

# Principles and Practices for Diesel Contaminated Soils

Volume IV

*Edited by*  
**Christopher P.L. Barkan**



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Contaminated Soils, Vol. IV**

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## **Principles and Practices for Diesel Contaminated Soils, Vol. IV**

*Edited by*

**CHRISTOPHER P.L. BARKAN**

**EDWARD J. CALABRESE and**

**PAUL T. KOSTECKI**



**Amherst  
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OF AMERICAN  
RAILROADS**

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## Biographies

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GIF

Edward J. Calabrese is a board certified toxicologist who is 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 the author of more than 270 papers in scholarly journals, as well as 23 books, including *Principles of Animal Extrapolation; Nutrition and Environmental Health*, Vols 1 and 2; *Ecogenetics: Safe Drinking Water Act: Amendments, Regulations and Standards; Petroleum Contaminated Soils*, Vols, 1, 2 and 3; *Ozone Risk Communications and Management; Hydrocarbon Contaminated Soils*, Vols. 1, 2, 3 and 4; *Hydrocarbon Contaminated Soils and Groundwater*, Vols. 1, 2, 3 and 4; *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; Contaminated Soils; Diesel Fuel Contamination; Risk Assessment and Environmental Fate Methodologies, and Principles and Practices for Petroleum Contaminated Soils*. 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). Dr. Calabrese also serves as Chairman of the International Society of Regulatory Toxicology and Pharmacology's Council for Health and Environmental Safety of Soils (CHESS) and Director of the Northeast Regional Environmental Public Health Center at the University of Massachusetts.

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 risk assessment and risk management research for contaminated soils for the last eight years, and is coauthor of *Remedial Technologies for Leaking Underground Storage Tanks*, coeditor of *Soils Contaminated by Petroleum Products and Petroleum Contaminated Soils*, Vols. 1, 2 and 3, and of *Hydrocarbon Contaminated Soils*, Vols. 1, 2, 3 and 4; and *Hydrocarbon Contaminated Soils and Groundwater*, Vols 1, 2, 3 and 4, of *Contaminated Soils: Diesel Fuel Contamination, Vols. 1,2,3, and 4; Principles and Practices for Petroleum Contaminated Soils*, Vols 1, 2 and 3; and *Risk Assessment and Environmental Fate Methodologies*. Dr. Kostecki's yearly conferences on hydrocarbon contaminated soils draw hundreds of researchers and regulatory scientists to present and discuss state-of-the art solutions to the multidisciplinary problems surrounding this issue. Dr. Kostecki also serves as Managing Director for the International Society of Regulatory Toxicology and Pharmacology's Council for Health and Environmental Safety of Soils (CHESS), as Executive Director of the Association for the Environmental Health of Soils (AEHS). He is an editorial advisor to the *Journal of Soil Contamination* and *SOILS* magazine, as well as on the editorial board of the *Journal of Human and Ecological Risk Assessment*.

## Preface

### Proceedings of 1994 Symposium on Remediation of Diesel Fuel Contaminated Soil

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Sponsored by the Association of American Railroads  
Research and Test Department

North American industry, including railroads, must compete in a highly competitive global economy in which the regulatory and operating constraints vary from country to country. Environmental regulations in North America are often more stringent than most of the rest of the world. Although the public and environmental health of North Americans may benefit from these regulations, they impose costs on the operation of North American companies that do not apply to many of their international competitors. In the world marketplace these added costs must be offset by greater efficiencies and/or quality differentials. Railroads are one of the major North American transportation modes, consequently their costs, including the cost of compliance with environmental regulations, can affect the price of North American goods reaching the market.

The largest single component of railroads' environmental compliance costs is the cleanup of sites contaminated by leaks and spills of petroleum products. Most of these releases occurred in an era before their potential impact on the environment was understood. The discovery of the contamination at Love Canal in 1976 changed our perception, if not our understanding, of the risk posed by chemical contamination of soil and groundwater, and many of the regulations regarding cleanup of contaminated sites were developed in the atmosphere of uncertainty and fear that followed. Political considerations often dictated that the development of regulations and standards precede detailed scientific understanding of the risk to human and environmental health posed by contaminated sites.

As our scientific knowledge has advanced we have come to understand that there are many factors that can mitigate the impact of contamination. This is particularly relevant to the petroleum products typically found at contaminated railroad sites. Application of this knowledge to cleanup requirements is important to North America's public and environmental health, as well as its economy. When resources are expended on the unnecessary cleanup of a site, it detracts from economic productivity and, more importantly, it can divert attention and resources away from other sites or activities that may pose greater marginal risk to human and environmental health. Optimal allocation of remediation resources is therefore of interest to government, industry and the public. The public has a right to expect that regulators will work with the regulated community to apply advances in scientific and engineering knowledge to the greatest extent possible.

The annual symposium on diesel contaminated soils, and the production of this volume, are intended to provide a forum to encourage the development and exchange of scientific, engineering and economic information related to railroad industry remediation issues. The contents of this volume are particularly timely because they principally bear on two major issues in remediation today: the expanding use of bioremediation techniques, and the application of risk-based criteria to site cleanup.

Just five years ago, bioremediation was still viewed with a great deal of skepticism. It is now a proven technique, and its effectiveness has been documented in many applications (including papers published in previous volumes in this series). A number of the papers included in this volume provide additional information on the steps required to successfully apply the technique, including some novel applications and circumstances of particular relevance to railroad industry users. In the broader sense, the value of bioremediation is its role as an economical method in which the hydrocarbon contaminants are converted by microbial activity into harmless byproducts, often without even requiring the removal of the contaminated soil. Biodegradation of the contaminants means that potential problems have been eliminated, not simply transferred to another location or environmental media.

Whereas bioremediation represents an economical technique to remove contaminants, the emerging use of more sophisticated risk-based cleanup criteria represents a scientific method to determine how much of the contaminant to remove at a particular site to adequately guard public and environmental health. In the past, cleanup levels for petroleum contaminated sites have often been arbitrary standards driven by the sensitivity of the analytical techniques in use. As these techniques have become more sensitive to trace levels of hydrocarbon contaminants, the cleanup requirements have become correspondingly more stringent, often with little consideration of how much this would benefit public or environmental health. Even when ostensibly risk-based criteria have been used, they have often been based on total petroleum hydrocarbon (TPH) levels. The TPH criteria is a non-specific analytical technique for measuring hydrocarbon mass. Frequently, risk-based criteria based only on TPH analyses rely on invalid assumptions regarding the chemical composition (and consequent toxicology and mobility) of the contaminants being measured in the soil and particularly the contaminants typical of railroad remediation sites. Too often the result is excessive, time consuming and costly site cleanup requirements. Several of the papers in this volume address this issue by presenting detailed information on the specific chemical compounds present at contaminated railroad sites, as well as the environmental mobility and bioavailability of these compounds, the sampling and statistical methods used to evaluate a site, and how to use this information when planning a site cleanup.

Bioremediation and risk-based cleanup criteria have a factor in common, successful use of either requires greater planning than has been necessary for more traditional approaches. This planning is more demanding of both the regulated community and the regulator. The regulated community may have to expend more time and money in evaluating the site, collecting necessary data and evaluating this information. Regulators must be willing to expend the time and resources to review the information to assure themselves that the proposed approach and criteria satisfies their obligation

to the public. The payoff for proper execution of these efforts will frequently be less costly remediation requirements that are commensurate with the risk posed by contaminated sites and consequently, better allocation of resources to cleanup contaminated sites in North America.

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The vitality and relevance of the annual diesel symposium and the resultant book would be impossible without the interest, support and participation of the railroad environmental community, in particular the members of the AAR Environmental Affairs Committee and its Environmental Engineering and Operations Subcommittee. The editors and railroad industry are grateful to the authors for their participation in the diesel symposium and their willingness to share the knowledge they have gained pertinent to the remediation of railroad sites. Special thanks to Martina Schlauch for her assistance with the technical preparation of the diesel symposium and book, to Linda Rosen for her energetic support of the annual conference, and the staff at AEHS for their patience and persistence in bringing together the materials presented in this volume.



