. Because the volume of sludge in Lagoon 3 was greater than expected, the entire volume of solidified sludge could not be stockpiled within the lagoon. To address this issue, solidified sludge was also stockpiled west of Lagoon 3. Plastic sheeting was laid out in this area prior to staging of solidified sludge.

For sludge solidification batches processed at the northern end of Lagoon 3 and in all of the remaining lagoons, mixing operations were conducted in pits excavated out of previously compacted solidified sludge. Use of these pits allowed for better control of the mixing ratios and easier mixing. As sludge was processed in each lagoon, new mixing pits were excavated. Periodic relocation of the pits improved efficiency by keeping the mixing operations close to the areas where sludge was being collected.

Throughout the preliminary portion of this project, sludge was processed at a rate of six batches per day. Each batch consisted of approximately 25 tons of sludge, 25 tons of boiler fly ash and 6 tons of portland cement. During solidification activities at Lagoon 4, daily production was increased to 8 batches a day. During solidification activities at Lagoon 6, daily production was increased to 10 batches a day and subsequently to 12 batches a day. Daily production increases were realized by increasing the number of mixing pits and by improving traffic flow patterns at the site. Solidification of sludge was completed in January 1997.

Compaction of Solidified Sludge

Placement and compaction of solidified sludge was performed using the tracked excavators and the D-6 bulldozer. Sludge was placed back into the lagoons in 12-inch loose lifts. The bulldozer was rolled a minimum of three times over each complete lift prior to placement of material for the subsequent lift. To accelerate the rate at which solidified sludge could be placed at the site, a large-capacity, articulated dump truck was mobilized to the site during the final stages of sludge solidification operations. This unit was used during operations at Lagoon 6 and for placement of material above all of the lagoons.

Dust Suppression

Because of the large volumes of boiler fly ash and portland cement used during this project, it was necessary to take steps to control the amount of dust released during

sludge solidification. Boiler fly ash was delivered to the site in sealed hopper trucks, and was transferred directly from the trucks to the mixing pits. Because each truck carried approximately 25 tons, it was not necessary to measnre fly ash weight (other than to record the delivered weight) prior to mixing. Portland cement was also delivered to the sire in sealed hopper trucks, and was transferred from the trucks to a temporary storage tank located at the site. A scale on the storage tank was used to measure the weight of portland cement delivered to the mixing pit for each batch. The portland cement storage tank was connected to a dust collection baghouse that captured dust generated during transfer operations. For dust suppression during transfer of solidification agents to the mixing pits, a welded steel "mixing box" was used. The mixing box was placed in the bottom of the mixing pit and transfer hoses were connected to the top of the box. The mixing box was removed from the pit when transfer of agents was completed for each batch.

Surface Grading at the Site

The surface of the lagoons site was graded to promote drainage of surface water away from the area where solidified sludge was placed. The solidified sludge was graded such that a crown was formed along the east-west centerline of the site. This crown created surface slopes of approximately two percent on the northern and southern halves of the area to be capped. In addition to the crown, the surface of the site was also sloped from west to east at a grade of approximately two percent. This two percent slope roughly approximates the existing ground surface at the site.

A 1978 aerial photogtaph of the lagoons site was obtained to determine the extent of the area where solidified sludge would be placed and where the GCL would subsequently be installed. This photograph was used to accurately determine the locations of former Lagoons 1 and 2 which have since been backfilled with soil. The area at the site within which solidified sludge was placed included (and was limited to) the combined original footprints of all six lagoons.

In addition to the surface grading performed in rhe area where solidified sludge was placed, several other areas of the site were also graded to promote non-erosive surface drainage at the site. The exposed surface of the soil berm that surrounded Lagoon 6 on the north, east and south sides was regraded from a relatively steep slope to more shallow (2 feet horizontal for every 1 foor vertical) slope. A soil berm, also sloped at 2:1 was constructed along the southwestern edge of the area to be capped to allow surface drainage off the south edge of the cap. Shallow drainage ditches were excavated along the western edge of the area to be capped. These ditches will help divert surface water away from the area where solidified sludge was placed.

Site Closure During Winter Months

The lagoons site was closed following completion of sludge solidification, placement and final grading operations. It was necessary to cease construction activities on this project over the remaining winter months because the GCL manufacturer recommended that the GCL not be installed during sub-freezing temperatures. To prevent erosion at the site while construction activities were suspended, a soil stabilization product was applied to the surface of the site. The product selected for this application was Road Oyl™ which is manufactured by Soil Stabilization Products Co., Inc. Road Oyl™

is a resin-modified emulsion, and is applied as a liquid. The manufacturer recommended that the Road Oyl™ be diluted when used for temporary soil erosion control. Undiluted, this product can be used to create high-strength temporary road surfaces. For this project, a 3:1 ratio (water: Road Oyl™) was used to adjust the strength of the product.

Road Oyl™ was applied to the surface of the site in February 1997 and closnre operations were ceased for the remainder of the winter. Project activities resumed at the site in April 1997. No evedience of soil erosion was observed at the site.

Installation of the Geosynthetic Clay Liner

To minimize the possibility for migration of contaminants contained in the solidified sludge; a geosynthetic clay liner (GLC) was installed at the site. For this project, the Bentofix™ GCL system was selected. This product is distributed by Fluid Systems. This particular GCL is constructed from woven geotextiles and bentonite. The GCL serves as a low permeability barrier between surface water and the solidified sludge. Compacted clay was initially specified for this project, however, the GCL was substituted as an alternative that is easier to properly install, and will typically have a lower permeability than compacted clay. VaDEQ reqnired that the liner have a lower permeability than the soil underlying the lagoons. As discussed previously the permeability of the GCL was lower than any of the soil samples that were collected from the lagoons.

The liner was delivered to the site in 15.5-foot by 125-foot rolls. Each roll was covered with plastic sheeting to prevent product degradation by exposure to sunlight and to prevent premature hydration of the bentonite. According to the manufactnrer of this product, extended exposure to sunlight can cause degradation of the geotextile fabric covering the GCL. Additionally, if the bentonite becomes hydrated prior to deployment, the rolls become extremely heavy, and there is potential for the bentonite to migrate within the liner, possibly preventing formation of a uniform impermeable barrier when installed.

As recommended by the manufacturer, the liner was installed with a 12-inch overlap along the ends (the 15.5-foot dimension) of adjoining rolls, and a 10-inch overlap along the sides of adjoining rolls. All overlapped areas were additionally sealed by applying 0.25 pounds per linear foot of loose, granular bentonite. Rolls were installed such that overlapping sections were "shingled" from higher to lower elevations. Shingling of the sheets inhibits passage of infiltrating surface water between the overlapped rolls.

A two-foot deep by two-foot wide anchor trench was excavated around the perimeter of the area to be capped. The liner was installed into the anchor trench, and the trench was backfilled with previously excavated soil. To avoid excavating into solidified sludge, the anchor trench was installed at the toe of the soil berms located at the edge of the area to be capped. This allowed for capping of a slightly larger area than that covered by the six former lagoons.

Placement of Soil at the Site

Clean fill material was transported to the site to cover the GCL. Because this fill material was essentially of topsoil quality it was also used as a source of topsoil for this project. To achieve topsoil quality, the fill soil was amended by mixing in lime prior to

seeding with native grasses. A sample from the source of fill was collected and analyzed for TPH. TPH was not detected in the soil sample.

As recommended by the GCL manufacturer, all liner material deployed on any given day was completely covered with soil on the same day. No installed material was left uncovered overnight. Additionally, the GCL was not installed when site conditions were extremely wet or during rainfall events. Soil cover was placed in 15-inch loose lifts and was subsequently compacted such that its installed thickness was 12 inches. Styrofoam grade stakes were used to ensure that 12 inches of soil cover was achieved uniformly over the site. Six inches (after compaction) of topsoil was installed above the 12 inches of soil cover. This provided a good medium for grass to grow at the site and brought the total installed thickness of the soil cover to 18 inches. This is considered an adequate soil cover for protecting the GCL from expected frost penetration depths in Virginia. Figure 3 shows the final elevations in the capped area of the site after all soil was placed above the GCL.
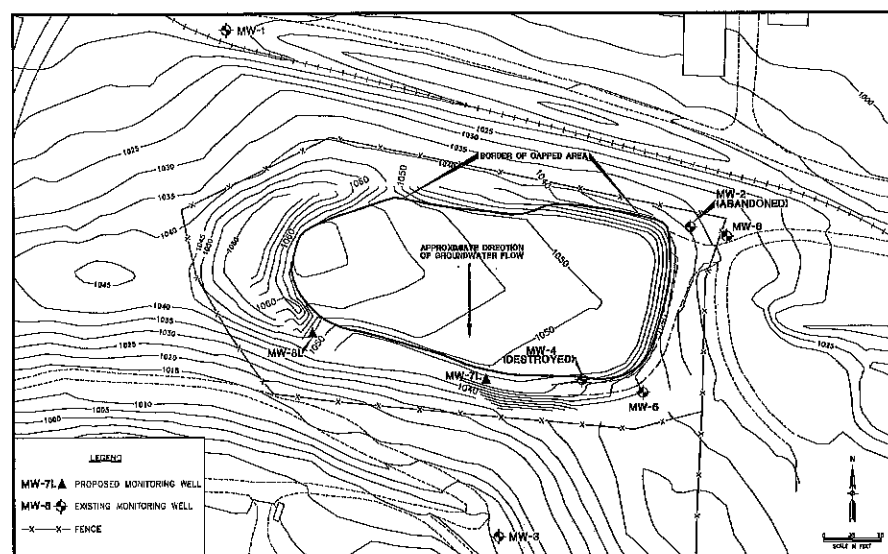
Figure 3   Final elevations at the lagoons site

POST-CLOSURE CARE OF THE SITE

As required in the approved closure plan, Norfolk and Western will be required to perform certain post-closure activities at the lagoons site to ensure that the cap system is performing properly. In addition, regular groundwater monitoring is required at the site following closure. Future use of the lagoons site is restricted by the presence of the GCL-based cap system. Any future operations planned for the site should not include excavation or other intrusive construction activities. The site gate will remain locked at all times. Norfolk and Western will install "No Trespassing" signs on the site perimeter fence.

Care and Maintenance of the Cap System

The site will be inspected on a regular basis by Norfolk and Western. These inspections will be performed monthly for the first year following closure and quarterly thereafter. The following activities will be performed as necessary:

- The grass will be mowed (minimum of twice per summer);
- Bare spots will be replanted with grass and fertilized (during the growing season);
- Any plant species with deep roots or any woody species will be immediately removed from the surface of the cap;
- Any depressions or areas of erosion will be repaired; and
- Gaps in the perimeter fence will be repaired.

An inspection form will be used to document observations and maintenance performed at the site.

Groundwater Monitoring

As specified in the approved closure plan, groundwater will be monitored at the site for a period of 10 years after closure. According to previous studies, the predominant groundwater flow direction is to the south. Three monitoring wells that have been approved for post-closure monitoring are located at or near the lagoons site. These wells are designated MW-1L, MW-5L and MW-6L and are shown on Figure 3. Two additional wells will be installed at the site to provide complete, downgradient perimeter monitoring of the site. These proposed wells are designated as MW-7L and MW-8L and are also shown on Figure 3.

MW-2L was abandoned prior to closure and MW-3L is considered too far from the site to provide pertinent groundwater data. In addition, MW-4L was accidentally destroyed during closure activities. Because MW-5L, is reasonably close to the former location of MW-4L it is proposed that MW-4L not be replaced. To help account for the loss of MW-4L, the formerly proposed location of MW-7L has been moved slightly to the east.

As specified in the closure plan, Norfolk and Western will collect samples from the monitoring wells and analyze for the following parameters and constituents:

- Totals metals by EPA Method 6010;
- Total volatile organic compounds (VOCs) by Method 8010;
- Total petroleum hydrocarbons (TPH) by EPA Method 8015;
- Specific conductance (field measurement); and
- pH (field measurement).

In addition to the analyses listed, each well will also be gauged for groundwater elevation during each sampling event.

CONCLUSIONS

Table 3 lists the quantities of wastes and other materials that were processed on this project.

TABLE 3   Summary of Project Quantities

Materials processed	Quantity processed
Water treated	1,186,000 gallons
Sludge processed	11,800 tons
Solidified sludge placed	22,570 cubic yards
Fly ash used	14,600 tons
Portlaud cement used	2,800 tons
GCL installed	105,000 square feet
Clean fill placed	5,500 cubic yards
Contaminated debris disposed	140 cubic yards
Non-contaminated debris disposed	80 cubic yards

Treatment and disposal of petroleum-based wastes has been an important issue at industrial facilities for many years. Use of surface impoundments (lined and unlined) for disposal of petroleum wastes was historically a common practice at industrial facilities, including facilities owned and operated by the railroad industry. As demonstrated by this project, it is possible to perform cost-effective closure of these sites while providing long-term protection of the environment. Because this project was completed without transporting large volumes of waste off-site, closure costs were reduced dramatically. Other on-site treatment methods were considered for this site, including biotreatment and low-temperature thermal desorption. When compared to in-situ solidification, these technologies proved to be more costly.

QUESTIONS AND ANSWERS

Q. You mentioned groundwater monitoring at the end of the study. I am curious as to whether or not there was any groundwater impacts and what drove the need for the liner if there weren't any groundwater impacts?

As I said in one of the early slides, there were low levels. A couple of the MCL's for metals and volatile organics were exceeded at the site. So there was limited groundwater impact prior to the project.

Q. Is that one of the main reasons for requiring the liner?

Yes

Q. Did you look at the option of remediation in-situ rather than digging it out, solidifying, and then placing it back in?

We did not look at that option.

CHAPTER 4

COST-MANAGED CLOSURE OF SPILL SITES ON RAILROAD MAINLINES

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INTRODUCTION

The release of diesel fuel from railroad locomotive derailments or grade-crossing accidents often results in soil impacts directly beneath mainline railroad tracks. A common approach to corrective actions at these sites has been excavation and subsequent disposal or treatment of the impacted soil. The cost of corrective actions involving excavation can be high, particularly if railroad tracks must be removed to excavate impacted soils from below or adjacent to the tracks. Additionally, track removal results in the loss of revenue associated with the disruption of the railroad's commercial traffic. The excavation of impacted soil from beneath the tracks may also be unnecessary from a risk-based viewpoint. Innovative corrective actions at railroad spill sites can minimize costs by using alternatives to track removal.

Corrective action case studies from spill sites are presented to provide economic comparisons of alternatives to track removal. Actual costs for completed innovative corrective actions are compared with estimated costs that would have been incurred if track were removed to excavate impacted soil. Those estimated costs include costs associated with lost revenue from disruption of commercial railroad traffic. The case studies that are presented have been closed or are in final closure phases by the state regulatory agencies.

CASE STUDIES

Case Study #1 - Bioventing System between Double Mainline

Spill Information and Site Conditions

Approximately 200 gallons of diesel fuel was released during a grade-crossing accident in rural west central Minnesota. Nearly all the fuel was released between double mainline railroad tracks making excavation of impacted soil impractical based on mainline track downtime. The remainder of the fuel was sprayed along the railroad right-of-way. Site geology consists of railroad track ballast overlying silty sand.

Initial response activities included recovering a small quantity of fuel using absorbent material and excavating impacted soil in the railroad right-of-way for thermal treatment.

Remediation Activities

To determine the presence or absence of fuel on the water table, a monitoring well was installed between the double mainline railroad tracks. The monitoring well was installed by positioning the drilling rig over one of the mainline tracks. The other mainline was kept open allowing freight trains to pass. Figure 1 shows the drilling rig positioned on top of the trackbed. Free-phase fuel was not observed on the water table. Subsurface soil, groundwater and biotreatability samples were collecting during monitoring well installation.

Analytical results indicated no groundwater impacts were present. Also, biotreatability results were favorable. Based on the favorable results, the monitoring well was converted to a bioventing well to treat impacted subsurface soils.

Conclusions

Soil cleanup goals were achieved after operating the bioventing system for one year. The site was subsequently closed by the state regulatory agency. Total cost for the project was approximately $90,000.
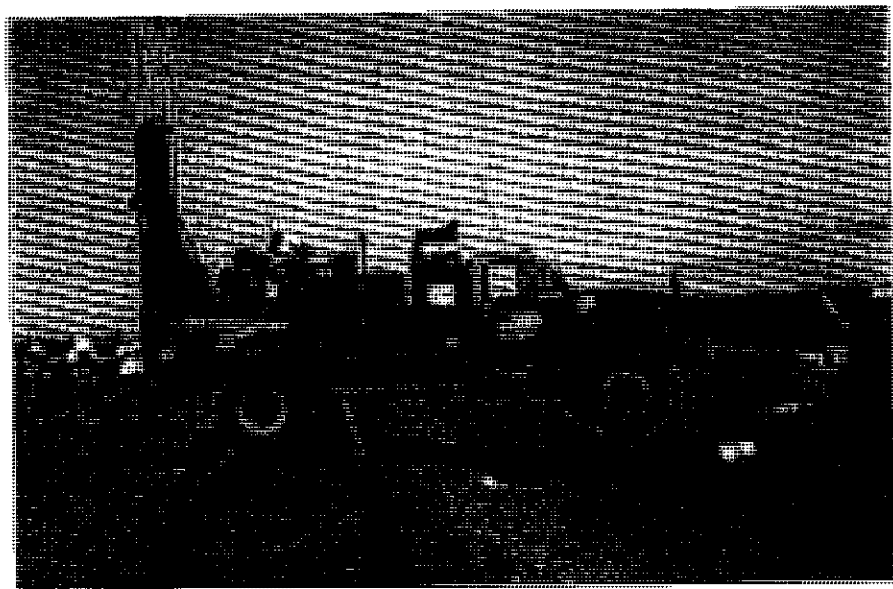
Figure 1   Drilling rig positioned on top of the track bed

Case Study #2 - Shallow Diesel Fuel Recovery Trench

Spill Information and Site Conditions

Approximately 1,200 gallons of diesel fuel was released through a broken site glass on a locomotive fuel tank in rural western Minnesota. Diesel fuel was subsequently observed seeping from the side of the railroad track bed into an adjacent drainage ditch. Geology below the trackbed consists of topsoil overlying silty clay, which was acting as an impermeable layer.

Initial response activities included removing ponded diesel fuel and water from the drainage ditch using pumps and placing absorbent material in the ditch to recover seeping diesel fuel.

Remediation Activities

Approximately 100 cubic yards of impacted soil present in the drainage ditch was excavated and thermally treated. At the spill location, a shallow trench approximately 15 feet wide and 2 feet deep was excavated to just below the clay surface. A slotted PVC pipe and riser were placed in the trench to intercept the seeping diesel fuel. Placement of the recovery pipe is shown on Figure 2. The trench was then backfilled with coarse gravel so that the spilled diesel fuel could easily enter the trench. Monthly site inspections were conducted to recover diesel fuel from the interceptor pipe and gravel backfill.

Conclusions

Site closure was gained after 15 inspections. Total costs associated with the initial response and remediation activities were approximately $90,000.
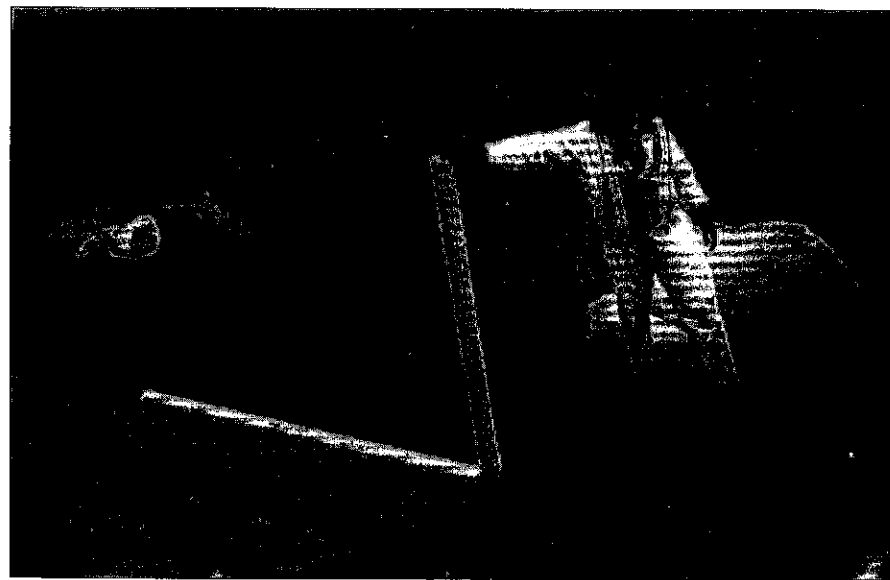
Figure 2   Placement of recovery pipe

Case Study #3 - Site Investigation between Triple Mainline

Spill Information and Site Conditions

Approximately 5,000 gallons of diesel fuel was released during a head-on collision of two freight rrains. The incident occurred on a triple mainline, commuter train corridor in a major U.S. city. Because of rhe busy rail corridor, shutdown of the track was impractical. A stormwater drainage ditch is located adjacent to the railroad tracks. Site geology consists of 3 to 4 feet of ballast overlying clay.

Initial response activities included constructing an over/under dam within the drainage ditch and excavating shallow recovery trenches on both sides of the tracks. However, very little of the spilled diesel fuel was recovered.

Remediation Activities

Due to the quantity of diesel fuel spilled and subsequent small amount initially recovered, a network of monitoring wells was installed using a conventional drilling rig on both sides of the tracks to locate the remaining fuel. A significant amounr of free phase diesel fuel was observed in two monitoring wells located adjacent to the drainage ditch. Emergency actions were taken to prevent the diesel fuel from seeping into the ditch. A 100-foot fuel interceptor/groundwater depression trench was installed between the monitoring wells and the ditch.

The trench was operated for approximately one year with mixed success. The state regulatory agency insisted on additional investigation to determine where the temainder of the spilled fuel was located. The only area of the site not yet investigated was beneath the triple mainline tracks. Interruption of the mainlines tracks was not feasible, therefore alternative investigation methods would have to be considered. Using a portable jack hammer, ten 3/4 -inch monitoring wells were installed between the rails of the mainline tracks. Diesel fuel was observed in one of the newly installed monitoring wells, and fuel recovery activities were initiated. However, it was apparent based on results of the site investigation conducted beneath the mainline tracks that nearly all of the fuel had adsorbed into the underlying clay soil.

Conclusions

Monitoring of selected wells continues at the site, however, closure is imminent. Total costs associated with the initial response and remediation activities were approximately $250,000.

Case Study #4 - On-Site Air Stripping System

Spill Information and Site Conditions

In February 1996, 27 railcars including pressurized tank cars of anhydrous ammonia and liquid propane derailed. Integrity of the derailed liquid propane tank cars was not compromised during the incident. However, one of the anhydrous ammonia tank cars was badly damaged. Nearly all of the anhydrous ammonia volatilized from the damaged tank car. Because of the sub-zero temperatures near the boiling point of anhydrous ammonia at the time of the incident, approximately 1,000 gallons of liquid ammonia spilled from the damaged railcars mixed with snow to form concentrated ammonium hydroxide. Fluctuating temperatures during the days following the incident caused increased snow melt and movement of the impacted water within the drainage ditch located adjacent to the railroad tracks.

Remediation Activities

Vacuum trucks were used to remove the concentrated ammonia/water mixture at several locations within the ditch. The recovered mixture was treated at a local publicly owned treatment works (POTW). Still, a large volume of impacted water remained in the ditch. Because the impacted water was contained in the ditch, in-situ treatment methods were considered. Air stripping was chosen as a cost-effective option for reducing the ammonia concentration of the impacted water in the ditch.

A manifold system consisting of one-inch diameter pipes with randomly drilled holes was constructed and placed into the ditch. The manifold system was initially connected to a high volume air compressor, but later replaced with a blower unit. The air stripping unit is shown in Figure 3. To augment the air stripping process, water was pumped from the downstream end of the ditch upstream and sprayed through high-pressure nozzles. Surface water samples were collected periodically for both field testing and laboratory analysis. Based on analytical results, ammonia concentration of the water in the ditch decreased two orders of magnitude from 14,000 to 450 mg/L in one month of operation.

Conclusions

Even though the air stripping unit was reducing the concentration of the impacted water, the state regulatory agency required the removal of approximately 100,000 gallons of water from the ditch. Analytical results indicated this removal action did not

Figure 3   Air stripping unit

Site remediation goals are frequently defined in terms of residual total petroleum hydrocarbon (TPH) levels in soil. Because of the recalcitrant nature of weathered petroleum wastes, these goals may not be attainable. The n-alkanes, which are easily degraded, are often absent or present at low concentrations. The remaining hydrocarbons ate more difficult to degrade. These include structurally complex alkanes such as pristane and phytane, 4- to 6-ring polynuclear aromatic hydrocarbons (PAHs), cycloalkanes, asphaltenes and polar compounds. It is widely accepted that biodegradation of these hydrocarbon classes is considerably slower than that for fresh crude oil.

Soil used in this investigation was obtained from a former oil refinery at Lovell, Wyoming that has been inactive since the late 1950s. The facility refined crude oil from the northern Wyoming basin, and also reprocessed used motor oil. A total of 52,000 cubic yards of petroleum contaminated soil was excavated from four waste lagoons in the fall of 1995 and stockpiled prior to on site bioremediatiou. Bioremediation at the former Lovell refiuery site has three objectives: (1) improvement of soil physical properties by addition of organic bulking agents; (2) breakdown of persistent soil clods containing high levels of petroleum contaminants; and (3) biodegradation of recalcitrant petroleum contaminants commensurate with remediation goals within a reasonable time frame.

A bench scale investigation was conducted prior to implementing full-scale bioremediatiou in order to optimize the process. The purpose of this chapter is to present the results of that investigation. The investigation had three objectives. First, organic and inorganic soil amendments were evaluated for their effectiveness in enhancing biodegradation by improving physical properties and nutrient availability. Second, the bioavailability of highly weathered petroleum contaminants was evaluated over a 110-day period using gas chromatography/mass spectrometry (GC/MS) analytical methods. The third objective was to evaluate the effectiveness of using hopanes as a conserved internal standard to monitor the biodegradation losses of n-alkanes, TPHs, PAHs and steranes. A supplemental investigation was also conducted by the National Environmental Technology Applications Center (NETAC) to determine the effectiveness of adding innovative products to accelerate hydrocarbon biodegradation.

EXPERIMENTAL PROCEDURES

Soil for this investigation was obtained from a 52,000 cubic yard stockpile of contaminated soil from an inactive refinery site in Lovell, Wyoming. Contaminated soil was excavated from four on-site waste lagoons in 1995. Soil for bench scale testing was obtained from two locations within the stockpile. Stockpiled soils have salt encrusted surfaces containing sodium and magnesium sulfates. Cation exchange capacity was determined using U.S. EPA Method SW-846-9081. Total Kjeldahl nitrogen (TKN) was analyzed using U.S. EPA Method 351. Available NO_3N was estimated using a calcium sulfate extraction. Available P was estimated using a Mehlich 2 extraction procedure. Sulfate was analyzed using U.S. EPA Method SW-846-9038. Heterotrophic microorganisms were determined 30 days after addition of bulking agents by most ptobable number (MPN) using the agar plate method. The carbon to nitrogen (C:N) ratio was calculated nsing an estimated 45 percent C content in 30,000 mg/kg TPHs and TKN. The C:N ratio was calculated without consideration of either native soil organic matter ot added bulking agents. Test soil was air dried and sieved through

6.25mm screen openings to remove debris. Sieved soil was thoroughly homogenized by coning and quartering, then placed in individual pans (30 cm by 23 cm by 10 cm) for bench scale testing. The soil or soil/bulking agent mixture was placed in pans to a depth of six to eight cm. Soil mixtures were monitored for 110 days.

Both organic and inorganic bulking agents were added to the test soil to improve aetation. Supplemental nutrients were not added to the test mixtures. One of the bulking agents, a composted wastewater sludge, contained approximately six percent N (C:N 8.3:1). Mixtures 5, 6 and 9 received this high N sludge compost. Mixtures 4, 7 and 8 received a second compost containing less than one percent N (C:N 42:1). Sawdust was used in all mixtures with the exception of Mixture 1, the control. Mixture 2 contained a mixture of soil and sawdust. Four of the eight mixtures contained sand in varyiug amounts. Table 1 shows the composition of the various soil mixtures.

Soil aeration was accomplished by thorough mixing once per week for two minutes using a steel trowel. Mixtures were watered twice weekly to maintain a soil water content between 20 and 25 percent (dry wt. basis). Cautiou was applied not to overwater the mixtures to prevent damaging soil structure. This was particularly difficult with Mixture 1 because of the absence of any bulking agent. The contaminated soil was also hydrophobic, requiriug several minutes to absorb added water. This is a typical characteristic of soil containing high levels of petroleum hydrocarbons, and probably results from oily coatiugs on normally hydrophilic soil particles.

Soil samples were collected for analysis at startup and biweekly thereafter for a 110 day period. However, sampling was discontinued after Day 70 for Mixtures 2, 4, 7 and 8. These mixtures exhibited very low levels of hydrocarbon biodegradation, probably due to N deficiency. On Days 84 and 96, duplicate samples were collected from Mixtures 5, 6 and 9 by repeating the process below to evaluate sampling and analytical precision. Soil sampling procedures were as follows. Soil in each tray was mixed for two minutes. Five subsamples were collected, one from the center and one near each corner of the tray. These subsamples were thoroughly mixed aud the composite sample placed in a glass jar for subsequeut analysis.

TABLE 1   Test Mixtures Used for Petroleum Biodegradation Study

Mixture 1	Conraminared Soil (CS)
Mixture 2	CS + Sawdust (SD),100% CS vol.[a]
Mixture 4	CS + Compost (10% CS wt.) + SD (150% CS vol.)
Mixture 5	CS + Sludge Compost (10% CS wt.) + SD (150% CS vol.)
Mixture 6	CS + Sand (33% CS wt.) + Sludge Compost (10% CS wt.) + SD (150% CS vol.)
Mixture 7	CS + Sand (33% CS wt.) + Compost (10% CS wt.) + SD (150% CS vol.)
Mixture 8	CS + Sand (100% CS wt.) + SD (200% CS vol.) + Compost (20% wt.)
Mixture 9	CS + Sand (33% CS wt.) + SD (200% CS vol.) + Sludge Compost (10% CS wt.)

[a] Additions of bulking agents were made based on either weight or volume of contaminated soil.

Additional soil samples were collected from the Lovell refinery site to determine whether normalizing field TPH data to hopanes would improve sampling precision. Twenty seven soil samples were collected to a depth of 50 cm using a power-driven sampler 7.6 cm in diameter fitted with an inner acrylic sleeve. The 2,300 cm³ sampler was driven into the soil by a front-end loader fitted with an adaptor bracket designed for the sampler. Samples were air dried, thoroughly homogenized, sieved and ground in a Dayton electric mill. The fraction finer than 1 mm was analyzed for TPH and hopanes. A previous investigation showed no statistically significant difference in TPH results between screened soil greater or less than 1mm. Data precision was evaluated by comparing differences in standard deviation between normalized and non-normalized data.

All soil samples were analyzed using either gas chromatography/mass spectrometry (GC/MS) in the selected ion monitoring (SIM) mode, or gas chromatography/flame ion detection (GC/FID). The GC/MS SIM method is a compilation of U.S. Environmental Protection Agency (U.S. EPA) Method 8015B, SW846, D3328, Marine Safety Laboratories Notice 5200.9, and several other methods used by the U.S. Coast Guard, Environment Canada, and other laboratories currently developing methods for SIM oil analysis and oil characterization techniques. These methods were developed to characterize oils based on standard oil fingerprinting techniques, PAH and PAH homologue patterns, saturated hydrocarbon patterns and distributions, and sterane and triterpane compounds. The GC/MS system was calibrated using five oil and five hopane/sterane standards at 1.0, 5.0, 10, 25 and 50 µg/ml. All samples were quantified using the average response factor obtained from the calibration range, or the response factors from the calibration check. The hopane compound had only a four-point calibration because the standard could not be prepared at a 50 µg/ml level due to volume restrictions. Before analysis each day, the system was tuned with 50 ng of Decaflurotriphenylphosphene (DFTPP). Samples were quantified for saturated hydrocarbons, PAHs and the PAH homologues, hopanes and steranes using the internal standard method. The TPH concentrations were quantified using the external standard method. The TPH concentration was calculated for each sample by manually integrating the area of the chromatogram produced by extracting Ion 85, and dividing by the average response factor from the calibration range. Ion 85 is a widely known representative ion of hydrocarbons not subject to phthalate or other interferences.

Where quantification of TPHs only was required, a GC/FID method was used. The advantage of this method is its speed relative to GC/MS methods. Use of this method requires a reference oil for calibration. A source oil was not available from the Lovell refinery site. Therefore, a reference oil was prepared by extracting pure product from the samples as a calibration standard. Thirty grams of soil was extracted with methylene chloride by shaking vigorously. Methylene chloride extract was evaporated and the weight of residual oil determined gravimetrically. The residual oil was redissolved in methylene chloride and passed through an alumina column to remove any polar compounds which may have contributed to the total weight. The extract was evaporated again, and the remaining oil weighed. The calibration range was prepared from the site oil and the response factors were determined by tabulating the peak heights or area sum of the entire oil fingerprint against the mass injected. The TPH calibration range was prepared from a standard of 38,000 mg/kg prepared from the site soil. Oil was also gravimetrically determined from samples which were Soxhlet extracted to check for anomalies. It was concluded that the same oil fingerprint was produced using either

method. A minimal amount of light end hydrocarbons was lost in the process, which should not affect the response factors generated from the prepared oil fingerprints. The GC/FID was calibrated using five standards at 440, 880, 2,200, 4,400 and 11,000 µg/ml. Samples were either quantitated using the average response factor for the calibration range on the day the instrument was calibrated, or the response factor from the daily calibration check of a 2,200 mg/mL standard. As outlined in U.S. EPA Method 8015B, calibration checks were also analyzed at the end of each batch.

The samples were extracted using the Soxhlet method outlined in U.S. EPA Method SW-846. Briefly, 30 grams of soil was spiked with 500 mL of 400 mg/mL surrogate solution which contains d_{10}-anthracene, 5-a-androstane and d_{62}-triacontane. The samples were extracted with 300 mL of methylene chloride using Soxhlet apparatus for 16 hours. The extracts were then concentrated to final 10 mL volume. Prior to instrument analysis, 20 mL of 500 mg/mL internal standard containing 1,4-d_4-dichlorobenzene, d_8-naphthalene, d_{10}-acenaphthene, d_{10}-phenanathrene, d_{12}-perylene was added to a one mL aliquot. Matrix spike and matrix spike duplicate (MS/MSD) samples were prepared in each batch, if provided, by spiking selected PAHs, baa-20-cholestane, and 17b(H),21b(H)-hopane (moretane). One blank was extracted along with each batch of samples.

Most of the data presented in this report were normalized to hopanes. Two compounds, C29 hopane (17a(H),21b(H)-30-norhopane) and C30 hopane (17a(H),21b(H)-hopane) were selected for this purpose because they were most abundant. Use of hopanes is widely recommended in the oil literature for normalizing biodegradation data (Peters and Moldowan 1993, and Bragg et al. 1994). To normalize the data, the target analyte for a given sampling time was divided by selected hopanes (Federal Register, September 15, 1994).

The following procedures were followed by NETAC in a supplemental study designed to test the effectiveness of four bioremediation products. The products included Inipol EAP-22, a liquid oleophilic fertilizer, Vita-Bugg, an ammonium phosphate oleophilic fertilizer, System ET-20, a proprietary microbial inoculum and oleophilic fertilizer, and B&S Industrial, a proprietary microbial inoculum and fertilizer. The product's manufacturers and/or distributors supplied the products and recommendations for application rates for this study. The products were evaluated using a flask test with contaminated soil from the Lovell site. The study was conducted for 60 days. Controls included a background sample containing petroleum-contaminated soil with no treatment additions, and a nutrient supplemented sample with a designated nutrient additive. Sample analyses included microbiological and chemical analysis, and continual respirometric measurements. Sample analyses were performed on Day 0, 30 and 60. For each time point, microbiological analysis, sample extraction, GC/MS analysis and/or TPH by GC/FID analysis was completed. Soil was air dried to a low moisture content, and mixed in a V-mixer for two hours to uniformly distribute petroleum contaminants. A conserved internal marker was added and mixed into the soil matrix to determine extraction efficiencies and facilitate quantifying the level of biodegradation. After mixing, the soil was divided into separate aliquots of one to two kg for each of the control, nutrient and treatment additions. The study consisted of four biological additive treatments and two controls run in triplicate. Soil samples were placed in 250 Erlenmeyer flasks and a sufficient amount of tap water added to provide a minimum moisture content of 20 to 25 percent of dry weight during the course of the study. After

addition of the appropriate treatment according to vendor specifications, each flask was stoppered with a plug and tube permitting airflow via a respirometer as a measure of microbial activity. The soil was agitated weekly to simulate tilling. The study was performed at ambient room temperatures (22 °C). Respirometric measurements were made continuously to qualitatively measure microbial activity. One set of flasks was attached to a Columbus Instrument *Micro-Oxymax* model respirometer. The instrument monitors O_2 uptake and CO_2 production. The instrument refreshes the atmosphere of the flask when either the initial O_2 concentration level declines by 0.5%, or the initial CO_2 level increases by 0.5% over the initial values.

RESULTS

Soil characteristics are listed in Table 2. Soil from the Lovell site is a very uniform silty clay that becomes massive when wet and readily forms dense clods. The bioavailability of petroleum contaminants is restricted due to limited flux of moisture, oxygen and nutrients, and the affinity of clay colloids for structurally complex hydrocarbons. Improvement of soil physical properties is a prerequisite for optimizing the bioremediation process. Exchangeable sodium was low enough to prevent dispersion of clays and loss of aggregate stability. The high population of heterotrophic microorganisms shows that inhibitory or toxic effects were absent. Total Kjeldahl N is 560 mg/kg, with a C: N ratio based on 30,000 mg/kg TPH of 24:1. Relative levels of available phosphorus (P) and potassium (K) ranged from medium to very high. Several organic and inorganic bulking agents were added to improve soil aeration. The mixtures are presented in Table 2. Mixture 1, which did not receive bulking agents, remained cloddy throughout the 110-day test period. The remaining mixtures were loose and friable. All mixtures were moderately hydrophobic, probably due to petroleum coatings on soil surfaces. The sampling and analytical precision for three soil mixtures in which duplicate samples were collected is presented in Table 3.

The chromatograms in Figure 1 provide a comparison of petroleum hydrocarbon biodegradation between unamended soil (Mixture 1) and soil that received sand, sawdust and high N sludge compost as bulking agents (Mixture 6). Figures 2a and 2b show the loss of n-alkanes in Mixtures 1, 5, 6 and 9 and 2, 4, 7 and 8, respectively. The data in these figures were normalized to hopanes as a stable internal standard. The stability of hopanes makes them particularly useful as biomarkers in bioremediation studies (Peters and Moldowan 1993). Figures 3a and 3b show a comparison between non-normalized and normalized TPH data, respectively. Twenty-seven soil samples were also collected from the former Lovell Refinery Site to evaluate the effect of normalization on data quality. The standard deviations in TPH for normalized and non-normalized data represented 6.5 and 14.5 percent of the mean values, respectively.

Figures 4a and 4b compare the biodegradation losses of pristane and phytane, respectively, in amended and unamended soil mixtures. Both compounds have been used as biomarkers, at least in early stages of bioremediation (Butler et al. 1991). Figures 5 and 6 show the loss of TPHs and PAHs, respectively, in amended and unamended soil mixtures. Most petroleum hydrocarbons were contained within the unresolved complex mixture. The PAHs in contaminated soil were predominantly 3- and 4-ring compounds. Sterane concentrations were very stable in both amended and unamended soil mixtures over the 110-day test period.

TABLE 2   Soil Characteristics and Bench Scale Test Conditions for Petroleum Biodegradation Study

Soil pH	7.0 - .7.6
Soil Texture	Silty Clay
Cation Exchange Capacity (meq/100 g) [a]	58
Exchangeable Sodium (meq/100 g) [a]	4
Total Kjeldahl Nitrogen (mg/kg) [b]	560
Nitrate Nitrogen (relative level) [c]	Very Low
Avail. Phosphorus (relative level) [d]	Medium to Very High
Avail. Potassium (relative level) [d]	High to Very High
Sulfate (mg/kg) [e]	2,100
Soil Structure	Massive (wet); Friable, Subangular Blocky (moist)
Soil Temperature	17 - 20°C
Soil Moisture (% dry wt.)	20 - 25
Heterotrophic Microorganisms (cfu/g) [f]	$3.8 \times 10^6 - 1.5 \times 10^9$
Total Petroleum Hydrocarbons (mg/kg) [g]	30,000
Carbon: Nitrogen [h]	24:1

[a] Cation exchange capacity and exchangeable sodium analyzed using USEPA Method SW-846-9081.
[b] Total Kjeldahl N analyzed using USEPA Method 351.
[c] Nitrate N extractable in calcium sulfate.
[d] Available P extractable in a Mehlich 2 solution.
[e] Sulfate analyzed using USEPA Method SW-846-9038.
[f] Heterotrophic microorganisms determined by most probable number (MPN) using the agar plate method.
[g] Analyzed for total petroleum hydrocarbons using USEPA Method 8015B by GC/FID.
[h] Based on 45 percent estimated carbon in petroleum hydrocarbons.

DISCUSSION

GC/MS chromatograms shown in Figure 1 represent data from two contaminated soil mixtures sampled at Days 0, 29, 70 and 110. Mixture 1, the control, contained petroleum contaminated soil with no added bulking agent. The rapid loss of n-alkanes in Mixture 6 was similar to that for Mixtures 5 and 9, which also received high N sludge compost as one of the bulking agents. Enhanced biodegradation in these mixtures compared to the control was probably due to high N availability in mixtures amended with sludge compost. This is consistent with results reported by Atlas (1995), who studied oil biodegradation on marine shorelines. He found the most important parameter affecting the rate and extent of oil degradation was the ratio of nitrogenous nutrients to oil load in the interstitial water. Atlas (1995) noted that addition of nutrients typically increases the rate of oil biodegradation by about three to five times that

TABLE 3   Sampling and Analytical Precision Duplicate Samples from Soil Mixtures 5, 6 and 9

| Soil Mixture	Hydrocarbon Class	Precision (relative percent difference)	
		Day 84	Day 96
5	n-alkanes	6%	2%
5	PAHs[a]	1%	35%
5	Steranes	21%	16%
5	TPH[b]	10%	15%
6	n-alkanes	26%	18%
6	PAHs	38%	26%
6	Steranes	23%	2%
6	TPH	18%	9%
9	n-alkanes	57%	23%
9	PAHs	10%	31%
9	Steranes	3%	11%
9	TPHs	6%	2%

[a] PAHs - Polycyclic aromatic hydrocarbons
[b] TPH - Total petroleum hydrocarbons

of an untreated control. It is generally accepted that availability of nutrients, particularly N, limits the biodegradation of petroleum hydrocarbons in both soil and marine environments (Bragg et al 1994).

The paired chromatograms in Figure 1 provide considerable evidence for the weathered nature of oily wastes. At Day 0, chromatograms for Mixtures 1 and 6 were nearly identical. The oil fingerprints show a characteristic Gaussian distribution of the n-alkanes from about C8 through C36. These peaks are easily identified due to their characteristic even spacing. Intermixed with n-alkanes are an abundance of branched alkanes, including the isoprenoids pristane and phytane. The phytane peak is dominant in the chromatograms, which indicates this oil has lost possibly 75 to 90 percent of its n-alkane concentrations. Ratios of C_{17}/pristane and C_{18}/phytane are typically greater than 2.0 for fresh crude oils. Oil from the Lovell site has C_{17}/pristane and C_{18}/phytane ratios of approximately 1.0 and 0.5, respectively. Because the distribution of n-alkanes has remained gaussian, this weathering process is directly attributable to biodegradation, not evaporation. Further indication of biological weathering is the pronounced unresolved complex mixture (UCM), which contains cyclic and structurally complex alkanes. In fresh crude oils and refined products, the UCM is also present, but is usually suppressed by a higher proportion of resolved to unresolved peaks.

The paired chromatograms also show a progressive loss of n-alkanes over the 110-day period for both mixtures, but at very different rates. Mixture 6 illustrates enhanced biodegradation in soil amended with a high N bulking agent. Chromatograms for both
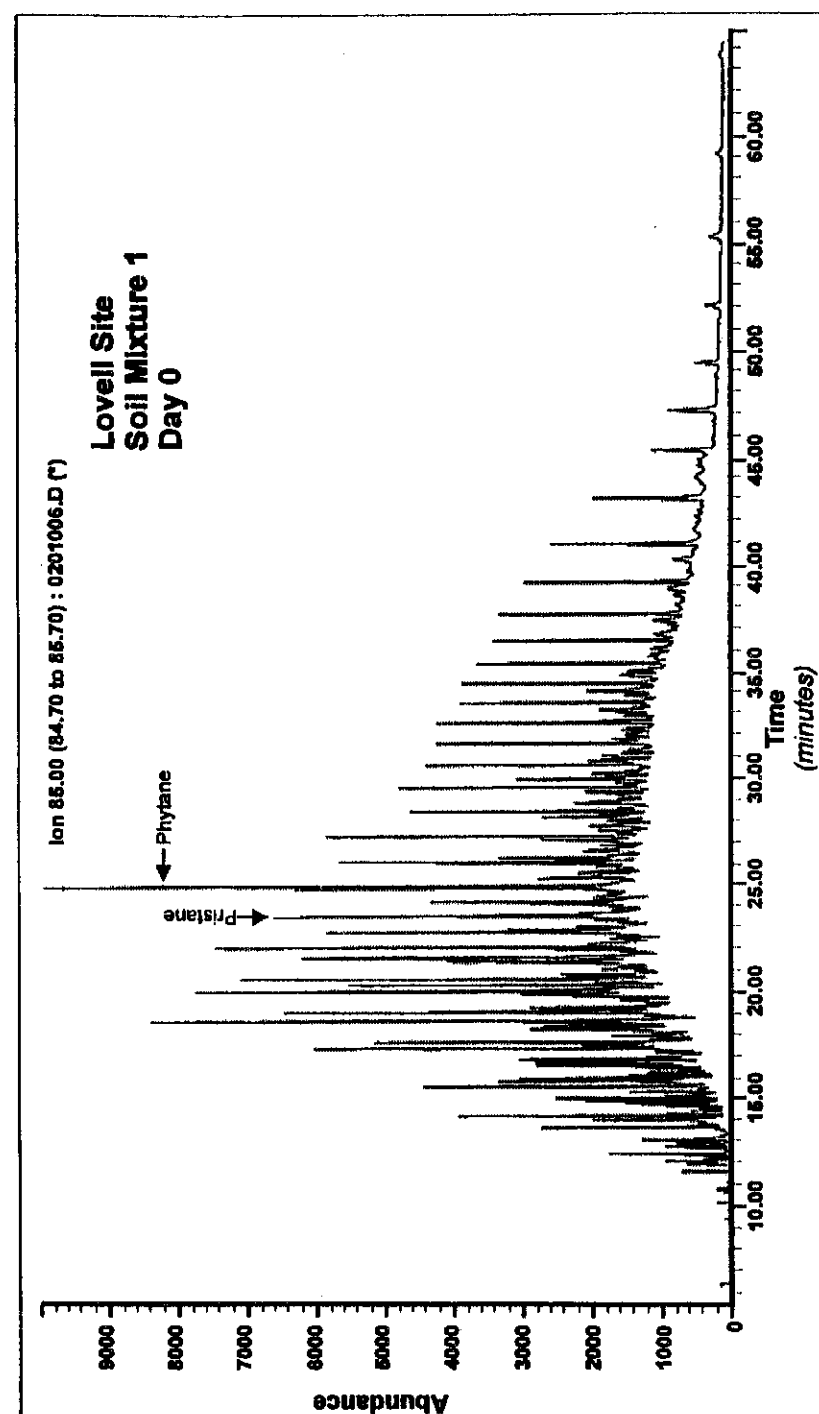
Figure 1   Chromatograms for Soil Mixtures 1 and 6 that show the relative difference in petroleum hydrocarbon biodegradation

Figure 1   continued
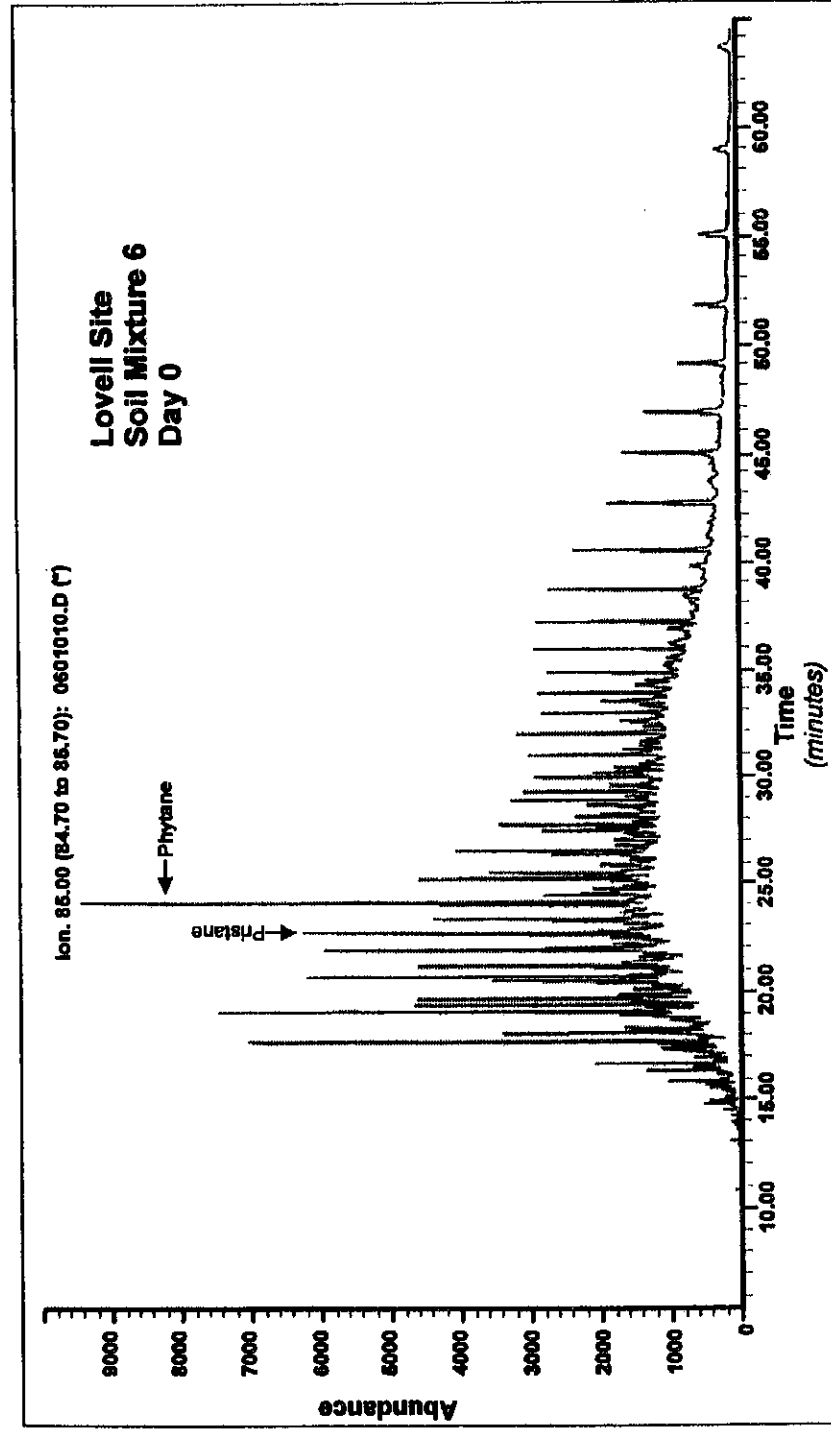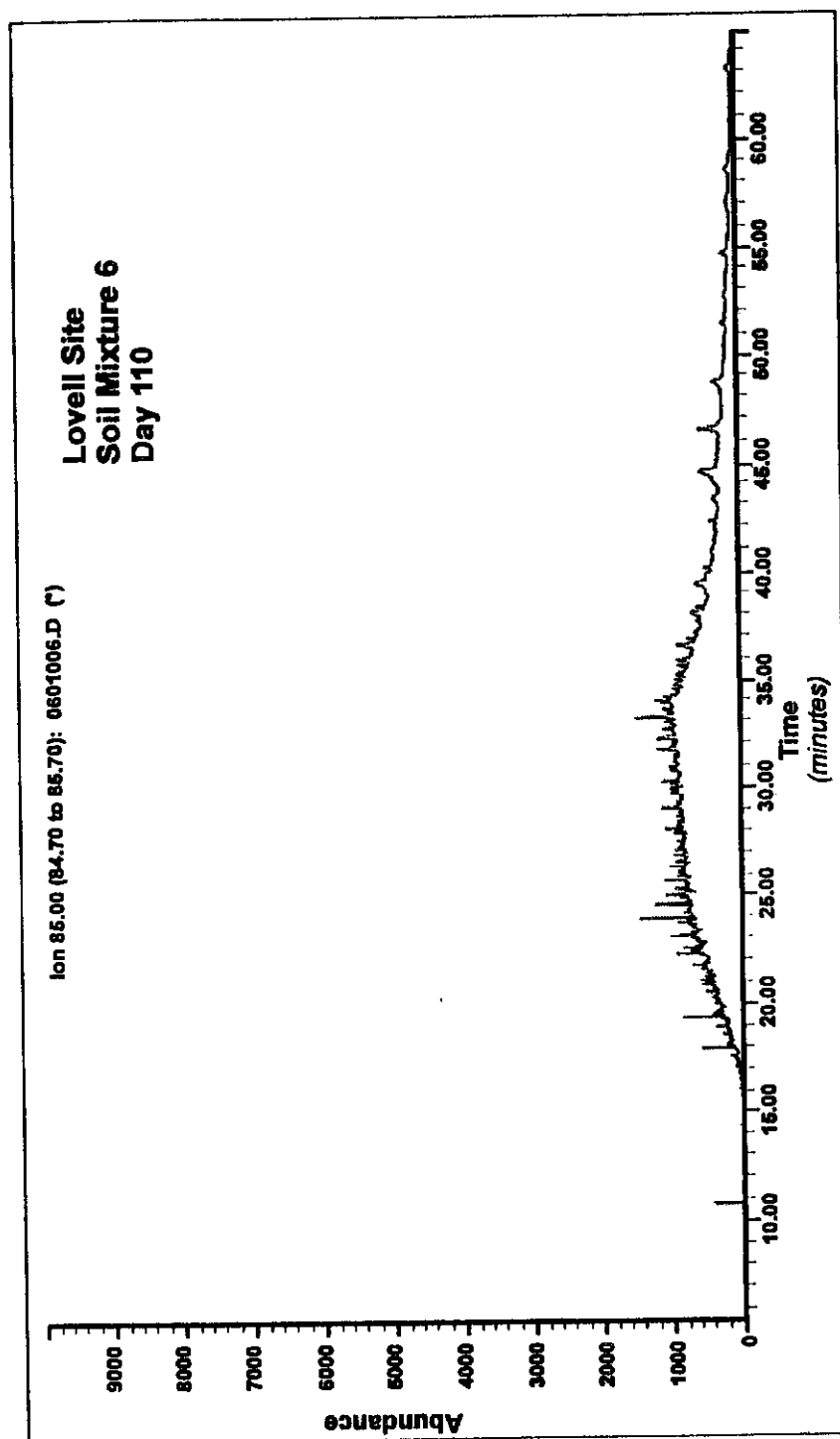
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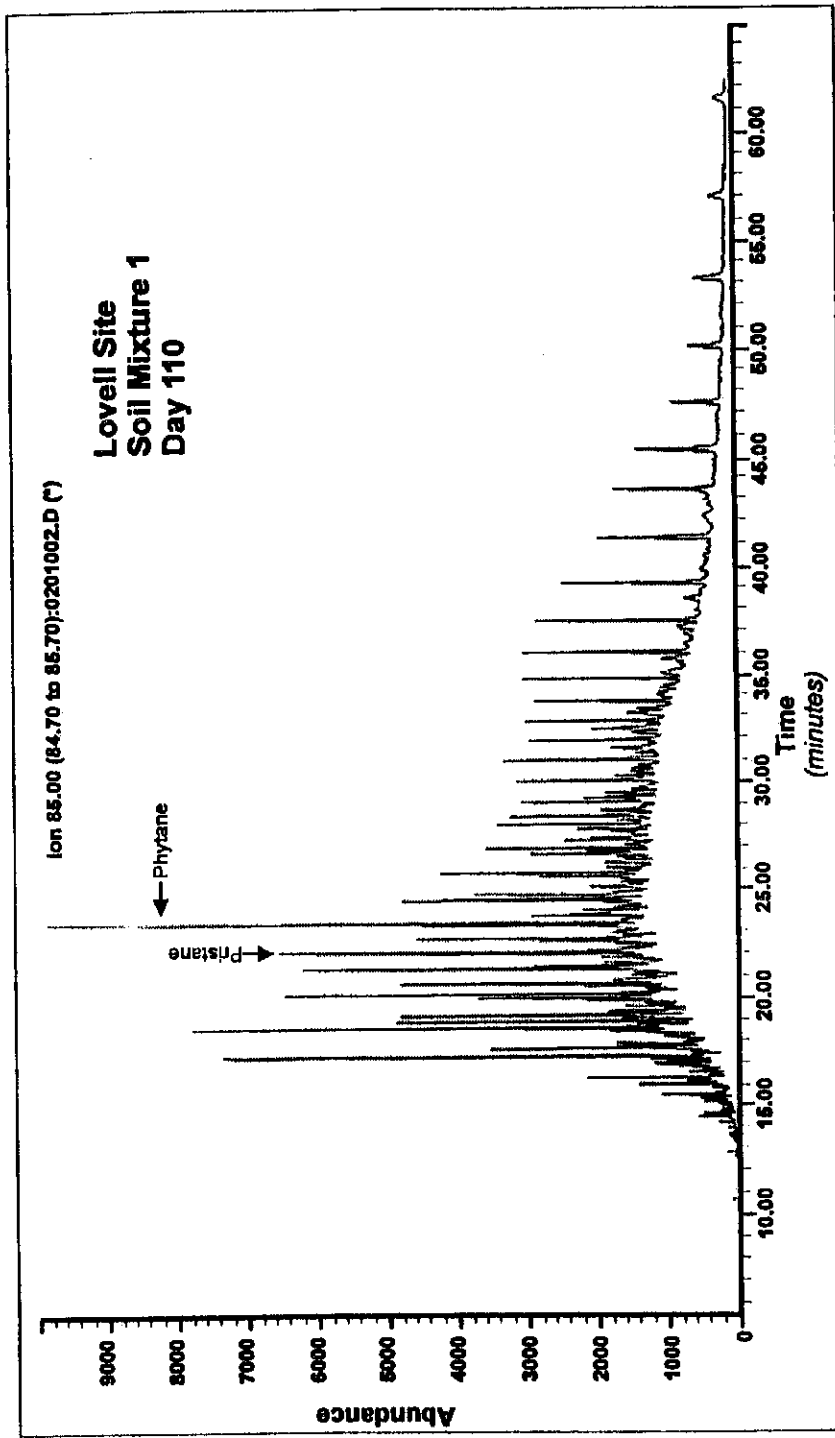
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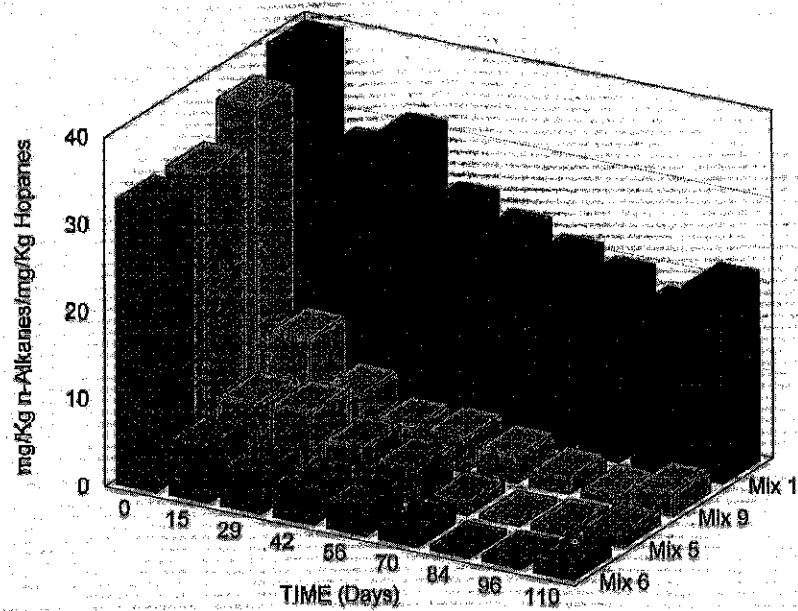
Figure 2a   **Loss of saturated hydrocarbons from petroleum contaminated soil mixtures containing a high-nitrogen analysis sludge compost bulking agent compared to an unamended contaminated soil**
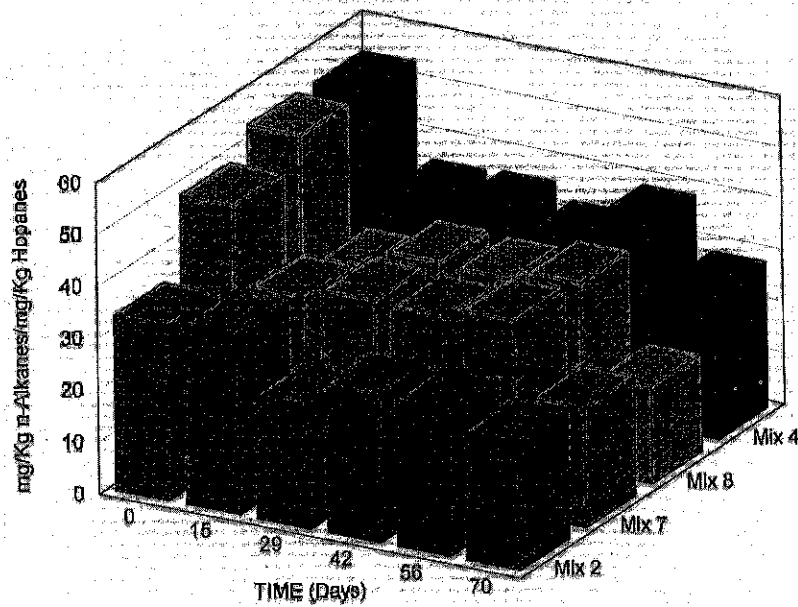
Figure 2b   **Loss of saturated hydrocarbons from petroleum contaminated soil mixtures containing bulking agents with low or moderate nitrogen levels**

Total Hydrocarbons (Non-Normalized) —●— Total Hydrocarbons (Normalized)
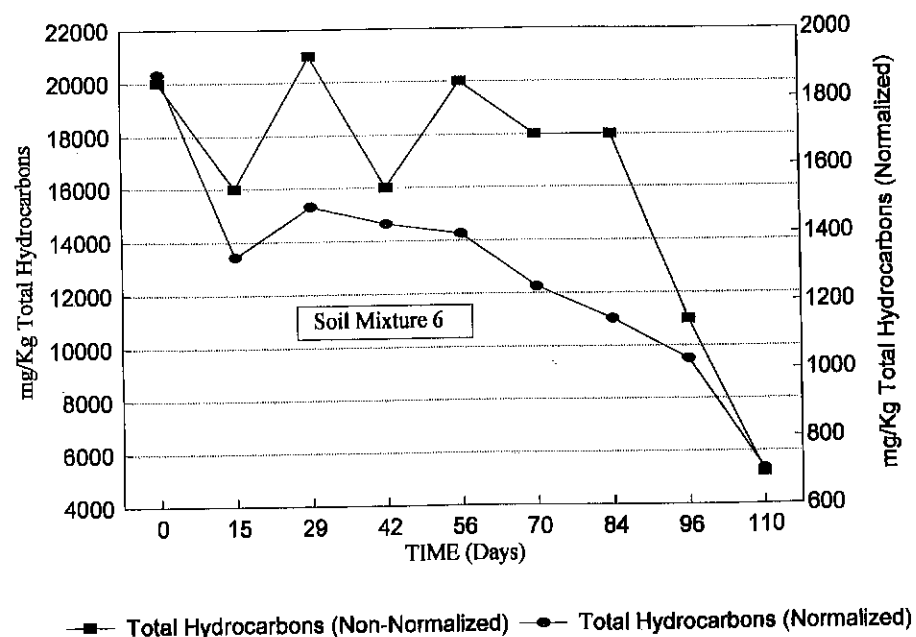
Figure 3   Biodegradation of total hydrocarbons vs. time using both normalized and non-normalized data

Figure 4b   Loss of phytane from petroleum contaminated soil mixtures

Figure 4a   Loss of pristane from petroleum contaminated soil mixtures
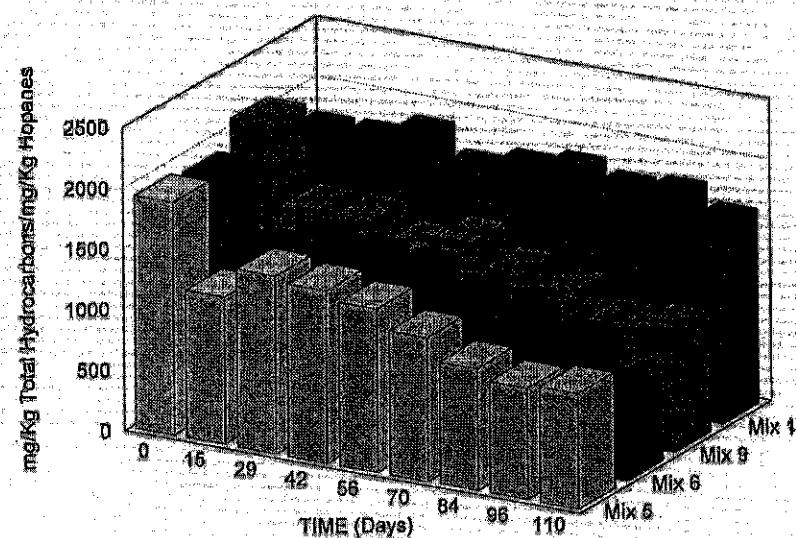
Figure 5   Loss of total hydrocarbons from petroleum contaminated soil mixtures containing a high nitrogen analysis sludge compost bulking agent compared to an unamended contaminated soil

Figure 6   Loss of PAHs from petroleum contaminated soil mixtures

mixtures over the first 70 days also show the loss of low boiling point normal and branched alkanes, probably by evaporation due to intensive mixing. During this period, the lower end of the chromatographic envelope became trunca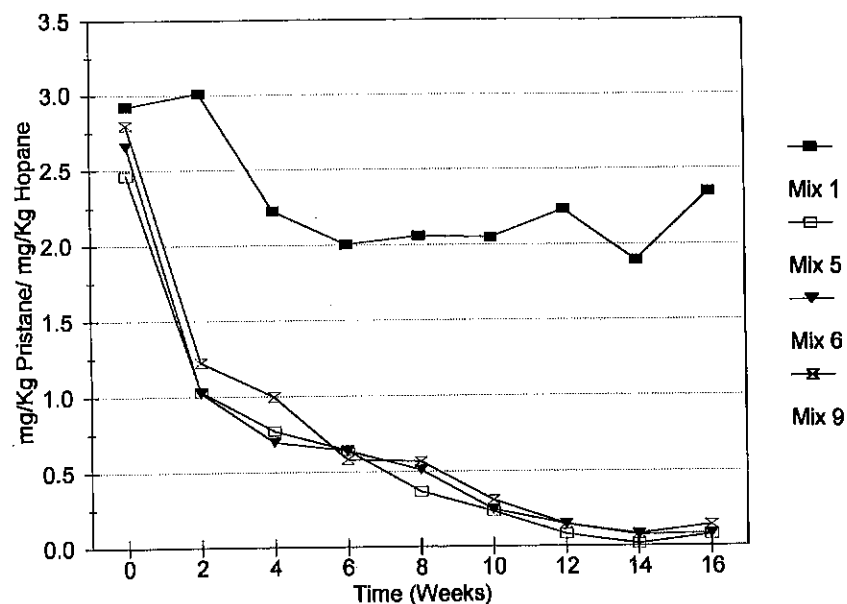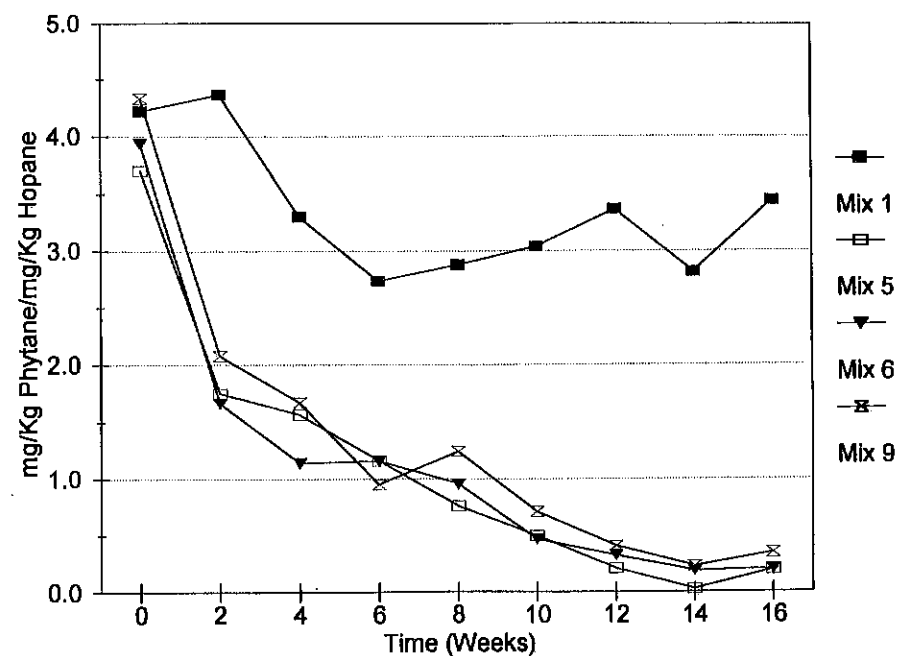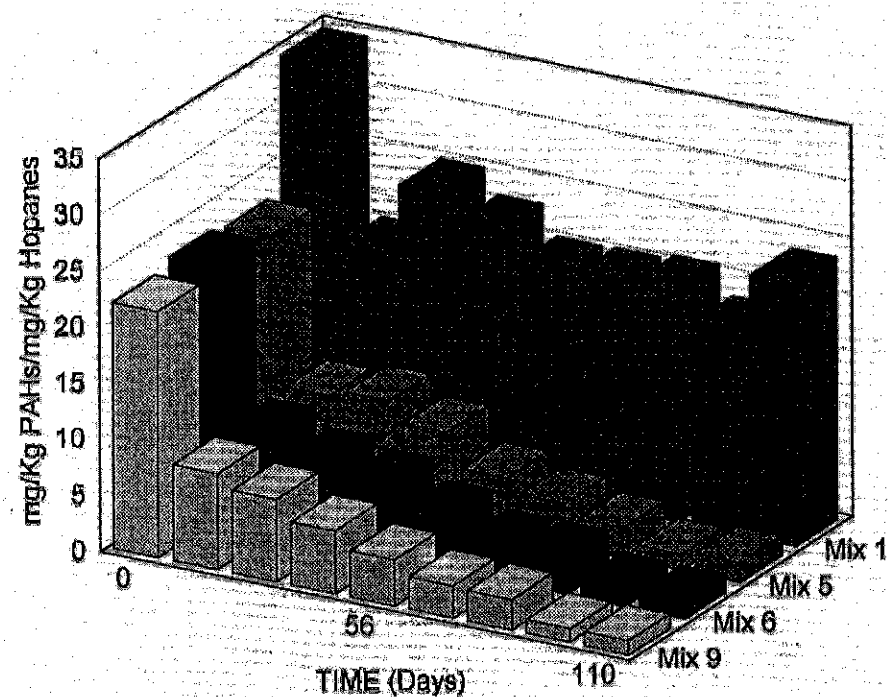ted and receded toward higher carbon (C) numbers. Evaporative losses deplete all hydrocarbons of the same volatility regardless of structural complexity. Microbial degradation, on the other hand, attacks compounds over a much wider molecular weight range than either evaporation or dissolution. According to Bartha and Atlas (1977), n-alkanes between C_{10} and C_{25} are the most readily utilized by microorganisms. Evidence for biodegradation is apparent from the decrease in n-alkanes relative to adjacent, structurally complex compounds of similar boiling point and solubility. This process is evident in chromatograms from both mixtures, but was much more rapid in Mixture 6. The initial ratios of C_{17}/pristane and C_{18}/phytane were nearly identical in both mixtures at Day 0. At Day 110 these ratios were distinctly different. In Mixture 1, the final C17/pristane and C18/phytane ratios were approximately 0.6 and 0.3 respectively. In Mixture 6, after only 29 days these ratios had declined to approximately 0.2 and less than 0.1, respectively. By Day 110, all C17 and C18 were absent, and the isoprenoid biomarkers pristane and phytane had nearly disappeared. Wang and Fingas (1995) noted the inadequacy of, pristane and phytane as biomarkers when conditions favor an advanced stage of biodegradation, but also noted they may be useful early indicators of biodegradation.

In Mixture 1, the relative size of the UCM remained nearly constant throughout the full treatment period, indicating no biodegradation of complex branched or cyclic alkanes. In Mixture 6, however, these compounds began to rapidly disappear after Day 70. By Day 110, the UCM was reduced to approximately one half that present at Day 70. The last chromatogram for Mixture 6 is typical of an advanced stage of weathering, in which normal and isoprenoid alkanes have virtually disappeared, and only complex branched and cyclic hydrocarbons remain. Because crude oils are never fully degraded, they always leave some complex, black tarry residue containing a high proportion of asphaltic compounds. According to Atlas (1995) the toxicity of this tarry residue is very low, which is fortunate because asphaltic compounds are very stable.

Normal alkanes are the most readily degradable petroleum hydrocarbons. Figures 2a and 2b show a comparison of n-alkane losses between soil mixtures containing bulking agents with low to moderate N contents and mixtures containing high N analysis sludge compost. Figure 2a shows a dramatic difference in loss of n-alkanes between the unamended soil (Mixture 1) and amended soil (Mixtures 5, 6 and 9). The rapid biodegradation of n-alkanes in these mixtures is probably due to sufficiency of N rather than improved soil physical properties. Evidence for this can be seen by comparing results from Mixtures 2 and 5, which both contained sawdust as the primary bulking agent. Addition of sawdust reduced soil bulk density and improved aeration in both mixtures. Mixture 5 also contained high N analysis compost, while Mixture 2 did not. In both mixtures, n-alkanes were nearly identical at Day 0. In Mixture 2, there was no evidence of biodegradation during the first 15 days. By contrast, in Mixture 5, the ratio of n-alkanes to hopanes had declined from approximately 33 at Day 0 to 7 at Day 15. When Mixture 2 was discontinued at Day 70, the ratio of n-alkanes to hopanes was 20, while the ratio in Mixture 5 had declined to 2. There were no discernible physical differences between these mixtures. Both appeared to be loose, friable and well aerated when moist. Lack of biodegradation in Mixture 2 during the first 15 days was probably not due to a microbial induction effect, because all other mixtures including the control exhibited losses of n-alkanes during the same period. A similar comparison was made between Mixtures 7 and 9. Both contained contaminated soil, sand, sawdust and compost, but Mixture 9 contained high N analysis compost. In Mixture 7, the ratio of n-alkanes to hopanes declined from 48 to 30 between Days 0 and 15, with little change thereafter. Mixtures 4 and 8 exhibited the same degradation pattern as Mixture 7. All three mixtures contained the lower N analysis compost. The ratio of n-alkanes to hopanes in Mixture 9 declined from 37 to 15 between Days 0 and 15; by Day 110 n-alkanes were almost completely absent.

The rapid loss of n-alkanes from Mixtures 5, 6 and 9 is evidence of enhanced biodegradation. The markedly slower degradation of n-alkanes in Mixtures 2, 4, 7 and 8 after 15 days suggests biodegradation was limited by nutrient availability. Although soil physical conditions were improved by addition of bulking agents in all these mixtures, the rate of biodegradation was not. With a very high C:N ratio, sawdust may have induced an N deficiency and limited biodegradation of n-alkanes. Evidence for either a sufficiency or deficiency of N is only indirect, however, because available forms of N were not measured prior to or during the biodegradation process. Such measurements can be misleading because soil microorganisms frequently utilize available N as rapidly as it is mineralized from organic N. Use of total N provides a better estimate of N availability in an active bioremediation system, provided soil conditions are optimal for

mineralization of organic N. Availability of phosphorus (P) is seldom cited in the literature as limiting petroleum biodegradation in either the soil or marine environment. Phosphorus-limited biodegradation in the present study was unlikely because the relative level of available P in soil extracts ranged from medium to high (Table 1).

Hopanes have been used successfully as an internal reference to quantify the biodegradation of crude oil components in oiled beach sediments (Butler et al, 1991). For a given stage of hydrocarbon biodegradation, the ratio of total hydrocarbons to hopanes remains constant and only declines when biodegradable hydrocarbons are lost from the system. The C_{29} and C_{30} hopanes are considered the best biomarkers because they are the most degradation-resistant and usually the most abundant in the C_{29} to C_{35} range (Wang and Fingas, 1995). Oily wastes in beach environments and soils vary widely in both depth and lateral extent. Use of normalized biodegradation data eliminates much of this spatial variability. Bragg et al (1994) reported standard errors for non-normalized data from oiled beach sediments ranged from 19 to 46 percent of mean values, while normalized data had standard errors of only 2 to 8 percent. Because oil distribution was heterogeneous, they emphasized oil concentration data alone was insufficient to demonstrate bioremediation was effective. Use of hopane-normalized data provided the key to determining a statistically significant effect of fertilizer addition versus an untreated control.

The distribution of oily wastes in soil is also highly variable, and use of hopanes to monitor petroleum biodegradation should be equally valuable. Figure 3 presents both non-normalized and normalized data for TPH biodegradation. The non-normalized data were highly variable due to uneven contaminant distribution. Normalizing these data eliminated most of the variability caused by uneven spatial distribution of hydrocarbons. The effect of normalizing soil data from our bench scale study was somewhat surprising, because all soil was thoroughly mixed prior to sample collection. The greatest benefit of normalization is expected to be from field soil data. We collected 27 soil samples from the former Lovell Refinery Site prior to treatment, and analyzed them for TPHs. Non-normalized data from all samples had a standard deviation of 14.5 percent of the mean. Normalized TPH data from the same sample set had a standard deviation of only 6.5 percent of the mean. These samples were relatively large (2,300 cm³), and entire samples were air dried and thoroughly homogenized prior to selecting an aliquot for analysis. When smaller volumes of soil are sampled in the field and not thoroughly mixed, standard deviations can be much higher.