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## CHAPTER 1

# Characterization of Weathered Diesel and Bunker Oil in Soil and Groundwater

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### INTRODUCTION

Regulation of spilled petroleum in soils and groundwater has been the subject of substantial debate between industry and governmental agencies since the early 1980s. At the heart of the controversy rests two fundamental issues; first, the constituents within the petroleum mixture that should be regulated, and second, the environmental risk posed by the various petroleum constituents. We would add a third issue, that being the need for distinguishing between fresh petroleum spills and highly weathered petroleum in soil and groundwater as to the differential risk they pose. The focus here is to present evidence that weathered fuel oil represents a very different characteristic than gasoline or diesel fuel, which are the basis for regulatory cleanup thresholds and as such should be remediated in a manner more consistent with the risk they may represent to the public health and the environment.

Oliver et al.,<sup>1</sup> have compiled state regulations for petroleum throughout the 50 states. Their survey found that 42 states used a surrogate mixture analysis, total petroleum hydrocarbons (TPH) as the primary guidance for cleanup of petroleum sites. Thirty-five of these 42 states also apply volatile organic analysis in concert with TPH analysis. A few states, notably California, do not specify a generic cleanup level in soil or water, but rather publish guidelines by geographic district that are used as action levels.<sup>2</sup> Strangely, even as Congress and the U.S. Environmental Protection Agency are proposing to strengthen the use of risk assessment based cleanups and the establishment of national risk protocols,<sup>3</sup> rarely do states make cleanup determinations based on constituent risk. Moreover, site specific hydrogeology, and vadose soil properties generally are not applied when assessing environmental impacts to potential receptors. A few states such as Oregon are moving away from the mixture (TPH) technique and are beginning to regulate on the basis of specific constituent analysis, most often including benzene, toluene, total xylenes, ethylbenzene (BTXE), and polyaromatic hydrocarbons (PAHs).

Recently ASTM<sup>4</sup> published its draft guidance on corrective action at petroleum release sites in which it specifically discourages the use of TPH values as a basis for making corrective action decisions. The authors of the ASTM guidance contend that TPH is limited in utility to identifying boundaries of affected areas and pinpointing "hotspots." Given the present regulatory methods and the probable move to more risk based assessments, the development of a clear understanding regarding site specific and constituent specific petroleum chemistry is critical.

## CHEMISTRY OF PETROLEUM

In general, petroleum types most frequently facing environmental cleanups include gasoline, diesel fuel, jet fuel, and heavy fuel oil. Distinct from these petroleum classes are weathered materials in soil and groundwater which have undergone degradation or transformation by abiotic and biotic processes. It is instructive to understand the distinction among these classes and their properties as they lead directly to the application of appropriate analytical techniques and chemical specific toxicity.

Gasoline is essentially a complex mixture of hydrocarbons that boil below 200°C. Individual hydrocarbons in this boiling range are those which contain from four to twelve carbon atoms. Gasoline related hydrocarbons fall into three general types: paraffins (e.g., n-nonane), olefins (e.g., hexene), and aromatics (e.g., benzene). There are approximately 500 members of this series of compounds, most of which have been found in gasoline. While the contribution of various compounds in gasoline vary by their origin, five compounds make up 29% of the gasoline fraction and another 20 compounds constitute 59%.

Diesel fuels are classified as middle distillates and are denser than gasoline. Distillate fuel oils are vaporized and condensed during a distillation process and thus have definite boiling range. Diesel fuel No. 2 is used in the automotive and railroad industries and contains hydrocarbons predominantly in the C<sub>10</sub> to C<sub>20</sub> range. It is comprised of the same classes of compounds as gasoline, with the exception being a wider range of hydrocarbons having a boiling point range of 160-360°C. Diesel contains minor amounts of PAHs including phenanthrene (429 mg/Kg), fluoranthene (37 mg/Kg), pyrene (41 mg/Kg), benz[a]anthracene (1.2 mg/Kg), and benzo[a]pyrene (0.6 mg/kg).<sup>5</sup> A comprehensive review of the chemistry of diesel fuels was performed by Griest et al.<sup>6</sup> This study characterized the chemistry of 11 diesel fuels. Results of this work showed the amount of benzene present at trace levels, <0.01 to 0.08 mg/Kg.

Bunker C fuel oil, or Bunker No. 6 oil is among a number of heavy fuel oils which are comprised of pitch, reduced crude oil, and fractionator bottoms. Historically, these oils were manufactured by removing what was left from refining crude petroleum. Bunker C oil is a solid at room temperature. Weathered bunker oil will generally not begin to boil below 300°C.

## ANALYTICAL TECHNIQUES

There are five analytical methods routinely employed for the determination of petroleum in soil—all are EPA methods: 418.1 total recoverable petroleum hydrocarbons; 8015 (Modified) total petroleum hydrocarbons; 8020 BTXE; 8270 semi-volatile compounds; and 8240 volatile organic compounds. Of these methods, 8015M and 418.1 are the most widely applied. California modified the standard EPA Method 8015 to gasoline and diesel fuel analysis from leaking tanks. The method uses a temperature programmable gas chromatograph (GC) with a flame ionization detector (FID). The column is heated from 40 to 265 °C in 10 °C increments.<sup>7</sup> The method does not report individual compounds, and as can be seen from its operating range, cannot evaluate highly weathered diesel or residual fuel oils, as they boil well above the maximum temperature. Method 418.1 is an infrared spectrophotometric procedure<sup>8</sup> in which an extract using fluorocarbon-113 is quantified using the C-H stretch band at about 2930 cm<sup>-1</sup> against a standard containing n-hexadecane, isooctane, and chlorobenzene, all of which are representative of light fuel but not weathered diesel or heavy fuel oils.

Use of GC techniques for direct component analysis in heavy residual fuel or weathered diesel is beset by many potential problems. The number of possible components in any given molecular weight range increases markedly with the molecular weight, and there is a drop in differences in physical properties among similar structural forms. Unless the sample has been fractionated by other techniques to reduce the complexity, component analysis by GC is very difficult at best. In light of this problem the coupling of GC with spectrometric techniques which can provide a better resolution of the molecular character should be applied. Absent the ability to determine what compounds or types of compounds comprise the weathered diesel or bunker fuel mixture, a true analysis of its environmental significance cannot be determined. As such, the appropriate method for analyzing petroleum in soil or groundwater is GC-mass spectrometry (GC/MS).

Method 8270 is a GC/MS technique. It can be used to determine the types of semi-volatile compounds in soil extracts or groundwater. This method is applicable to most neutral, acidic, and basic organics that are soluble in methylene chloride; noteworthy among these are PAHs.<sup>9</sup> It can also provide a breakdown of hydrocarbons by carbon number but not by specific structure in the heavy fuel range (C<sub>20</sub> to C<sub>38</sub>). The reason for the lack of resolution by structure is that the MS identifies compounds principally in terms of molecular type and weight. Nevertheless, the method provides a good qualitative insight as to the carbon distribution within the mixture.

The importance in understanding the hydrocarbon distribution is tantamount when applying a risk assessment approach to cleanup. For example, it is known that alkanes and alkenes have limited toxicity and are of low solubility in water.<sup>10</sup> It is also known that as the number of aromatic rings increases or the number of carbon atoms increases, solubility and toxicity decrease. Thus when evaluating weathered diesel and heavy fuel products, the properties of these compounds have a direct bearing on the mixture's potential significance to the public health and the environment.