The precision of field soil data usually ranges from 40 to greater than 100 percent, and 40 percent is considered ideal (Mason 1983). Duplicate soil samples were collected from three soil test mixtures in the bench scale study to measure sampling and analytical precision. Soil samples were collected from Mixtures 5, 6 and 9 on two sampling events, Day 84 and Day 96. Table 3 shows the total precision associated with these samples. The average relative percent difference (RPD) between duplicate samples was 17 percent, with a range from 1 to 57 percent. The effect of normalization on data precision was not evaluated because hopanes were not analyzed on duplicate samples. Based on the data cited above, it seems reasonable to expect that normalizing these data would have substantially increased data precision. These results represent ideal conditions where a small soil volume (3 to 4 liters) was thoroughly mixed prior to sample collection. Much lower precision (higher RPD) occurs when smaller samples are collected without mixing. Barth et al. (1989) examined the components of variance for

soil data from an NPL site sampled for PCBs. They found 92 percent of the total variation came from the sample location, while only 8 percent was introduced after the sample was taken. Less than one percent of the total variation was attributable to the analytical process, yet that is where the majority of quality assurance (QA) resources are usually focused. Use of normalized soil data can substantially increase field data precision. The improvement in data quality has several important benefits: it provides better documentation of bioremediation in the field; it facilitates measuring compliance with a cleanup standard; it permits more accurate evaluation of products designed to enhance hydrocarbon biodegradation; and it reduces the cost of monitoring by permitting collection of fewer soil samples.

Previous estimates of biodegradation have often relied on the ratios of biodegradable components such as n-alkanes to less biodegradable components such as isoprenoids. Both pristane and phytane, highly branched isoprenoids, have been used for this purpose. Changes in these ratios may provide an early indication of biodegradation, but isoprenoids are in fact biodegradable under optimal environmental conditions (Tabak et al. 1991). Because of this, their use as an internal standard underestimates the extent of biodegradation. Figures 4a and 4b compare the biodegradation losses of pristane and phytane, respectively, in both amended and unamended soil mixtures using normalized data. In Mixture 1, the unamended control, biodegradation of pristane and phytane occurred only during the first four to six weeks, with little or no change thereafter. Although data for Mixtures 2, 7 and 8 are not presented, losses of pristane and phytane were similar to the control. By contrast, loss of pristane and phytane was both rapid and uniform in Mixtures 5, 6 and 9. The initial decline of pristane and phytane in the unamended soil followed by lack of degradation is indicative of a nutrient-limited system. Use of either pristane or phytane, as biomarkers in our study would definitely have underestimated the extent of biodegradation.

Figure 5 shows the biodegradation of TPH as determined by GC/FID analysis. Most of the hydrocarbon compounds contained in these soil samples are part of the UCM, comprised of structurally complex alkanes and cycloalkanes. The relative proportion of these compounds in weathered oils is high, and they are generally resistant to biodegradation, even under optimum environmental conditions. The slow decline of structurally complex hydrocarbons is in marked contrast to the rapid decline of n-alkanes in the same mixtures (Figure 2a). In Mixture 1, the unamended control, loss of TPH over the 110-day test period was only 7 percent. In Mixtures 5, 6 and 9, which contained high N analysis sludge compost, TPH losses were 50, 62 and 52 percent, respectively. The relatively slow decline of TPH in these mixtures indicates that structural complexity rather than nutrient availability may have limited hydrocarbon biodegradation. The slowing tendency of utilization is caused not only by substrate depletion, but also because remaining hydrocarbons are structurally less degradable than the ones that have already disappeared (Wang and Bartha, 1990). For this reason, kinetic data generated during early stages of bioremediation should not be used to predict hydrocarbon losses during later stages. Use of kinetic data is also complicated in the case of crude oils and hydrocarbon fuels because they contain numerous individual hydrocarbons, each of which is utilized at a different rate.

Microorganisms may have the metabolic capability to mineralize PAHs and yet fail to do so because the compounds are insoluble, sorbed or otherwise unavailable to the cell. The bioavailability of PAHs is often limited because of low solubility and

sorption onto soil colloids (Loehr and Webster 1996). Soils from the Lovell Site have uniform silty clay textures with a high potential for PAH sorption. In spite of this, PAH bioavailability does not seem to have been reduced. The biodegradation of PAHs in amended and unamended soil mixtures is presented in Figure 6. In the control mixture, 41 percent of PAHs were lost over the 110-day test period. Losses of PAHs in Mixtures 2, 4, 7 and 8, which are not shown in Figure 6, ranged from 30 to 48 percent after 70 days. The moderate loss of PAHs in these mixtures was similar to that of the control, and was expected because of limited N availability. In the three mixtures containing higher N levels, PAH losses were rapid, from 90 to 93 percent over 110 days. In this study, the predominant PAHs were degraded more completely than TPH. This is in agreement with results reported by Bossert et al (1984). They simulated landfarm conditions over a 1,280-day period by periodic additions of oily sludge to test soil. They found 85 percent of predominant PAHs were degraded compared to 47 percent of TPHs. In their study, 3- and 4-ring PAHs comprised 96 percent of the total. When viewed as a class, PAHs in our study were eliminated more rapidly than TPHs. It should be noted, however, that PAHs in oily waste from the Lovell Site comprise only 1.3 percent of total hydrocarbons.

At the start of this bench scale study, naphthalenes, fluorenes, dibenzothiophenes and phenanthrenes comprised approximately 95 percent of total PAHs. The most prevalent of these were the structurally complex, highly methylated homologues, which are more resistant to biodegradation than their parent compounds (Dragun 1988). At the end of the 110-day test period, the relative proportion of PAHs within each group of compounds had changed. The distribution of dibenzothiophenes was typical. At Day 0, the parent compound in Mixtures 5, 6 and 9 represented 5 percent of all dibenzothiophenes. The methyl-, dimethyl- and trimethyldibenzothiophenes represented 19, 36 and 38 percent of the total, respectively. At Day 110, the parent compound had been reduced to less than 1 percent. The methyl, dimethyl and trimethyl homologues of dibenzothiophene had been altered to 7, 29 and 63 percent, respectively. These data show that the least complex dibenzothiophenes were most easily degraded, while the trimethyl homologue was quite persistent. The same biodegradation pattern existed for all PAHs in this study, regardless of the extent of total PAH loss. The most stable PAHs within each group were the highly methylated homologues.

The 4-ring pyrenes and chrysenes, which represented only 5 percent of total PAHs, were less easily degraded than the 3-ring PAHs. Losses of pyrenes in Mixtures 5, 6 and 9 were 52, 54 and 56 percent, respectively, over 110 days. Losses of chrysenes for the same mixtures were 31, 38 and 19 percent; respectively Bossert et al (1984) found pyrene, with its more condensed structure, to be more stable than chrysene. In our study, however, pyrenes were degraded more rapidly than chrysenes. The more recalcitrant 5- and 6-ring PAHs were also present, but at concentrations too low to permit quantitative comparisons.

The stability of steranes and hopanes is well recognized. Because of the limited duration of our study, we assumed both groups of hydrocarbons would be stable. Figure 7 confirms the stability of total steranes relative to the two most prominent hopanes. The relatively high sterane concentration at Day 0 in Mixture 1, the control, is probably an anomaly. Data from Mixtures 2, 4, 7 and 8 are not shown, but were very similar to the control. Peters and Moldowan (1993) noted that some oils exposed to heavy weathering show significant alteration of both hopanes and steranes, with hopanes
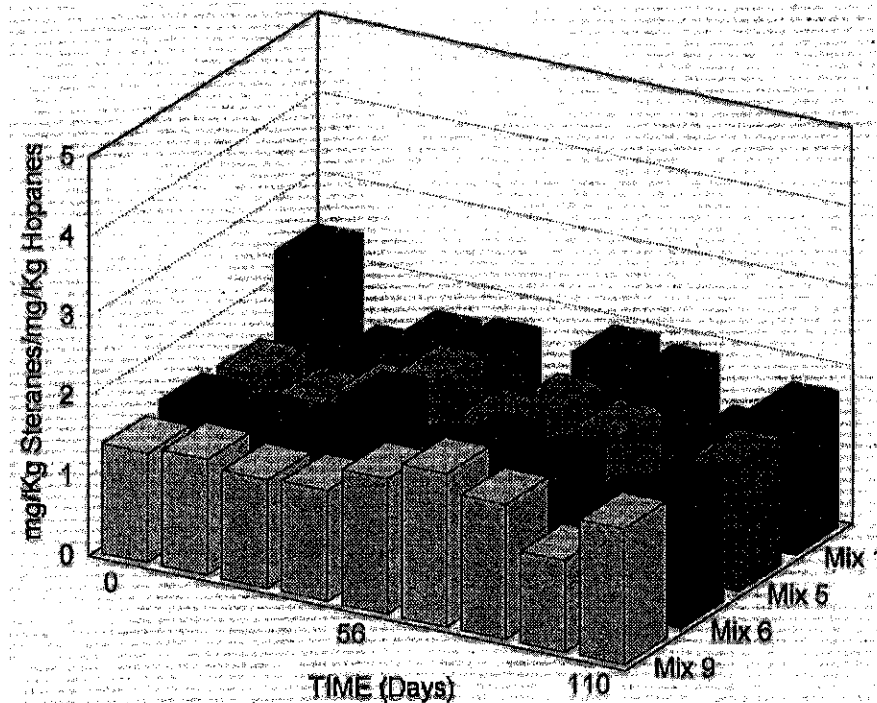
Figure 7 Loss of steranes from petroleum contaminated soil mixtures

being somewhat more stable. Lin et al (1989) reported that C_{30} steranes are more resistant to biodegradation than the C_{27} through C_{29} homologues. We examined chromatograms from mixtures that demonstrated enhanced biodegradation, and found no evidence of sterane degradation. We also examined chromatograms from the same mixtures for evidence of hopane alteration. Chromatograms from Day 0 were compared to those from Day 110. All were found to be identical. For our study, selection of either steranes or hopanes as a conserved internal standard would have been appropriate.

In the supplemental study conducted by NETAC, the oleophilic fertilizer product Vita-Bugg[TM] was more effective than three other bioenhancement products plus the control, as determined by degradation of n-alkanes. For the Vita-Bugg[TM] treatment, an overall reduction of 82 percent was observed for n-alkanes in 60 days. Removal of PAHs for two of the three test products and the control were relatively similar, ranging from 37 to 52 percent. The Vita-Bugg[TM] treatment was selected for field testing at the former Lovell Refinery Site to determine whether its full-scale application is cost effective. This product will be compared to a conventional fertilizer treatment and a control using a replicated, randomized block design.

CONCLUSIONS AND RECOMMENDATIONS

Use of high N sludge compost as a bulking agent accelerated the biodegradation of petroleum hydrocarbons when compared to an untreated control and to soil mixtures

containing bulking agents lower in total N. Chromatograms after 110 days from high N soil mixtures indicated an advanced stage of weathering in which normal and iso-prenoid alkanes had virtually disappeared, and only complex branched and cyclic hydrocarbons remain. Loss of TPHs in high N soil mixtures ranged from 50 to 62 percent for the test period. The relatively slow decline of TPHs in these mixtures indicates that structural complexity rather than nutrient availability may have limited hydrocarbon biodegradation. Losses of PAHs were rapid in mixtures containing sufficient N, ranging from 90 to 93 percent over 110 days. It should be noted, however, that 95 percent of total PAHs were comprised of 2- and 3-ring compounds. Of the 4-ring PAHs, pyrenes degraded more readily than chrysenes, even though pyrene has a more condensed structure. The most stable PAHs within each group were the highly methylated homologues Both steranes and hopanes were stable in all soil mixtures. Use of hopane-normalized data eliminated most of the data variability caused by uneven spatial distribution of contaminants. The resulting increase in data precision has several important benefits. It provides better documentation of bioremediation in the field. It permits more powerful statistical treatment of data for purposes of measuring effectiveness of innovative treatments or compliance with a cleanup standard. Use of normalized data also reduces the cost of monitoring by permitting collection of fewer soil samples.

Results of this study will be used to expedite the full scale bioremediation process at the former Lovell Refinery Site and to test the effectiveness of an oleophilic fertilizer treatment under field conditions. Field testing will occur concurrently with full scale treatment operations. Treatment effectiveness in the field will be measured using a fully randomized block design, in which an oleophilic fertilizer will be compared to conventional commercial fertilizer, composted cattle manure, and an untreated control. When treating crude oil wastes, analytical data should be normalized to an internal standard such as hopanes. If oleophilic fertilizer is found to be cost-effective after a three to four month test period at the Lovell Site, it may be selected for full scale treatment. Because oil at the Lovell Site is highly weathered, analytical data will be carefully examined during the treatment process to determine whether recalcitrant hydrocarbons will degrade within a reasonable time frame. If compliance with a numerical cleanup standard is difficult to obtain, (cleanup goals will be negotiated based on actual risks to human health and the environment), it is important to explore other options for negotiating successful cleanups. A site-specific risk assesment may determine that TPH levels in excess of 10,000 mg/kg are acceptable, primarily because levels of potentially carcinogenic PAHs are usually quite low in crude oil wastes. Another option would be to develop a phased cleanup approach, where land treatment bioremediation is followed by low-maintenance phytoremediation. Phytoremediation may be effective in reducing potentially carcinogenic PAHs while at the same time eliminating or substantially reducing routes of exposure to contaminated soil. At some sites, the cost of phytoremediation may be offset by the revenue gained from production of a saleable crop. Determination of a weathering index for crude oil wastes in soil is also recommended in order to determine the extent to which petroleum wastes are biodegradable. A numerical weathering index would be based on the relative percentages of hydrocarbon classes, such as n-alkanes, aromatics, asphaltenes, resins, the remaining unresolved complex mixture, and polar compounds. The index could be combined with rapid bioslurry treatability data to determine the extent of treatment attainable by

bioremediation. This is valuable information when deciding whether bioremediation is an acceptable remedial technology as well as estimating the level of treatment attainable under optimum field conditions.

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CHAPTER 6

A CALIFORNIA CASE STUDY FOR LEAVING PETROLEUM-AFFECTED SOIL IN PLACE

A Cooperative Program Between Buyer, Seller, and Regulatory Agency

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INTRODUCTION

Based on the results of an October 1995 study by Lawrence Livermore National Laboratory, the State of California Water Resources Control Board issued broad new guidance for the evaluation and management of petroleum sites within the State. The new guidance encourages the use of bioremediation and natural attenuation for petroleum sites that meet certain criteria to be classified as "low risk" sites, and has significantly changed the way petroleum sites can be managed in California. Based on this general, state-wide guidance, regional and local regulatory agencies developed their own approaches for resolving sites affected by petroleum hydrocarbons. Using a new approach for petroleum-affected sites, Geomatrix Consultants, Inc. (Geomatrix) embarked on a risk-based evaluation of a historic rail yard to facilitate regulatory closure and support a real estate transaction. The project was unique because:

- We successfully applied a risk-based approach to obtain closure of the rail yard where petroleum product could be visually observed in the soil using a recently-adopted guidance document for petroleum sites developed by the Regional Water Qnality Control Board, Sau Francisco Bay Region.
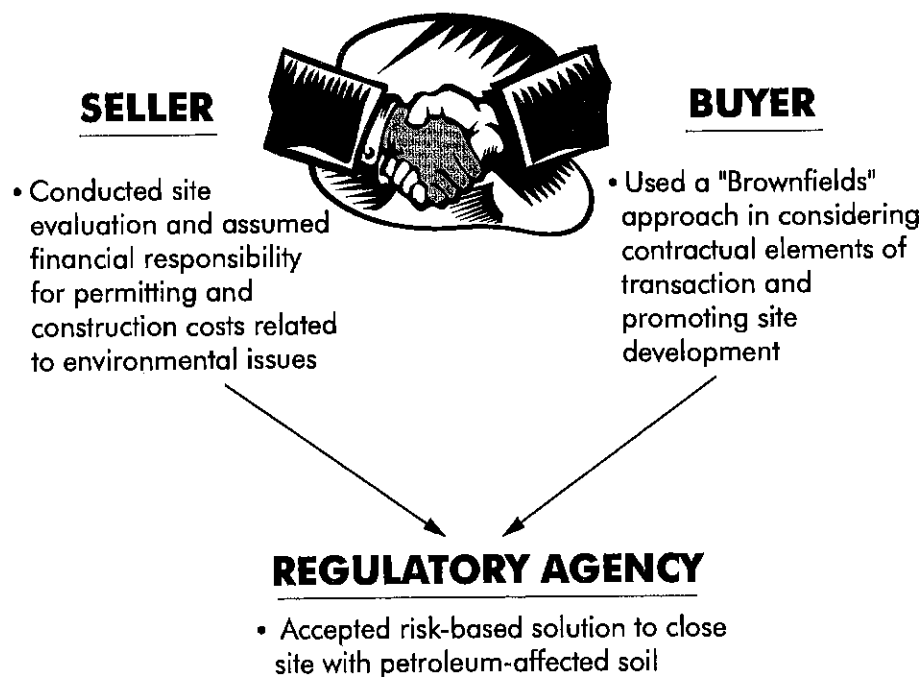
- Using a "Brownfields" approach, the sale of the property was contractually tied only to regulatory closure with no clauses for present or future mitigation of petroleum-stained soil.
- A critical partnership between the seller and the buyer, which allowed them to work jointly with the oversight regulatory agency, facilitated resolution of the environmental site closure and paved the way for development of the property on schedule and within cost patameters that were acceptable to both parties (Figure 1).

This chapter describes the regulatory perspective under which the project was performed, the results of the risk-based evaluation relative to the regulatory guidance, and the environmental considerations associated with the transaction that were resolved during the course of the project.

PROJECT BACKGROUND

Regulatory Perspective

Lawrence Livermore National Laboratory (LLNL), at the tequest of the State of California Water Resources Control Board (SWRCB), performed a survey of over a

SELLER

- Conducted site evaluation and assumed financial responsibility for permitting and construction costs related to environmental issues

BUYER

- Used a "Brownfields" approach in considering contractual elements of transaction and promoting site development

REGULATORY AGENCY

- Accepted risk-based solution to close site with petroleum-affected soil

Figure 1   Partnership

thousand leaking underground fuel tanks (LUFT), in California and examined the regulatory framework under which LUFT sites were administered. The results of its work were published in a 1995 report entitled *California Leaking Underground Fuel Tank (LUFT) Historical Case Analyses*. LLNL found that petroleum plumes (dissolved benzene) tend to stabilize close to the source area and rarely impact drinking water wells. The LLNL report also indicated that passive bioremediation may be the only remedial action necessary to protect groundwater quality in the absence of free product that contains soluble constituents ("source"). Based on the results of its study, LLNL proposed significant changes in the requirements for cleanup of LUFT sites in California, including application of risk-based decision-making rather than numerical standards in resolving petroleum releases and use of passive bioremediation once the fuel leak source has been removed rather than active remediation, where appropriate. The LLNL study focused on benzene, toluene, ethylbenzene and xylenes (BTEX) only; at the time of the study, there was little groundwater data for gasoline additives (methyl-tertiary-butyl ether [MtBE]) and additives were not evaluated in the LLNL study.

In December 1995, the SWRCB concurred with the findings of the LLNL study, and instructed the nine regional water quality control boards and other fuel leak oversight agencies withiu the State to "Proceed aggressively to close low-risk soil only cases." The SWRCB further recommended that the oversight agencies require monitoring only to evaluate plume stability for low-risk groundwater cases (for example, cases where only shallow groundwater is impacted and no drinking water wells are within 250 feet of the fuel leak).

It was within this broad framework that, in January 1996, the Regional Water Quality Control Board, San Francisco Bay Region (RWQCB) developed its *Supplemental Instructions*, which outlined the RWQCB's approach for determining and regulating low risk fuel sites within its jurisdiction. These instructions classified low risk soil or groundwater sites, and recognized that certain petroleum products such as degraded diesel and crude oil may not be soluble enough to degrade gtoundwater quality. Hence, these products may not be considered a "source" requiring removal. The RWQCB's Supplemental Instructions further stated. "For old releases, the absence of current groundwater degradation is often a good indication that residual [petroleum] concentrations present in the soil are not a source of pollution."

With this new guidance in place, Geomatrix proceeded in June 1996 with an expedited, risk-based evaluation of a former rail yard where previous work by another consultant revealed the presence of residual petroleum product in soil.

Site Information

The site is a former rail yard that occupies approximately 6.5 acres in a city in northern California and is located immediately to the north of the downtown commercial area. It is bounded to the north by active railroad tracks. A creek, which is tidally-influenced and discharges to nearby San Francisco Bay, is adjacent to the western site boundary. Public streets bound the site to the south and east (Figure 2).

On average, approximately 2 to 3 feet of fill is present throughout the site overlying silty clay (Bay Mud), except at the levee along the creek. In this area, the depth of the fill averages approximately 5 feet. The depth to groundwater at the site varies seasonally between approximately 1.5 feet to 5 feet below ground surface (bgs).

Historically, the site was used as rail yard since the late 1800s, and former facilities
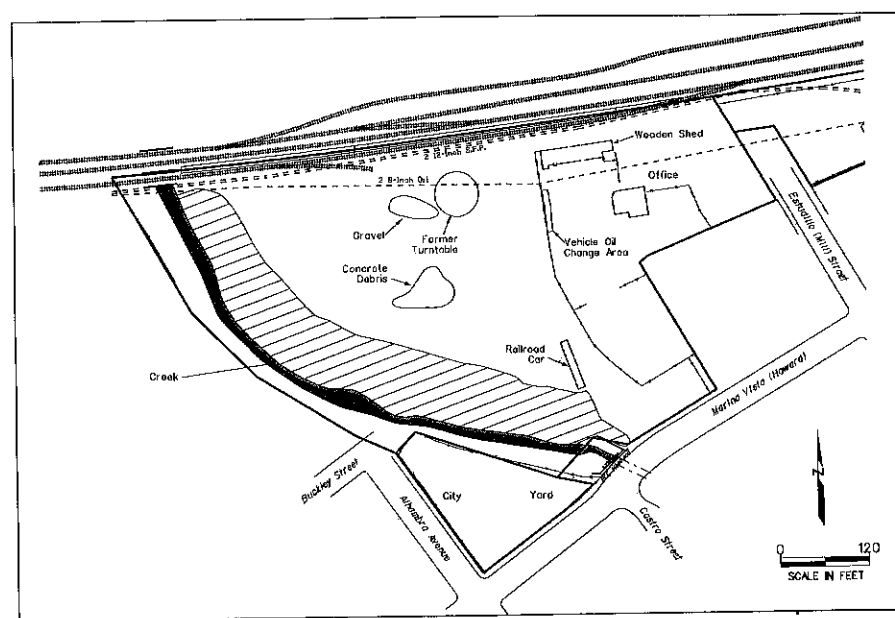
Figure 2   Site plan

located on the site included railroad tracks within the central portion of the site and a turntable in the north-central portion of the site. The levee along the creek was constructed in the late 1950s. Land use at the time of the site evaluation included railroad and city corporation yards, which were used primarily for material storage, Amtrak depot, and associated parking lots. Additionally, active underground fuel distribution pipe lines were present along the northern site boundary.

Planned Future Use

The buyer plans to redevelop the property as a regional transit hub, and will construct a passenger rail station, and asphalt-paved bus turnaround and parking areas. Also included in the plan is extensive regrading of the levee along the creek to develop a "green belt" area and enhance flood control along the creek.

Conclusions of Previous Investigations by Others

Prior to the real estate transaction and on behalf of the buyer, an initial investigation was performed by another consultant to evaluate whether significant environmental impacts had occurred at the site from recent or historical land uses. For this investigation, soil and grab groundwater samples were collected near historical or existing site features and along the levee. From the results of the investigation, the consultant concluded that soil and groundwater were environmentally impacted, and that site mitigation likely would be required prior to and during redevelopment of the property. The highlights of the initial investigation findings included:

- Total petroleum hydrocarbons (TPH) in the diesel and motor oil ranges were detected in soil at concentrations up to 110,000 and 5,300 milligrams per kilogram (mg/kg), respectively.
- Petroleum-affected soil was in contact with groundwater.
- Petroleum product was observed in soil
- "Free product" was reported.

RISK-BASED INVESTIGATION PROGRAM AND RESULTS

For the initial investigation, TPH data were used as a general indicator of soil and groundwater quality at the site. TPH is an aggregate measurement and is limited in application because it does not measure specific fuel-related components (such as aromatics) and cannot be used to directly assess solubility and human health risk (Zemo, et. al, 1995a). Therefore, to assess whether the detected TPH could be left in place given the RWQCB criteria for a "low risk soils case" and the planned future site use, we developed a risk-based investigation program that consisted of an aggressive sampling and constituent-specific analytical program.

In considering the possibility of closing the site as a low risk soils case, we noted that the laboratory reports from the initial site investigation had indicated that the chromatographic pattern for 33 of the 35 samples with TPH detections did not resemble the respective fuel standards. TPH analyses are subject to positive interference by non-petroleum hydrocarbons such as biogenic materials resulting from intrinsic biodegradation (Zemo and Synowiec, 1995b). The laboratory comments were an important indicator that this type of interference was occurring in the samples. The information suggested that degraded or biogenic hydrocarbons probably were present in the samples and were partially or wholly contributing to the TPH quantification. This information further suggested that the degraded TPH likely was not an ongoing source to groundwater degradation.

To complete the risk-based evaluation, additional data were collected to assess:

- the extent of reported separate-phase product and potential for it to act as a source of dissolved petroleum to groundwater, and
- the distribution and concentrations of chemicals of potential concern in soil and groundwater and their potential to impact human or ecological receptors.

Soil and groundwater samples were analyzed for specific constituents: polynuclear aromatic hydrocarbons (PAHs), benzene, toluene, ethylbenzene and xylenes (BTEX), and other volatile organic compounds (VOCs), and metals. No TPH analysis was performed for the risk-based evaluation, except for the groundwater samples that were collected near the creek. There are no TPH criteria relevant to the site, and as previously stated, the aggregate TPH measurement is not used in California to assess risk to human health. The TPH analysis for groundwater samples collected near the creek was performed at the request of the RWQCB for taste and odor and ecological considerations.

Application of Results for Site Closure

From the data collected during the additional investigation, we were able to favorably address the criteria established by the RWQCB and demonstrate that the site qualified as a low risk soil case that warranted closure. With respect to the criteria, our conclusions are presented in Table 1.

TRANSACTIONAL CONSIDERATIONS

A critical component of the success of the environmental aspects of the project was the partnership that developed between the buyer and seller. As a developer with a planned site use, the buyer had a stake in the resolution of the environmental site closure and associated transactional issues. The partnership evolved as the sales negotiations and additional environmental investigation proceeded, and allowed for a "Brownfields" approach to be applied to the transactional considerations and assumptions regarding potential costs during and subsequent to site development.

Contract negotiations hinged on two primary aspects: 1) the seller would obtain regulatory closure for all environmental issues relative to the planned future site use as a transit hub; and, 2) financial responsibility would be assumed by the seller for all permitting and construction costs related to potential environmental issues that could result if regulatory closure allowed for chemical constituents to remain in place. The potential site development costs were the cornerstone of the transaction: the seller would not have proceeded readily with the property sale if there were excessive construction costs or long-term cost liability related to environmental issues; significant negotiations that could be involved with these issues could have impacted the buyer's funding sources and overall site development schedule. Conversely, the buyer could not fund potential environmental costs outside the projected costs of the planned development. Resolution of the potential cost issues was a priority for both parties. With this in mind, analysis of potential near- and long-term environmental costs were estimated by the buyer's consultant and Geomatrix while the risk-based investigation was underway.

Using the initial data generated for the site, the two consultants did not share a common vision for the outcome of the risk-based evaluation and costs that could be related to the development of the site under a risk-based closure scenario. Although the environmental consultant for the buyer agreed with the concept of a risk-based closure, it believed that the closure could only be achieved with removal of a significant volume of the petroleum-affected soil (assuming it would be a long-term "source" to groundwater degradation), and that, based on the likely presence of other constituents in site soil, special soil handling procedures would be required throughout the site development. Specifically, with respect to estimating potential costs to mitigate environmental issues during and after site development, the major assumptions between the two consultants differed as presented in Table 2.

These differing assumptions translated to more than $500,000 difference in estimated site development and management costs associated with potential environmental issues. The key component to Geomatrix's cost-estimating exercise was assuming that the petroleum-affected soil did not pose a threat to human health and the environment. As previously described, this assumption was ultimately demonstrated through a constituent-specific, risk-based analysis at the site. The costs estimated by Geomatrix were within the bounds of the seller's parameters for the sale to proceed. The buyer

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TABLE 1   Site Conditions Relative to Regulatory Criteria

Investigative Results	RWQCB Criteria
Petroleum was bound in soil matrix throughout north-central and eastern portions of the site, and no free flowing separate phase was observed. BTEX and other soluble constituents generally not present.	No ongoing petroleum sources to groundwater, including free product, exist.
Soil and groundwater data collected during two investigative programs incorporated into site analysis.	The site is adequately characterized.
Results indicated groundwater unaffected by BTEX, PAHs, and VOCs. Petroleum in soil is immobile and insoluble, and unlikely to affect water quality.	Little or no groundwater impact currently exists.
No groundwater impact exists; therefore, no potential drinking water receptors could be impacted by the site.	No water wells, deeper drinking water aquifers, surface water, or other sensitive receptors are likely to be impacted.
Constituents detected in the soil included PAHs and metals at low concentrations. A screening-level human health risk evaluation on aggregated data concluded that conditions do not present a significant risk to human health.	The site presents no significant risk to human health.
Site groundwater affected only by dissolved metals at concentrations less than California ambient water quality criteria, and poses no ecological risk to the creek.	The site presents no significant risk to the environment.

Based on the data and its evaluation relative to the criteria, the RWQCB authorized closure of the site as a low risk soils case, with no conditions, such as mitigation of petroleum-affected soil or long-term monitoring.

agreed with Geomatrix's overall assumptions and approach for a risk-based closure, and, hence, proceeded with the transaction.

Although removal of petroleum-affected soil was not targeted as a goal, it was recognized that excavation and handling of petroleum-stained soil likely would occur during site grading. To address this issue and remain within the established cost parameters, the buyer agreed to have the seller develop specifications for handling of petroleum-stained soil for incorporation into the overall grading bid package and periodically monitor the grading activities to ensure compliance with the specification.

TABLE 2   Primary Assumptions for Cost Estimate to Resolve Site Environmental Issues

Buyer's Consultant	*Seller's Consultant (Geomatrix)*
Risk-Based Closure	
Hazardous material would be left on site, requiring capping and long-term cap maintenance.	Because the risk-based closure considered risk to human health and the environment, no materials would be present on site that would require isolation, and therefore, no capping would be necessary.
Removal of Petroleum-Stained Soil	
All petroleum-stained soil could act as a long-term source to groundwater degradation and should be removed from the site. Significant soil disposal costs would be incurred.	Later-boiling petroleum hydrocarbons that are insoluble and not a long-term source to groundwater were detected in site soil and would remain on site unless excavated as part of the planned site grading. Minimal soil disposal costs would be incurred
Other Site Development Considerations	
Remediation planning, oversight, and reporting would be required.	No specific remediation would be required, but provisions would be made in the contractor specification package for handling petroleum-stained soil, if encountered.
All construction personnel to be health and safety-trained.	Personnel involved with site grading and utility installation to be health and safety-trained.

With this partnering approach, site grading began in July 1997. The buyer and the seller, working together, minimized project costs and contractor down-time related to petroleum-stained soil. Ultimately, less than 100 cubic yards of petroleum-stained soil was separately stockpiled for disposal during an earthmoving operation of approximately 5000 cubic yards.

CONCLUSIONS

Environmental issues at a historic rail yard were successfully closed using a newly-established regulatory guidance that allowed for a risk-based evaluation and demonstration that petroleum-affected soil did not pose a long-term source to groundwater degradation. The environmental closure, in conjunction with the partnership that developed between the property buyer and seller as resolution of the environmental issues proceeded, facilitated site closure with the regulatory agency, the property transaction, and ultimately, development of the property on schedule and within cost parameters that were acceptable to both parties.

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CHAPTER 7

CASE STUDY: LANDFILL CAP REMEDIATION PROJECT AT A FORMER RAIL YARD

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INTRODUCTION

NES, Inc. (NES) recently completed the design and construction of a landfill capping project at a former rail yard. The purpose of this capping project was to contain waste material generated from historical railroad maintenance operations. In addition to the design technical specifications and contract drawings, NES prepared a remedial work plan, a health and safety plan, a contingency plan, obtained the required permits, and is responsible for the operation and maintenance for the project. Operation and maintenance planning are detailed and a landfill cap inspection example as prepared by NES is provided in this chapter.

The Union Road site ("the site") is a Class 2 site as defined by the New York State Department of Environmental Conservation (NYSDEC). The site was once a railroad maintenance and classification yard and is located in Cheektowaga, NY. Coal ash, grease and oil from locomotive and rail car repairs were routinely disposed of in large marshy pit located near the rail yard. When the rail yard was closed in 1955 and the property was sold (in 1959), the "tar pit" remained. In the early 1980's the existence of the "tar pit" was brought to the attention of county and state environmental agencies. It was found that some of the wastes from this pit had moved through the marsh and into nearby Deer Lik and Slate Bottom Creeks.

A thorough investigation of the site and careful consideration of several alternatives were performed in the late 1980's and early 1990's. It was determined that the best way to remediate the site was to consolidate the wastes and contaminated soil and sediment in a contained disposal area to be built on site.

Remedial Work Plan

As part of the closure process, a remedial work plan was required to demonstrate that all areas within the site were addressed to the satisfaction of the regulatory agency. For this project, the major activities included:

- Excavation of 22,000 cubic yards of contaminated soils and placement within the on-site disposal area;
- Placement of a 13 foot high, 140 foot wide gabion basket wingwall and 260,000 square feet of reno mattresses;
- Installation of 2,200 linear feet of a three foot wide slurry wall cut-off trench;
- Construction of a dual liner landfill cap covering 7.7 acres; and
- Excavation of contaminated soil within the former roundhouse area with subsequent topsoil placement and seeding over six acres.

Other, less critical site activities included:

- Clearing and grubbing activities on over 15 acres of the site;
- Wetland and tar pit dewatering and excavation activities;
- Monitoring well installation;
- Dewatering well pump and controls installation;
- Pre-cast concrete building and duplex pump station installation; and
- Sanitary sewer connection installation for groundwater discharge.

Support activities included:

- Construction of a new site entrance road;
- Construction of temporary site access roads; and
- Staging of field offices and related equipment.

Pertinent Design Operations

Design work undertaken included the following pertinent operations:

- Development and implementation of a site specific health and safety plan;
- Preparation of design plans and technical specifications;
- Preparation of contract documents;
- Contingency planning;
- Permitting; and
- Operation and maintenance planning.

Other design work and support services included:

- Remediation cost efficiency;

- Preparation for and use of surveying control/services;
- Construction contract administration; and
- Community relations.

Health and Safety Plan

The health and safety plan prepared for this hazardous waste site addressed the following topics: scope of work, site history, physical description, health and safety personnel, emergency information, site control and security, site worker protection, and off-site impacts.

The health and safety program was used as a tool that permitted every employee and subcontractor to incorporate safety into the work plan. This policy ensures both employees and the site personnel near the work zone areas, a safe and healthy workplace.

The health and safety plan is comprised of the written program requirements utilized as a foundation for site specific compliance and planning, namely:

- Corporate commitment;
- Medical surveillance program;
- Worker protection and safe worker practices;
- Respiratory protection program;
- Permit -- entry confined spaces;
- Hazardous waste site operations;
- Control of hazardous energy sources;
- OSHA audit and recordkeeping compliance;
- Emergency action plan; and
- Hazard communications.

Personal monitoring equipment was required during site construction phases of the project and was incorporated into the proposed health and safety plan for remedial construction activities. Engineering controls were incorporated into the design. The health and safety plan developed for this project included a decontamination procedure for each operational unit area.

Contingency Plan

A contingency plan was developed for remedial design activities to be used during construction in case of emergency and unforeseen situations. Regulatory understanding of all Federal, state, and local requirements for the handling of hazardous waste and construction debris was required. Site meetings, reviews, and close client and regulatory contact was planned to insure proper design. Internal coordination was required and procedures were proposed to incorporate this interaction and coordination into the work undertaken during the design and contract administration service provided.

Permitting

Permits for this project were prepared and submitted to applicable jurisdictions, namely:

- Notice of intent (NOI) for storm water discharges associated with industrial activity under the SPDES general permit;
- Highway work permit, County of Erie, Department of Public Works, Division of Highways, New York;
- Section 401 water quality certification;
- Nationwide permit 33 CFR 330, Appendix A Sec. No. (38);
- Town of Cheektowaga, New York -- tree removal permit.

Plans and Specifications

The plans and specifications were prepared in CSI format for competitive bid. The project was divided into tasks, each headed by a separate task leader. A team approach was used to complete the remedial design report and the contract documents for this project.

Remedial Operations

Project remedial tasks defined in the contract documents included:

- Mobilization
- Clearing and grubbing
- Erosion control
- Groundwater discharge
- Excavation/landfillcap
- Wetland excavation
- Roundhouse remediation
- Stream restoration
- Well installation
- Utilities/general expenses

- Downstream investigation
- Downstream remediation
- Project management
- Meeting with NYSDEC
- Public relations
- Surveying/QA control
- Health and safety
- O & M planning
- Litigation support

Operation and Maintenance Planning

Prior to completing the environmental remediation construction work at this inactive hazardous waste site, NES began operation and maintenance program planning for the remainder of the project. The project remediation plan calls for 30 years of site operation, maintenance, and monitoring that will involve inspections on the following completed remedial activities and installed remedial system:

- Gabion baskets and reno mattress;

- Slurry wall cutoff trench;
- Landfill cap utilizing a geosythetic and HPDE liner;
- Contaminated soil excavation and backfill activities;
- Landfill cover with topsoil and seeding;
- Dewatering well pumps, controls, and a duplex pump station;
- Discharge to city sanitary transmission system; and
- Other seeded areas along with erosion and sediment control systems.

Maintenance following the remedial construction will involve periodic site inspections of fencing and gates, the pumping system, as well as the cap and slurry wall system. Vegetative plantings and turf require periodic maintenance, such as pruning, mowing, and replacement, as uecessary.

All facilities must be properly operated and maintained, including but not limited to sysrems of treatment and control and related appurtenances that were installed and are being utilized to achieve compliance with the conditions of any order or agreement with the governing jurisdiction. Proper operation and maintenance include effective performance, adequate funding, adequate operation staffing and training, as well as adequate laboratory and process controls, including quality assurance procedures.

Plan Purpose

The purpose of an Operation and Maintenance Plan is to familiarize personnel and authorities with the:

- Appropriate operation of installed systems;
- Basis of design;
- Description of equipment and facilities at the site; and
- Program for operation and maintenance.

Following the construction and completion of remedial activities at this inactive hazardous waste site landfill capping construction project, an operation and maintenance program was prepared. An effective program will extend equipment life and reduce unexpected equipment failures.

An adequate program is intended to ensure the following:

- Agreement on the project plan for system shut-downs and crisis operations;
- Improved coordination and cooperation of operation with maintenance personnel and regulatory agencies;
- Improved time management program and use of personnel;
- Increased understanding and awareness of equipment;
- Maintenance of spare part inventory;

- Presentation of a lubrication and maintenance schedule;
- Presentation of an established plan for maintenance and contingency operations;
- Reduction in costs for emergency repairs;
- Regular procedural inspection of equipment; and
- Repeated calibration and adjustments.