## STUDY DESIGN

Southern Pacific Transportation Company has routinely been collecting speciated hydrocarbon data in soils and groundwaters from sites containing weathered diesel fuel and Bunker C oil since 1992. As a result, a substantial data set has been generated characterizing these weathered mixtures in a variety of settings. In this work a diverse series of sites are selected based on depositional history and physiographic setting. Sites chosen include an arid environment at Imlay Nevada, central mountain setting in Dunsmuir California, two central valley California sites, and a southern coastal environment. In all, the data set contains over 300 soil samples, and in excess of 200 groundwater samples. Geotechnical properties of the various affected soils were also collected in an effort to correlate depositional properties and hydrocarbon species with the ultimate objective of aiding the design of remedial technologies.

## PHYSICAL PROPERTIES OF SOIL

Physical properties of vadose soils at each of the sites have been collected. A minimum of two samples were analyzed in every soil type with a total of 43 samples cataloged in the database. Data are available for soil type, grain size, pH, specific gravity, total porosity, moisture content, density, and hydraulic conductivity.

**Soil Type:** Soil types range across a wide spectrum from gravels to clays and include organic clays, clays, poorly-graded sand with silt, clayey sand, silty sand, and poorly-graded sand.

**Grain Size Distribution:** Grain size distribution data are cataloged in terms of percent gravel (retained on #4 sieve; approximately >4 millimeters), sand (pass #4 sieve and retained on #200 sieve; approximately >0.07 millimeters and <4 millimeters), and fines (pass #200 sieve; approximately <0.07 millimeters). Test results for site soils indicate gravel ranging from 0 to 67%, sand ranging from 2 to 93%, and fines ranging from 4 to 98%. The arithmetic means for each size group are 6% for gravel, 27% for sand, and 67% for fines.

**pH:** Soil pH ranged from 6.4 to 8.6 and averaged 7.4.

**Specific Gravity:** Specific gravity of soil samples ranged from 2.51 to 2.79 and averaged 2.70.

**Total Porosity:** Total porosity of soil samples ranged from 21.0 to 48.3% and averaged 31.3%. When evaluated by soil horizon (A vs. B vs. C horizons), the data show no systematic variation with location or with depth other than soils tend to be finer grained with increasing depth, which would be expected.

**Moisture Content:** Moisture content ranged from 5.1 to 36.7% and averaged 12.5%. The moisture content was generally higher in the deeper samples. There was no adjustment for variations in seasons in which samples were taken.

**Dry Density:** Dry density ranged from 89.6 to 130.8 pounds per cubic foot (pcf) and averaged 107.4 pcf. The data show no systematic variation with site or with depth.

**Saturated Vertical Hydraulic Conductivity:** Measured vertical hydraulic conductivities ranged from  $1.5 \times 10^{-8}$  centimeters per second (cm/sec) to  $1.0 \times 10^{-1}$  cm/sec and averaged  $4.3 \times 10^{-4}$  cm/sec. The average dispersion in conductivity values by site was two orders of magnitude and the dispersion among designated soil types was approximately 0.45 order of magnitude. Measured hydraulic conductivity for A horizon soil averages  $4.1 \times 10^{-4}$  cm/sec while the measured hydraulic conductivity for B horizon and below averages  $7.1 \times 10^{-6}$  cm/sec.

**Acute Toxicity:** A total of 11 samples from the sites were submitted to a laboratory for acute toxicity (fish bioassay) analysis. All 11 samples had an acute aquatic 96-hour  $LC_{50}$  greater than 750 mg/l.

A summary of physical properties statistics is provided in table 1. Four soil types were encountered frequently: SM, SC, ML, and CL. These four classes provide a wide range of characteristics from coarse sandy soil (SM) to fine clays (CL). Data in Table 2 catalogs properties by these soil classes.

## PETROLEUM CONSTITUENTS IN SOIL

Soil samples were analyzed for one or more of several classes of compounds including total petroleum hydrocarbons (TPH), volatile organic compounds (BTXE), polynuclear aromatic hydrocarbons (PAH), and speciated hydrocarbons by carbon number. The data set contains samples with TPH ranging from 50 mg/Kg to over 35,000 mg/Kg.

**BTXE:** Aromatic volatile compounds were detected in only 19 out of 279 samples analyzed by Method 8020 or 8260 (modified). The volatile fraction of diesel 2 (TVPH) contributed a minimum of 0%, maximum of 7% and average of 2% in the mixture.

**PAHs:** 47% (112 detections) of 236 samples analyzed contained at least one PAH. Of the 16 PAHs analyzed for by EPA Methods 8310 and 8100, none were detected in more than one-third of the sample population. Chrysene, fluoranthene, and pyrene were detected in trace quantities the most frequently, with 69, 61, and 47 detections, respectively. Mean concentrations for PAHs developed include an assumption that non-detects are equivalent to one-half the detection limit for samples with at least one detectable PAH. For samples with no detectable PAHs, the total PAH is the value of the highest detection limit. Given these assumptions, total PAHs ranged from non-detectable in the majority of samples to a maximum contribution of 14.1% in soils containing weathered bunker sludge, and an average of 0.18% of total petroleum hydrocarbons. The distribution of PAHs by carbon number was assessed by grouping PAHs according to carbon chain length. Contribution by carbon number was then evaluated by comparing the average concentration of each carbon number (e.g., the average  $C_{12}$  concentration is equivalent to the sum of average concentrations of acenaphthylene and acenaphthene) to the sum of the average PAH concentrations:

Table 1. Mean Physical Properties of Soils

Test Method	Mean Values by Soil Type			
	N=6	N=7	N=12	N=7
Sieve Analysis <sup>(1)</sup> ASTM C136 (Percent Passing by Weight)				
3/4"	100	100	100	100
1/2"	99.9	100	100	100
3/8"	99.1	100	100	100
#4	98.7	99.9	100	100
#10	97.3	99.9	100	100
#20	95	99.6	100	99.7
#40	93.2	98.7	99.6	99.2
#60	86.1	93.7	97.1	98.4
#100	63.5	67	86.3	93.3
#200	35.4	19.2	62.9	67.4
Percent Gravel <sup>(2)</sup>	1.7	0.1	0	0
Percent Sand <sup>(2)</sup>	60.9	80.7	37.1	32.6
Percent Silt <sup>(3)</sup>	12.3	13.1	28.3	47.4
Percent Clay <sup>(3)</sup>	25.1	6.1	34.6	20
ASTM Classification	SC	SM	CL	ML
Bulk Specificity Gravity ASTM D854	2.64	2.63	2.65	2.63
Bulk Moisture Content ASTM D2216 (percent)	10.3	6.8	16.5	11.3
Maximum Dry Density ASTM D1557 (pcf)	121	100.2	108.9	110.5
Permeability ASTM D1084 (cm/sec)	3.1 x 10 <sup>-5</sup>	1.4 x 10 <sup>-3</sup>	6.2 x 10 <sup>-5</sup>	1.8 x 10 <sup>-6</sup>

Note: (1) Based on US Standard Sieve Sizes. (2) Based on percent retained (#200 sieve size). (3) Based on percent passing (#200 sieve size).