Items to be considered in the operation and maintenance program are quite variable, dependent on the remedial activities undertaken during construction, the type(s) of remedial systems installed, and the intended length of operations, in this case 30 years from the completion of remedial activities.

An example outline of the items considered for this remedial hazardous waste landfill project, with groundwater monitoring, sediment and erosion control, and dewatering operations involved consideration of the following items:

1. Records of groundwater monitoring information for a remedial project will involve the review of, the tabulation and reporting of, as well as, the long-term storage of information. This information includes:

- Inspection logs,
- Photographs,
- Analytical data including:
- Analytical technique utilized,
- Date, exact place and time of sampling or measurement,
- Date analysis was performed,
- Name of individual and firm who performed analysis,
- QA and QC data; and
- Results of analyses.

2. Permit requirements for tabulation and reporting of data and the storage of records are reviewed and adhered to, thus insuring environmental regulatory compliance.

Investigation Areas and Maintenance Responses

Investigation areas and maintenance responses for the installed hazardous waste landfill cap will include the inspection areas and responses for this site as listed in Table 1.

An example of an inspection report for visit documentation, was prepared for all remedial activities to be monitored. Follow-up documentation of operation and maintenance measures taken resulting from an inspection, are also required. Figure 1 presents an example of a landfill cap inspection report template for field use by operation and maintenance personnel.

Another separate inspection report template similar to the example presented in Figure 1 is to be utilized by personnel for the inspection of other completed remedial

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TABLE 1   General Inspection Areas and Maintenance Responses

Inspection Areas	Maintenance Response
Unhealthy vegetative growth	Apply fertilizer, reseed, and/or irrigate.
Excessive vegetative growth	Mow vegetation. Prevent excessive and large root growth
Large vegetative and root growth	Prevent excessive and large root growth
Surface erosion	Apply mulch to areas affected and reseed. Direct runoff away from damaged areas.
Washouts	Addition of compacted backfill.
Sediment and erosion controls	Repair and replace.
Burrowing rodents	Consult professional exterminator. Backfill burrows.

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activities that must be field reviewed for operation and maintenance (see Operation and Maintenance Planning section for activity listing).

Field Reference Resource

The intent of any operation and maintenance program is to provide a reference resource and highlight documentation storage of site information. Design and as-built information along with shop drawings and manufacturers' submittals are essential to the program. These documentation items include:

- Approved shop drawings;
- As-built plans and specifications;
- Manufacturer's manuals;
- Manufacturer's catalogs;
- Design and as-built calculations; and
- Other applicable information (vendor and manufactures contacts, spare part requirements, etc.).

In addition, the following documentation has been assembled and will be referred to often during operation and maintenance activities:

- Consent agreement or order with governing jurisdiction;
- Standard operating procedures;

Figure 1. Example Landfill Cap Inspection Form

Date: _____ Inspector: _____ Weather Condition _____

Project _____ Location _____

The inspector to provide a detailed condition survey information in a format that is consistent with the item under inspection.

Item of Inspection for Landfill Cap	Location of Site Inspection (Be Specific)	Site Condition Comment by Inspector	Recommended Operation and Maintenance Measures to be Implemented	Date of Implementation of Recommended Measures and Comment
Soil Placement				
Vegetative Growth (Excessive or Unhealthy)				
Clay Membrane				
HPDE Liner				
Monitoring Well and Gas Vent Boots				
Surface Erosion				

Distribution: Inspector Field File, Project Manager, Office File

Figure 1   Example landfill cap inspection form

- Pertinent and governing rules and regulations (Federal, state, local); and
- Permits.

Standard Operating Procedures were developed and must be reviewed prior to initiation of the operation and maintenance program. Thus, maintenance personnel have a quick reference and have been exposed to the procedures to be followed in the office and the field during the operation and maintenance period.

CONCLUSION

An operation and maintenance program for this environmental hazardous waste remediation project has been planned, information for field use has been assembled, volume-format in a three-ring binder and the information has been distributed to all key personnel. Copies are kept on file at the site, and will be at the State jurisdiction level in the future. The operation and maintenance volume format provides the user with all available site information in one general place for ease of access.

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Remedial Design Report, Union Road Site, NES, Inc., April 1995.

Operation, Maintenance and Monitoring for a Hazardous Waste Site, New York State Department of Environmental Conservation, April 20, 1992 Memorandum.

CHAPTER 8

PHYTOREMEDIATION OF FUEL OIL CONTAMINATED SOIL

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INTRODUCTION

There is an emerging trend in the environmental industry toward using less active remedial technologies. Phytoremediation, the use of vegetation for remediation of soil, sediments and water, is a technology that holds promise to cost effectively address sites contaminated with moderately hydrophobic compounds, such as petroleum hydrocarbons, chlorinated solvents, ammunition wastes, and excess nutrients (Schnoor et al., 1995). In addition, phytoremediation holds promise toward cleanup of sites contaminated with heavy metals (Azadpour and Matthews, 1996) and sites with recalcitrant organics, such as manufactured gas plants and refineries (Schwab and Banks, 1994). Plants remediate contaminants via three mechanisms: direct update and accumulation of nonphytotoxic metabolites into plant tissue or volatilization through plant tissue; release to exudates and enzymes that stimulate microbial activity and biochemical transformations; and enhancement of mineralization in the rhizosphere (Schnoor et al., 1995).

Certain trees uptake large volumes of water and can actually be used to treat contaminated groundwater. At a site in New Jersey, concentrations of nitrate in groundwa-

ter were significantly reduced following implementation of a *TreeMediation*™ program (Gatliff, 1994). In this current study, rhizosphere processes in a species of *phyreatophyte* are employed to stimulate the biodegradarion of an aged fuel oil spill in Wisconsin.

OBJECTIVE

The objective of the project is ro remediate soil and fill materials within the four hotspots at the facility to below 1000 milligrams per kilogram (mg/kg) diesel range organics (DRO), as requited by the Wisconsin Department of Natural Resources (WDNR). Excavation and treatment of the soil materials was not a preferred option, based on the potential costs associated with segregating construction debris from soil and risks inherent in excavating at a facility with a long operational history.

Site Description

Operations began at this site in the early 1900s. A heterogeneous mixture of fill material was used to extend the property boundary west within the adjacent river (Figure 1). During the late 1970s a section of below-ground piping transferring No. 2 fuel oil from a larger aboveground storage tank (AST) to a smaller day use AST failed, resulting in a subsurface release. Approximately 15,000 gallons (56,800 liters) of fuel oil were recovered from shallow trenches installed at the site. Concentrations of hydrocarbons constituents in groundwater ate below current WDNR-established groundwater quality standards.

Investigations at the site have determined that highly affected soil (concentrations greater than 1,000 ppm DRO) remain in four generalized hotspots at the site (Figure 1). The site is underlain by 3 to 15 feet (.9 to 4.6 m) of heterogeneous fill material, comprised of wood timbers, sawdust, construction debris, clay, sand and gravel. The depth of the water table ranges from 3 to 9 feet (.9 to 2.7 m) and the water table slopes west, toward the adjacent river. Three of the hotspots (Hotspot 1, 2 and 4) are below a hard-packed gravel equipment storage area and Hotspot 3 is located below a vegetated area along the river.

MATERIALS AND METHODS

Soil Sampling and Analysis

Soil samples were collected and analyzed during May 1994, October 1995 and April 1996. Backhoe test pits were completed during May 1994 to allow collection of soil samples that were used to determine initial concentrations of DRO in soil, microbiological populations, microbiological respirometry rates, and for performing accelerating biovent tests. Six soil samples were collected from three test pits and were screened in the field visually, and with a flame ionization detecror. Soil samples were collected from depths of between 3 feet and 5 feet (.9 to 2.7 m) below land surface, which represents the capillary fringe. Soil samples were also collected during October 1996 and May 1996 to determine the perimeter and initial concentration of DRO in each of the horspots. Soil samples were collected during these evenrs using hollow stem augers and standard splitspoon sampling techniques.
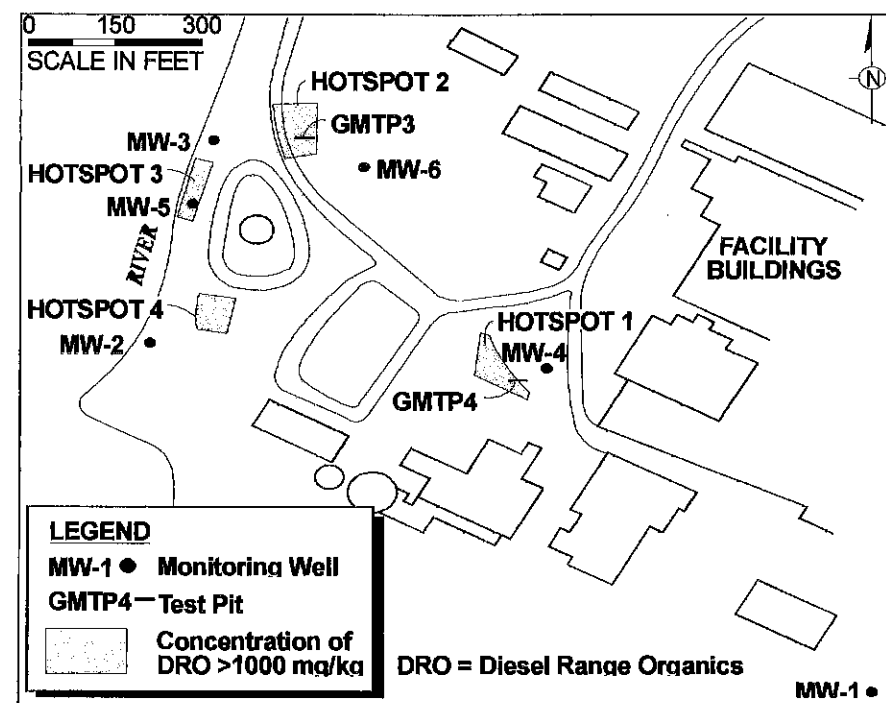
Figure 1   Site layout and location of four soil hotspots

Soil samples for DRO analysis were submitted to a WDNR-certified laboratory for analysis and chromatograms were supplied by the laboratory. Soil samples for microbiological enumeration, respirometry and accelerated bioventing testing were performed by Acurex Environmental of Research Triangle Park, North Carolina.

Microbiological populations were determined using standard spread plate count procedures and soil respiration rates were determined using a Micro Oxymax respirometer utilizing methods that were suggested by the equipment manufacturer.

Accelerated Biovent Tests

Accelerated biovent tests were performed on two of the six soil samples (Soil Samples GMTP3/4-5 and GMTP4/4-5), based on the results from the initial DRO analyses and microbiological enumerations. Accelerated biovent testing was perforined for a 24 week period with sacrificing of sample aliquots for DRO or respirometry testing at Weeks 0, 2, 4, 6, 13 and 24.

Samples for the accelerated biovent tests were first homogenized and were placed in 500 ml Erlenmeyer flasks equipped with rubber stoppers and tubing. The samples were not amended with uutrients other than air during the tests and the tests were performed at room temperature. Humidified air used during the test was supplied through plastic tubing by a diaphragm air pump and was pumped through the sample vessel at an air flow rate equivalent to 4 pore volume exchanges per day.

Agronomic Assessment

Soil samples were collected from Hotspot 2 and Hotspot 3 during June 1995 to determine potential phyto-toxic effects on tree root development and concentrations of agronomic constituents of interest. The bench top root development study was performed by Applied Natural Sciences (ANS) of Fairfield, Ohio using soil collected from Hotspot 2 and Hotspot 3 and cuttings from willow trees indigenous to the site. Soil and cutrings were refrigerated by ANS until July 1995. Cuttings were removed from the refrigerator, transplanted into sand and rooted. The rooted cuttings were planted and were monitored for leaf and root development. After two months of development, willow and hybrid poplar plants were transplanted into soil collected from Hotspot 2 and Hotspot 3. Plant growth was observed for a period of 6 weeks, when plants were harvested and root systems were evaluated. Soil samples were submitted to Servi -Tech Inc. of Dodge City, Kansas for testing of constituents including nitrate and ammonia nitrogen, phosphorous, potassium, zinc, iron, manganese, copper, sulfur, calcium and sodium. Soil samples were also analyzed for pH, soluble salts (as specific conductance) and percent organic matter.

RESULTS AND DISCUSSION

Soil DRO and Microbiological Analysis

Concentrations of DRO exhibir a wide degree of variability, both across the site and within each of the four hotspots. Although there does not appear to be a lateral trend in elevated concentrations of DRO, the highest concentrations were present within the capillary fringe. Concentrations of DRO in samples collected from the six backhoe testpits completed at the site ranged from 40 mg/kg to 5,000 mg/kg. The results from the microbiological enumerations indicated that a viahle population of microbes capable of degrading fuel oil were indigenous to soil at the facility. Populations of heterotrophs in colony-forming units per gram (CFU/g) ranged from 1.1×10^5 CFU/g to 4.1×10^6 CFU/g, and populations of diesel degrading microbes ranged from 5.7×10^3 CFU/g to 9.5×10^5 CFU/g.

Accelerated Bioventing Tests

The results from DRO analyses performed on aliquots of Soil Samples GMTP3/4-5 and GMTP4/4-5 are presented in Figure 2. After an initial apparent increase in DRO concentrations between Weeks 2 and 4, a significant decrease in DRO was observed during the testing. Overall concentrations of DRO in the soil samples decreased during the laboratory bioventing testing between 40% and 90% from the concentrations measured at the onset of the test. The initial increase in measured DRO in the soil samples is attributed to one or a combination of the following: 1) variability of the DRO resulting from heterogeneities inherent in the soil material; 2) presence of intermediate constituents related to the micro-environment changing from anaerobic to aerobic conditions that may have mirrored DRO in the analysis or 3) by-products of degradation of wood cellulose mirroring a fuel oil chromatography signature (as reported by Edelman and Girard, 1994).
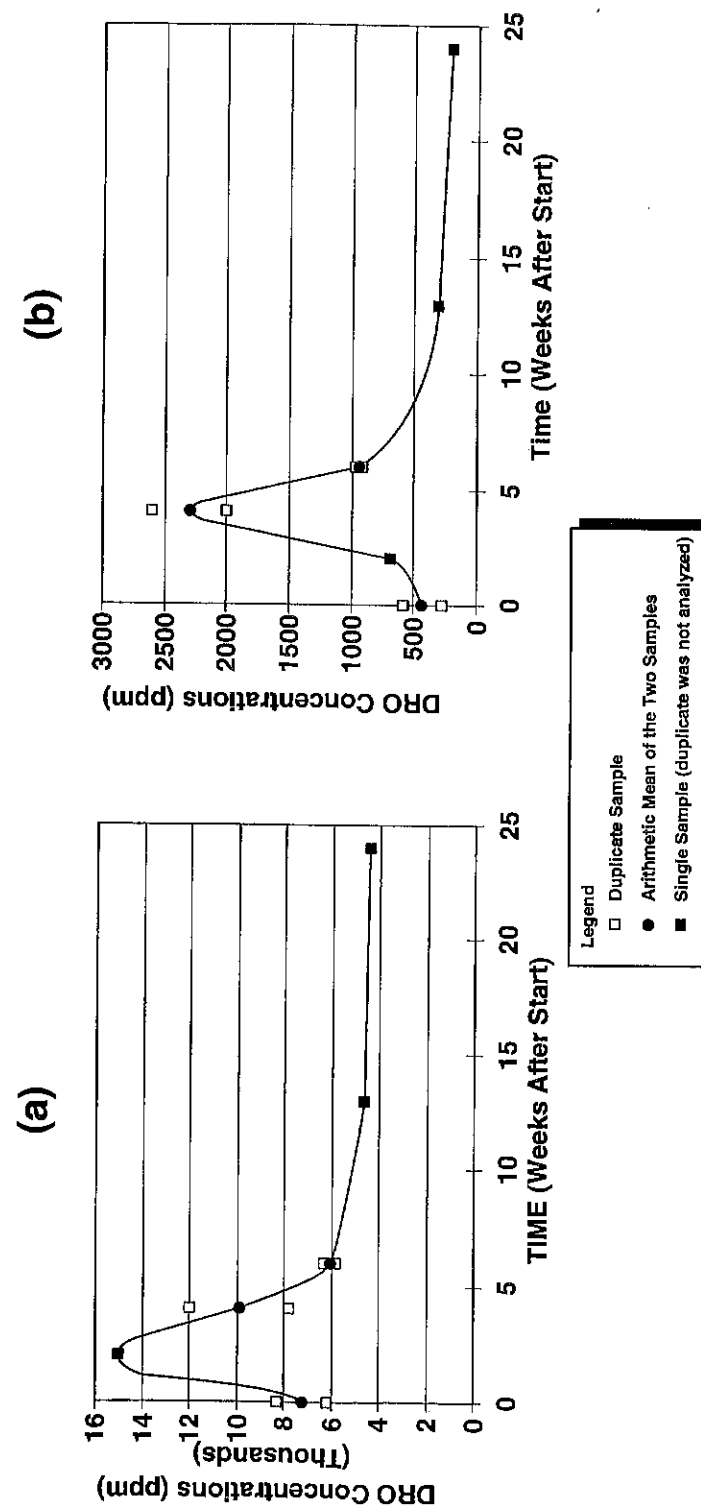
Figure 2   Trends in DRO concentration during accelerated biovent test, (a) soil sample GMTP4/4-5 soil sample GMTP4/4-5 (b) soil sample GMTP3/4-5

Patterns in DRO Chromatograms

The chromatograms from the sample aliquots collected at the onset of the accelerated biovent tests were compared to chromatograms from aliquots collected at the end of the tests. Chromatograms of aliquots from soil sample GMTP4/3-5 collected at the onset of the test and at the end of the test are presented in Figure 3. Comparison between the initial and final chomatograms suggests a relative decrease in shorter chained (earlier eluting) hydrocarbons and relative increase in longer chained (later eluting) hydrocarbons during the accelerated bioventing testing. This comparison supports a conclusiou that decreasing DRO was related to biodegradation of shorter chained hydrocarbons. Based on the decreasing DRO and patterns observed in the chromatograms during the accelerated bioventing testing, in-situ bioremediation was selected for implementation in the four hotspots. In-situ biological alternatives that were considered included in-situ bioventing and phytoremediation. Phytoremediation was selected as the alternative based on the low cost for implementation and monitoring.

Agronomic Assessment

Both hybrid poplars and willows showed good aerial growth during the root development portion of the agronomic assessment. However, the willows showed a more pronounced tendency to establish rooting within the DRO contaminated soil. The laboratory results from analysis performed during the agronomic assessment showed concentrations of constituents wete within an acceptable range for tree growth, however, relatively high concentrations of soluble salts in the subsurface could be a potential concern to tree growth at the site. Based on the results from the agronomic assessment, it was determined that a willow species would be planted in the 4 soil hotspots.

Tree Planting

Hybrid willow trees (Prairie Cascade) were planted in the four hotspots during the week of May 13, 1996. The trees were planted roughly at a spacing of 8 feet (2.4 m), with a total of 300 trees planted. Trees in hotspot 2 following planting are presented in Figure 4.

Trees were planted using *TreeMediation*^{TM}, a proprietary process developed by ANS which focuses rooting activity and rhizosphere development in the zone of contamination. Site visits were made periodically through the summer months of 1996 to monitor the growth of the trees. Precipitation amounts were monitored in the area, however, unusually heavy precipitation during Summer and Fall 1996 precluded the need for supplemental watering.

Tissue Analysis

Plant tissue samples were collected from trees in the four horspots during October 1996 to determine the necessity and nature of a fertilizer program. "Yellowing" of leaves was noted in a porrion of the trees in Hotspot 1 and insect damage was apparent in several of the trees, particularly within Hotspot 3. Nitrogen, phosphorous and potassium (primary nutrients) were found at concentrations comparable to reported concentrations in leaves of orange, almond and apple (trees with commonly reported leaf nutrient content). However, samples collected from leaves that exhibited "yellowing"
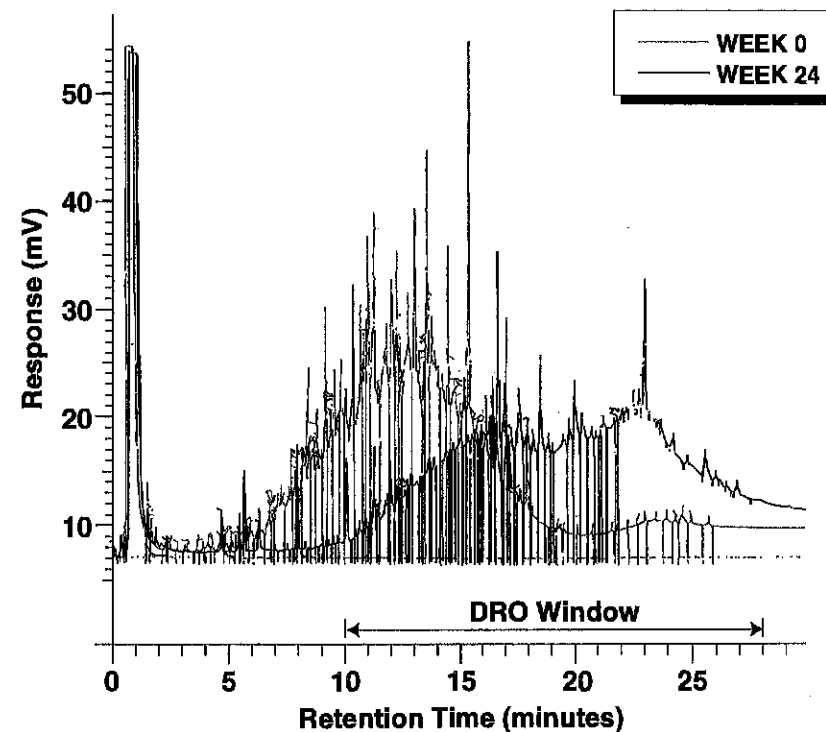
Figure 3   **Chromatograms of aliquots from GMTP4/4-5 collected at the beginning of the 24 week accelerated biovent test and at the end of the test. Note a shift to the right and a relative decrease in the magnitude of the peaks in the chromatograms**

Figure 4   Trees in hotspot 2 following May 1996 planting

contained lower concentrations of nitrogen than leaves that exhibited normal green color. Based on the results from tissue sampling, a fertilization program was implemented beginning in Fall, 1996. The program has consisted of surface applications of high nitrogen fertilizer in the rows between the trees during October 1996 and April 1997. Subsequent tissue analysis indicates that levels of primary nutrients in trees with leaves that had formerly "yellowed" has increased, and the number of trees with yellowing leaves has been greatly reduced. The fertilization program is expected to continue on a semi-annual basis. Insecticide was applied to the trees in April 1997 and appears to have substantially reduced the insect damage. A photograph of Hotspot 2 taken in September, 1997 is presented in Figure 5. Trees across the site grew an average of 5 feet to 6 feet in the first 16 months of the phytoremediation program.
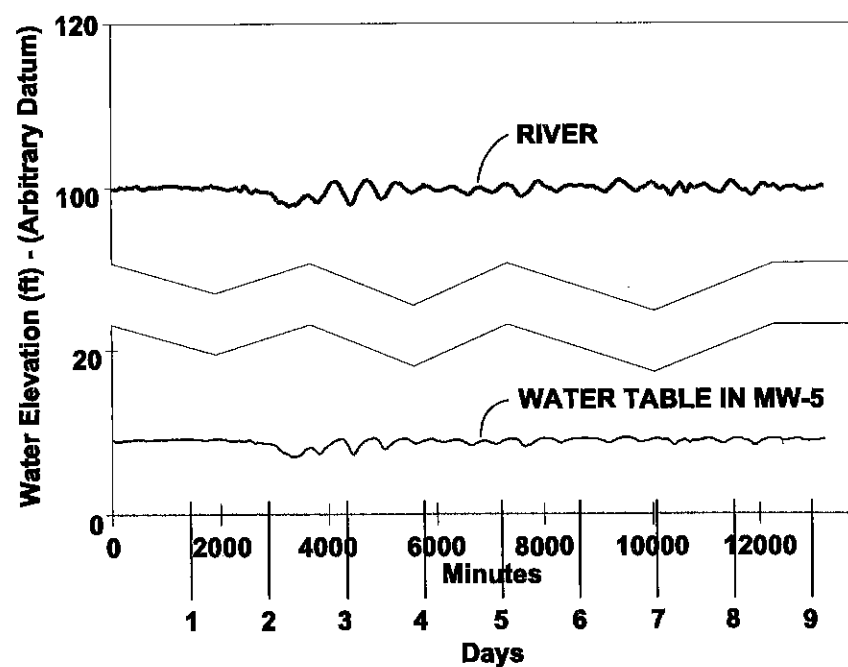
Trends in Water Levels

Water levels in a water table Monitoring Well MW-5 located in Hotspot 3 and water levels in the adjacent river were recorded during Spring 1997 to determine background trends in water levels. Water levels were measured and recorded in 10 minute increments during a 9 day period using pressure transducers installed in the well and the river. The measurement period occurred from April 30, 1997 to May 7, 1997 prior to leaves emerging during the Spring. The results from the water level measurements are presented as hydrographs in Figure 6. The depth to water ranged from approximately 9 to 10 feet in Monitoring Well MW-5 during the measurement period and the water table elevation in the monitoring well mirrors the river elevation. Future measurements in the river and selected monitoring wells will aid in determining the effect of the tree roots on the water table.

Future Activities

Plant tissue samples will be collected on an annual basis to monitor nutrient concentrations in the trees and to help evaluate the fertilization program. The fertilization program will continue on a semi-annual basis. Insecticide applications are expected to continue on an annual basis, as necessary. The water level monitoring program will continue on a semi-annual basis as the trees mature to monitor the effect of tree growth on shallow groundwater. Direct observations of root growth in one or more hotspots is scheduled for Fall, 1997. These direct observations will aid in determining the extent that roots penetrate downward and laterally across the hotspots. Soil DRO samples will be collected during Fall 1999 (3 years from planting) to monitor the progress of biodegradation within the rhizosphere of the trees.

Figure 5　**Trees in hotspot 2 in September 1997. Trees have grown an average of five feet to six feet in height during first sixteen months of the phytoremediation program**

Figure 6　**Trends in water elevation in monitoring well MW-5 and adjacent river from April 30, 1997 to May 7, 1997**

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CHAPTER 9

PHYTODEGRADATION OF PCP AND PAH CONTAMINATED SOIL USING PERENNIAL RYEGRASS

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INTRODUCTION

Phytoremediation is the use of plants for the in situ cleanup of contaminated soils, sediments, and water. The specific technology described in this chapter, phytodegradation, is the use of perennial ryegrass to remediate surface soils contaminated with organic chemical wastes. Some organic contaminants have been shown to be more rapidly removed in planted soils (rhizosphere) than in unplanted soils, including chlorinated solvents (Gordon), pesticides (Licht), and nitroaromatic explosives (Schnoor). Pentachlorophenol (PCP), and some polyaromatic hydrocarbons (PAHs) may biodegrade more rapidly in planted soils than in unplanted soils.

The ability of plants to enhance biodegradation seems to be based, in part, on plant root exudates. Plants release into the soil organic chemical exudates (sugars, acids, alcohols, and proteins) which can enhance biodegradation in the following ways: (1) the exudates stimulate soil microorganisms in the rhizosphere (the zone immediately surrounding the plant root) by serving as a food source. Rhizosphere soils contain 10 to 100 times more metabolically active microoganisms than unplanted soils; (2) exudates from the roots contain enzymes which can transform organic contaminants; (3) exudates can stimulate cometabolic transformations of contaminants by soil microorganisms.

Another important mechanism in phytoremediation may be that plants themselves can take up and detoxify certain organic contaminants in the course of normal plant metabolism. Phytokinetics' personnel have conducted laboratory-scale studies using crested wheatgrass (*Agropyron cristatum*). The fate of uniformly radiolabeled PCP, added to soil at a concentration of 100 milligrams per kilogram (mg/kg), was compared in three planted and three unplanted systems. Employing a specifically designed flow-through test system, a budget was maintained for the PCP-derived radiolabel, and the extent of mineralization and volatilization of the radiolabel was monitored during a 155-day test.

In the unplanted systems, an average of 88 percent of the total radiolabel remained in the soil, and only 6 percent was mineralized. In the planted systems, 33 percent of the radiolabel remained in the soil, 22 percent was mineralized, and 36 percent was associated with plant tissue.

Other tests using the same system were conducted with radiolabeled pyrene (initial concentrations of 100 mg/kg soil). The onset of mineralization occurred sooner in planted systems (mean = 45 days) than in unplanted systems (mean = 75 days). However, the extent of radiolabeled pyrene mineralization was the same in the two types of systems.

A non-remediative function of plants is to stabilize soils against erosion by wind and water. Grasses appear to be ideal for both phytoremediation and erosion control because their fibrous root systems form a continuous dense rhizosphere.

For phytoremediation to be effective, soil contaminants must be in the surficial soil, within the root zone of plants (top two to three feet), and must be present at non-phytotoxic levels. Although phytoremediation may be cost effective, especially for larger sites, it is slower than more intensive approaches (such as excavation or ex situ treatments) and may require several growing seasons.

The Site

This project was accepted into the Emerging Technology Program in 1995 for a two year greeenhouse and field trial. Under the Emerging Technology Program, Phytokinetics, Inc. (Phytokinetics), evaluated phytodegradation for surficial soils contaminated with PCP and PAHs from the McCormick & Baxter (M&B) Superfund site in Portland, Oregon.

The McCormick Baxter facility is a former wood treating plant. The facility produced treated wood products from 1944 until closure in the 1980s. The facility was closed in 1988 when the company filed for bankruptcy. During the operations creosote, pentachlorophenol (PCP), and solutions of arsenic, chromium, copper and zinc were used.

Located on the banks of the Willamette River, the site is surrounded by heavy industrial development. The future use of 40 acres of Portand riverfront property however, is possibly intended to be commercial, perhaps a public marina. Thus the risk receptors at the site are the River, the workers on the site, the neighbors, and the future patrons. The PCP treatment goal was tentatively set for 50 ppm. Initial core sampling indicated that the contaminants were concentrated in the top six inches of soil, with concentrations in samples from the 6-12 inch profile decreasing to less than 30% of the shallow soil.

Phase I

For the Phase I test, soil was collected on site in drums and shipped to the Logan greenhouses. After homogenization the soil was sampled and analyzed. The results showed a well mixed soil with concentrations of:

PCP average	162 ppm
Total PAHs average	298 ppm

The first phase, which began in March 1996, had the objectives of determining plant species for use in the field study, determining appropriate nutrient levels for the optimal conditions for plant growth, and predicting the rate and extent of degradation for the field study.

Two phototoxicity tests were conducted examining seed germination and root elongation of four grass species, perennial ryegrass, tall fescue, timothy and orchard grass. A test was conducted on uncontaminated soil and the contaminated soil from the site. The initial test subjects were determined from the literature and conversations with a Portland area agronomist. The plant specie with the best germination rate was perennial ryegrass (*Lolium perenne*).

The soil columns were planted and placed according to a randomized block design. Four treatments were established, each with eighteen replicates. The treatments were A) planted; B) unplanted nutriated; C) unplanted and unnutriated, and D) a second planted set. None of the treatments can be considered a pristine or undisturbed control, because the effect of excavating, shipping, mixing, and packing into columns had at least the effect of stimulating microbial activity through aeration. The greenhouse columns setup is shown in Figures 1 and 2.

Columns were sampled by removing the plants and soil from the column, then dividing the soil into top and bottom sections. Sampling occurred at 2, 6, and 11 months from planting. The results for PCP (Figure 3), show a quick decrease from the initial concentration of 162 ppm in the planted soil, to around 60 ppm by the 2 month sampling, and to below the 50 ppm target by the 6th month. There was no further decrease from the sixth to eleventh month. There was a slower decrease in the unplanted soil in the second and sixth month, but by the eleventh month the unplanted replicates were showing almost the same remediation as the planted treatments. The unplanted, unamended columns showed almost no decrease at the second month, and significant decrease in both the sixth and eleventh months. The concentrations of the planted at two months, the unplanted at six months, and the unamended at eleven months are similar and within the standard deviation of the treatments as shown in Figure 3.

The same pattern was noted in the low-ring PAH compounds, for example in pyrene, (Figure 4). The planted treatment decrease quickly, and the other treatments approach the same endpoint over time. The five and higher ring PAHs showed little change regardless of the treatment, as in benzo(a)pyrene (Figure 5).

Phase II

The second phase, which began in April 1996, took place at McCormick & Baxter. The field test phase consisted of two growing seasons. For both seasons, as in the green house study, contaminant removal rates were compared in planted and unplanted (nutriated) soils, as well as in unplanted unamended soils. The latter treatment was a

Figure 1   Phase I greenhouse study experimental set-up

Figure 2   Phase I greenhouse study experimental set-up
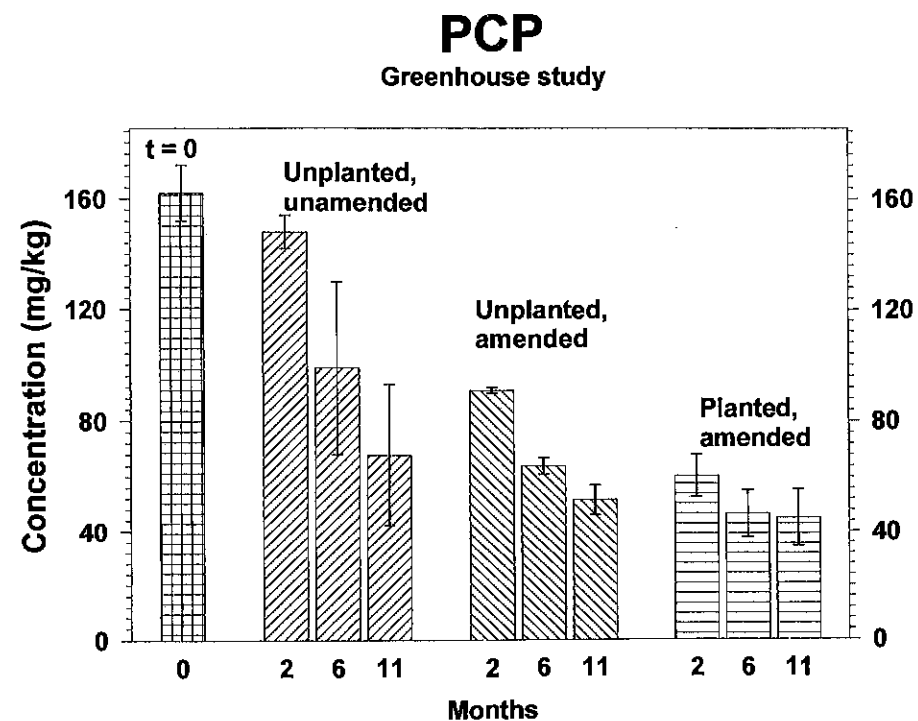

Figure 3   PCP concentrations in phase I greenhouse study with standard deviations
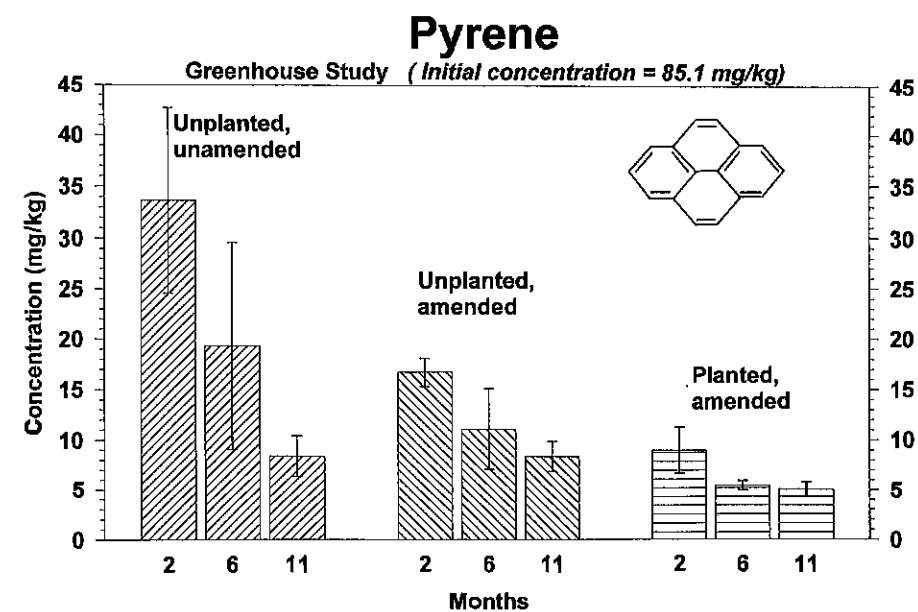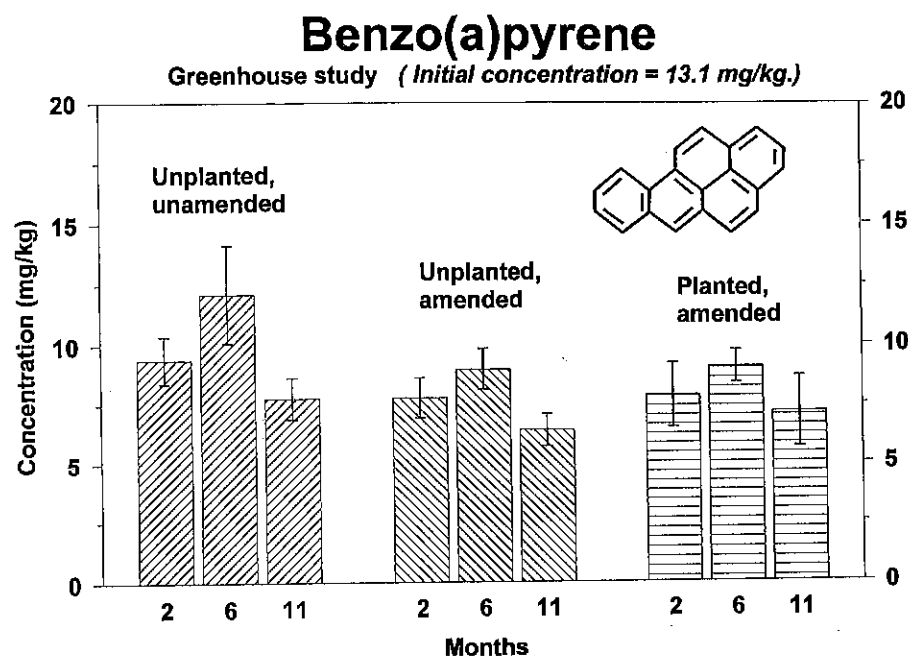

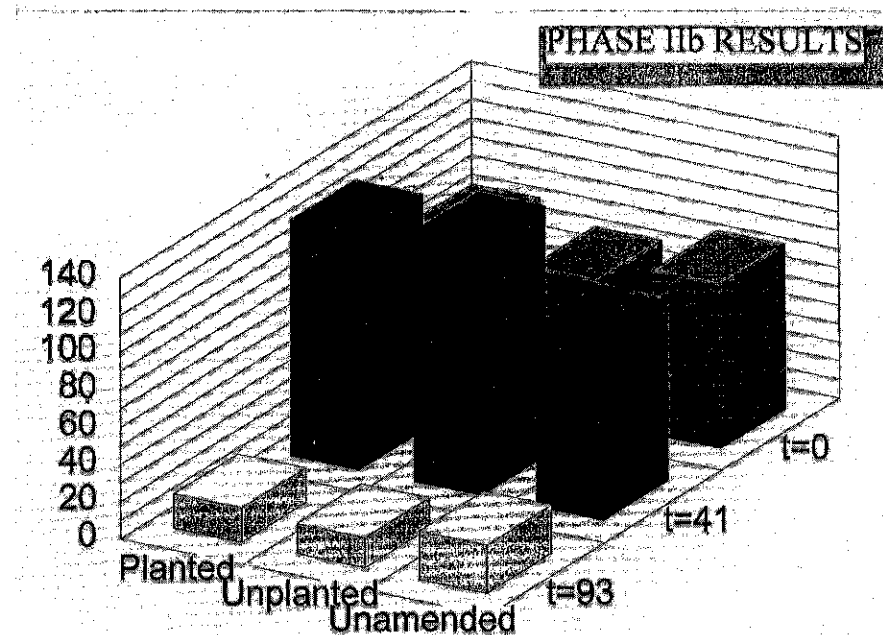**Figure 4   Pyrene concentrations in phase I greenhouse study**

Figure 5   **Benzo(a)pyrene concentrations in phase I green-house study**

true control in that nothing was done in the treatment plot except sample. This setup was intended to allow assessment of rates of phytodegradation, enhanced bioremediaiton (landfarming), and of natural (intrinsic) bioremediation.

In the first year the plots were established in an area almost devoid of vegetation. Baseline sampling in the area had discovered a highly variable media and contaminant mix, so the plots were arranged in what was hoped to be a reasonably homogenous contamination strata. Samples were only taken at two points during the growing season, at planting (t=0), and at the end of the season, seven months following planting. At the seventh month sampling both the planted and landfarming treatment plots showed marked decreases in concentrations relative to their starting points. Sampling variation made definite conclusions difficult, though the average concentrations for PCP were down below 50% of the initial concentration, and the PAHs of up to four rings showed similar decreases.

It was decided to move the treatment plots for the second year because the contaminants were degraded to the point where further changes would be difficult to quantify. The new plots were arranged as a randomized block with three treatments and four replications. Samples were taken more frequently, with four sample times during the growing seasons at 41 days, 90 days, 128 days, and 179 days. Samples were composited to try to bring down variability. Data was corrected for moisture content. Despite these efforts, the data variability was very high, with little to distinguish between the treatments, as indicated in Figure 6.

Figure 6   **PCP concentrations in phase IIb (second year) field study**

CONCLUSION

Phytodegradation of PCP and low-ring PAHs was accelerated as compared to conventional biodegradation in the greenhouse phase of this study. The contaminant endpoints in the soil at this site using this plant species on this contamination was similar regardless of treatment. Aeration, nutrient addition, and irrigation made contributions to the degradation of the contaminants.

Nutrient addition had a sufficiently large enough effect on biodegradation in the field study that there was no observable rhizosphere effect; that is there was no opportunity for the plants to enhance the microbial degradation as the microbes had sufficient resources without the plants.

The highly non-uniform distribution of analytes in the study area may have masked some effects of time and treatment. Soil moisture was also highly variable between treatment plots, with the planted plots being somewhat drier than the unvegetated area.

CHAPTER 10

TPH ANALYTICAL VERIFICATION PROTOCOL FOR MULTIPLE FIELD SITES

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INTRODUCTION

This chapter summarizes a research program supported by the Association of American Railroads (AAR) for the verification of an innovative analytical approach for quantifying carbon fractions which comprise Total Petroleum Hydrocarbons (TPH) in soil. A series of diesel-impacted soil samples were collected from four geographically diverse member company railroad sites for this program and subjected to extensive analysis and evaluation.

The focus of this research program is the innovative TPH method called the direct analysis approach that was developed by Shell Development Company. It provides information that can be used to establish risk-based cleanup goals for soil. Conventional TPH analytical methods do not provide information for risk characterization; instead, conventional methods yield results which can only be compared to unscientific numerical TPH standards, which may not reflect real environmental risk. A risk-based evaluation protocol developed by the Total Petroleum Hydrocarbon Criteria Working Group incorporates the results of the direct analysis approach and is described below in greater detail.

The results of this study offer strategic benefits and potential cost savings to railroad companies. The verification program for a scientifically defensible analytical method for diesel TPH can be incorporated into a risk-based approach for determining cleanup

goals. This will allow companies to focus remedial efforts on the reduction of real risks. There would be no real benefit to cleaning up soil at a site to a numerical standard of 100 ppm TPH, for example, if a risk-based analysis shows that adequate site-specific protection could be derived from a cleanup level of 1,500 ppm. Also, when a railroad company is faced with planning strategically for the management of multiple sites, a defensible risk-based approach would allow the company to focus first on sites that pose the greatest environmental risks.

The remainder of this introduction presents the goals of the TPH analytical method verification program, background information on the Total Petroleum Hydrocarbon Criteria Working Group protocols, and a summary of the benefits of this program for the railroad industry.

Goals of the TPH Verification Study

The goals of this research program are to:

- Verify the robustness of the direct analysis method for TPH in diesel-impacted soils, when applied to a variety of samples of different soil types, environmental settings, and contaminant histories
- Begin building a database of information on the characteristics of weathered diesel in soils, which will support the development of a cost-effective characterization program for risk-based applications
- Provide support for a risk-based approach for evaluating diesel releases at railroad sites, leading to more cost-effective cleanup programs

Many railroad companies are faced with the prospect of addressing environmental impacts at sites where groundwater and soil have been impacted by releases of diesel fuel, bunker C, and/or lube oil. Often the TPH cleanup requirements are quite low, and do not reflect a scientific approach to risk reduction. For example, the same TPH standard applied to gasoline releases may also be required for diesel releases, even though the fuels differ significantly in toxicological and environmental properties.

The AAR, as part of the Total Petroleum Hydrocarbon Criteria Working Group, has investigated strategies for developing risk-based soil cleanup levels at petroleum hydrocarbon sites as an alternative to regulatory numerical TPH criteria. In its research efforts, AAR has chosen to focus on the development of strategies relevant to diesel fuel, as this is the petroleum form of greatest interest to member companies.

While there is a growing acceptance and appreciation of risk-based cleanup approaches, many state regulatory agencies are skeptical about risk-based approaches for TPH sites, for a number of reasons:

- There is a need for a well-documented method for analyzing TPH so that the results can be used in a risk analysis.
- The comparability of new analytical methods with conventional TPH analyses needs to be verified and understood.

- The relationship between TPH risk calculations and agency-accepted calculations and toxicity parameters must be clearly communicated.

AAR continues to make progress in these areas, as indicated by the results of the research program summarized in this report. In its 1996 publication, *Risk-Based Determination of Soil Clean-Up Goals for Diesel-Contaminated Sites in the Railroad Industry,* AAR outlined the theoretical basis for risk-based derivation of clean-up goals for diesel-impacted soils. In its 1997 publication, *Comparison of Analytical Methods for Total Petroleum Hydrocarbons in Soil,* comparative laboratory results between candidate methods applicable to risk analysis and conventional TPH methods were presented, for replicates of a single soil sample from a railroad site.

One of the benefits of this research program is that railroad sites in four states and four diverse geographical areas have been evaluated. The ultimate goal of this process is to educate the regulatory community in each state that alternative approaches for TPH management will be protective of human health, and will result in real reductions of risk.

Background of the Total Petroleum Hydrocarbon Criteria Working Group Approach

AAR's research program used procedures established by the Total Petroleum Hydrocarbon Criteria Working Group (Working Group) as a starting point. This national consortium of representatives from government, industry, consulting, and academia has been active since 1993 in the development of scientifically based strategies for determining risk-based soil cleanup levels at petroleum hydrocarbon sites. The group recognizes that TPH is a gross measurement, which is applied to many different complex mixtures of petroleum hydrocarbons. TPH concentrations are not indicative of risks, because the same TPH concentration can have different composition and different risk. The group also recognizes that current risk evaluation approaches do not apply to complex petroleum hydrocarbon mixtures, measured as TPH.

During the past four years, the Working Group has formulated an approach for developing risk-based soil cleanup levels protective of human health at hydrocarbon-contaminated sites. In general terms, this approach evaluates the risk from TPH as a whole, as the sum of hydrocarbon fractions, as determined by:

- The chemical class of the hydrocarbon compounds (aliphatic or aromatic), and
- The carbon equivalent fraction, determined by the retention time on a gas chromatographic (GC) column relative to straight chain aliphatic compounds of known carbon number

The Working Group selected thirteen hydrocarbon fractions, as presented in table 1.

The hydrocarbon fractions were assigned toxicological and fate and transport characteristics, based on a review of available data for surrogate compounds, or for mixtures representative of the fractions. For this research effort, a total of sixteen fractions including the aliphatic fraction $>C_{21}$ to C_{35}, were determined analytically using the direct analysis procedure. This was a reflection of the specific compounds used in

TABLE 1   Total Petroleum Hydrocarbon Criteria Working Group — Carbon Equivalent[a] Aromatic and Aliphatic Fractions

Carbon Equivalent Aromatic Fractions	Carbon Equivalent Aliphatic Fractions
C_5 to $\leq C_7$ (Benzene)[b]	$C5$ to $\leq C_6$
$>C_7$ to $\leq C_8$ (Toluene)[c]	$>C_6$ to $\leq C_8$
$>C_8$ to $\leq C_{10}$	$>C_8$ to $\leq C_{10}$
$>C_{10}$ to $\leq C_{12}$	$>C_{10}$ to $\leq C_{12}$
$>C_{12}$ to $\leq C_{16}$	$>C_{12}$ to $\leq C_{16}$
$>C_{16}$ to $\leq C_{21}$	$>C_{16}$ to $\leq C_{21}$
$>C_{21}$ to $\leq C_{35}$	

[a]Carbon equivalent fractions are determined by the retention time on a GC column, relative to straight chain aliphatic compounds of known carbon number
[b]Benzene is the only aromatic compound in this fraction
[c]Toluene is the only aromatic compound in this fraction

calibration (i.e., benzene and toluene for aromatics, hexane and heptane for aliphatics).

There are currently no toxicological or fate and transport parameters available for the $>C_{21}$ to $\leq C_{35}$ aliphatic fraction. This fraction is equivalent to white mineral oil, and is believed to have low bioavailability, toxicity, and environmental mobility [MADEP, 1996; TPHCWG, 1997]. As a conservative approach for risk assessment purposes, the $>C_{21}$ to $\leq C_{35}$ aliphatic fraction is evaluated as $>C_{16}$ to $\leq C_{21}$.

The Working Group approach is applied within the framework of the American Society for Testing and Materials' (ASTM) Risk-based Corrective Action (RBCA) Specification E1739-95 [ASTM, 1995]. The RBCA framework integrates established risk and exposure assessment practices with remedial action selection. A tiered approach allows the decision-maker to weigh the cost of additional site-specific evaluations against the benefits of less conservative cleanup criteria at each tier. Key elements of the RBCA framework are source characteristics, exposure pathways, and receptors.

Risk-based screening levels, or RBSLs, are calculated during a screening level or Tier 1 RBCA analysis. Calculation of RBSLs for TPH differs from the typical RBCA approach because a chemical mixture, rather than a single chemical, is evaluated. First, potential carcinogenic effects are evaluated separately, since the presence of potential carcinogens in TPH would typically drive the cleanup analysis. For example, carcinogenic effects would be associated with benzene or certain polycyclic aromatic hydrocarbons (PAHs), if present. If potential carcinogens are not present, or are present below regulatory or risk-based levels, fate and transport information is combined with non-carcinogenic reference dose information and reference concentrations developed by the Working Group to establish RBSLs for individual hydrocarbon fractions. The individual fraction RBSLs are combined with site-specific mixture composition data to calculate mixture-specific "whole" TPH RBSLs.

Benefits of the TPH Analytical Verification Program to the Railroad Industry

The important elements of the TPH verification research program and the expected benefits to the railroad industry are summarized below and discussed in detail in the following sections:

- comparison of total petroleum hydrocarbon results determined by the direct analysis method to TPH results determined by conventional methods;

- evaluation of hydrocarbon fraction distribution, at a given site and from site to site;

- evaluation of differences in hydrocarbon distribution between surface and subsurface soil samples;

- comparison of leaching results using synthetic precipitation leaching procedure (SPLP) with predicted values using Working Group fate and transport parameters; and

- development of a sampling and analysis strategy for risk-based evaluation of diesel-impacted railroad sites.

Comparison of Direct Analysis Method TPH to Results Determined by Conventional Methods

These comparisons provide additional data on the suitability and applicability of the direct analysis TPH method, as a substitute for conventional TPH analytical methods currently required by state regulatory agencies. Documented correlations between the direct analysis method and conventional methods will provide regulatory agencies with the information they need to accept the use of the direct method with hydrocarbon fractionation for risk analysis. At the same time, the less expensive first part of the direct analysis method for TPH can be substituted for conventional methods to define the extent of diesel contamination at a given site. This will preclude the requirement to use the direct analysis method and conventional methods in parallel for every sample at a site, and ultimately will result in lower analytical costs for railroad companies.

Evaluation of Hydrocarbon Fraction Distributions within Sites and from Site to Site

The potential value of this research element is high, in that under the Working Group approach, the risk associated with a petroleum hydrocarbon is closely tied to its fraction distribution. Before this study was completed, the degree of consistency of hydrocarbon fraction distribution for weathered diesel fuel had not been documented for multiple sites. The results of this study indicate that the hydrocarbon fraction distribution in aged diesel is relatively consistent from site to site. An understanding of the fraction distribution variability will help to determine the number of samples needed for a typical RBCA analysis at railroad diesel sites. This will give railroad companies a better understanding of the number of samples needed to characterize diesel contamination, and thus an improved estimate of the sampling and analytical costs at a site.

Hydrocarbon Distribution Comparison for Surface and Subsurface Soil Samples

The ASTM method evaluates different exposure pathways for surface soil contamination (0 to 3 feet) and for subsurface contamination (>3 feet in depth). Results indicate that, in general, there is not a significant difference in hydrocarbon distributions between surface and subsurface soil samples. This determination will be useful in the design of future sampling programs for risk analysis. The results indicate that surface samples may be sufficient for characterizing the distribution of petroleum compounds for risk analyses for sites without groundwater contamination. This could reduce the number of samples analyzed by fractions and limit the sampling effort to quick and inexpensive hand augering.

Comparison of Leaching Results Using SPLP and Predicted Values

By comparing actual leaching results with those predicted using fate and transport parameters selected by the Working Group, there is a potential to define lower risks for a site than theoretical transport parameters would normally indicate. This evaluation indicates that actual leaching results yield a lower leaching factor, and thus a higher, less conservative RBSL. This information will help an environmental manager to decide whether the additional expense of SPLP analyses is justified. Furthermore, in some cases, actual test results have better acceptance by regulators than application of calculated transport parameters in risk models.

Sample Collection and Analysis Strategies

This research program will lead to the development of a sampling and analysis strategy that can be applied to diesel-impacted railroad sites in general by a variety of contractors. This includes sample collection equipment and collection protocols; sample depths (i.e., surface and subsurface); numbers and locations of samples to be collected; factors affecting decision-making processes in the field; numbers and types of analyses to be performed; and types of evaluations to be made in reviewing analytical results. Consistency in a RBCA sampling and analytical approach for railroad sites will help to build a reliable database on diesel contamination, and further regulatory acceptance of the data.

Benefits Summary

In summary, the benefits of the TPH analytical protocol verification study are:

- Development of information which can be distributed to the United States Environmental Protection Agency (USEPA) and state regulators to facilitate the acceptance of RBCA in general, and the use of a risk-based approach for diesel fuel in particular.
- Reduction of and/or improvement in the estimation of sampling and analytical costs for railroads, by establishing a methodology for deriving the appropriate data for RBCA analyses.
- Use of risk-based approaches to reduce cleanup costs and associated liability reserves.

FIELD SAMPLE COLLECTION PROGRAM

Soil samples were collected from four railroad facilities located in the following areas of the United States:

- Southeastern rail yard;
- North-Central rail yard;
- Midwestern rail yard; and
- West Coast derailment site

The general procedures used to select soil sampling locations and collect samples are described below. The remaining sections summarize diesel fuel usage, site conditions, and sample collection strategies at the individual sites.

General Procedures

Before sample collection began at each site, site personnel were consulted to obtain information on the history, layout of previous structures, and activities associated with diesel handling. Surface soils were examined for indications of previous spills or releases. The goal was to obtain samples from areas known or suspected to have been impacted by diesel fuel in the past, but where there were no longer active releases of diesel. Areas were avoided where other types of hydrocarbons, such as gasoline or lubricants, were known to have been managed. Generally, sampling locations were downgradient of fuel storage or fueling areas.

The field sampling team was prepared to collect soil samples with either a hand auger, or, if conditions were not suitable for hand augering, with a mechanically driven device called the PreSIT^sm system, which is fitted with 1-inch split spoons for sample collection. At all four sites, conditions were suitable for hand augering. This method of sampling was used because it yielded a larger sample volume.

The hand auger was advanced to the top of the water table, or to a maximum depth of six feet below the ground surface. At three of the four sites, two composite samples were collected from each boring, a surface soil sample (composited from ground surface to a maximum depth of three feet below ground surface) and an unsaturated zone subsurface soil sample (composited from below the surface soil interval to a maximum depth of six feet below ground surface). The groundwater table was extremely shallow at the West Coast derailment site, and only one composite surface soil sample was collected from each boring. No samples were collected below the water table. One background sample location, unimpacted by diesel fuel but of a similar soil type, was selected at each location. Samples for matrix spikes were also collected from these background samples. Upon completion of sample collection, each soil boring was backfilled with bentonite pellets and hydrated with potable water, or abandoned according to the direction of site personnel. The hand auger was decontaminated between boring locations with isopropyl alcohol and deionized water.

In addition to samples collected for standard analyses, two samples per site, one surface and one subsurface, were collected from each site for determination of pH and grain size, and one subsurface sample per site was collected for permeability testing. The samples collected for these physical parameters were representative of observed conditions in all site samples. A geotechnical laboratory provided a specialized 6-inch

sampling tube for collection of the subsurface sample for permeability testing. First, a shovel was used to dig down to the desired depth, and then the sample collection tube was driven down six inches to collect the sample. Finally, the tube was retrieved without disturbing the collected soil.

Soils from each sampling zone were logged, composited in a clean contaiuer, and placed into appropriate sampling containers for shipment to the laboratory. Packing and shipping of samples followed standard procedures provided in the field sampling and analysis plan, to minimize sample container breakage, leakage, or cross contamination, and to provide a cleat record of sample custody from collection to analysis. These procedures include proper labeling, completing a chain of custody, packing the containers individually with protective material to prevent breakage, and using ice as a preservative. Sample shipment occurred via an overnight express service that guaranteed 24-hour delivery.

Southeastern Rail Yard Site

This site currently operates as a rail car maintenance facility. In past years it was used for diesel fuel storage and fueling of locomotives.

Summary of Diesel Fuel Usage

Fixed fueling and fuel storage at this site reportedly ceased in 1990, although fneling of vehicles continues. Diesel storage and fueling structures for locomotives have been removed from the site. Diesel fuel was handled in two areas. There was a bulk storage area, which included a 500,000-gallon aboveground bulk storage tank located on a concrete pad within a retaining wall, piping, pumping facilities, and an unloading station. There was also a locomotive refueling area located approximately 700 feet from the bulk storage area, with a fueling apron and tracks, fueling racks, piping, and other equipment. Free product zones have been identified on top of the groundwater table underlying both the bulk storage and refueling areas. Subsurface product recovery from the top of the water table and other remedial actions are ongoing at the site, although not in the former bulk storage area, according to site personnel.

Site Conditions

Only the concrete containment for the storage tank remains at the former bulk storage area, as all other materials have been demolished and disposed offsite. The site is relatively level, with a drainage ditch located to the north of the former bulk fueling atea. Drainage in the area of sample collection appears to be mainly through percolation. Soils encountered consisted of fine, medium, and coarse sands, cinder fragments, wood debris from rail ties, and roots. The water table was encountered at approximately three feet below the ground surface. Grouudwater reportedly may rise to within one to two feet of the ground surface during wet summer months or following storms.

Sample Collection

Samples were collected in the former bulk storage area rather than the former refueling area because conditions in this area were most representative of aged diesel impacts. Currently there are material storage and equipment maintenance activities in

the former refueling area, and the potential exists for hydrocarbon impacts unrelated to diesel fuel. Eight sample borings were advanced. Eight borings were in the undisturbed area south of the old dike as shown on Fignre 1. A backgronnd sample, not shown on Figure 1 was collected from the eastern property boundary, approximately three-quarters of a mile east of the stndy area, in an area unimpacted by fuel handling activities. One surface and one subsurface soil sample were collected at each boring location. Because the water table was very shallow, encountered ar approximately three feet below the ground surface, surface soil samples were all collected from 0 to 1.5 feet, and unsaturated zone subsurface soil samples were collected from 1.5 to 3 feet. Samples
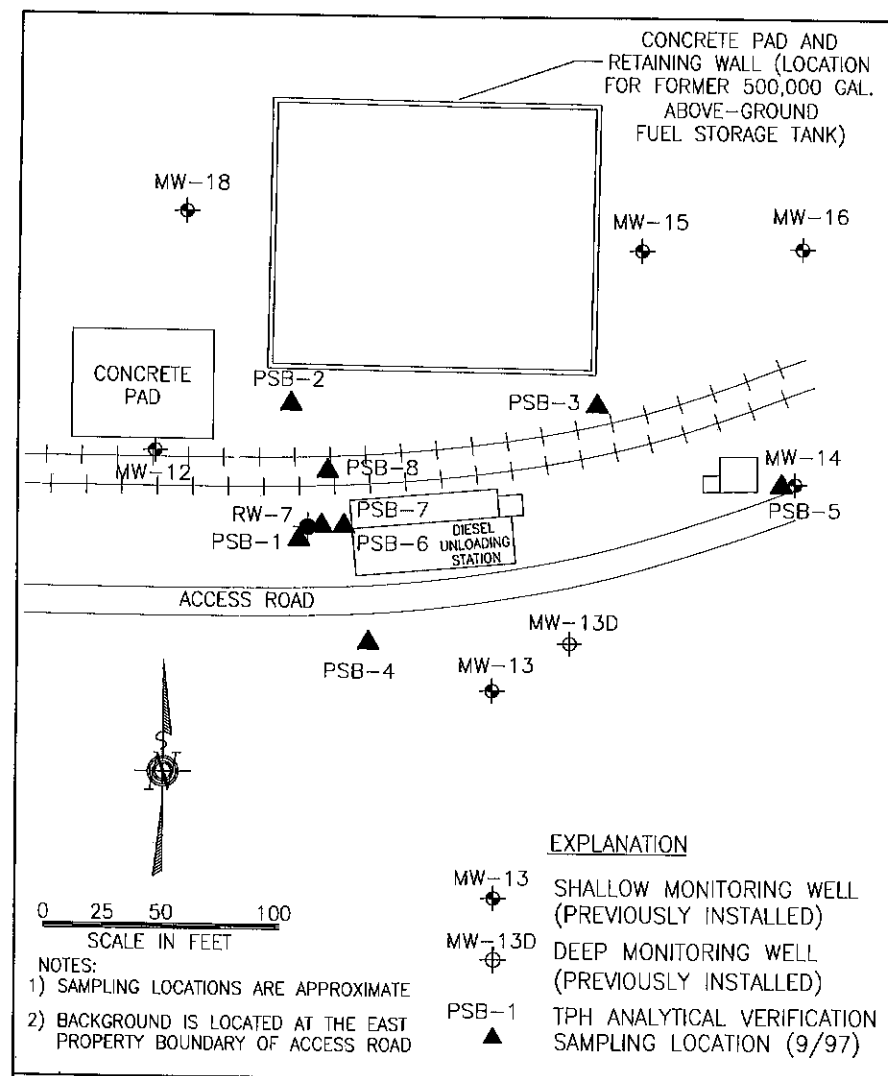
Figure 1   TPH Investigation Area — Southeastern Rail Yard

were collected in areas where previous investigations had indicated elevated organic vapor concentrations. No organic vapor analyzer was available at this site to confirm earlier findings. All sample locations except for the background location indicated visual staining or hydrocarbon odor, ranging from slight to strong.

North-Central Rail Yard Site

This site is currently an active rail yard, although it is no longer operating as a fueling facility. This site has been in use as a rail yard facility since the steam locomotive days.

Summary of Diesel Fuel Usage

Fueling operations were formerly conducted in the area of the locomotive roundhouse and turntable. In 1973, fuel seepage into a nearby river downgradient of the fueling area was noted, and the railroad took action to abate the seepage. Free product recovery and abatement equipment was installed, including a fueling pad, control wells, piping, and storage tanks. Since abatement activities were initiated, more than 150,000 gallons of fuel have been recovered from the subsurface. Fueling activities ceased in 1984, and the roundhouse, turntable, and other structures related to fueling have been demolished. An enhanced product recovery system was installed in 1997, which utilizes a recovery trench downgradient of the fueling area.

Site Conditions

This rail yard site is covered with cinder fill. Site personnel explained that the cinders were generated from cleaning the coal-burning steam locomotives. Subsurface soil was comprised of a mixture of sand, typically coarse, and cinders. The apparent surface water drainage pattern is from the former fueling area, across the investigation area, and toward a nearby river. At a nearby monitoring well, the depth to groundwater was observed to be approximately 11 feet below ground surface. Free product was noted on top of the groundwater.

Sample Collection

The general location of the investigation area is indicated in Figure 2. Eight borings were installed within the investigation area, in an area between the former fueling area and a product recovery trench near the river. This investigation area was selected because it was likely to contain diesel-impacted soils, but was some distance away from the former fueling area and zones of free product. Also, the area was sufficiently removed from active rail lines for safe working conditions. A background soil sample was collected at the northern end of the rail yard facility, several hundred feet from the former fueling area. The background sample consisted of sand with some cinders. All borings were installed to six feet below ground surface. In each boring, a surface soil sample was collected from the 0 to 3-foot interval, and an unsaturated zone subsurface soil sample was collected from the 3 to 6-foot interval. Varying degrees of hydrocarbon odor and staining were observed at all boring locations except the background location. All samples collected in the field were field screened for organic vapors using a photoionization detector (PID). All samples, including the background samples, yielded readings ranging from 64 to 125 ppm.

Midwestern Rail Yard Site

This site is currently used for switching rail cars. In years past, it was also used to fuel locomotives and as a trailer-on-flat-car (TOFC) facility.

Summary of Diesel Fuel Usage

Fueling and fuel storage at this site was discontinued in 1988. The above ground diesel fuel storage tanks were removed and the fueling racks were decommissioned in 1994. A pump house and a roundhouse have also been removed. This site has undergone various phases of environmental investigation but no remediation activities have occurred at the site.
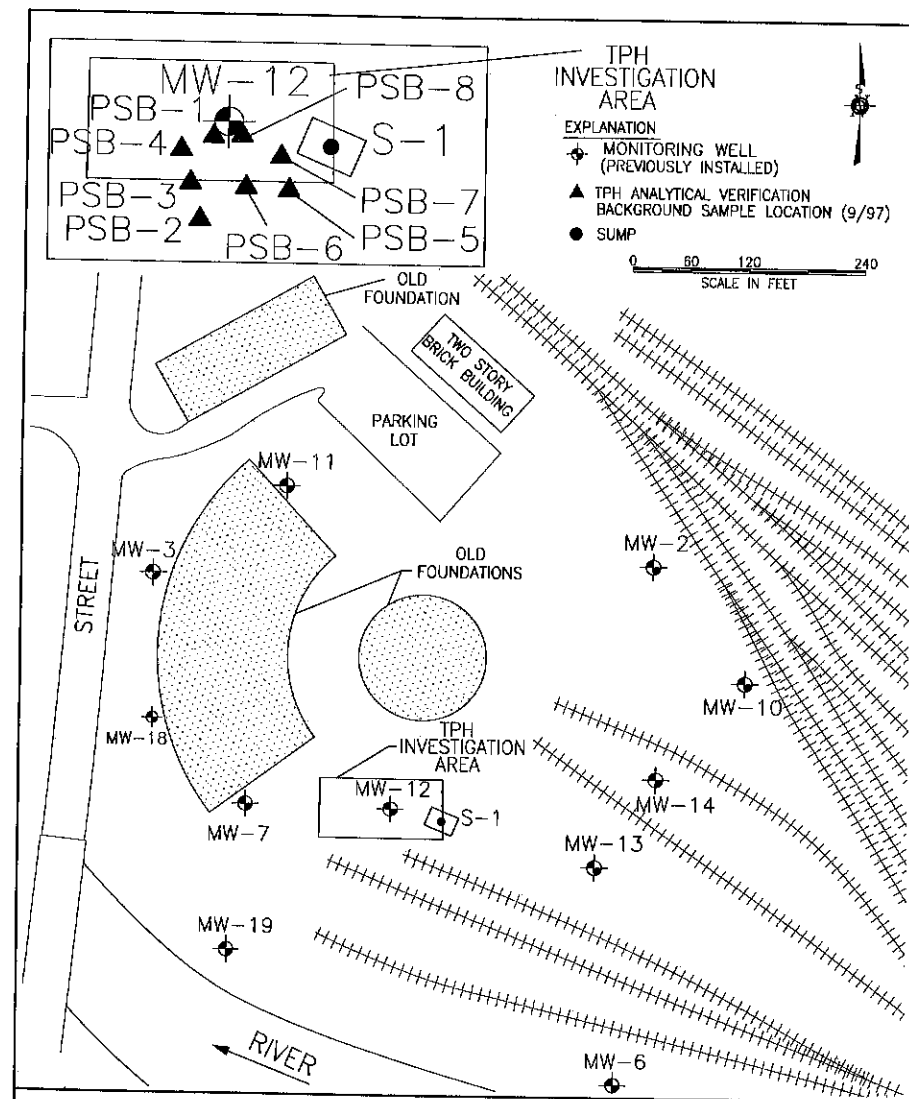

Figure 2   TPH Investigation Area — North Central Rail Yard

Site Conditions

Structures have been removed in the area of investigation and the site graded with native soils. The ground surface is generally flat, with no obvious pattern of surface water runoff, and is sparsely vegetated. Soils encountered were medium sands, with a limited amount of gravel fill in the upper inches in some locations. The groundwater table was below six feet, the maximum sampling depth; the depth to groundwater is reportedly 9 to 10 feet, with groundwater flow toward a nearby river.

Sample Collection

The area selected for soil sampling, with a detail of sample locations, is provided in Figure 3. Eight borings were completed within this area, with the selection of locations based on previous sampling results which had indicated TPH impacts. A background soil sample was collected approximately one-half mile northeast of the sampling area, in a location unaffected by runoff from the fueling area. All borings were completed with a hand auger to a depth of six feet, with a surface soil sample (0 to 3 feet below ground surface) and a subsurface soil sample (3 to 6 feet below ground surface) collected from each boring. Hydrocarbon impacts were noted in each of the borings completed within the investigation area, as indicated by varying amounts of odor and staining. A PID was used to screen samples in the field; readings were observed to be very low, that is, less than 10 ppm.

West Coast Derailment Site

The West Coast site, unlike the other three sites, is not a former fueling facility. Instead, it is a site where a locomotive derailed in 1993, spilling diesel fuel onto the track and drainage ditch.

Summary of Site Conditions and Diesel Fuel Release

In November 1993, a locomotive derailed on a spur line located near a marine bay on the West Coast. The locomotive fuel tank was ruptured and approximately 3,000 gallons of diesel fuel were released. The fuel flowed into a shallow swale on the western side of the track, to a storm drain at the lowest point in the swale, and into slough, or swampy area. Emergency response efforts contained and removed much of the fuel. However, an estimated 800 gallons of diesel fuel infiltrated into the soils and were not recovered during cleanup operations. Subsequently, investigation activities were conducted to assess the magnitude and extent of diesel contamination.

A concrete and asphalt driveway was installed across the track and on top of the derailment area three years after the spill occurred. This driveway provides vehicle access to a private company. Soils within the area sampled ranged from silty sand and clayey silt to silty clay, with rock fragments (ballast), wood, and brick in some locations. The water table was found to be shallow, between two to three feet below the ground surface.

Sample Collection

Ten soil borings were installed in the derailment area, as indicated on Figure 4. However, samples were collected for analysis at only seven of the locations. Samples

were not analyzed from borings PSB-4, PSB-6, and PSB-7 because there were no visual indications of diesel impacts, and the soils appeared to contain clean fill. One background boring was installed and sampled approximately 200 feet north of the derailment location, on the west side of the tracks, and on the north edge of the gravel driveway. The boring locations within the known fuel release area were selected based upon accessibility, and concentrations of fuel constituents found in soils during
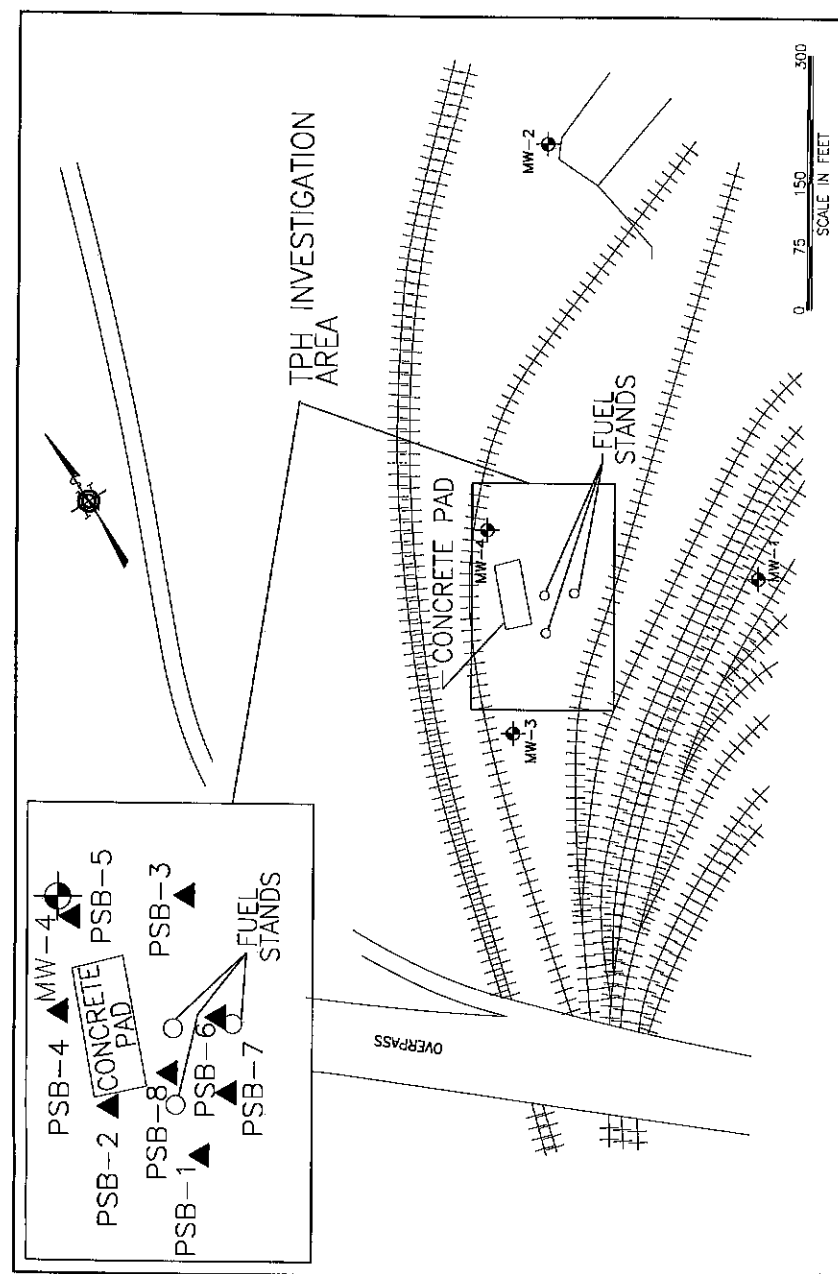

Figure 3   TPH Investigation Area — Midwestern Rail Yard

previous investigations. The asphalt and concrete paving which had been installed over the area after the derailment complicated access to potentially impacted areas. All borings were installed to the top of the groundwater table, ranging from two to three feet below the ground surface. Because of the shallow depth of the borings and the high water table, only one composite sample was collected from each boring sampled. Soils observed during the boring and sampling process did not appear to be impacted by hydrocarbons. There was no staining observed, and only boring (PSB-1) indicated a slight hydrocarbon odor.

ANALYTICAL APPROACHES

This section presents the research and conventional analytical procedures used in this program, and the information gained from the various analyses. The selection of certain samples for specified analyses is described.

Direct Analysis Procedures for TPH

The direct analysis procedure, developed by the Shell Development Company [AAR, 1996], is a gas chromatographic (GC) procedure for determining the overall hydrocarbon profile of a petroleum mixture. The method separates the total petroleum hydrocarbons between C_5 and C_{35} (TPH) into aliphatic and aromatic components, and into thirteen fractions.

The direct analysis procedure is presented schematically in Figure 5. As part of this procedure, three individual analyses are performed. The steps in the analyses, and the information derived from TPH analyses without fractionation and with fractionation into aliphatic and aromatic compounds, are discussed below.

Direct Analysis without Fractionation

For this study, representative 20-gram portions of soil were first extracted into n-pentane to remove the hydrocarbon from the soil. A portion of the n-pentane extract was then injected onto the GC column for separation of the individual components according to boiling point. The analytical system was calibrated with a series of n-alkane markers ranging from C_8 (n-octane) to C_{35} (n-pentatriacontane). This initial analysis allows for the determination of the carbon distribution of the hydrocarbon material present in the soil sample. Figure 6 shows a typical chromatographic profile for diesel fuel [AAR, 1996]. This material shows a distinctive hydrocarbon distribution pattern, which allows for the determination of the type of material present.

Diesel fuel is produced from the distillation of crude oil. It is comprised of a complex mixture of aliphatic and aromatic hydrocarbons with lesser amounts of heavier hyproducts. In a fresh diesel fuel, the primary constituents are normal (straight chain) alkanes. This contributes to high cetane ratings in the fuel, for a high quality, better burning fuel. The hydrocarbon range will vary slightly with each manufacturer, but diesel fuel consists primarily of hydrocarbons in the C_9 to C_{25} range with the most predominant components in the C_{14} to C_{17} range.

As the diesel fuel weathers, the n-alkanes are eventually lost due to environmental and biological processes. In a weathered diesel fuel, branched-chain and cyclic hydrocarbons begin to dominate. The sharp peaks of the chromatogram disappear and typically a broad "hump" is produced. This is a result of the inability of the GC column to

separate the numerous isomeric compounds that coelute under the analytical conditions.