Table 2. Speciated Hydrocarbons in Soil by Soil Class

Hydrocarbon Range	SC		SM			CL			
	N. Cal	C. Cal	N. Cal	C. Cal	NV	N. Cal	C. Cal	S. Cal	NV
	%	%	%	%	%	%	%	%	%
C <sub>9</sub> -C <sub>10</sub>	-	-	-	-	-	-	-	-	-
C <sub>10</sub> -C <sub>11</sub>	-	-	-	-	-	-	-	-	-
C <sub>11</sub> -C <sub>12</sub>	-	-	-	-	-	-	0.2	-	-
C <sub>12</sub> -C <sub>13</sub>	1.4	-	-	0.1	0.3	-	1	-	-
C <sub>13</sub> -C <sub>14</sub>	1.9	-	-	0.2	1.2	-	1.7	0.2	0.4
C <sub>14</sub> -C <sub>15</sub>	3.8	-	-	1.1	4.9	0.2	4	1.1	1.8
C <sub>15</sub> -C <sub>16</sub>	2.5	2.2	0.1	0.7	2.8	0.3	1.9	0.8	2
C <sub>16</sub> -C <sub>18</sub>	6	1.8	1.3	5	11	2.7	9.5	5.1	4.6
C <sub>18</sub> -C <sub>20</sub>	11.2	4.6	4.7	11.9	15	8.5	15	11	8
C <sub>20</sub> -C <sub>22</sub>	15.1	9	9.3	17.9	16	15.8	17	15	11
C <sub>22</sub> -C <sub>24</sub>	10.7	8.1	10.4	13.1	10	13.3	11.5	11	12
C <sub>24</sub> -C <sub>26</sub>	12.3	19	12.1	11.7	9.2	12.3	9.5	10	11
C <sub>26</sub> -C <sub>28</sub>	11.2	12	17.2	13.1	9.2	14.3	10	12	16
C <sub>28</sub> -C <sub>30</sub>	11	15	18.2	10.8	8.5	13.3	8.5	13	15
C <sub>30</sub> -C <sub>32</sub>	6.4	18	15.1	7.5	6.5	9.5	5.5	10	10.6
C <sub>32</sub> -C <sub>34</sub>	6.5	16	12.8	7	5.8	10	5	11	8.2

Note: % = percent of total hydrocarbons. - = Compound not detected within hydrocarbon range.

C <sub>10</sub>	10.6%	C <sub>16</sub>	10.2%
C <sub>12</sub>	12.4%	C <sub>18</sub>	15.3%
C <sub>13</sub>	8.1%	C <sub>20</sub>	14.2%
C <sub>14</sub>	17.5%	C <sub>22</sub>	11.7%

**Speciated Hydrocarbons:** As mentioned at the onset of this article, measuring petroleum in soil or groundwater as a function of general TPH is of limited utility other than for general screening purposes. Speciated hydrocarbon data were compiled from all five sites and the mean distributions are presented in Table 2 as a function of soil class.

There does not appear to be any discernible difference in hydrocarbon species as a function of either soil class or site meteorological conditions. The weathered heavy bunker oil has been resident in all the various soils for at least 15 years and in some cases over 50 years. What can be readily seen is the distribution of species is highly skewed to hydrocarbons with more than 25 carbon atoms. Every soil type is comprised of at least 38% by mass of constituents with 24 carbon atoms or greater, and four of the nine categories exhibit greater than one-half of the resident mass as 24 carbon atoms and larger. Viewing the data from a potential risk modeling perspective, the average contribution of semi-volatile hydrocarbons (<C<sub>16</sub>) is less than 5% of the total hydrocarbon mass present. Dispersion of data across a given site or soil type was found to be very limited; this phenomena is believed to have resulted due to the long time periods under which degradation, volatilization, and diffusion have been allowed to act at these sites. Representative hydrocarbon distributions, partitioned by fine and coarse grained soil, are depicted graphically in Figures 1 and 2.

#### PETROLEUM CONSTITUENTS IN GROUNDWATER

Residual petroleum hydrocarbons were speciated in groundwater samples at the two central California sites and the north central California site. These facilities provide a sharp contrast for comparison purposes. The aquifers being tested at both central valley sites are comprised of sandy silts having an average conductivity less than  $1 \times 10^{-4}$  cm/s, whereas the Dunsmuir Yard in north central California is located on the banks of the Sacramento River where groundwater flows through rivertine gravels. Mean concentrations and percent contributions of petroleum constituents are compiled in Table 3 for two sites, and with Dunsmuir, both a weathered diesel and weathered bunker fuel zone exists, allowing for cross comparison between diesel and bunker fuel.

Table 3. Groundwater Hydrocarbon Speciation at Two Sites

Hydrocarbon Constituent	Dunsmuir, Bunker Oil		Roseville		Dunsmuir, Diesel	
	mg/l	% <sup>1</sup>	mg/L	%	mg/l	%
C <sub>10</sub>	ND <sup>2</sup>	0	0.17	0.8	ND	0
C <sub>11</sub>	ND	0	0.26	1.2	ND	0
C <sub>12</sub>	ND	0	0.31	1.4	0.03	0.8
C <sub>13</sub>	0.5	0.9	0.44	2.0	0.15	3.5
C <sub>14</sub>	0.9	1.5	0.61	2.8	0.19	4.6
C <sub>15</sub>	0.13	2.1	0.79	3.6	0.26	6.1
C <sub>16</sub>	0.16	2.8	0.87	4.0	0.28	6.7
C <sub>17</sub>	0.21	3.7	1.00	4.8	0.32	7.6
C <sub>18</sub>	0.25	4.3	1.20	5.4	0.35	8.4
C <sub>19</sub>	0.30	5.2	1.20	5.6	0.38	9.0
C <sub>20</sub>	0.38	6.5	1.30	6.0	0.39	9.2
C <sub>21</sub>	0.39	6.8	1.40	6.5	0.37	8.9
C <sub>22</sub>	0.41	7.1	1.50	6.7	0.30	7.0
C <sub>23</sub>	0.39	6.8	1.50	6.9	0.26	6.1
C <sub>24</sub>	0.41	7.1	1.50	6.7	0.22	5.4
C <sub>25</sub>	0.41	7.1	1.20	5.6	0.17	4.1
C <sub>26</sub>	0.39	6.8	1.10	5.2	0.13	3.1
C <sub>27</sub>	0.32	5.6	1.10	5.0	0.11	2.6
C <sub>28</sub>	0.30	5.2	1.00	4.8	0.12	2.8
C <sub>29</sub>	0.27	4.6	0.96	4.4	0.06	1.4
C <sub>30</sub>	0.25	4.3	0.83	3.8	0.04	1.0
C <sub>31</sub>	0.20	3.4	0.57	2.6	0.03	0.8
C <sub>32</sub>	0.16	2.8	0.44	2.0	0.03	0.6
C <sub>33</sub>	0.13	2.2	0.31	1.4	0.01	0.3
C <sub>34</sub>	0.11	1.9	0.22	1.0	ND	0
C <sub>35</sub>	0.07	1.2	0.05	ND	ND	0
C <sub>10</sub> to C <sub>20</sub>	1.57	27	8.15	37	2.35	56
>C <sub>20</sub>	4.21	73	13.68	63	1.85	44

<sup>1</sup>% means percent of total hydrocarbons. <sup>2</sup>ND means not detected.

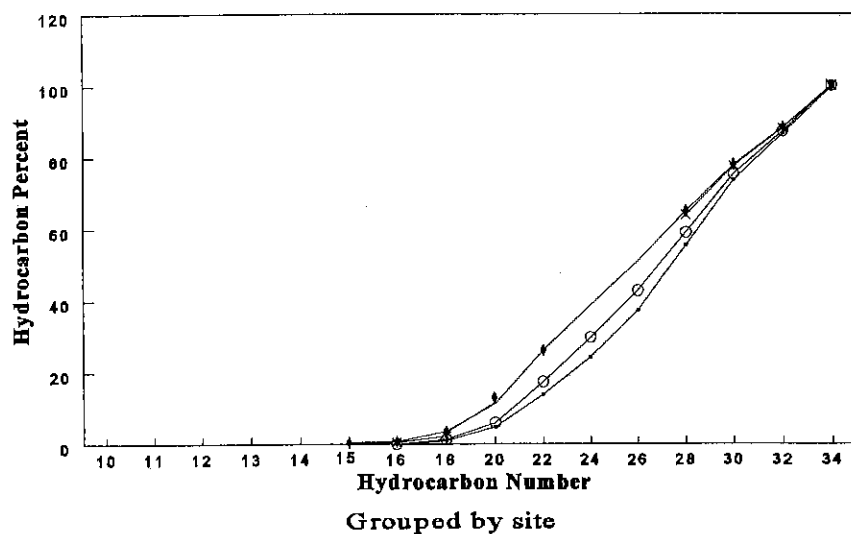


Figure 1. Distribution of hydrocarbon species in coarse grained soils.