A careful examination of the chromatograms from the initial n-pentane extract of the soils can provide information on the total hydrocarbon distribution, the type of material present, and a general evaluation of the weathering of the material. This procedure was performed on all soil samples collected, including background samples.
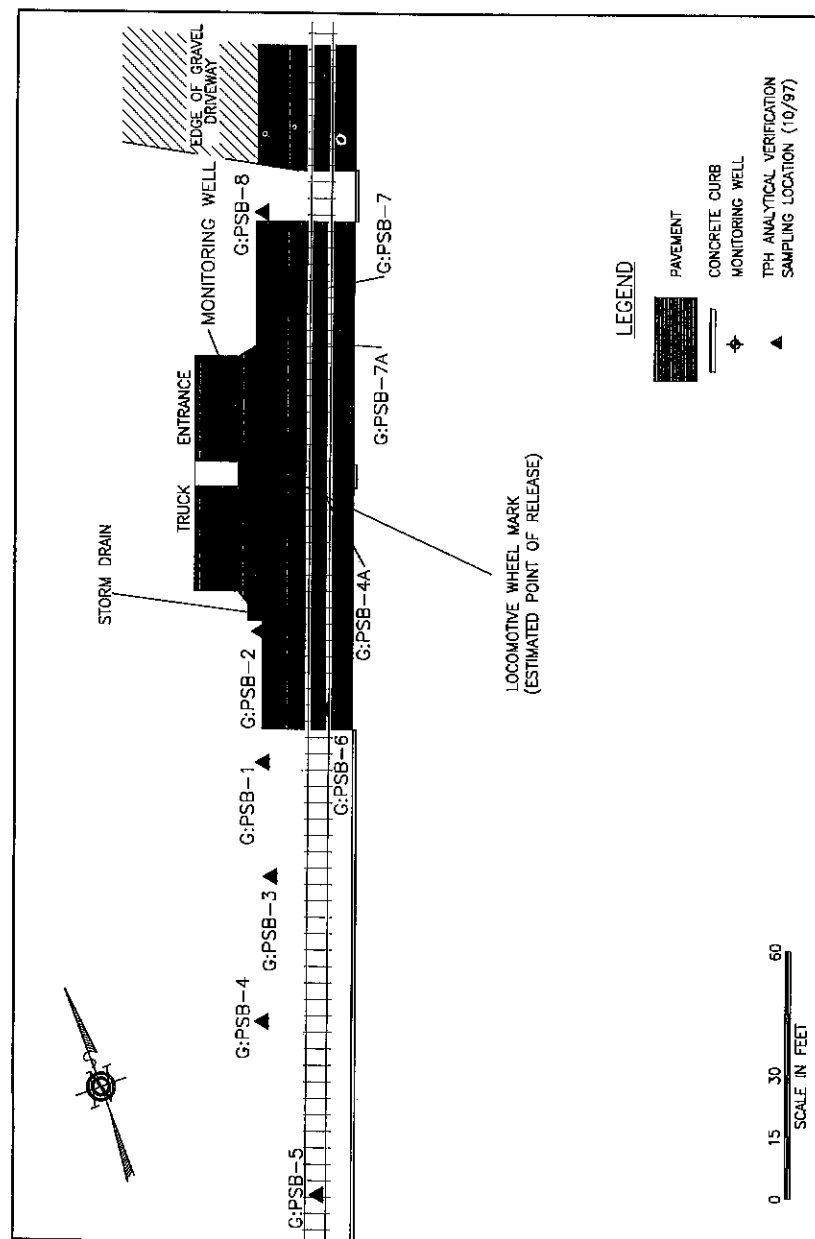

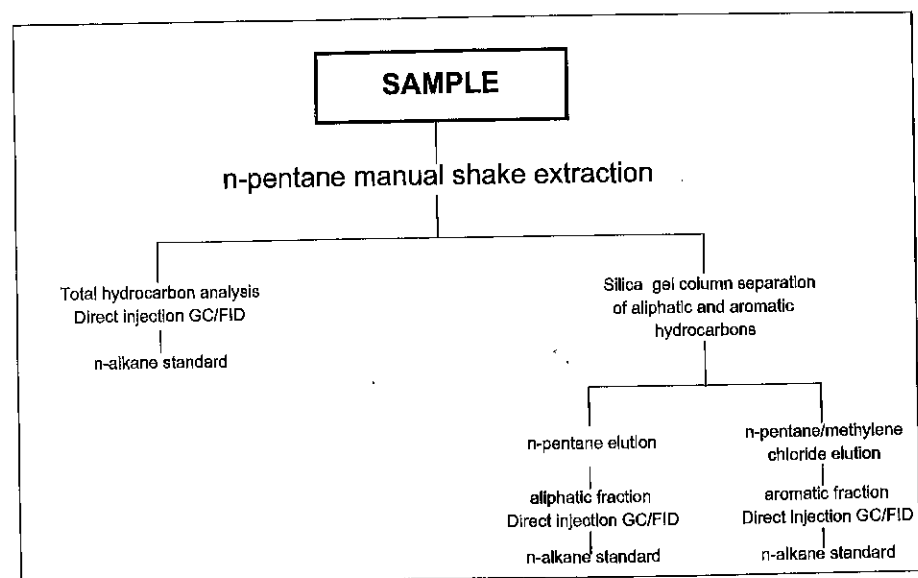**Figure 4   TPH Investigation Program Sample Location — West Coast Derailment Site**

Figure 5   Direct Analysis Scheme — C$_8$ to C$_{35}$

Direct Analysis Procedure for TPH Following Fractionation

After the initial analysis was performed, an additional portion of the n-pentane extract was separated into aliphatic and aromatic fractions using silica gel column chromatography. The extracts were transferred to the silica gel column. The aliphatic hydrocarbons were eluted from the column using n-pentane. The n-pentane eluates were then analyzed using the same GC conditions used for the initial n-pentane extract. The silica gel column was next eluted with n-pentane/methylene chloride (2:1 v/v). This eluate contains the aromatic hydrocarbon fraction. A third GC analysis was then performed to determine the carbon ranges for the aromatic hydrocarbons.

The data obtained from these GC analyses are for the application of the Working Group approach for determining risk-based soil cleanup levels at petroleum hydrocarbon sites. Data were calculated for the hydrocarbon fractions in the C$_8$ to C$_{35}$ range. This information was calculated for all soil samples collected, including background samples.

Fraction Analysis for the C$_6$ and C$_7$ Ranges

The data for the C$_6$ and C$_7$ hydrocarbon ranges were determined using a purge-and-trap GC coupled with a mass spectrometer (MS) according to USEPA method 8260A [USEPA, 1994]. This procedure was used for two reasons. A single run GC analysis for all components involved in the Working Group methodology must be able to adequately resolve hydrocarbon constituents across a wide boiling point range (69°C - 490°C). This results in long chromatographic run times in order to separate the constituents. Special techniques, such as cryogenic cooling, decreased temperature ramp rates, and the use of wider diameter capillary GC columns are necessary to allow
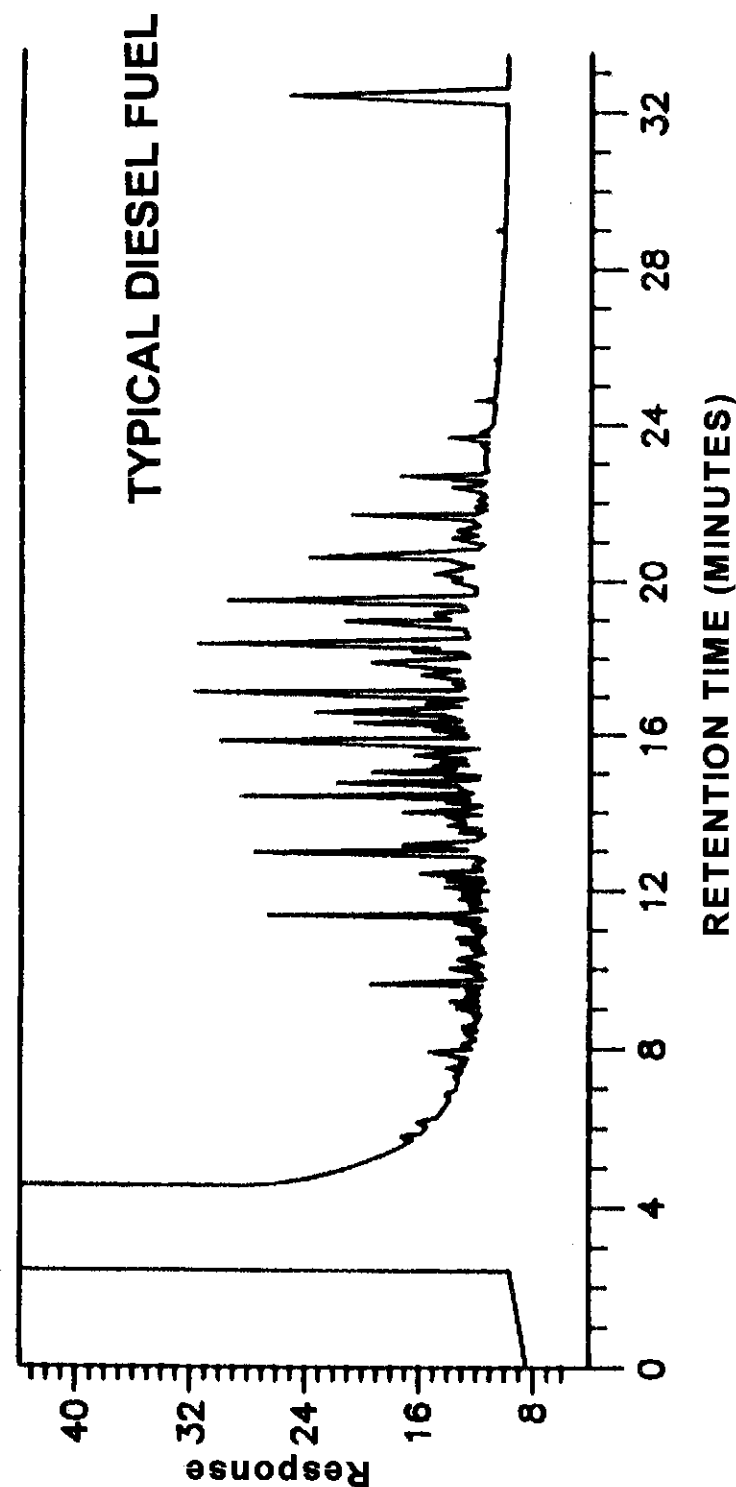
**Figure 6   Typical Chromatographic Profile of Diesel Fuel**

for separation of the individual hydrocarbons of higher molecular weight. However, this makes it more difficult to resolve the C_6 hydrocarbon from the solvent (C_5) peak. Starting the run at C_8 shortens the analysis time and eliminates the need for cryogenics in the analysis.

The second, and primary reason for using the GC/MS procedure for the C_6 and C_7 ranges, is the significant effect that benzene (C_6 aromatic) plays in risk calculations. The use of the GC/MS procedure allows benzene to be determined at the 5-25 μg/kg (ppb) level, whereas the direct analysis procedure is sensitive to approximately 5 mg/kg (ppm), a detection range which may not be suitable in some regulatory applications.

The USEPA method 8260A analysis was performed for all samples, including background samples. Individual analyses were performed for n-hexane, n-heptane, benzene and toluene to represent target constituents for the C_6 and C_7 fractions.

Total Organic Carbon

The total organic carbon (TOC) content of each of the site soils, with the exception of the background samples, was determined using the dichromate method developed by SECOR Geochemistry [SECOR, 1997]. Organic material in the soil sample is oxidized to carbon dioxide by dichromate under acidic conditions:

$$Cr_2O_7^{2-} + 3C + 16H^+ \rightarrow 4Cr^{3+} + 3CO_2 + 8H_2O \qquad (1)$$
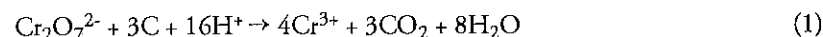
The Cr^{3+} produces a blue/green color, which is measured colorimetrically using a spectrophotometer. The amount of Cr^{3+} determined is used to calculate the amount of organic carbon using the stoichiometry given in Equation 1.

This analysis was used to determine if a correlation between TOC content and the TPH content of the site soils could be determined.

Total Petroleum Hydrocarbons by Conventional Methodologies

All site soils, with the exception of the background samples, were analyzed using two conventional TPH analytical techniques, the American Petroleum Institute (API) GC method for diesel range organics (DRO) [API, 1993] and USEPA method 418.1 [USEPA, 1983], which is an infrared (IR) spectroscopic technique.

The TPH method developed by the API uses methylene chloride to extract the hydrocarbon from the soil sample. The methylene chloride extract is injected onto a GC column where separation of the individual constituents occurs. DROs are defined as having a boiling point between 170°C and 430°C and an alkane range of C_{10} and C_{28}.

The USEPA procedure is based upon the principle that carbon-hydrogen bonds absorb infrared light in the vicinity of 2930 cm^{-1} (3.4μm). To perform the analysis, the organic materials in the sample are removed by a solvent extraction using 1,1,2-trichloro-1,2,2-trifluoroethane (Freon-113). Freon-113 does not contain carbon hydrogen bonds, and therefore does not produce IR absorptions that would interfere in the analysis. Because the Freon-113 extracts other nonpetroleum hydrocarbon material, silica gel is added to the extract. The silica gel is used to adsorb polar organic compounds such as animal fats and other nonpetroleum hydrocarbons. The IR spectrometer is calibrated with a synthetic standard containing 37.5% hexadecane, 37.5% isooctane, and 25%

benzene. The IR absorption of the sample extract is then compared with that of the calibration standard to obtain a TPH value. This result is then used to calculate the amount of TPH in the original sample.

These conventional TPH analytical approaches were used in addition to the direct analysis procedure, so that there would be a basis of comparison. A previous AAR study [AAR, 1997] indicated that there was relatively good correlation between the conventional TPH analytical methods and the direct analysis method for diesel fuel. It was postulated that there would be a good correlation between the three analytical methods for the diesel-impacted study sites. Differences could occur if a site were to contain a large amount of heavy (>C_{28}) or light (<C_{10}) hydrocarbons. If the results were as expected, data obtained from a diesel fuel site previously characterized by one of the two conventional procedures could still be of use to the risk assessment. The complete direct analysis procedure could be applied to a few selected samples from the site to obtain the proportions of aliphatic and aromatic compounds. These proportions could then be applied to the previous results, saving time and money in extensive resampling efforts.

Polynuclear Aromatic Hydrocarbons by GC/MS/SIM

As is the case with benzene, the presence of certain polynuclear aromatic hydrocarbons (PAHs), particularly benzo(a)pyrene and dibenzo(a,h)anthracene, could have significant impacts on any risk assessment due to the carcinogenic effects of these chemicals. Therefore, analysis for PAHs was performed on the surface and subsurface soil samples, which exhibited the highest amount of aromatic hydrocarbons from each site, as determined by the direct analysis procedure.

The analysis was performed using USEPA method 8270B [USEPA, 1994] modified to operate the GC/MS system in the selective ion monitoring (SIM) mode. SIM refers to the use of a mass spectrometer to acquire and record ion current at certain, selected mass per charge values. By monitoring only a few selected ions, the output from the electron multiplier (detector) can be integrated over a longer period of time, thus enhancing the signal-to-noise ratio. This allows sensitivity increases of 100 to 1,000 times over conventional GC/MS procedures.

By performing this procedure on the samples with the highest levels of aromatics from each site, the maximum PAH readings were obtained. These numbers could be used in a risk assessment to provide a conservative estimate of carcinogenic PAH risk for the site.

Synthetic Precipitation Leaching Procedure

The USEPA developed the Synthetic Precipitation Leaching Procedure (SPLP), USEPA method 1312 [USEPA, 1994], to determine the mobility of both inorganic and organic constituents present in liquids, soils, and wastes. For a soil, the sample is extracted with 20 times its weight of extraction fluid. The extraction fluid used is dependent on the region of the country where the site is located. If the sampling location is east of the Mississippi River, a pH 4.20 extraction solution is used. If the sampling location is west of the Mississippi River, a pH 5.00 extraction solution is used. The soil sample is extracted for 18 ± 2 hours, after which time the sample is filtered and the resultant fluid is subjected to analysis.

For this study, one sample from each site was selected for SPLP extraction, followed by analysis of the extract for total hydrocarbons and PAHs. The sample selected was the one with the highest concentration of hydrocarbon material.

The purpose of this procedure was to compare actual leaching results with those predicted using the fate and transport parameters selected by the Working Group. This could help to define lower risks for a site than transport parameters would normally indicate.

Permeability, Grain Size, and pH

Two samples from each site, one surface and one subsurface, were analyzed for grain size using ASTM method D422 (sieve and hydrometer) [ASTM, 1990] and pH. The pH of the soil was determined on a 1:1 slurry (25 grams of sample and 25 mL of deionized water) after being tumbled for thirty minutes.

The grain size distribution yields information on the soil type (percentage of sand, silt, and clay, and descriptive term, e.g., silty sand). Soil pH was determined because it may influence the leachability of organic constituents. This allows for an evaluation of recoveries of hydrocarbon fractions from soils with different physical characteristics.

One subsurface soil sample from each site was collected for permeability analysis (undisturbed), using ASTM method D2434-74 [ASTM, 1990]. The soil permeability gives an indication of the ability of the soil to transport fluids. This data also provides information, which could be useful in determining the leachability of organic constituents from the soil.

ANALYTICAL RESULTS

Hydrocarbon Profiles

The hydrocarbon profiles for selected samples from each of the four study sites are presented and discussed below. These profiles were derived by performing the initial step of the direct analysis procedure. N-pentane extracts of soil samples were injected onto a GC column for separation of individual components according to boiling point. This initial step does not separate aliphatic and aromatic components. The chromatographic profiles show distinctive hydrocarbon distribution patterns indicative of the material present. Each of the chromatograms shows patterns typical of diesel fuel; in three of the four samples, other types of hydrocarbons are also indicated in the chromatograms.
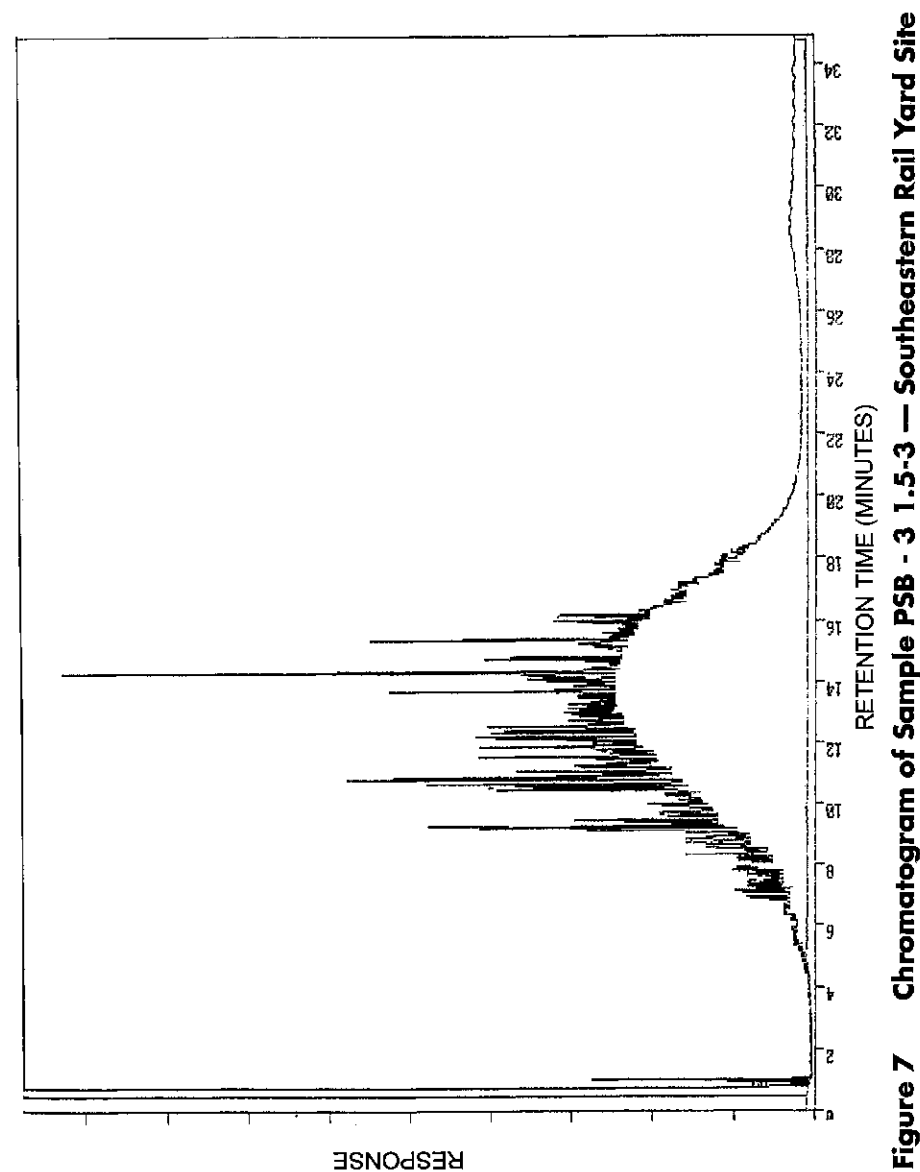
Southeastern Rail Yard

The hydrocarbon profile for the majority of the soils from the Southeastern Rail Yard site is consistent for a weathered diesel fuel. Figure 7 shows a chromatogram for sample PSB-3 (1.5-3'), which was typical of the soils from this site. The "hump" in the chromatogram is indicative of moderate weathering of the material. This hydrocarbon profile was similar for the surface and subsurface soils.

North-Central Rail Yard

Soil samples from the North-Central Rail Yard site showed generally lower levels of hydrocarbon material than those from the Southeastern Rail Yard site. Figure 8 shows

a chromatogram for sample PSB-1 0-3', which is somewhat different than that obtained from the Southeastern Rail Yard site. While this material shows the same characteristic "hump," it elutes earlier, more in the range of what would be expected of kerosene. This pattern is consistent for the soils throughout the site. Reportedly, lighter (lower boiling point) locomotive fuels were used in cold climates, compared to fuels used in the southeastern United States. In addition, the samples show some late-eluting residue that is heavier than what would be expected from a diesel fuel.

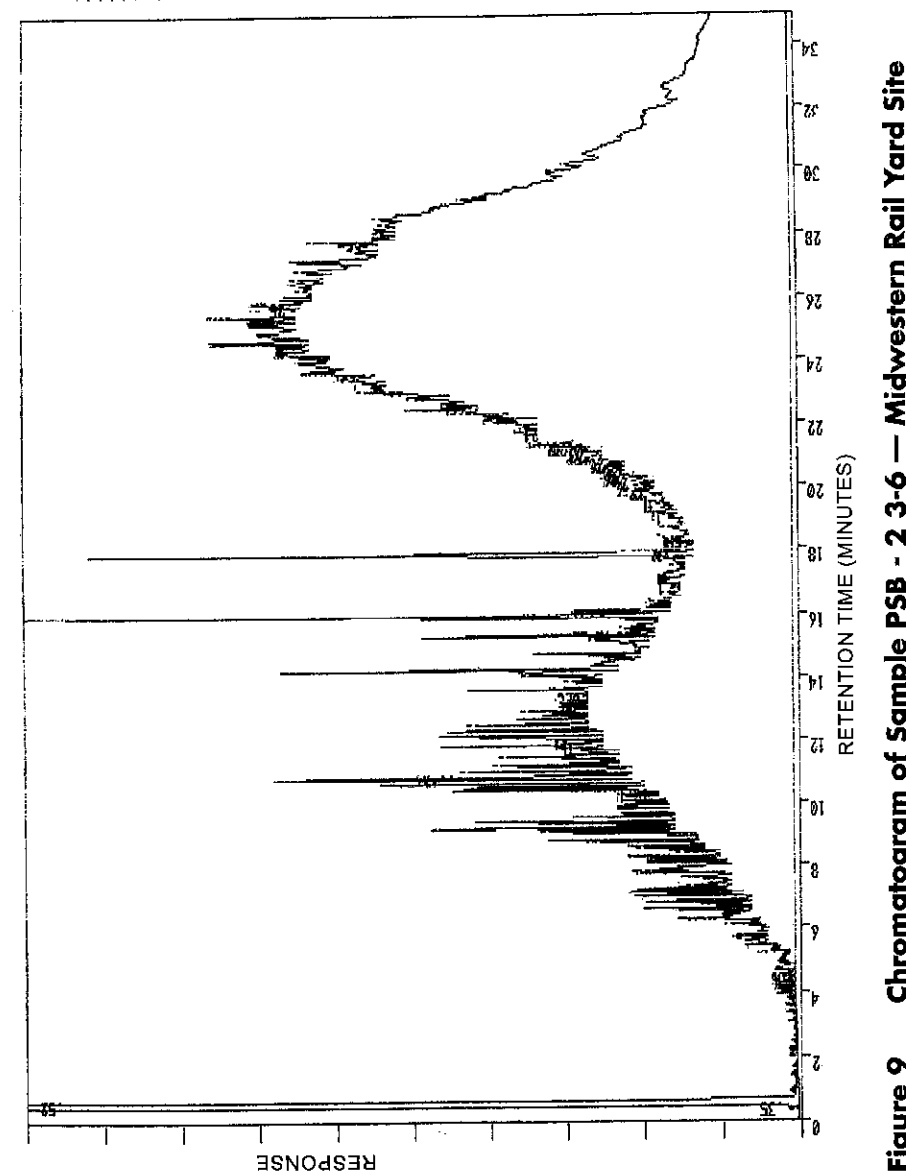Figure 7   Chromatogram of Sample PSB - 3 1.5-3 — Southeastern Rail Yard Site

Midwestern Rail Yard

The differentiating characteristic of the soils from the Midwestern Rail Yard site is the presence of a well defined lubricating oil pattern in addition to diesel fuel in the higher concentration samples. Figure 9 shows a chromatogram for sample PSB-2 3-6', which clearly shows the presence of both materials. The lubricating oil is indicated by the "hump" on the right-hand side of the chromatogram. The relative amount of each material varies across the site from primarily diesel with a small amount of lubricating oil, to a relatively equal mixture of the two. Also, in several cases, the lubricating oil is the dominant product.

Figure 8   Chromatogram of Sample PSB - 1 0-3 — North Central Rail Yard Site
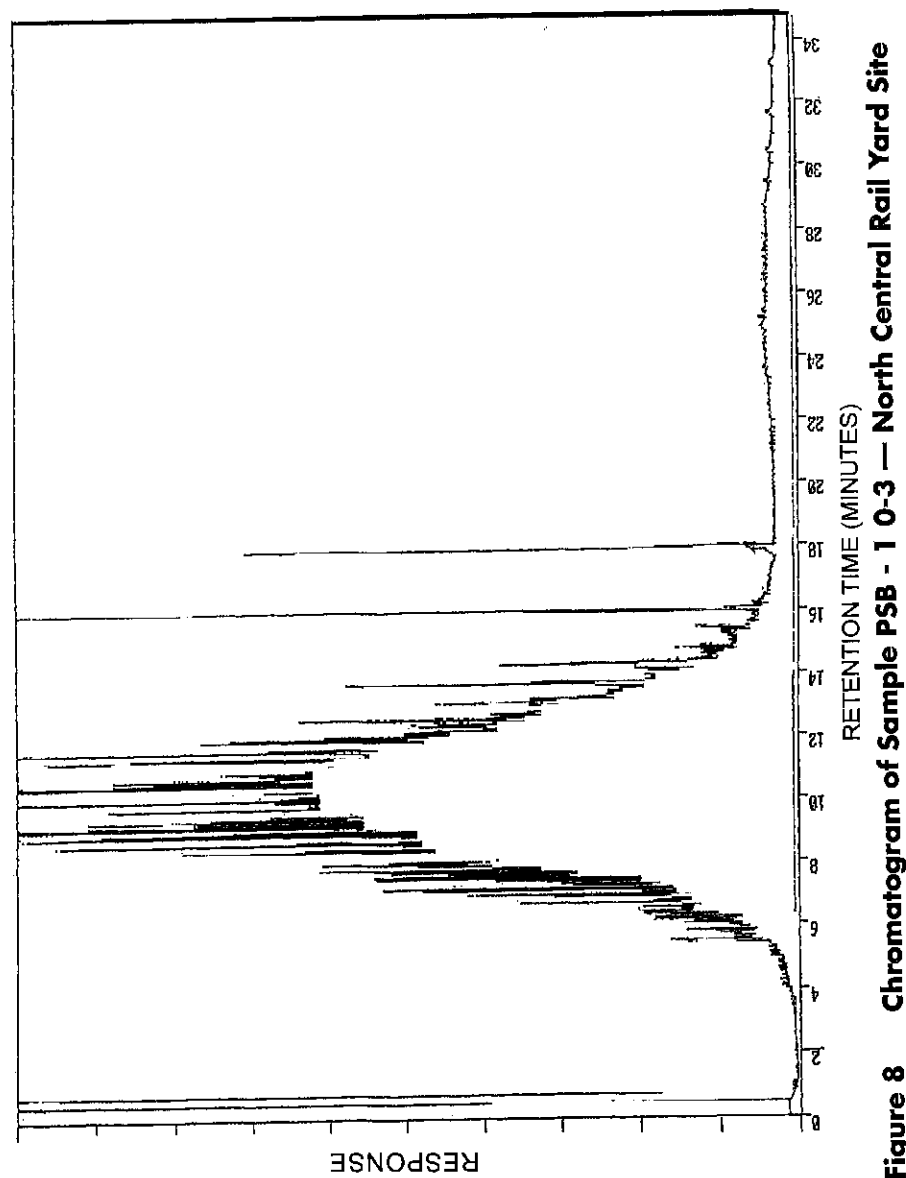
West Coast Derailment Site

Although some of the organics present in the samples from the West Coast Derailment site are consistent with a weathered diesel fuel, the majority of the organics are not. A significant amount of the material present elutes later than C_{35}, and apparently some well beyond C_{44} (the maximum temperature available by the procedure used). Figure 10 is a chromatogram for sample PSB-1 0-2.5', which shows the weathered diesel fuel and the unidentified high molecular weight material. The two large peaks at retention times 15.9 and 17.8 minutes are surrogate compounds (chloro-octadecane and o-terphenyl) which were added to the sample prior to extraction.
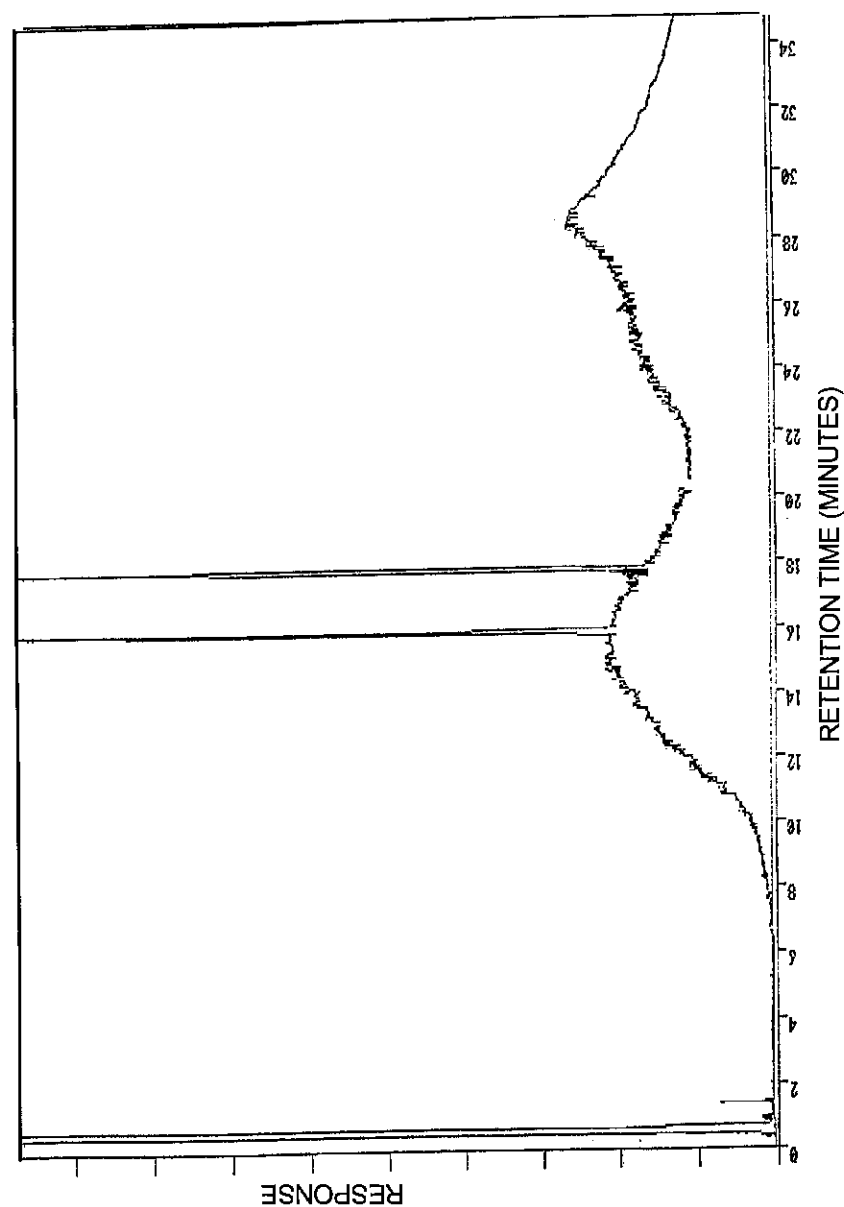

Figure 9   Chromatogram of Sample PSB - 2 3-6 — Midwestern Rail Yard Site

Figure 10   Chromatogram of Sample PSB - 1 0-2.5 — West Coast Derailment Site

Total Petroleum Hydrocarbon Results by Various Methodologies

Analytical Results

This section presents the results for total petroleum hydrocarbons for the direct analysis procedure (USEPA 418.1), as well as the total organic carbon results for each of the sites. Results are presented for both surface and subsurface soils. All results are reported on a dry-weight basis. The symbol "ND" means that the fraction was not detected. The detection limit is given in parentheses following "ND."

Tables 2 through 5 present the results for each of the sites. Only surface soil samples were taken from the West Coast Derailment site. Table 5 presents results for the background sample as well as for the individual soil samples from the West Coast Derailment site. The background sample is inclnded because it showed detectable levels of hydrocarbons at concentrations approximating those found in the site samples. The background samples from the other sites did not show detectable levels of hydrocarbons by the direct analysis procedure and therefore were not analyzed by the other methodologies.

The average results for the direct analysis, API, and USEPA TPH analyses for each of the sites are illustrated graphically in Figures 11 and 12 for surface and subsurface soils, respectively. Average values were computed by using the detection limit for those samples reported as ND. The results show general consistency in terms of the hydrocarbon concentrations, and the relative concentrations using the different TPH methods, between the surface and subsurface soils at the North-Central and Midwestern sites. At the Southeastern site, surface soil hydrocarbon concentrations were about half the concentrations, on the average, of the subsnrface soils, although the relative concentrations using the different TPH methods were similar. The differences in concentrations at this site may be indicative of leaching and surface degradation in this relatively warm, wet climate. These differences could also be indicative of the soil intervals sampled. At the Southeastern site, the water table was shallow, and the surface and subsurface soils were taken from 0-1.5' and 1.5 to 3.0', respectively. At the North-Central and Midwestern sites, the surface and subsurface soil intervals were 0-3' and 3-6', respectively.

In all cases, the total organic carbon value was higher than any of the hydrocarbon methodology results. This indicates that at each of these sites, there is naturally occurring organic matter present in addirion to the hydrocarbon. The largest difference between organic carbon and hydrocarbon results was at the North-Central Rail Yard site.

At three of the four sites (North-Central, Midwestern, and West Coast), the hydrocarbon results generally followed the pattern:

Direct GC < API GC < USEPA IR

At these locations, the hydrocarbon profiles revealed the presence of high boiling materials other than diesel fuel. In cases like these, it is expected that the USEPA IR procedure would yield higher values than the chromatographic techniques. The GC procedures are limited by boiling point considerations. The API procedure quantifies materials with boiling ranges to C_{28}, while the direct analysis procedure, as applied for this study, quantifies materials to C_{35}. The USEPA IR procedure is not bound by boiling point considerations, and will determine any molecular weight material as long as it

TABLE 2　Petroleum Hydrocarbon and Organic Carbon Data Southeastern Rail Yard Site (mg/kg - dry weight)

Location	Direct Analysis GC	API GC	USEPA IR	TOC
Surface Soils				
PSB-1 0-1.5'	457	345	994	19,400
PSB-2 0-1.5'	10,589	15,300	13,200	34,100
PSB-3 0-1.5'	8,456	14,600	13,200	32,300
PSB-4 0-1.5'	344	240	440	44,400
PSB-5 0-1.5'	ND (118)	117	217	35,600
PSB-6 0-1.5'	8,941	14,100	17,300	42,100
PSB-7 0-1.5'	8,123	10,800	9,610	30,500
PSB-8 0-1.5'	12,466	18,800	16,300	39,600
Average	6,187	9,288	8,908	34,638
Subsurface Soils				
PSB-1 1.5-3'	6,943	10,100	7,500	23,400
PSB-2 1.5-3'	22,893	33,600	22,600	58,000
PSB-3 1.5-3'	23,928	31,400	23,000	44,500
PSB-4 1.5-3'	ND (125)	18	229	14,100
PSB-5 1.5-3'	ND (117)	23	35	1,240
PSB-6 1.5-3'	13,783	25,100	22,000	47,200
PSB-7 1.5-3'	25,313	32,700	26,100	50,300
PSB-8 1.5-3'	17,978	31,900	20,100	51,000
Average	13,885	20,605	15,196	37,613

TABLE 3　Petroleum Hydrocarbon and Organic Carbon Data — North Central Rail Yard Site (mg/kg - dry weight)

Location	Direct Analysis GC	API GC	USEPA IR	TOC
Surface Soils				
PSB-1 0-3'	2,545	6,710	8,400	47,800
PSB-2 0-3'	181	340	400	33,100
PSB-3 0-3'	ND (115)	165	96	2,300
PSB-4 0-3'	201	420	1,180	45,600
PSB-5 0-3'	2,954	4,770	13,800	70,900
PSB-6 0-3'	ND (122)	540	270	79,700
PSB-7 0-3'	ND (125)	380	610	45,300
PSB-8 0-3'	163	860	960	47,500
Average	801	1,773	3,215	49,100
Subsurface Soils				
PSB-1 3-6'	5,159	7,700	7,700	52,100
PSB-2 3-6'	328	900	670	25,700
PSB-3 3-6'	339	540	620	35,000
PSB-4 3-6'	394	950	2,130	52,400
PSB-5 3-6'	361	670	1,520	37,800
PSB-6 3-6'	ND (118)	90	80	33,900
PSB-7 3-6'	586	500	1,700	54,100
PSB-8 3-6'	ND (136)	510	770	46,800
Average	928	1,483	1,899	42,225

TABLE 4   **Petroleum Hydrocarbon and Organic Carbon Data — Midwestern Rail Yard Site (mg/kg - dry weight)**

Location	Direct Analysis GC	APIGC	USEPA IR	TOC
Surface Soils				
PSB-1 0-3'	6,255	10,700	10,900	20,000
PSB-2 0-3'	13,899	6,000	23,000	42,200
PSB-3 0-3'	843	2,900	3,000	24,900
PSB-4 0-3'	1,397	2,100	3,300	10,600
PSB-5 0-3'	2,385	3,400	2,900	6,600
PSB-6 0-3'	7,235	11,700	9,200	21,200
PSB-7 0-3'	8,805	10,100	12,800	39,400
PSB-8 0-3'	10,161	15,400	19,600	44,400
Average	6,373	7,787	10,588	26,163
Subsurface Soils				
PSB-1 3-6'	10,883	11,700	12,000	13,400
PSB-2 3-6'	2,269	4,800	8,900	12,900
PSB-3 3-6'	9,248	13,600	11,800	16,800
PSB-4 3-6'	4,036	6,800	5,400	7,300
PSB-5 3-6'	5,493	6,400	6,500	8,300
PSB-6 3-6'	7,846	10,000	11,400	15,600
PSB-7 3-6'	6,822	8,100	8,500	12,100
PSB-8 3-6'	7,340	9,990	13,700	15,000
Average	6,742	8,924	9,775	12,675

TABLE 5   **Petroleum Hydrocarbon and Organic Carbon Data Surface Soils — West Coast Derailment Site (mg/kg - dry weight)**

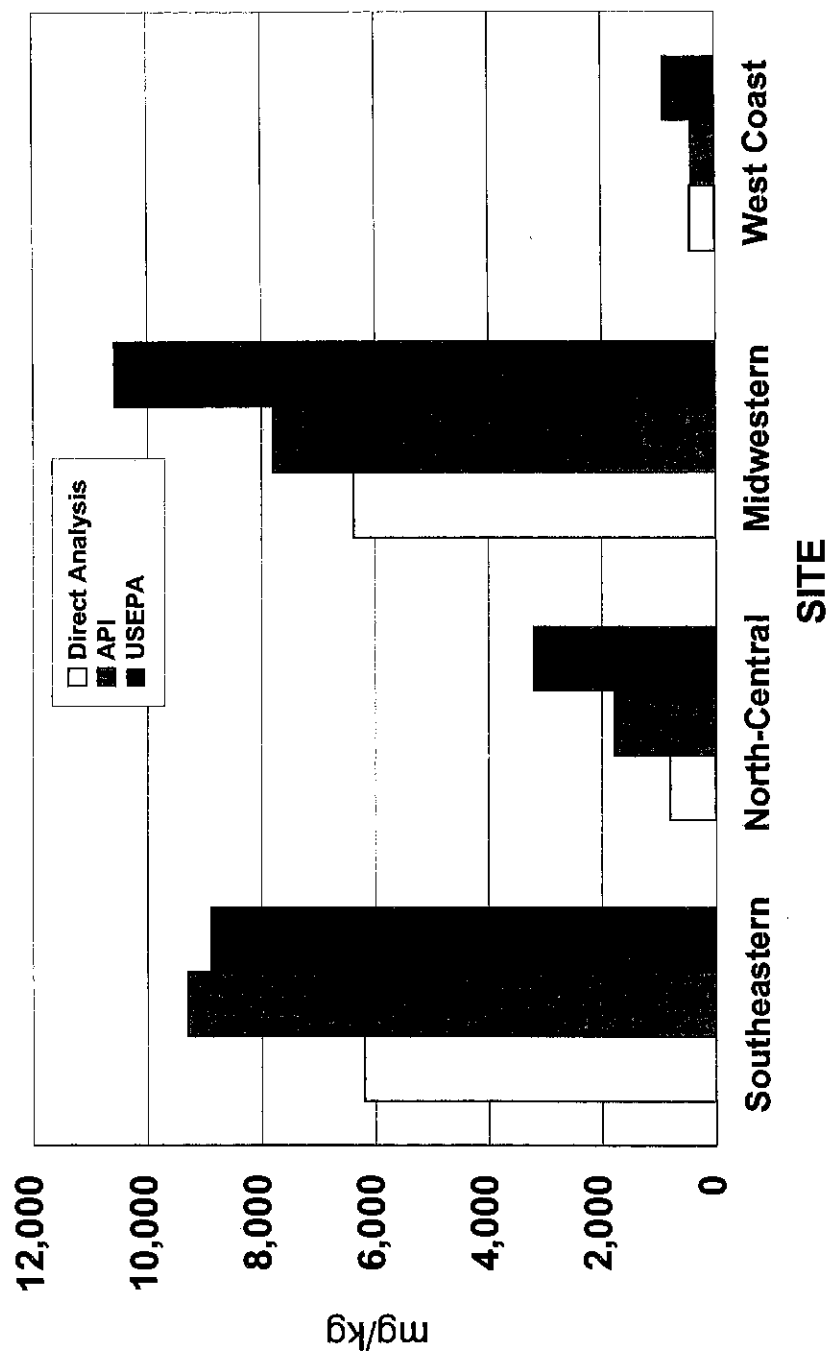| Location	Direct Analysis GC	API GC	USEPA IR	TOC
Background	600	510	590	8,400
PSB-1 0-2.5'	830	457	1,350	15,100
PSB-2 0-2.5'	405	260	1,040	20,600
PSB-3 0-2.5'	257	230	760	13,500
PSB-4A 0-3'	366	500	670	4,700
PSB-5 0-2'	150	150	270	4,800
PSB-7A 0-3'	478	390	600	2,900
PSB-8 0-2.5'	636	910	1,740	32,300
Average	446	414	919	13,414

Figure 11   Comparison of Hydrocarbon (TPH) Results (Surface Soils)
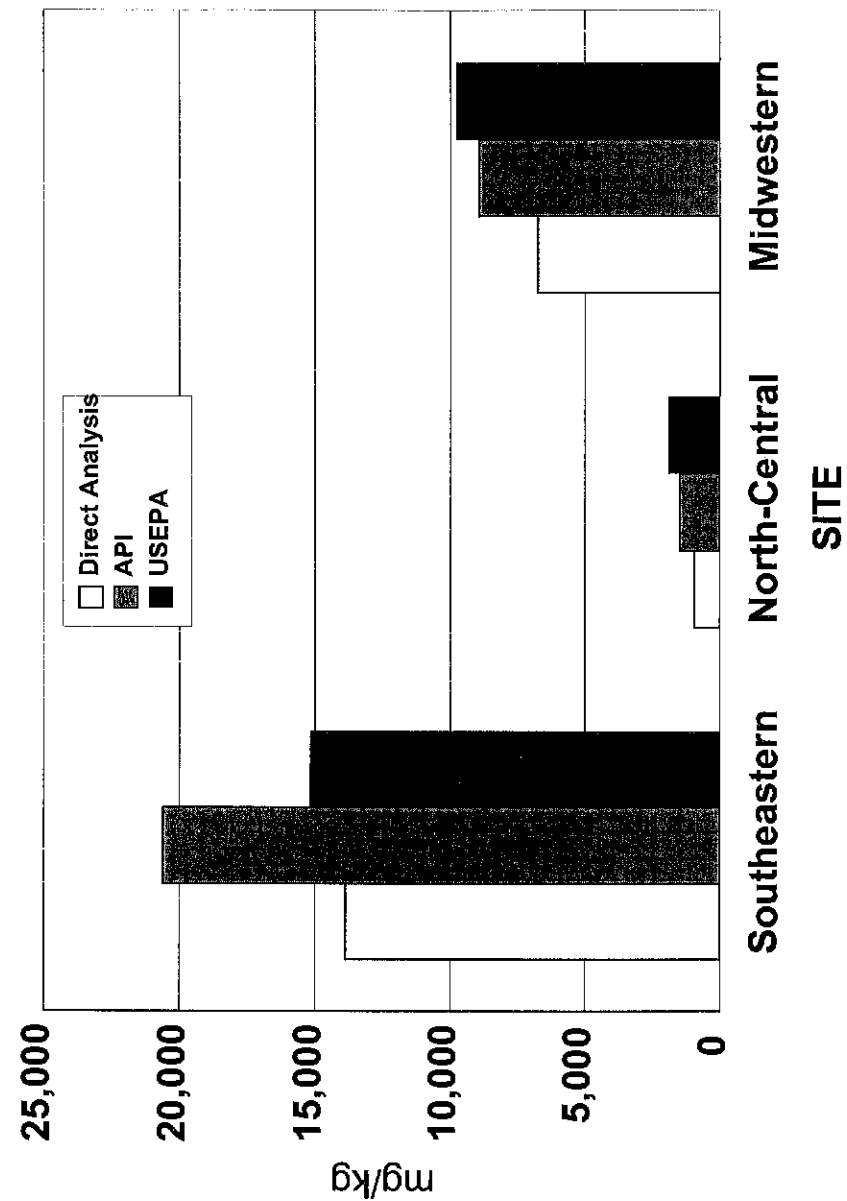

Figure 12

Comparison of Hydrocarbon (TPH) Results (Subsurface Soils)

is soluble in the extraction solvent. Therefore in cases where a significant portion of the hydrocarbon material is greater than C_{28} or C_{35}, the IR procedure normally shows higher results.

The greater value for the API procedure versus the direct analysis procedure may be the result of differing extraction efficiencies for the extraction solvent employed. Some of the "uondiesel" related hydtocarbons in the $>C_{21}$ range may not be as soluble in the n-pentane used in the direct analysis procedure as rhey are in the methylene chloride used in the API method.

The results for the Southeastern Rail Yard site showed closer agreement between the hydrocarbon methodologies. This site showed weathered diesel fuel to be the dominant hydrocarbon present. With the exception of PSB-1 0-1.5, there was little heavy material present outside of the diesel range. Thus, it would be expected that the results would show less variability at this site. The direct method, on average, gave slightly lower results. This may be due to the weathering effects of the material, making it slightly more difficult for the n-pentane to extract all of the hydrocarbon constituents from the soil matrix.

Statistical Comparison of TPH Results

A statistical comparison was made to determine if the direct analysis procedure is statistically similar to the IR and/or the API methods. The statistical analysis cousisted of comparing the results of the three methods in a multiple comparison test (i.e., analysis of variance, or ANOVA), post-hoc tests, and correlation analysis. A summary of the results of the statistical analyses are presented in Table 6A and 6B.

Nondetect Values. Samples, which were nondetect for any of the analytical methods, were adjusted to a concentration of 0.0 mg/kg. The following nondetects occurred in the analytical data:

- Southeastern Rail Yard site surface soil: 1
- Southeastern Rail Yard site subsurface soil: 2
- North Central Rail Yard site surface soil: 3
- North Central Rail Yard site subsurface soil: 2

The USEPA considers the Shapiro Wilks W-test appropriate for analyzing environmental data [USEPA, 1992]. If the W-test indicated that the original data was not normally distributed, the data was log-transformed (natural logarithm). If the log-transformed data was not normally distributed, then it was assumed to be distribution-free (i.e., nonparametric).

The Southeastern and Midwestern Rail Yard site and West Coast Derailment site surface soil data were normally distributed, as well as the Midwestern Rail Yard site subsurface soil data. The Southeastern Rail Yard site subsurface soil data were all distribution-free. The North-Central Rail Yard site surface soil had oue data set, which was distribution-free (i.e., direct analysis method), while the subsurface soil data sets were all log-normally distributed.

Multiple Comparisons. The three TPH analytical methodologies were evaluated to determine if one or all of the methodologies provided statistically significant differ-

TABLE 6A, 6B   TPH Verification Study Statistical Summary

Site	Soil	Methods	Correlation	
			API	IR
Southeastern Rail Yard Site	surface soil	DA	S	S
		API	—	S
	subsurface soil	DA	S	S
		API	—	S
North-Central Rail Yard Site	surface soil	DA	NS	S
		API	—	NS
	subsurface soil	DA	S	S
		API	—	S
Midwestern Rail Yard Site	surface soil	DA	NS	S
		API	—	S
	subsurface soil	DA	S	NS
		API	—	S
West Coast Derailment Site	surface soil	DA	NS	S
		API	—	S

Site	Soil	ANOVA	Post-hoc tests for differences between data sets					Notes
			Tukey	N-K	Duncan	Scheffe	Dunnett	
Southeastern Rail Yard Site	surface soil	NS	NS	NS	NS	NS	NS	All three methods equal
	subsurface soil	NS	NS	NS	NS	NS	NS	All three methods equal
North-Central Rail Yard Site	surface soil	NS	NS	NS	NS	NS	DA vrs IR DA vrs API	All three methods equal
	subsurface soil	NS	NS	NS	NS	NS	NS	All three methods equal
Midwestern Rail Yard Site	surface soil	NS	NS	NS	NS	NS	NS	All three methods equal
	subsurface soil	NS	NS	NS	NS	NS	NS	All three methods equal
West Coast Derailment Site	surface soil	S	NS	NS	DA vrs IR API vrs IR	API vrs IR	NS	The IR method may over-estimate TPH

Notes:
DA = Direct Analysis Method
IR = USEPA IR Method 418.1
API = API GC DRO Method
S indicates statistically significant, and NS indicates not significant, at the 0.05 level.
—indicates method not correlated against itself

ences in the TPH analyses. If all of the three data sets within a site and soil were normally distributed, a one-way ANOVA was conducted. If one or more of the data sets were log-normally distributed, and the remaining data sets were normally distributed, a one-way ANOVA was conducted on the log-transformed data. If one or more of the data sets were distribution-free, then the nonparametric Kruskal-Wallis test was used. These tests are discussed further in USEPA guidance [USEPA, 1992].

Southeastern Rail Yard Site:

The surface soil data were all normally distributed, therefore an ANOVA was used to detect differences. The F-test and p-value of the ANOVA was 0.49 (0.62), indicating that there were no significant differences between the three method data sets. The subsurface soil data were all nonparametric, and the Kruskal-Wallis test indicated no significant difference between the method data sets (0.69 (0.51)).

North-Central Rail Yard Site:

The surface soil data were log-normally distributed and nonparametric, therefore the Kruskal-Wallis test was used to detect differences. The Z-score and p-value of this test was 3.89 (0.14), indicating that there were no significant differences between the three method data sets. The subsurface soil data were all lognormal, and the ANOVA indicated no significant difference between the method data sets (1.10(0.35)).

Midwestern Rail Yard Site:

The surface soil data were all normally distributed, therefore an ANOVA was used to detect differences. The F-test and p-value of the ANOVA was 1.21 (0.32), indicating that there were no significant differences between the three method data sets. The subsurface soil data were all normally distributed, and the ANOVA indicated no significant difference between the method data sets (2.37 (0.12)).

West Coast Derailment Site:

The surface soil data were all normally distributed, therefore an ANOVA was used to detect differences. The F-test and p-value of the ANOVA was 4.61 (0.02), indicating significant differences between the three method data sets at the 0.05 level.

Post-hoc Tests. Multiple comparison tests identify the existence of significant differences between data sets, but do not indicate which of the individual data sets differ. Post-hoc tests were developed for this purpose. Five post-hoc tests were used to test the data:

- Tukey's studentized range test
- Newman-Keuls multiple range test
- Duncan's multiple range test
- Scheffe's multiple comparison test
- Dunnett's multiple comparison test

These tests are generally applied if a multiple comparison test indicates that a significant difference exists between data sets. However, the post-hoc tests were applied to all of the site/soil comparisons. There were no significant differences reported for the Southeastern and Midwestern Rail Yard surface and subsurface soils, or for the North-

Central Rail Yard site subsurface soils.

The ANOVA and Kruskal-Wallis tests indicated no significant differences in the North-Central surface soil. However significant differences between the direct analysis and API methods, and the direct analysis and IR methods, were found when using the Dunnett's multiple comparison test (i.e., the direct analysis method provided consistently smaller TPH values). Dunnett's multiple range test is not particularly conservative in comparison to some of the other post-hoc tests, and its robustness against non-normality is not well understood. Since the more conservative Tukey's and Newman-Keuls tests did not find a significant difference, it can be safely concluded that there is no significant difference between the direct analysis method and the IR or API methods for surface soils from the North-Central Rail Yard site.

The West Coast Derailment site surface soils were shown to contain a significant difference by the one-way ANOVA. Duncan's multiple range test showed a significant difference between the direct analysis and IR methods and between the IR and API methods (i.e., the IR method provided consistently greater TPH values than the other two methods). However, Scheffe's multiple comparison test only identified a significant difference between the API and IR data sets (i.e., the API method provided consistently smaller TPH values than the IR method). Scheffe's test is generally more conservative that the Duncan's method, and in addition has a fixed error rate. The results of the post-hoc tests therefore indicate that the IR data set provides consistently higher values than the API data set, and may provide significantly higher values than the direct analysis data set, for surface soils from the West Coast Derailment site.

Correlation Analysis. The multiple comparison and post-hoc tests indicate which sets of data may be statistically different. However, each of the eight samples collected from each site and soil (seven samples for the West Coast derailment site) were paired (i.e., each sample was analyzed for TPH using the three methodologies). The ANOVA and Kruskal-Wallis tests do not account for pairing, but treat each data set as a collection of random data points. A correlation analysis was conducted to determine if, when comparing two data sets from within the same site and soil, the magnitudes of the samples change at the same time (i.e., do low TPH values as reported for the direct analysis method correspond to low TPH values for the API method).

The type of correlation analysis selected is dependent on the data distribution. Normal or log-normally distributed data pairs were analyzed using Pearsons product-moment correlation, while those containing a nonparametric data set were analyzed using Spearmans rank correlation. All correlation analyses were conducted at the 0.05 level of significance.

Southeastern Rail Yard Site:

The correlation analysis indicated a significant correlation among the three methods within the surface and subsurface soil data sets.

North-Central Rail Yard Site:

The correlation analysis indicated a significant correlation among the API and IR, and direct analysis and IR methods, but a nonsignificant correlation between the direct analysis and API surface soil samples. The subsurface soil samples were significantly correlated.

Midwestern Rail Yard Site:

The correlation analysis indicated a significant correlation among the direct analysis and IR methods, but a nonsignificant correlation between the direct analysis and API, and the IR and API, surface soil samples. The subsurface soil samples were significantly correlated for the direct analysis and API methods, and the API and IR methods, but were not significant for the direct analysis and IR methods.

West Coast Derailment Site:

The correlation analysis indicated a significant correlation among direct analysis and IR methods, and the API and IR methods, but a nonsignificant correlation between the direct analysis and API surface soil samples.

Summary. As indicated in Tables 6A and 6B, the statistical analyses show that in general, the three methods provide similar TPH values. However, a significant difference existed between the IR method results and the results obtained using either the direct analysis or the API methods in the West Coast site surface soil. There was no significant correlation between the direct analysis and API methods in the North-Central and Midwestern sites, and West Coast site surface soils. However, the subsurface soil correlations are significant for the North-Central and Midwestern sites. This result is unexplained, but does not appear to have an effect on the tests of significant difference .

Aliphatic and Aromatic Hydrocarbon Fractions

This section presents a summary of the results for the equivalent carbon distributions following the silica gel fractionation procedure in the direct analysis method. Average results for each site are presented in Tables 7 through 10. Only samples with a total hydrocarbon result of 500 mg/kg or greater were used for the average calculations. This represents a value of five times the detection limit and eliminates baseline noise, which may skew the numbers at low levels. The data in the tables are discussed below.

Approximate Carbon Number Range

The first column gives the approximate carbon number range used for quantitation. These ranges are based on n-alkane calibration standards and reflect the ranges used for risk evaluation by the Working Group. For example, the carbon range $>C_{12}$ to $<= C_{16}$ would include those hydrocarbons eluting at a retention time 0.01 minute after n-dodecane (C_{12}), up to and including the retention time of n-hexadecane (C_{16}).

TPH

The TPH value is the average value obtained by an analysis of the n-pentane extract without any fractionation of the sample into aliphatic and aromatic hydrocarbons. This result includes contributions from both hydrocarbon classes.

Aliphatic Hydrocarbons

The aliphatic hydrocarbons were calculated from an analysis of the pentane eluate following the silica gel fractionation procedure.

TABLE 7   Direct Analysis Analytical Results (Dry Weight Basis) Average of Eleven Samples — Southeastern Rail Yard Site

Approximate Carbon Number Range	TPH[1] (mg/kg)	Aliphatic Hydrocarbons (mg/kg)	Aromatic Hydrocarbons (mg/kg)	Aliphatics+ Aromatics (mg/kg)	Percent Recovery[2]
C_6 - $<=C_7$	NA	ND (0.025)	ND (0.025)	ND	NA
$>C_7$ - $<=C_8$	NA	ND (0.025)	ND (0.025)	ND	NA
$>C_8$ - $<=C_9$	6	11	6	17	283
$>C_9$ - $<=C_{10}$	69	76	5	81	117
$>C_{10}$ - $<=C_{12}$	869	695	68	863	99
$>C_{12}$ - $<=C_{16}$	6,193	3,918	1,951	5,869	95
$>C_{16}$ - $<=C_{21}$	5,899	3,726	1,795	5,521	94
$>C_{21}$ - $<=C_{35}$	1,411	736	444	1,180	84
Total	14,447	9,162	4,369	13,531	94
Relative Percent[3] Distribution	—	68	32	—	—

Notes:
[1] Results from direct anlaysis method without fractionation
[2] Calculated as (Aliphatics + Aromatics), divided by the TPH value obtained using the direct analysis method without fractionation, x 100.
[3] Calculated as total aliphatic or aromatic hydrocarbons divided by (Aliphatics + Aromatics), x 100.

TABLE 8   Direct Analysis Analytical Results (Dry Weight Basis) Average of Three Samples — North Central Rail Yard Site

Approximate Carbon Number Range	TPH [1] (mg/kg)	Aliphatic Hydrocarbons (mg/kg)	Aromatic Hydrocarbons (mg/kg)	Aliphatics+ Aromatics (mg/kg)	Percent Recovery[2]
C_6 - $<=C_7$	NA	ND (0.025)	ND (0.025)	ND	NA
$>C_7$ - $<=C_8$	NA	ND (0.025)	ND (0.025)	ND	NA
$>C_8$ - $<=C_9$	ND (5)	ND (5)	ND (5)	ND	NA
$>C_9$ - $<=C_{10}$	12	9	ND (5)	9	75
$>C_{10}$ - $<=C_{12}$	381	278	51	329	86
$>C_{12}$ - $<=C_{16}$	1,774	1,157	387	1,544	87
$>C_{16}$ - $<=C_{21}$	565	324	156	480	85
$>C_{21}$ - $<=C_{35}$	819	372	238	610	74
Total	3,551	2,140	832	2,972	84
Relative Percent[3] Distribution	—	72	28	—	—

Notes:
[1] Results from direct analysis method without fractionation
[2] Calculated as (Aliphatics + Aromatics), divided by the TPH value obtained using the direct analysis method without fractionation, x 100.
[3] Calculated as total aliphatic or aromatic hydrocarbons divided by (Aliphatics + Aromatics), x 100.

TABLE 9   Direct Analysis Analytical Results (Dry Weight Basis) Average of Sixteen Samples — Midwestern Rail Yard Site

Approximate Carbon Number Range	TPH [1] (mg/kg)	Aliphatic Hydrocarbons (mg/kg)	Aromatic Hydrocarbons (mg/kg)	Aliphatics+ Aromatics (mg/kg)	Percent Recovery[2]
C_6 - $<=C_7$	NA	ND (0.025)	ND (0.025)	ND	NA
$>C_7$ - $<=C_8$	NA	ND (0.025)	ND (0.025)	ND	NA
$>C_8$ - $<=C_9$	8	6	ND (5)	6	75
$>C_9$ - $<=C_{10}$	34	30	ND (5)	30	88
$>C_{10}$ - $<=C_{12}$	359	241	89	330	92
$>C_{12}$ - $<=C_{16}$	2,278	1,106	895	2,001	88
$>C_{16}$ - $<=C_{21}$	2,119	939	759	1,698	80
$>C_{21}$ - $<=C_{35}$	1,759	964	385	1,349	77
Total	6,557	3,286	2,128	5,414	83
Relative Percent[3] Distribution	—	61	39	—	—

Notes:
[1] Results from direct anlaysis method without fractionation
[2] Calculated as (Aliphatics + Aromatics), divided by the TPH value obtained using the direct analysis method without fractionation, x 100.
[3] Calculated as total aliphatic or aromatic hydrocarbons divided by (Aliphatics + Aromatics), x 100.

TABLE 10   **Direct Analysis Analytical Results (Dry Weight Basis) Average of Three Samples — West Coast Derailment Site**

Approximate Carbon Number Range	TPH [1] (mg/kg)	Aliphatic Hydrocarbons (mg/kg)	Aromatic Hydrocarbons (mg/kg)	Aliphatics+ Aromatics (mg/kg)	Percent Recovery[2]
$C_6 - <= C_7$	NA	ND (0.006)	ND (0.006)	ND	NA
$>C_7 - <= C_8$	NA	ND (0.006)	ND (0.006)	ND	NA
$>C_8 - <= C_9$	ND (5)	ND (5)	ND (5)	ND	NA
$>C_9 - <= C_{10}$	ND (5)	ND (5)	ND (5)	ND	NA
$>C_{10} - <= C_{12}$	ND (5)	ND (5)	ND (5)	ND	NA
$>C_{12} - <= C_{16}$	93	76	ND (5)	76	82
$>C_{16} - <= C_{21}$	263	171	51	222	84
$>C_{21} - <= C_{35}$	290	108	81	189	65
Total	646	355	132	487	75
Relative Percent[3] Distribution	—	73	27	—	—

Notes:
[1] Results from direct anlaysis method without fractionation
[2] Calculated as (Aliphatics + Aromatics), divided by the TPH value obtained using the direct analysis method without fractionation, x 100.
[3] Calculated as total aliphatic or aromatic hydrocarbons divided by (Aliphatics + Aromatics), x 100.

Aromatic Hydrocarbons

The aromatic hydrocarbons were calculared from an analysis of the pentane/methylene chloride eluate following the silica gel fracrionation procedure.

Aliphatics + Aromatics

The total aliphatic + aromatic results are obtained from summing the results given in columns 3 and 4. Theoretically, this value should equal the value of the TPH result given in column 2.

Percent Recovery

The percent recovery result is obtained by dividing the result given in column 5 by the TPH result in column 2 and converting to a percentage. A value of 100% recovery would indicate that all material determined in the initial pentane extract was completely separated and recovered during the silica gel column fractionation procedure.

C_6 and C_7 Fraction Results

The results for the C_6 and C_7 fractions were obtained from the USEPA 8260 GC/MS methodology. Therefore, the TPH column shows the symbol "NA" for these fractions. Because there was no pentane extraction performed for these fractions, percent recovery calculations are also not applicable. The GC/MS procedure was used to determine if volatile organics (benzene and toluene) were present at low levels in the samples. Table 11 provides a list of the samples, which showed detectable levels of benzene or toluene during the study.

TABLE 11   **Benzene and Toluene Levels in Field Samples (mg/kg - dry weight basis)**

| Site	Location	Benzene	Toluene
Southeastern Rail Yard Site	PSB 6 1.5-3'	0.030	ND (0.025)
Southeastern Rail Yard Site	PSB 7 1.5-3'	ND (0.025)	0.038
Midwestern Rail Yard Site	PSB 6 0-3'	0.033	ND (0.025)
Midwestern Rail Yard Site	PSB 6 3-6'	0.057	ND (0.025)
Midwestern Rail Yard Site	PSB 8 0-3'	0.038	ND (0.025)

Relative Percent Distribution

The relative percent distribution given at the bottom of the tables gives an estimation of the amounts of aliphatic versus aromatic material in the sample. The result is calculated as illustrated in Figure 13.

Discussion of Fractionation Results

Fractionation Results: Analytical Trends

Southeastern Rail Yard Site: Weathered diesel fuel was the primary constituent at this site. The $>C_{12}$ - $<=C_{16}$ and the $>C_{16}$ - $<=C_{21}$ fractions were predominant in terms of weight percent of material, with approximately 84% of the hydrocarbon material being present in these two fractions. The average weight percent distribntion of aliphatic and aromatic fractions is illustrated in Figure 14.

Soil ⟶ Determine Total TPH (A)

⟶ Determine Aliphatic HCs (B)

⟶ Determine Aromatic HCs (C)
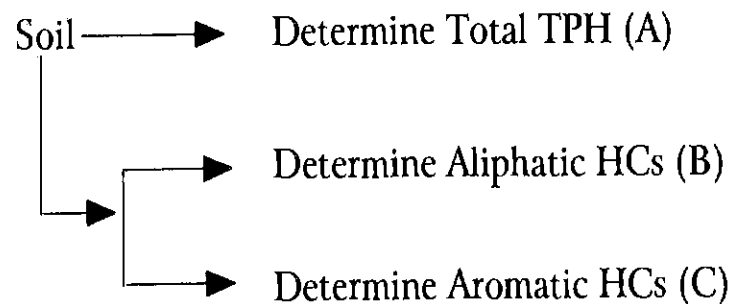
$$Percent\ Total\ Recovery = \frac{(B + C)}{A} * 100\%$$

$$Percent\ Aliphatics = \frac{(B)}{(B + C)} * 100\%$$

$$Percen\ Aromatics = \frac{(C)}{(B + C)} * 100\%$$

Figure 13

Hydrocarbon Recovery Calculations
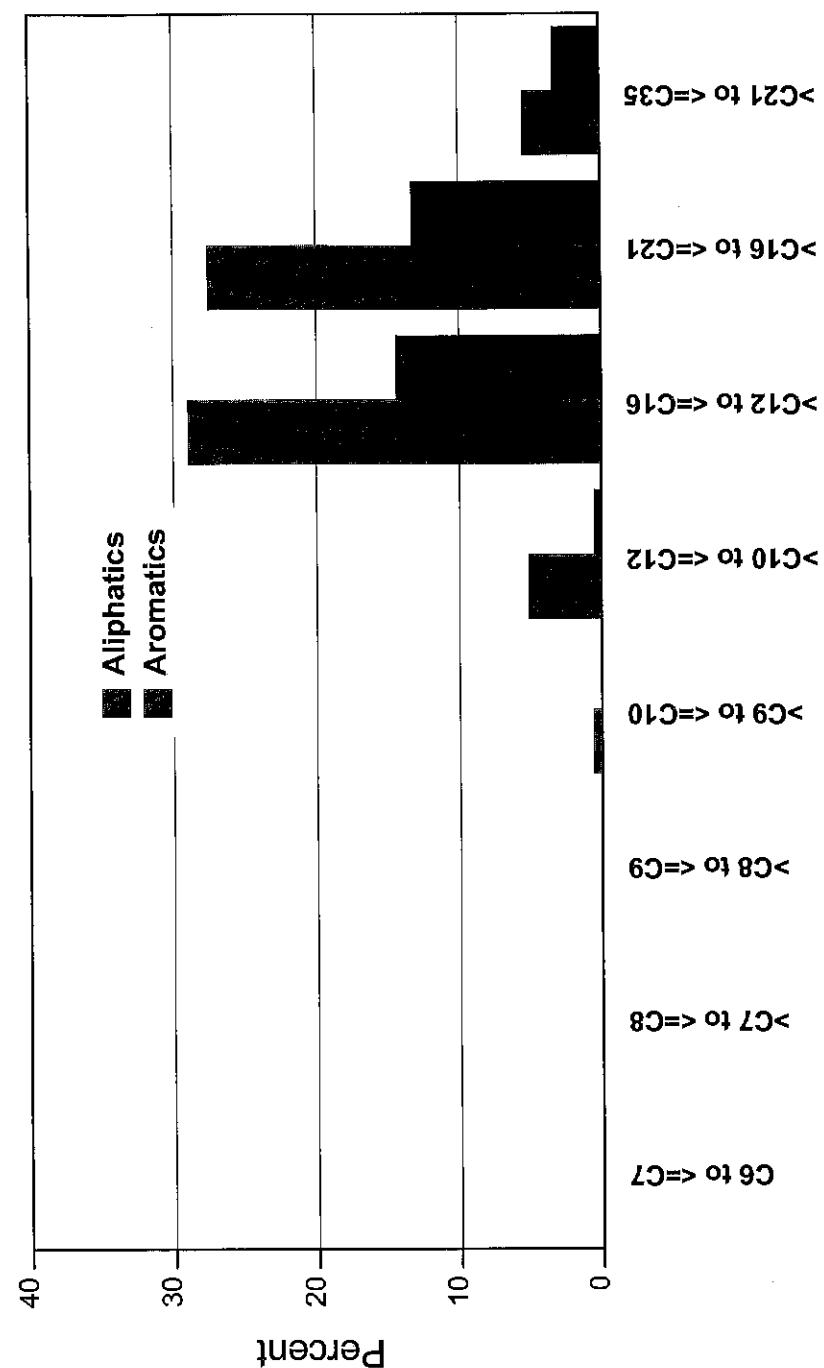
Figure 14

Average Hydrocarbon Fraction Distribution for Fractionated Samples (Weight Percent) — Southeastern Rail Yard
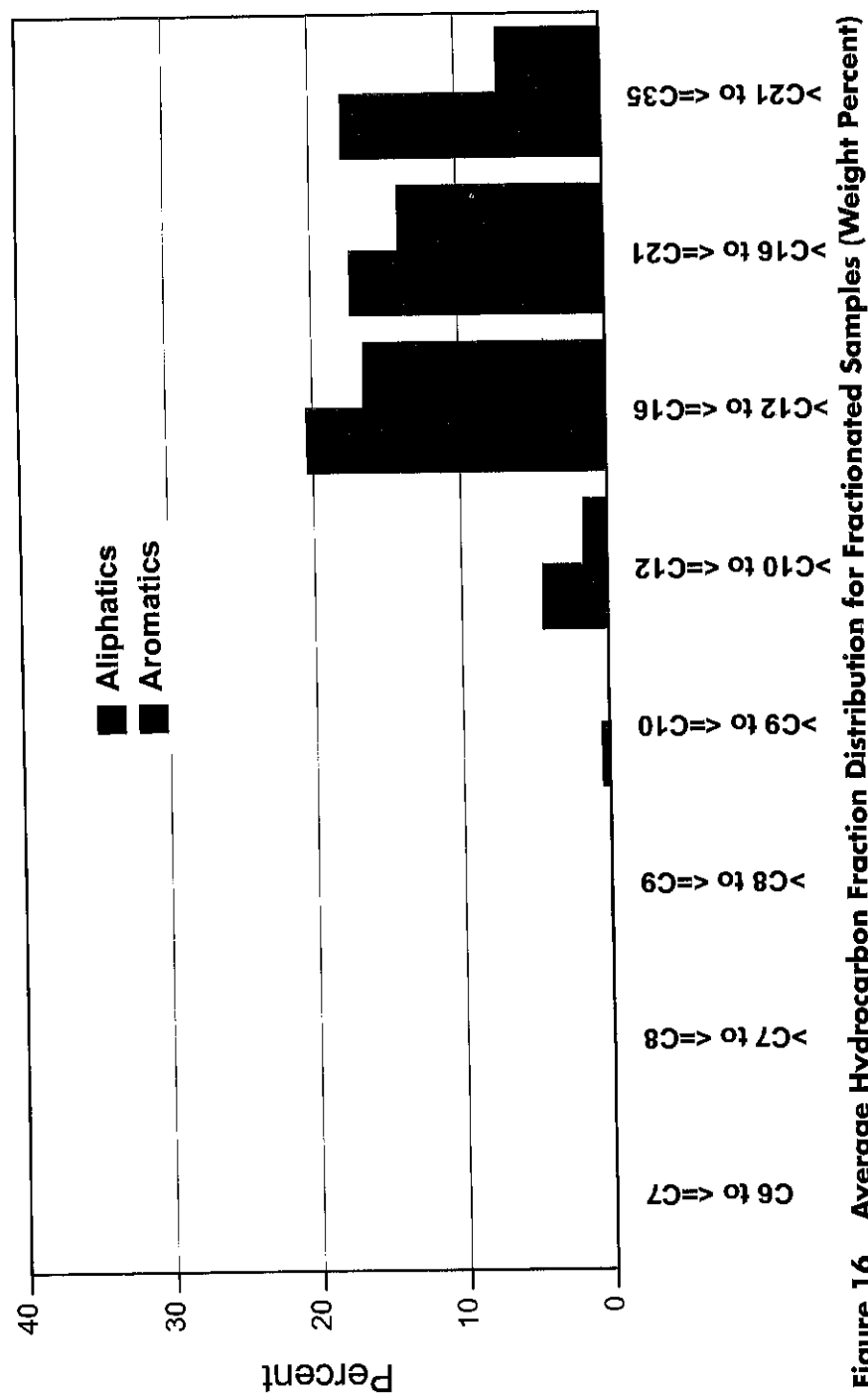
Figure 16   Average Hydrocarbon Fraction Distribution for Fractionated Samples (Weight Percent) — Midwestern Rail Yard
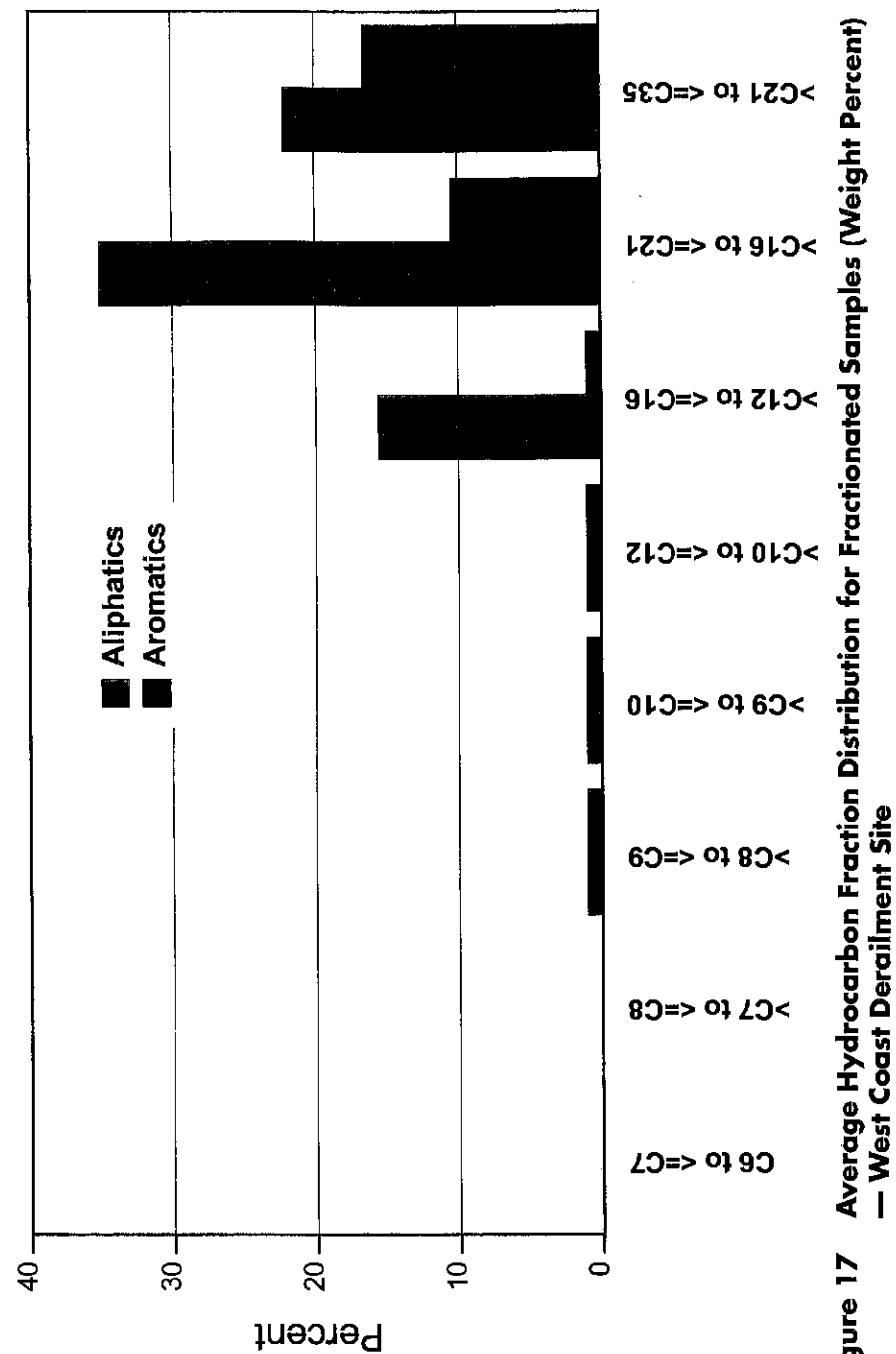
Figure 17   Average Hydrocarbon Fraction Distribution for Fractionated Samples (Weight Percent) — West Coast Derailment Site

The weight percent distribution for each aliphatic and aromatic fraction was calculated by dividing the mass within a specified carbon fraction by the total mass of aliphatics and aromatics. Prior to conducting a statistical analysis on these data, the following adjustments were made to the data sets.