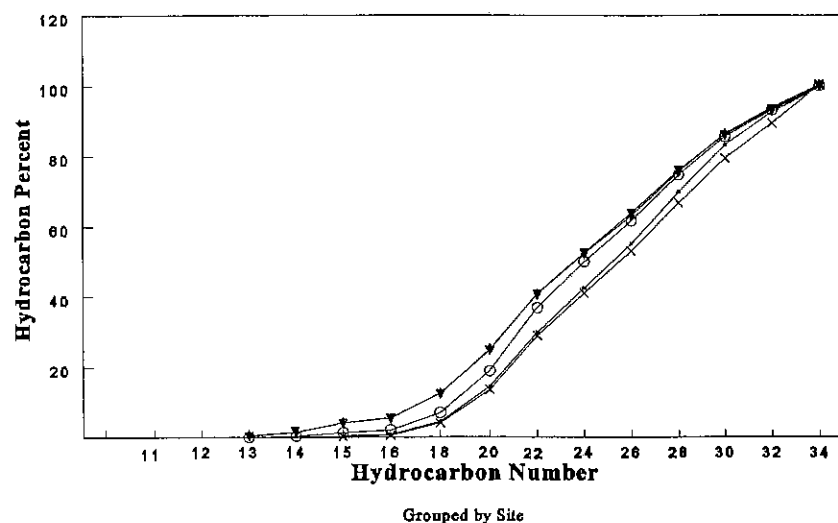


Figure 2. Distribution of hydrocarbon species in fine grained soils.

## CONCLUSIONS

The aim of this exercise was primarily to present the notion that there are distinct differences between fresh gasoline and diesel constituents and those which are found in highly weathered petroleum products. These weathered constituents are dominantly long chain, low solubility, and non-toxic compounds. Bioassay analyses are consistently above 750 mg/l. It would appear, based on the weight of this evidence and our growing knowledge of chemical exposure and toxicity, that the regulation of petroleum should be based on a thorough analysis of representative constituents, and cleanup determinations made on such information.

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**Questions and Answers:**

**Q.** What did the laboratory charge for the EPA Method 8270 speciation test? Did you feel it was significantly better than trying to identify diesel vs. Bunker C on chromatograms from a more classic EPA Method 8015?

**A.** I don't recall the exact cost. I think it was something like \$200. It's been our practice in the last couple of years to use 8270 speciated rather than asking for identification. It takes some of the subjectivity out of it. I know sometimes you get a report, an 8015 result, where they say it's weathered diesel. The data from 8270 are more comparable.

**Q.** It would be interesting to see what the difference is in the cost and if it's worthwhile.

**A.** Of course once you have established at a particular facility what your overall distribution is, you no longer have to run those EPA Method 8270 tests. I would not advocate that you run 8270 speciated all the time. You'd run your other indicator tests instead.

**Q.** In the last example that you had where you put in an interceptor trench, I was wondering when that was completed and how much of the relatively immobile heavy oils, the Bunker C oils, have actually been recovered. How is it going as far as trying to extract that?

**A.** It was completed at the end of last year. It's performing basically as designed. We don't see a lot of oil in it so far because it moves so slowly it's not yet fully penetrated that pack to reach the wells. As far as the flow in the wells, it's what was anticipated. It's working exactly as it was designed.

**Q.** The water table there fluctuated between 6 and 12 feet. Did you consider putting in the trench to intercept this heavy, relatively immobile material, and then cap it with asphalt? Did you consider doing what Brian Rice (Chapter 3) had spoken about, and batch processing that into part of the asphalt cover, or did you use any of the contaminated soil as part of the asphalt cover?

**A.** We did consider that but there were some other goodies in the mix that we could not live with so we had to go with the virgin asphalt.

**CHAPTER 2****Delineation of Diesel Fuel Soil Contamination at a Former Railroad Facility**

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**INTRODUCTION**

This chapter presents the results of a project to assess soil petroleum hydrocarbon (PHC) contamination at a former railroad facility. The introductory section provides information on the genesis of this project and PHC analysis. The field and data analysis methods used are then discussed and results presented. Finally, results are discussed and conclusions stated.

**Project Background**

In 1992 a railroad company requested that Terracon Environmental, Inc. (Terracon), conduct an assessment of subsurface conditions at a former facility located in the midwest. This facility was constructed during the 1850s within a city block containing approximately 29.5 acres and had been a target of military action during the Civil War. It was in continuous use until taken out of service in the 1960s. Both refueling and maintenance operations had historically been conducted on-site. By 1992, most of the facilities that had been located on it had been removed. Some tracks were still in place and in use, but the only remaining building was a former locomotive maintenance shop.

Railroads began using diesel engines on a limited basis in the 1920s. By the 1940s, they were in widespread use. Therefore, the release of diesel fuel at this site was a possibility. Railroad diesel fuel is similar to No. 2 diesel fuel, but may contain higher boiling range components.<sup>1</sup>

Four other consulting companies had previously performed intrusive assessment work at this site. This work as a whole indicated the presence of petroleum hydrocarbon (PHC) contamination in shallow soil and ground water. There were also indications of other possible soil contaminants. These were not material to this chapter and will not be discussed further herein. The PHC contamination was apparently diesel fuel. However, previous work failed to adequately assess site conditions, was of uncertain quality, and could not be validated.



## PHC Analysis

### TPH

Analysis for assessment of PHC contamination may be accomplished using the gross measure of total petroleum hydrocarbons (TPH) or by identification of specific compounds. Two different technological approaches are in common use for TPH analysis. These involve the use of either an infrared spectrophotometer (IR) or gas chromatograph (GC). In the former case, U.S. Environmental Protection Agency (USEPA) Method 418.1, modified with respect to the extraction of PHCs from soil samples, is generally used. In the latter case, since USEPA has not yet standardized practice, a number of essentially similar methods have been adopted by the states. Different detectors may be used with the GC; however, the flame ionization detector, which does not discriminate between the aliphatic and aromatic compounds present in PHC products, is commonly specified. The GC method appropriate for use in a given case must be tailored to the general type of PHC present. These have been variously labelled. For example, Iowa methods OA-1 and OA-2 are for "volatile" and "extractable" petroleum hydrocarbons, respectively, whereas similar methods in some other states use the American Petroleum Institute terminology of gasoline and diesel range organics.

There are advantages and disadvantages to the use of Method 418.1 and GC methods. The primary advantage offered by Method 418.1 in the past has been lower cost. In the short run, this will be affected by the increasing price of the Freon used for extraction in this method. The cost of suitable alternative extraction procedures will be a factor in the longer run as Freon use is phased out. Unfortunately, a number of biases are possible when Method 418.1 is used. With the exception of possible negative bias as a result of extraction inefficiency, GC methods are not affected by these. Additionally, the chromatogram produced by GC methods can be used for qualitative identification, by comparison to chromatograms of known products, as well as quantitation. For example, the difference between gasoline and diesel standard chromatograms is evident in Figure 1.

The biases that affect Method 418.1 have been well documented. Differences in absorbance between the standard and PHC products may result in either negative or positive bias. However, as discussed in more detail below, these would be expected to generally produce a positive bias. Other causes of negative bias are: (1) the relatively poor extraction efficiency of Freon; (2) loss of volatile compounds during extraction; and (3) removal of some aromatic compounds during the silica cleanup procedure. Other causes of positive bias are: (1) inclusion of higher molecular weight naturally occurring saturated hydrocarbons (e.g., plant waxes); and (2) IR dispersion caused by clay particles.<sup>2</sup>

The calibration standard used for Method 418.1 is "reference oil", composed of a mixture of 10, 15, and 15 ml each of the aromatic compound chlorobenzene and the aliphatic compounds isooctane and n-hexadecane, respectively. Because the wave number specified for calibration is  $2930\text{ cm}^{-1}$ , this would theoretically produce a positive bias, with the magnitude of the positive bias depending, in part, on the type of instrument used. The reason for this positive bias is that aliphatic compounds characteristically have an absorption maximum at about that wave number, while

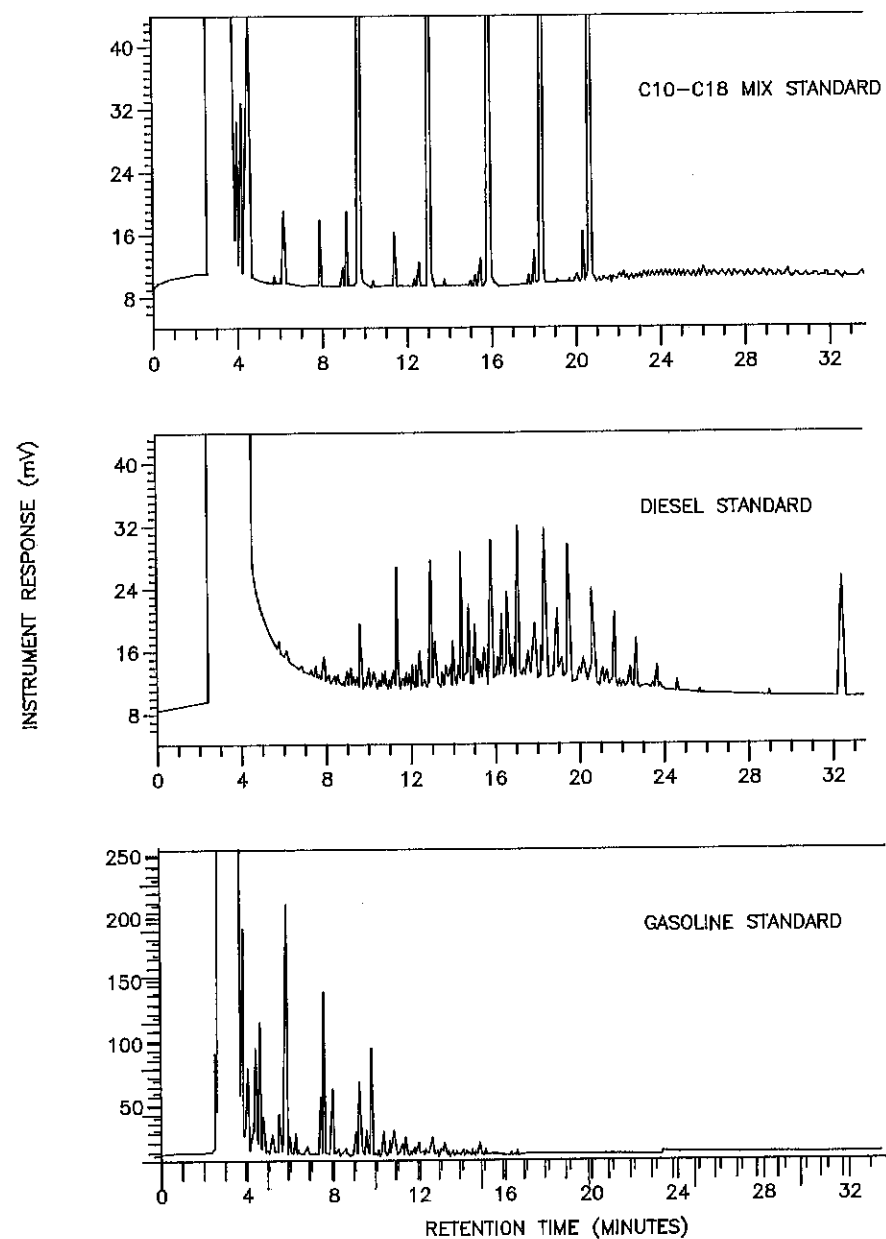


Figure 1. Laboratory GC chromatograms.

absorption maximums for aromatic compounds occur at wavenumbers exceeding 3000  $\text{cm}^{-1}$ . Therefore, the absorbance attributed to the calibration standard is really produced solely by the aliphatic compounds which comprise only 66.5% of the mass of hydrocarbons present in the "reference oil". This results in a potential 50% positive bias in comparison with mass distribution. Whether all of this bias is realized or not is influenced by two other factors:

The type of instrument used. Method 418.1 allows use of either a scanning spectrophotometer or wider band, fixed wavelength spectrometer. In the latter case, absorbance caused by aromatic compounds will be measured. However, since absorbance is proportional to the number of C-H groups rather than the total mass of hydrocarbons, the contribution of chlorobenzene in the reference standard will still be disproportionately small. Under these circumstances, chlorobenzene would be expected to produce 10.5% of the total absorbance of the standard while comprising about one-third of its mass fraction. This results in a potential 35% positive bias in comparison with mass distribution.

The nature of the PHC contamination involved and the resulting absorbance produced by it, the typical composition of diesel fuel, 75% aliphatic and 25% aromatic compounds, would indicate the potential for marginal positive bias for fresh No. 2 diesel fuel in comparison to "reference oil". This is consistent with what has been found in laboratory testing.<sup>3</sup> The impact of weathering on this bias is uncertain. To the extent that classes of compounds were differentially lost by weathering, the nature of this bias could change.

Figure 2 shows a spectrophotometer output plot of transmittance versus wavenumber for a 50 mg/l "reference oil" standard. The point of maximum absorbance on it, which would be used for calibration in this case, occurred at a wavenumber of approximately 2920  $\text{cm}^{-1}$ . The portion of the plot above a wavenumber of 3000  $\text{cm}^{-1}$ , which would not influence calibration, was produced by the aromatic compound portion of the standard.

#### Specific Compounds

Diesel fuel No. 2 is "essentially equivalent" to fuel oil No. 2. These products consist predominantly of hydrocarbons with carbon numbers in the range of  $\text{C}_{11}$  to  $\text{C}_{20}$ . They are complex mixtures and their "composition varies widely between sources and even between lots". The following are representative concentrations of single ring and polynuclear aromatic hydrocarbon (PAH) compounds which have been reported in No. 2 diesel fuel or No. 2 fuel oil:<sup>4</sup>

#### Single Ring

a. Benzene . . . . .	80 mg/Kg
b. Toluene . . . . .	800 mg/Kg
c. Ethylbenzene . . . . .	400 mg/Kg
d. Xylenes (total) . . . . .	2,700 mg/Kg

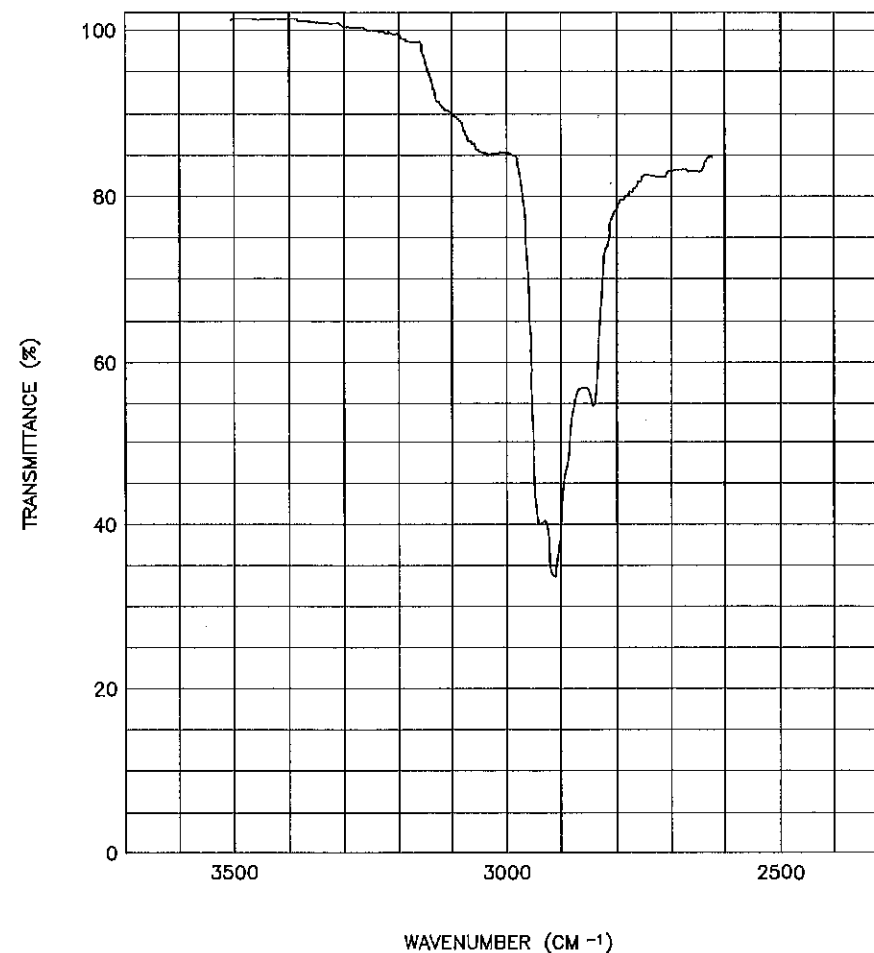


Figure 2. Method 418.1 spectrophotometer plot(50 mg/l Standard).