Non-Detect Values. Carbon fractions, which were nondetect were adjusted to the level of quantitation (LOQ) prior to calculating the weight percent distribution of that fraction. The total mass of each extraction is included in this adjustment. In samples where there were only one or two detections of carbon fractions within an extraction, and where these detections were only slightly higher than the LOQ, the samples were not included in the statistical analysis. The rationale behind this decision was that the calculation of weight percent distributions with the adjustment of nondetect carbon fractions to the LOQ in these particular samples resulted in distributions which were very dissimilar to those in which detects occurred in the majority of fractions.

Lower TPH Limit. An initial screening of data indicated that soil samples containing low TPH concentrations tended to have weight distribution percentages, which differed from those samples collected within the same site and soil. Therefore, samples containing less than 1,000 mg/kg TPH were eliminated from the data sets. The following samples were eliminated from the surface soils: two for Southeastern, three for North-Central, one for Midwestern Rail Yard sites, and all seven samples analyzed from the West Coast Derailment site. Seven of the North-Central subsurface soil samples were eliminated. The selection of 1,000 mg/kg TPH as the cut-off point was determined graphically, by plotting the total TPH extracted by the direct analysis method versus the sums of the total TPH from the aliphatic and aromatic extractions for the surface soil samples (Figure 18).

Selected Data. The soil samples selected for statistical analysis were determined after adjusting for nondetect values and eliminating samples with less than 1,000 mg/kg TPH concentrations. None of the West Coast Derailment site data qualifies under the above assumptions, therefore they are not included further in the statistical analyses. All of the subsurface soil samples exceeded 1,000 mg/kg TPH except for the North-Central site. The West Coast Derailment site is not included in the subsurface sample statistics, as the subsurface soil was not sampled at this site.

The statistical analysis consisted of observing the differences in carbon weight percent distributions across sites and soils. Comparisons between weight percent distributions for the suite of carbon fractions was not conducted. Rather, each particular carbon fraction was compared to the same fraction across sites, or across soils within a site. The statistic used for this purpose was the mean $\pm$ one standard deviation. In general, the 95% confidence limits of the mean were similar to the standard deviation range. However, in certain fractions, the confidence levels were extremely high, due to low numbers of samples selected for that fraction and the resulting high t-statistic. Therefore, the standard deviation range was determined to provide a reasonable estimate of similarities or differences between samples. For those carbon fractions where the ranges in standard deviations did not overlap, confidence limits were evaluated.
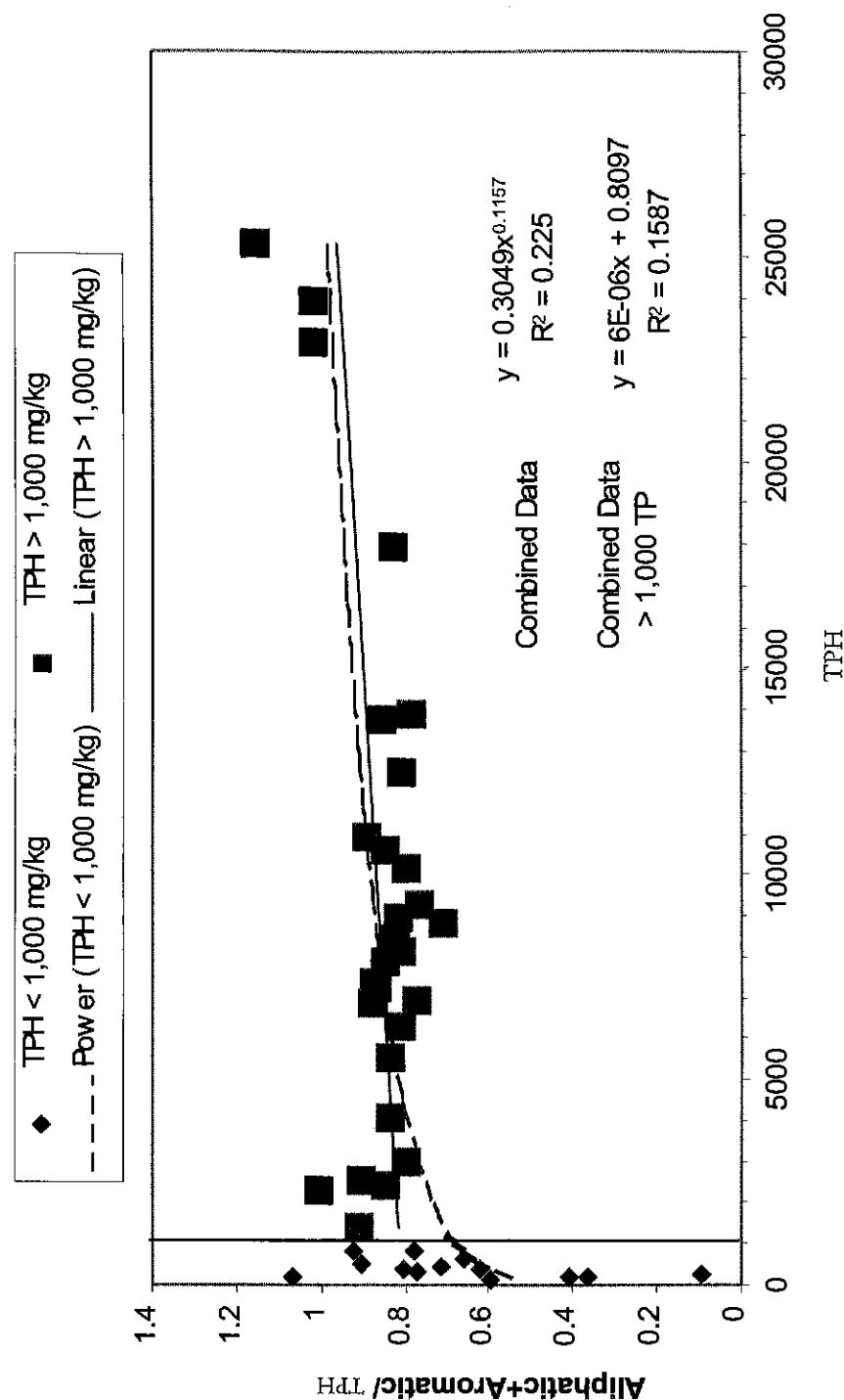
Figure 18   Combined TPH vs. Aliphatic + Aromatic Fraction Total for Surface Soils

All of the statistical analyses were conducted on the original data after the selection process for nondetect values and total TPH concentrations were completed. The data were not tested for distribution type, and no data transformations were performed.

Comparisons across Sites. The surface and subsurface soil samples were compared across three sites (the West Coast Derailment site was not included) to determine if any differences existed for particular weight percent distributions.

Surface Soil Comparisons between Sites. The results of the statistical analyses for the surface soils are presented in Table 12. When the original data was used (i.e, adjusted for nondetects, but not adjusted for TPH concentrations), the standard deviation range between North-Central and West Coast Derailment sites, and the Midwestern and West Coast Derailment sites, for the C_{16}-C_{21} fraction of the TPH did not overlap. For the aromatic fractions, the same relationship existed for the C_8-C_9, C_9-C_{10}, C_{10}-C_{12}, and C_{12}-C_{16} fractions. For the aliphatic fractions, all of the weight percent distributions relating the surface soils from all four sites had overlapping standard deviation ranges, indicating no significant difference between these sites.

When the data sets were adjusted both for nondetect values and TPH concentrations greater than 1,000 mg/kg, the West Coast Derailment site surface soil samples were excluded. However, there was no overlap in standard deviation ranges in the C_{16}-C_{21} fraction between Southeastern and North-Central Rail Yard sites. All other surface soil comparisons had overlapping standard deviation ranges.

Subsurface Soil Comparisons Between Sites. The results of the statistical analyses for the subsurface soils are presented in Table 13. No standard deviations were calculated for the North-Central site, as only one sample contained TPH at concentrations greater than 1,000 mg/kg. The standard deviation ranges for the TPH extraction did not overlap for the C_8-C_9, C_{10}-C_{12}, C_{12}-C_{16}, C_{16}-C_{21}, and C_{21}-C_{35} carbon fractions between the Southeastern Rail Yard and North-Central Rail Yard soils, and the C_{10}-C_{12}, C_{12}-C_{16}, C_{16}-C_{21} carbon fractions between the Southeastern and Midwestern Rail Yard soils. For the aliphatic fractions, all of the carbon fractions did not overlap between the Southeastern Rail Yard and North-Central Rail Yard, except for C_8-C_9. The C_{10}-C_{12}, C_{12}-C_{16}, and C_{16}-C_{21} carbon fractions did not overlap between the Southeastern Rail Yard and Midwestern Rail Yard subsurface soils. For the aromatic fractions, the C_6-C_7, C_{10}-C_{12}, C_{12}-C_{16}, and C_{16}-C_{21} carbon fractions did not overlap between the Southeastern Rail Yard and the North-Central and Midwestern Rail Yards. In addition, the Midwestern Rail Yard C_8-C_9 carbon fraction did nor overlap with that from the North-Central site.

Comparisons between Surface and Subsurface Soils, Within each Site. Surface and subsurface soil fraction distributions were compared within each site. The results of comparing the mean $\pm$ one standard deviation are summarized in Table 14. Because of the variability between replicates, very few differences, based upon the standard deviation range are discerned. The C_8-C_9 fraction differed between the surface and subsurface in at least one extraction for the Southeastern and North-Central sites. Other common differences between surface and subsurface soils include the C_{10}-C_{12} fraction. None of the Midwestern surface or subsurface soils overlap.

TABLE 12   Surface Soil Comparisons between Sites Based on +/- Standard Deviation

| | All data included | | | | Data w/o <1,000 mg/kg TPH | |
	North-Central	Midwestern	West Coast		North-Central	Midwestern
TPH				**TPH**		
Southeastern	x	x	x	Southeastern	C_{16}	x
North-Central		x	C_{16}	North-Central		x
Midwestern	x		C_{16}, Total			
Aliphatics				**Aliphatics**		
Southeastern	x	x	x	Southeastern	C_{16}	x
North-Central		x	x	North-Central		x
Midwestern	x		x			
Aromatics				**Aromatics**		
Southeastern	x	x	x	Southeastern	C_{16}	x
North-Central		x	$C_{8/9/10/12}$, Total	North-Central		x
Midwestern	x		$C_{8/9/14/12}$, Total			

Notes:
1.   X indicates that the standard deviation for all fractions overlap between these two sites.
2.   Carbon fraction number indicates that the standard deviations do not overlap between the two sites for the indicated fraction.

TABLE 13   Subsurface Soil Comparisons between Sites Based on +/- Standard Deviation without all data

| | All data included | |
	North-Central	Midwestern
TPH		
Southeastern	$C_{8/10/12/16/21}$	$C_{10/12/16}$
North-Central		x
Midwestern	x	
Aliphatics		
Southeastern	$C_{8/7/8/10/12/16/21}$	$C_{10/12/16}$
North-Central		x
Midwestern	x	
Aromatics		
Southeastern	$C_{6/10/12/16}$	$C_{6/10/12/16}$
North-Central		C_8
Midwestern	x	

Notes:
1.   X indicates that the standard deviations for all fractions overlap between these two sites.
2.   Carbon fraction number indicates that standard deviations do not overlap between the two sites for the indicated fraction.
3.   Only includes data where TPH is greater than 1,000 mg/kg.

TABLE 14 Comparisons between Surface and Subsurface Soils with all Data

	Southeastern	North-Central	Midwestern
TPH	$C_{8/9/10}$	C_8	None
Aliphatics	$C_{9/10}$	C_8	None
Aromatics	C_{10}	$C_{8/9}$	None

Notes:
Comparisons determined using +/- one standard deviation.
Carbon fraction numbers indicate that standard deviations do not overlap between the surface and subsurface soils for the fraction indicated.

Conclusions. A standard deviation was used as a statistic to differentiate individual carbon fraction weight distribution percentages between sites, and between soils within a site. No clear differences emerged. Generally, there was a large amount of variability between the replicates within each soil at each site, which masked any real differences that might have occurred between populations of weight percent distribution carbon fractions.

The C_{16}-C_{21} fraction differed between the Southeastern and North-Central Rail Yard surface soils for all three extractant categories. There were no apparent differences between the North-Central and Midwestern, nor the Southeastern and Midwestern, surface soils. For subsurface soils, the Southeastern Rail Yard generally contained weight percent concentrations that were different from those calculated for the Midwestern and North-Central Rail Yards. The West Coast Derailment site soil samples were not included in the statistical analysis due to low total TPH concentrations in the samples.

Comparisons between surface and subsurface soil weight percent distribution carbon fractions indicated that the C_8-C_9 through C_{10}-C_{12} carbon fractions might be used to distinguish separate soil horizons for the Southeastern and North Central Rail Yards. There was no apparent difference between surface and subsurface soils in the Midwestern site.

Based on the results of the simple statistical analysis conducted on the weight distribution percentages, it is difficult to distinguish differences or similarities between sites, or between the surface and subsurface soils within a site. A more complex statistical analysis of the data might provide more insight into their relationships.

Polynuclear Aromatic Hydrocarbons

Seven soil samples were analyzed for polynuclear aromatic hydrocarbons (PAHs) by GC/MS/SIM. A surface and subsurface soil sample were selected from the Southeastern, North-Central, and Midwestern Rail Yard sites. A single soil was selected from the West Coast Derailment site. Samples with the highest levels of total aromatic hydrocarbons from the direct analysis procedure were selected for analysis. In this way,

TABLE 15 Summary of Polynuclear Aromatic Hydrocarbon Results — Surface Soils (µg/kg - dry wt)

Site	Southeastern	North-Central	Midwestern	West Coast
Location	PSB- 8 (0-1.5')	PSB- 5 (0-3')	PSB- 8 (0-3')	PSB- 1 (0-2.5')
Naphthalene	8,600	490	2,400	ND (17)
Acenaphthylene	1,000	77	1,300	ND (17)
Acenaphthene	5,000	26	5,000	40
Fluorene	7,000	170	9,200	47
Phenanthrene	8,200	1,100	18,000	380
Anthracene	ND (55)	150	2,200	140
Fluoranthene	1,800	280	440	480
Pyrene	2,200	640	2,000	640
Benzo(a)anthracene	300	270	ND (180)	280
Chrysene	420	400	ND (180)	300
Benzo(b)fluoranthene	300	390	ND (180)	330
Benzo(k)fluoranthene	ND (55)	95	ND (180)	120
Benzo(a)pyrene	150	290	ND (180)	320
Indeno(1,2,3-cd)pyrene	170	290	ND (180)	190
Dibenz(a,h)anthracene	ND (55)	71	ND (180)	45
Benzo(g,h,i)pyrene	300	380	ND (180)	180
Total PAH	35,440	5,119	40,540	3,492

TABLE 16 Summary of Polynuclear Aromatic Hydrocarbon Results — Subsurface Soils (μg/kg - dry wt)

Site	Southeastern	North-Central	Midwestern
Location	PSB-3 (1.5-3')	PSB-1 (3-6')	PSB-3 (3-6')
Naphthalene	6,100	4,400	1,800
Acenaphthylene	1,600	ND (22)	610
Acenaphthene	6,700	220	4,800
Fluorene	1,800	1,300	8,100
Phenanthrene	27,000	1,100	17,000
Anthracene	ND (97)	130	2,400
Fluoranthene	1,800	140	1,100
Pyrene	1,800	200	280
Benzo(a)anthracene	210	100	350
Chrysene	280	97	320
Benzo(b)fluoranthene	200	98	250
Benzo(k)fluoranthene	ND (97)	89	80
Benzo(a)pyrene	99	62	150
Indeno(1,2,3-cd)pyrene	ND (97)	50	98
Dibenz(a,h)anthracene	ND (97)	ND (22)	36
Benzo(g,h,i)pyrene	124	78	110
Total PAH	63,913	8,064	37,484

results determined would be indicative of maximum PAH concentrations for the samples collected. The results are summarized in Tables 15 and 16.

Each of the target compound list PAHs were detected in at least one sample analyzed. The lighter (2 and 3 ring) compounds were present at the highest concentrations. Fresh diesel fuel contains a wide range of PAH compounds extending from naphthalenes (dominant) to phenanthrenes [Kaplan, 1994]. These compounds are more resistant to weathering effects than the normal alkanes and single ring aromatics. Therefore, even though the majority of the samples from the four sites showed at least moderate weathering, the PAH compounds were above detection levels using the GC/MS/SIM methodology. Naphthalene and the methyl substituted naphthalenes are the most soluble and biodegradable of the PAHs. The ratio of phenanthrene to naphthalene in the Southeastern and Midwestern Rail Yard sites provides another indication that this material has been subject to weathering processes. At these sites, the more resistant phenanthrene appears at concentrations equal to or greater than the naphthalene, indicating that naphthalene has been lost due to biological or environmental processes.

Leachate Testing

Sample Selection and Results

Three single samples from the Southeastern, North-Central, and Midwestern Rail Yard sites were selected to undergo leaching according to the Synthetic Precipitation Leaching Procedure (SPLP) as described in USEPA Method 1312 [USEPA, 1994]. The sample with the highest levels of PAHs was selected for analysis. Leachate testing was not performed on a sample from the West Coast Derailment site because of the inherently low levels of organics present in these samples.

Only the nonvolatile extraction portion of the SPLP was performed. Only five samples analyzed during the course of this study showed detectable levels of benzene or toluene (see Table 11). Even if all of the detected volatile organic material present, were to leach from these soils during the SPLP, the amount in the leachate would be below the detection limit of the quantitation procedure. This is due to a 1:20 dilution of the sample that occurs during generation of the SPLP leachate. That is, if a soil sample were found to contain 100 μg/kg (0.100 mg/kg) of benzene, the maximum amount that could be found in the leachate would be 5 μg/L (0.005 mg/L).

The generated leachates were analyzed for total hydrocarbons using the direct analysis method without fractionation, and for PAH compounds using the GC/MS SIM procedure. The results are summarized in Tables 17 through 19.

The results show that leaching was limited to the lighter constituents. For the PAHs, leaching was limited to naphthalene and trace levels of several 3-ring compounds. None of the heavier PAH compounds were present above the levels of detection. Similar results were obtained for the total hydrocarbon results. Leaching was limited to compounds of C_{12} or less.

Concentrations were below detection limits for individual fractions, although low concentrations below detection levels could be observed for lighter fractions. There was a total hydrocarbon concentration above the detection limit for the Midwestern Rail Yard site only. None of the heavier, $>C_{12}$, constituents were observed.

Leaching Factor Determination

The ultimate goal of the TPH analytical protocol verification study is to determine cleanup goals at petroleum-hydrocarbon contaminated sites in accordance with the Total Petroleum Hydrocarbon Criteria Working Group (Working Group) protocol. The Working Group protocol follows the risk-based corrective action (RBCA) framework developed by the American Society for Testing and Materials [ASTM, 1995].

The RBCA framework provides methods for estimating concentrations in environmental media, or risk-based screening levels (RBSLs), which pose minimal risk based on exposure factors and toxicity measures. One of the exposure pathways of concern is the leaching of contaminants from soils to groundwater. The soil to groundwater pathway of exposure is estimated by a leaching factor (LF), which relates the soil RBSL to the groundwater RBSL:

RBSL soil = RBSL groundwater/LF

The LF can be calculated through equations presented in the RBCA framework, or determined analytically from the results of laboratory analyses. This report calculates LFs by these two methods, and compares the results of the analyses for soils sampled by the AAR for the Working Group program.

Data. The PAH and SPLP leachate results described in the above sections were used in the leaching factor determination.

One soil sample per site was also analyzed for total organic carbon (TOC), which is a measurement of the fraction of organic carbon in a soil (foc). The soil moisture content was measured for each of these soils, and was used as the volumetric water content in the vadose zone (O_{ws}).

RBCA-Calculated Leaching Factor. The equation for the calculation of the leaching factor presented within the RBCA framework is:

$$F = Ps/(0_{ws} + KsPs + H0_{as})(1 + U_{gw}D_{gw}/IW)$$
where:

Ps = soil bulk density (1.7 g/cm^3)

0_{ws} = volumetric water content in the vadose zone soils (cm^3/cm^3) - soil specific

The soil-water partition coefficient (Ks) = foc * Koc, where:

foc = fraction of organic carbon in the soil - soil-specific (cm^3/cm^3)

Koc = organic carbon partition coefficient (cm^3/g) - chemical specific

RBCA default values proposed by the ASTM were used to calculate the LF, except for H, ks, O_{ws}, and foc, which were determined for individual soil samples or

TABLE 17   SPLP Leachate Results Southeastern Rail Yard Site — Soil PSB- 3 1.5-3'

Polynuclear Aromatic Hydrocarbons	
Parameter	Result (µg/L)
Naphthalene	25
Acenaphthylene	ND (0.5)
Acenaphthene	3
Fluorene	3
Phenanthrene	2
Anthracene	ND (0.5)
Fluoranthene	ND (0.5)
Pyrene	ND (0.5)
Benzo(a)anthracene	ND (0.5)
Chrysene	ND (0.5)
Benzo(b)fluoranthene	ND (0.5)
Benzo(k)fluoranthene	ND (0.5)
Benzo(a)pyrene	ND (0.5)
Indeno(1,2,3-cd)pyrene	ND (0.5)
Dibenz(a,h)anthracene	ND (0.5)
Benzo(g,h,i)perylene	ND (0.5)
Total Hydrocarbons	
Parameter	Result (mg/L)
Total Hydrocarbons	ND (4)

Note:

ND = Not detected. Number in parentheses indicates level of quantitation.

TABLE 18 SPLP Leachate Results North-Central Rail Yard Site — Soil PSB-1 3-6'

Polynuclear Aromatic Hydrocarbons	
Parameter	Result (µg/L)
Naphthalene	0.8
Acenaphthylene	ND (0.5)
Acenaphthene	ND (0.5)
Fluorene	ND (0.5)
Phenanthrene	ND (0.5)
Anthracene	ND (0.5)
Fluoranthene	ND (0.5)
Pyrene	ND (0.5)
Benzo(a)anthracene	ND (0.5)
Chrysene	ND (0.5)
Benzo(b)fluoranthene	ND (0.5)
Benzo(k)fluoranthene	ND (0.5)
Benzo(a)pyrene	ND (0.5)
Indeno(1,2,3-cd)pyrene	ND (0.5)
Dibenz(a,h)anthracene	ND (0.5)
Benzo(g,h,i)perylene	ND (0.5)
Total Hydrocarbons	
Parameter	Result (mg/L)
Total Hydrocarbons	ND (4)

Note:
ND = Not detected. Number in parentheses
indicates level of quantitation.

TABLE 19 SPLP Leachate Results Midwestern Rail Yard Site — Soil PSB-8 0-3'

Polynuclear Aromatic Hydrocarbons	
Parameter	Result (µg/L)
Naphthalene	1
Acenaphthylene	1
Acenaphthene	4
Fluorene	3
Phenanthrene	3
Anthracene	ND (0.5)
Fluoranthene	ND (0.5)
Pyrene	ND (0.5)
Benzo(a)anthracene	ND (0.5)
Chrysene	ND (0.5)
Benzo(b)fluoranthene	ND (0.5)
Benzo(k)fluoranthene	ND (0.5)
Benzo(a)pyrene	ND (0.5)
Indeno(1,2,3-cd)pyrene	ND (0.5)
Dibenz(a,h)anthracene	ND (0.5)
Benzo(g,h,i)perylene	ND (0.5)
Total Hydrocarbons	
Parameter	Result (mg/L)
Total Hydrocarbons	4

Note:
ND = Not detected. Number in parentheses
indicates level of quantitation.

TABLE 20   Leaching Factor Determination RBCA-Calculated Leaching Factors

Southeastern	Koc cm³/g	foc cm²/cm³	H cm³/cm³	Ks cm³/g	Pp g/cm³	Ps g/cm³	Ot cm³/cm³	Ows cm³/cm³	Oas cm³/cm³	Ugw cm/y	I cm/y	Ggw cm	W cm	RBCA LF
Naphthalene	844	0.045	0.017	37.98	2.65	1.7	0.358	0.136	0.222	2500	30	200	1500	2.17×10^{-3}
Acenaphthylene	2380	0.045	0.005	107.1	2.65	1.7	0.358	0.136	0.222	2500	30	200	1500	7.70×10^{-4}
Fluorene	3900	0.045	0.003	175.5	2.65	1.7	0.358	0.136	0.222	2500	30	200	1500	4.70×10^{-4}
Phenanthrene	8140	0.045	0.001	366.3	2.65	1.7	0.358	0.136	0.222	2500	30	200	1500	2.25×10^{-4}
North-Central	Koc cm³/g	foc cm²/cm³	H cm³/cm³	Ks cm³/g	Pp g/cm³	Ps g/cm³	Ot cm³/cm³	Ows cm³/cm³	Oas cm³/cm³	Ugw cm/y	I cm/y	Ggw cm	W cm	RBCA LF
Naphthalene	844	0.052	0.017	43.888	2.65	1.7	0.358	0.224	0.134	2500	30	200	1500	1.88×10^{-3}
Midwestern	Koc cm³/g	foc cm²/cm³	H cm³/cm³	Ks cm³/g	Pp g/cm³	Ps g/cm³	Ot cm³/cm³	Ows cm³/cm³	Oas cm³/cm³	Ugw cm/y	I cm/y	Ggw cm	W cm	RBCA LF
Naphthalene	844	0.025	0.017	21.1	2.65	1.7	0.358	0.098	0.260	2500	30	200	1500	3.90×10^{-3}
Acenaphthylene	2770	0.025	0.003	69.25	2.65	1.7	0.358	0.098	0.260	2500	30	200	1500	1.19×10^{-3}
Acenaphthene	2380	0.025	0.005	59.5	2.65	1.7	0.358	0.098	0.260	2500	30	200	1500	1.39×10^{-3}
Fluorene	3900	0.025	0.003	97.5	2.65	1.7	0.358	0.098	0.260	2500	30	200	1500	8.46×10^{-4}
Phenanthrene	8140	0.025	0.001	203.5	2.65	1.7	0.358	0.098	0.260	2500	30	200	1500	4.06×10^{-4}

Notes:

RBCA LF = Ps[Ows + Ks*Ps + H*Oas]*[1 + (Ugw*Ggw/I*W)]
Laboratory LF = SPLP Analysis/8270 Analysis

Ps = soil bulk density (g/cm3). RBCA default of 1.7 gm/cm3.
Pp = soil particle density (g/cm3). Standard default of 2.65 g/cm3.
Ows = volumetric water content (cm3/cm3). From lab sample moisture content.
Oas = volumetric air content (cm3/cm3). Ot-Ows.
Ot = total pore volume (cm3/cm3). 1-(Ps/Pb).

Ks = soil-water sorption coefficient (cm3/g). Ks = Koc*foc.
Koc = organic-carbon partition coefficient. Compound specific.

foc = fraction of organic carbon. Site specific TOC analysis.
Ugw = groundwater Darcy velocity (cm/yr). RBCA default of 2,500 cm/yr.
Ggw = groundwater mixing zone thickness (cm). RBCA default of 200 cm.
I = infiltration rate (cm/yr). RBCA default of 30 cm/yr.
W = width of source area parallel to groundwater flow direction (cm). RBCA default of 1,500 cm.

TABLE 21   Leaching Factor Determination Laboratory — Derived Leaching Factors

Site	Southeastern Rail Yard Site				
Location	PSB-3 (1.5-3)				
Analyte	8270 Analysis (µg/kg)	LOQ (µg/kg)	SPLP Analysis (µg/L)	LOQ (µg/L)	Laboratory Leaching Factor
Naphthalene	6,100	97	25	0.5	4.10×10^{-3}
Acenaphthylene	1,600	97	ND	0.5	NA
Acenaphthene	6,700	97	3	0.5	4.48×10^{-4}
Fluorene	18,000	580	3	0.5	1.67×10^{-4}
Phenanthrene	27,000	580	2	0.5	7.41×10^{-5}
Site	North-Central Rail Yard Site				
Location	PSB-1 (3-6)				
Analyte	8270 Analysis (µg/kg)	LOQ (µg/kg)	SPLP Analysis (µg/L)	LOQ (µg/L)	Laboratory Leaching Factor
Naphthalene	4,400	85	0.8	0.5	1.9×10^{-4}
Acenaphthylene	ND	22	ND	0.5	NA
Acenaphthene	220	22	ND	0.5	NA
Fluorene	1,300	22	ND	0.5	NA
Phenanthrene	1,100	22	ND	0.5	NA
Site	Midwestern Rail Yard Site				
Location	PSB-3 (0-3)				
Analyte	8270 Analysis (µg/kg)	LOQ (µg/kg)	SPLP Analysis (µg/L)	LOQ (µg/L)	Laboratory Leaching Factor
Naphthalene	2,400	180	1	0.5	3.48×10^{-4}
Acenaphthylene	1,300	180	1	0.5	7.69×10^{-5}
Acenaphthene	5,000	180	4	0.5	8.00×10^{-4}
Fluorene	9,200	180	3	0.5	3.26×10^{-4}
Phenanthrene	18,000	180	3	0.5	1.67×10^{-4}

Note:
LOQ = Limit of Quantitation

compounds. The input variables for the RBCA LF equation for each soil and compound are presented in Table 20, for those compounds, which were detected in both the Method 8270 and SPLP analyses.

Laboratory-Derived Leaching Factor. The laboratory LF was derived as the concentration of PAH leaching out of the soil (SPLP) divided by the concentration of PAH in the soil (Method 8270), and is presented in Table 21. Laboratory LFs were derived only for those compounds, which had a detected concentration for both the method 8270 and SPLP analyses, which were:

- Southeastern Rail Yard Site soil: naphthalene, acenaphthylene, fluorene, and phenanthrene
- North-Central Rail Yard Site soil: naphthalene
- Midwestern Rail Yard Site soil:naphthalene, acenaphthylene, acenaphthene, fluorene, and phenanthrene

Results. The results of the RBCA-calculated LFs are presented in Table 20, with laboratory-derived LFs presented in Table 21. In all cases, except for naphthalene in the Southeastern Rail Yard site soil, the laboratory-derived LF was less than the LF determined from the RBCA equation. The differences between the two methods were generally within an order of magnitude. Figure 19 indicates that naphthalene LF values did not have a high degree of association between the two methods of calculation. However, all the other LF values appeared to follow a linear trend.

These results show that the LF calculated from the ASTM RBCA framework is generally more conservative (higher) compared to the laboratory-derived LF. That is, the RBCA LF, in most cases, will result in a lower, or more conservative, soil RBSL for a given groundwater goal than the lower, site-specific, laboratory-derived LF, which will yield a higher, less conservative RBSL. The laboratory-derived LF represents a more realistic estimate of the transfer of PAHs from soils to groundwater, since it is based on real data.

Figure 19   Laboratory versus Calculated Leaching Factors

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Acronyms

AAR	Association of American Railroads
API	American Petroleum Institute
AST	aboveground storage tank
ASTM	American Society for Testing and Materials
BTEX	benzene, toluene, ethylbenzene and xylene
C:N	carbon to nitrogen
DAF	dissolved air flotation
DCE	dichloroethene
DO	dissolved oxygen
DRO	diesel range organics
EPA-ERTC	U.S. Environmental Protection Agency Environmental Response Team Center
f	soil fraction of organic carbon
G^{oc}C	gas chromatographic
GCL	geosynthetic clay liner
GC/FID	gas chromatography/flame ion detection
GC/MS	gas chromatography/mass spectrometry
IR	infrared spectroscopic
LLNL	Lawrence Livermore National Laboratory
LNAPL	light non-aqueous phase liquid
LUFT	leaking underground fuel tank
MCLs	maximum contaminant levels
MPN	most probable number
MS/MSD	Matrix spike and matrix spike duplicate
MTBE	methyl-tertiary-butyl ether
NETAC	National Environmental Technology Applications Center

NIST	National Institute of Standards and Technology
NYDSEC	New York State Department of Environmental Conservation
PAH	polynuclear aromatic hydrocarbons
PAH	polycyclic aromatic hydrocarbons
PCB	polychlorinated biphenyls
PCE	tetrachloroethene
PCP	pentachlorophenol
PID	photoionization detector
POTW	publicly owned treatment works
QA	quality assurance
RAPMA	Remedial Action Plan Monitoring Act
RBCA	risk-based corrective action
RBSLs	risk-based screening levels
REAC	Response, Engineering & Analytical Contract
RPD	relative percent difference
RWQCB	Regional Water Quality Control Board
SITE	Superfund Innovative Technology
SPLP	synthetic precipitation leaching procedure
SWRCB	State of California Water Resources Control Board
SIM	selected ion monitoring
SVOC	semi-volatile organic compounds
TCE	trichloroethene
TCLP	toxicity characteristic leaching procedure
TDS	total dissolved solids
TKN	total kjeldahl nitrogen
TOC	total organic carbon
TOFL	trailer-on-flat-car
TPH	total petroleum hydrocarbons
UCM	unresolved complex misture
U.S. EPA	United States Environmental Protection Agency
VaDEQ	Virginia Department of Environmental Quality
VC	vinyl chloride
VOC	volatile organic compounds
WDNR	Wisconsin Department of Natural Resources
XRF	x-ray fluorescence

Editor Biographies

ROGER P. ANDES is a Senior Environmental Research Engineer at the Association of American Railroads (AAR) where he oversees applied research in pollution prevention and remediation technologies for the railroad industry. Mr. Andes has a M.S. degree in Environmental Science from George Washington University. Prior to joining the AAR, he contributed to, produced, or reviewed and edited numerous reports on environmental monitoring, data analyses, and modeling programs for many industrial facilities, the Department of Energy, and for railroad operations at Amtrak. Current research at the AAR on site remediation has focused on the more accurate appraisal of risk from petroleum hydrocarbon contamination by methods proposed by the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG). Research reports for this effort co-authored by Mr. Andes include: *Risk-Based Management of Diesel-Contaminated Soil, R-897; Comparison of Analytical Methods for Use in Evaluating the Risk From Petroleum Hydrocarbons in Soil, R-903;* and *TPH Analytical Verification Protocol for Multiple Field Sites* (in preparation). Additionally, he has been an active participant in the Petroleum Environmental Research Forum (PERF) Risk Assessment Cooperative and the TPHCWG. Mr. Andes has played an important role reviewing and evaluating research plans by these groups in their efforts to contribute, obtain, and disseminate the latest information on advances in remediation technologies and risk assessment of contaminated sites. Mr. Andes is a member of the Scientific Advisory Board for the Annual Conference on Contaminated Soils, at which the Railroad Session papers in this book were presented.

CHRISTOPHER P.L. BARKAN recently accepted the position of Senior Scientist and Director of Railroad Programs at the University of Illinois at Urbana-Champaign. Prior to that he directed research for the railroad industry at the Association of American Railroads (AAR) in Washington, DC. At the AAR Dr. Barkan managed the railroad industry's research programs on pollution prevention, remediation technologies, hazardous materials transportation and tank car safety. Barkan continues to serve as the Deputy Project Director of the RPI-AAR Railroad Tank Car Safety Research and Test Project, a cooperative program of the tank car and railroad industries studying tank car safety. Barkan holds graduate degrees in biology from the State University of New York at Albany where he conducted research on the application of stochastic optimization models to ecological processes. He continued this work as a research fellow at the Smithsonian Institution's Environmental Research Center prior to joining the AAR Research and Test Department in 1988. His research at the AAR included the development and application of quantitative risk assessment models for rail transportation of hazardous materials, with particular emphasis on the environmental impact of chemical spills. Other environmental research for the railroad industry has included studies of the impact of rail lubrication, stormwater runoff characteristics, toxicity characteristic leaching procedure testing of railroad crossties, evaluation of the factors affecting successful application of in situ bioremediation and investigation of technology for recycling cleaning solutions used in railroad shops. Current projects include development of a standard locomotive fueling interface to prevent spillage during locomotive refueling and, developing new data on the chemical composition of weathered petroleum hydrocarbons typical of railroad sites. He serves on the steering committee of the Total Petroleum Hydrocarbon Criteria Working Group, a cooperative effort of industry, and government that has develop consolidated data and approaches to more effectively apply total petroleum hydrocarbon (TPH) and risk-based cleanup criteria to petroleum contaminated sites. Barkan is an author or editor of more than two dozen papers, reports and books on railroad environmental subjects.

EDWARD J. CALABRESE is a board certified toxicologist who is a professor of toxicology at the University of Massachusetts School of Public Health, Amherst. Dr. Calabrese has researched extensively in the area of host factors affecting susceptibility to pollutants, and is author of more than 300 papers in scholarly journals, as well as 24 books, including *Principles of Animal Extrapolation; Nutrition and Environmental Health,* Volumes 1 and 2; *Ecogenetic: Safe Drinking Water Act: Amendments, Regulations and Standards; Soils Contaminated by Petroleum: Environmental & Public Health Effects; Petroleum Contaminated Soils,* Volumes 1, 2 and 3; *Ozone Risk Communication and Management; Hydrocarbon Contaminated Soils,* Volumes 1-5; *Hydrocarbon Contaminated Soils and Groundwater,* Volumes 1-4; *Contaminated Soils,* Volumes 1-3; *Multiple Chemical Interactions; Air Toxics and Risk Assessment; Alcohol Interactions with Drugs and Chemicals; Regulating Drinking Water Quality; Biological Effects of Low Level Exposures to Chemicals and Radiation; Diesel Fuel Contamination; Risk Assessment and Environmental Fate Methodologies; Principles and Practices for Petroleum Contaminated Soils,* Volume 1-7 and *Performing Ecological Risk Assessments.* He has been a member of the U.S. National Academy of Sciences and NATO Countries Safe Drinking Water Committees, and the Board of Scientific Counselors for the Agency for Toxic Substances and Disease Registry (ATSDR). Calabrese also serves as Director of the Northeast Regional Environmental Public Health Center at the University of Massachusetts and Chairman of the BELLE Advisory Committee.

PAUL T. KOSTECKI, Associate Director, Northeast Regional Environmental Public Health Center, School of Public Health, University of Massachusetts at Amherst, received his Ph.D. from the School of Natural Resources at the University of Michigan in 1980. He has been involved with human and ecological risk assessment and risk management research for the last twelve years. Dr. Kostecki has co-authored and co-edited over 50 articles and 16 books on environmental assessment and cleanup including: *Remedial Technologies for Leaking Underground Storage Tanks; Soils Contaminated by Petroleum Products; Petroleum Contaminated Soils,* Volumes 1-3; *Hydrocarbon Contaminated Soils and Groundwater,* Volumes 1-4; *Hydrocarbon Contaminated Soils,* Volumes 1-5; *Contaminated Soils,* Volumes 1-3, *Principles and Practices for Petroleum Contaminated Soils,* Volumes 1-4; *Principles and Practices for Diesel Contaminated Soils,* Volumes 1-7; *SESOIL in Environmental Fate and Risk Modeling and Risk Assessment and Environmental Fate Methodologies.* Dr. Kostecki also serves as Associate Editor for the *Journal of Soil Contamination,* Chairman of the Scientific Advisory Board for *Soil and Groundwater Cleanup* Magazine as well as an editorial board member for the journal of *Human and Ecological Risk Assessment.*

In addition, Kostecki serves as Executive Director for the Association for the Environmental Health of Soils (AEHS). He is a member of the Navy's National Hydrocarbon Test Site Advisory Board and a member of the Steering Committee for the Total Petroleum Hydrocarbon Criteria Working Group.

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