PAHs	
a. Benzo(a)pyrene	1 mg/Kg
b. Chrysene	2 mg/Kg
c. Fluoranthene	40 mg/Kg
d. Fluorene	1,200 mg/Kg
e. 1-Methylnaphthalene	8,100 mg/Kg
f. 2-Methylnaphthalene	14,000 mg/Kg
g. Naphthalene	2,500 mg/Kg
h. Phenanthrene	400 mg/Kg
i. Pyrene	40 mg/Kg

The identification of such compounds at lower concentrations of the same relative order in environmental samples could be considered a characteristic indication of diesel fuel contamination (e.g., the presence of 1- and 2- methylnaphthalene and absence of benzene).

## METHODS

### General Field Work Plan

Terracon planned a three-phase assessment of this site. A uniformly-spaced sampling grid (this grid is shown in figures presented later in this chapter) was prepared to facilitate both field investigation work and later data analysis. This was altered as necessary due to conditions encountered in the field. The phases were:

Phase 1 - A Geoprobe systems van with hydraulically-driven piston samplers was used to sample at most grid locations for initial horizontal and vertical characterization of soil contamination. Probes were generally driven to a maximum depth of 15 feet below ground level with samples being taken at 5 feet intervals. Samples were screened in the field for (TPH) using an onboard (GC). Splits of some of these samples were also submitted to a commercial analytical laboratory for confirmation. The PACE, Inc. (PACE), laboratory in Lenexa, Kansas, was selected for this work.

Phase 2 - Additional soil sampling was subsequently performed using conventional drilling and sampling equipment during the installation of monitoring wells at remaining grid locations. In addition to 10 relatively shallow monitoring wells (i.e., 15 feet BGL), there were five deep monitoring wells (i.e., 65 to 75 feet BGL) installed as nested pairs at locations MW-1, MW-2, MW-3, MW-4, and MW-5. Location MW-1 was essentially an upgradient background well located to the northeast of the portion of the site of primary concern. Monitoring well installation and associated sampling were accomplished with a Central Mine Equipment (CME) Model No. 75 drilling rig equipped with 4-1/4 inch ID hollow-stem augers and split-barrel samplers. Samples were generally taken at 5-foot intervals, except in the case of the monitoring well in the most contaminated area of the site (MW-9). In that case, samples were also taken at depths of 8 and 12 feet BGL to obtain more precise depth

information. All of these samples were submitted to PACE for analysis. Additionally, PACE and Terracon's soils laboratory analyzed soil samples from selected locations for physical and chemical properties relevant to evaluation of contaminant transport.

Phase 3 - Ground water sampling and aquifer testing were performed. All ground water samples were submitted to PACE for analysis.

### Analytical Methods

#### Field

All soil samples obtained using the Geoprobe systems van were screened in the field for TPH using a GC. Deionized water, methanol, and hexane were first added to a known mass of sample to extract semivolatile PHCs from the soil matrix. The resulting hexane supernatant, with contaminants, was then analyzed.

The Geoprobe van was equipped with a Shimadzu Corporation GC-14A GC having a J&W DB-624 capillary column (0.53 mm x 30 m) flame ionization and 10.2 eV lamp photoionization detectors (FID and PID, respectively), and a Shimadzu C-R4AD integrator. The GC was calibrated with a No. 2 diesel fuel soil check sample of certified quality obtained from Environmental Resource Associates, Arvada, Colorado. This was used to generate a single response factor for quantitation. Operating parameters were altered during initial GC runs to find a procedure that produced the best response in the shortest time. It was found that commencing the run at a column temperature of 140°C held for 4 minutes, and then ramping it up at a rate of 10°C/minute to 210°C (where it was held for the remainder of the run) achieved these objectives. A run time of 25 minutes was adequate in all cases. Furthermore, it was found that when no target compound peaks were produced during the first 15 minutes of the run, none would occur during the last 10.

#### Laboratory

For regulatory reasons, modified USEPA Method 418.1 was used to analyze all soil and ground water samples submitted to PACE. This procedure was carried out using a spectrophotometer. A subset of selected soil and ground water samples was also analyzed for TPH by Iowa method OA-2. The GC utilized for this was equipped with the specified J&W DB-5 capillary column (0.32 mm x 30 m) and a flame ionization detector (FID). The method also permits use of a mass spectrometer (MS) as the detector. Samples were extracted with methylene chloride prior to analysis. OA-2 specifies an initial oven temperature of 50°C for 4 minutes. The temperature is then ramped up at a rate of 8 °C/minute to 280°C (where it is held for 33 minutes). Calibration is accomplished by first identifying the PHC contamination involved through comparison of the sample chromatogram with chromatograms of various commercial products. The one "most nearly matching the sample... (is) used for response calibration." Whereas OA-2 allows use of a single response factor when certain criteria are met or a three point calibration curve, standard PACE procedure is to use a five point calibration curve.

A subset of selected soil and ground water samples was also analyzed for specific volatile and semivolatile organic compounds (VOCs and SVOCs, respectively). Analysis for these was performed using USEPA GC/MS Methods 8240 and 8270.

#### Analytical Quality Assurance

In view of the uncertain quality of previously collected data, the railroad company involved was particularly concerned about data quality and accepted incorporation of a substantial quality assurance element into the sampling and analysis plan for this project. This included both field and laboratory elements. Field GC analysis quality control (QC) included the use of a standard method, analysis of method blank, duplicate, and triplicate samples, and splits with PACE. The field element of laboratory QA required submittal of duplicate soil and ground water samples, analysis of the same sample by both IR and GC methods, and soil and ground water check samples. Additionally, equipment rinse samples were submitted as a check on field decontamination methods. Laboratory analysis QC called for the use of standard methods and performance of standard laboratory QC samples. These consisted of method blank, laboratory control, and matrix spike/matrix spike duplicate (MS/MSD) samples. Furthermore, selected ground water samples were analyzed for an expanded list of analytes that allowed the performance of ion and dissolved solids concentration balance calculations. This constituted a further check on analytical data quality.

#### Data Analysis

Data were manually and electronically analyzed. First, data were manually tabulated and plotted on site diagrams. Next, they were statistically summarized, geostatistically contoured, and used to model site conditions using computer programs. The programs used for these purposes were GEO-EAS, GRAPHER, SURFER, and SPILLCAD.

## RESULTS

#### Site Hydrogeology

This site is located within the broad alluvial floodplain of a major river and the materials involved are typical for such a location. A generalized lithologic profile (with qualitative field observations) and particle size distribution curves for selected soil samples are presented as Figures 3 and 4, respectively. With the exception of thin depths of fill in some areas of the site, the shallow soils consist of clays and silts. It is also noteworthy that field classifications generally indicated clay or silty clay where laboratory data indicated silty clay or clayey silt. In two of the deep borings, thicknesses of sandy silt or sand were observed prior to reaching sand, at depths of 55 to 60 feet. One boring was drilled to a depth of 75 feet to confirm the location of underlying limestone.

Representative site assessment information on shallow (clays and silts) and deep (sand) zone characteristics is as follows:

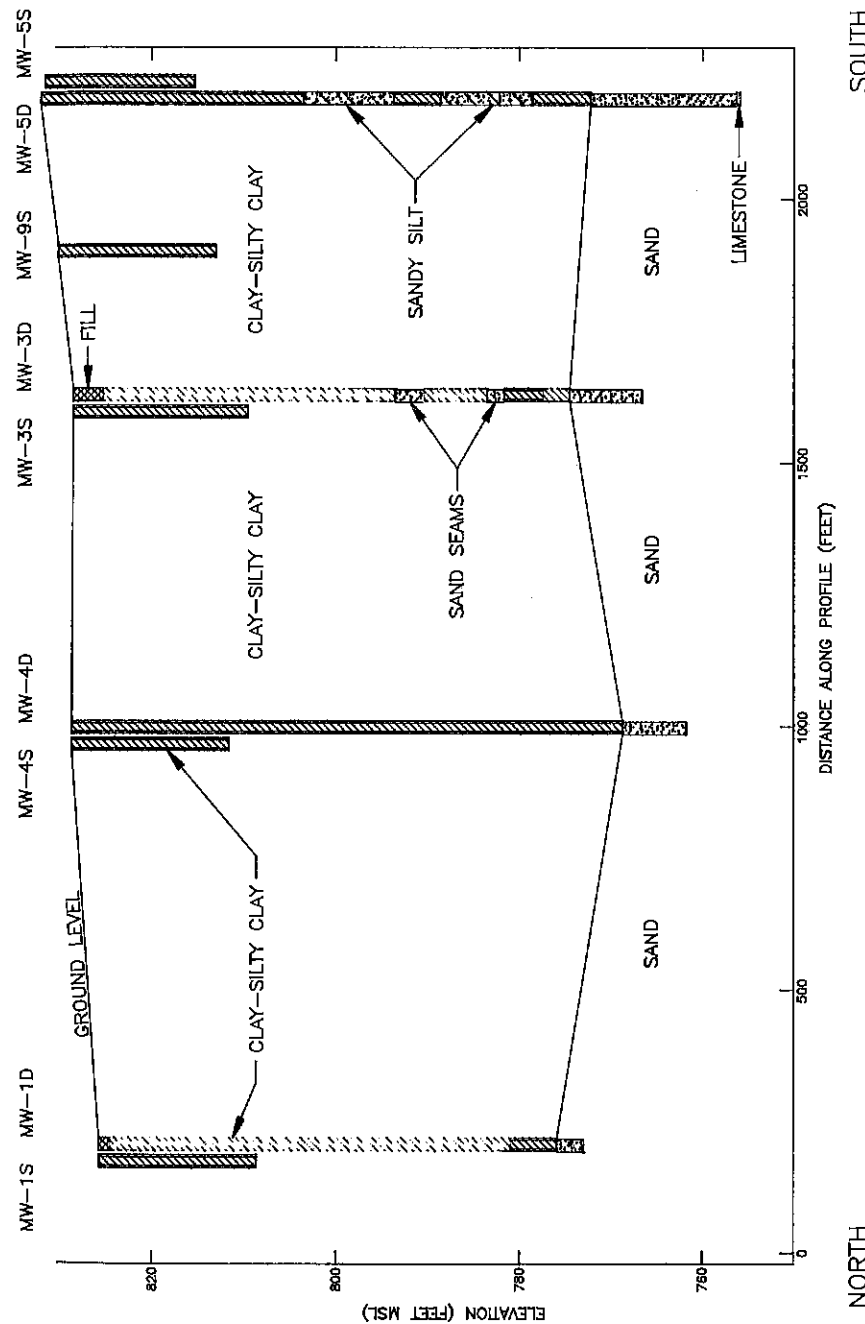


Figure 3. Generalized lithologic profile.



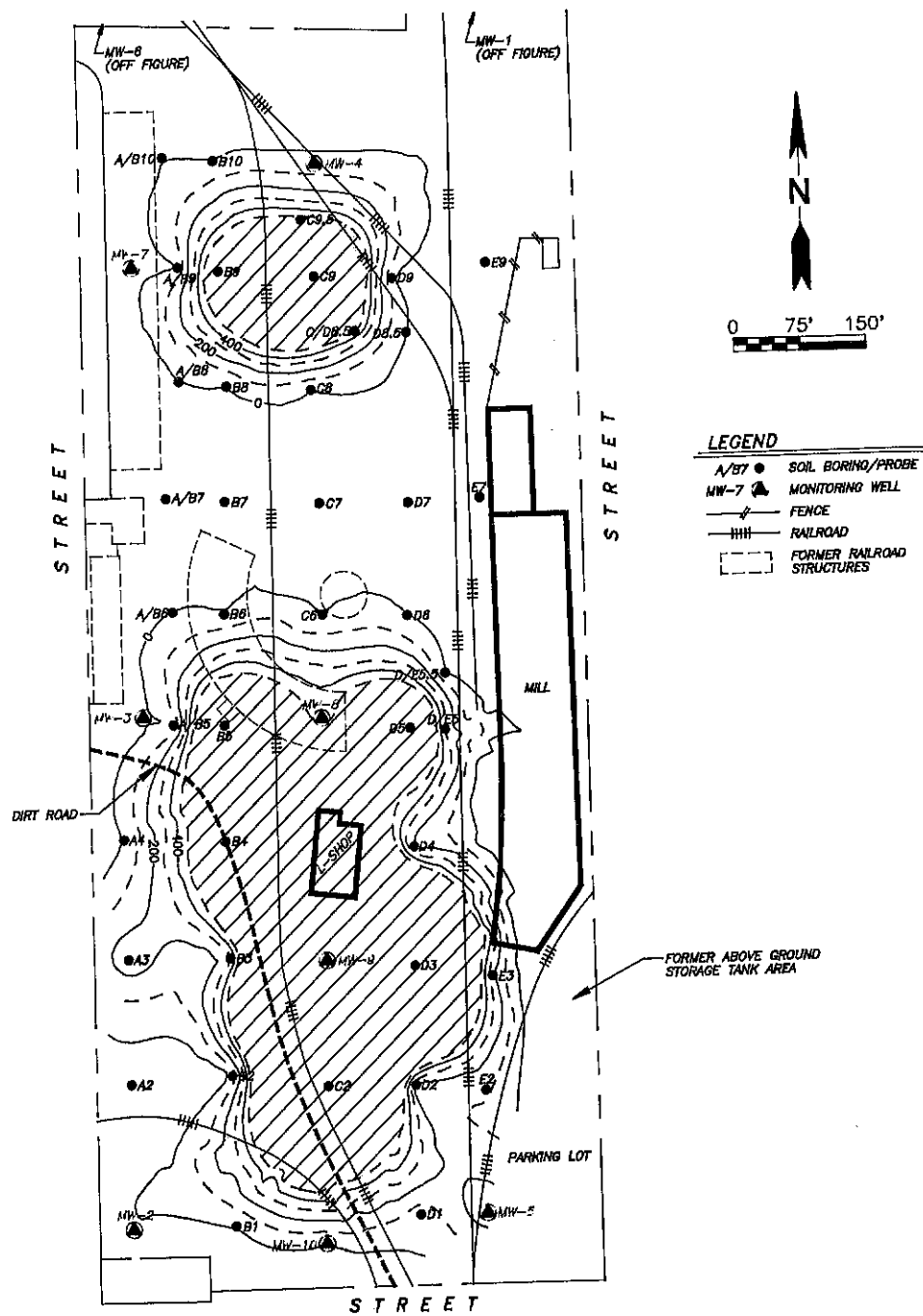


Figure 5. Soil TPH (mg/Kg) (10 feet BGL combined data set).

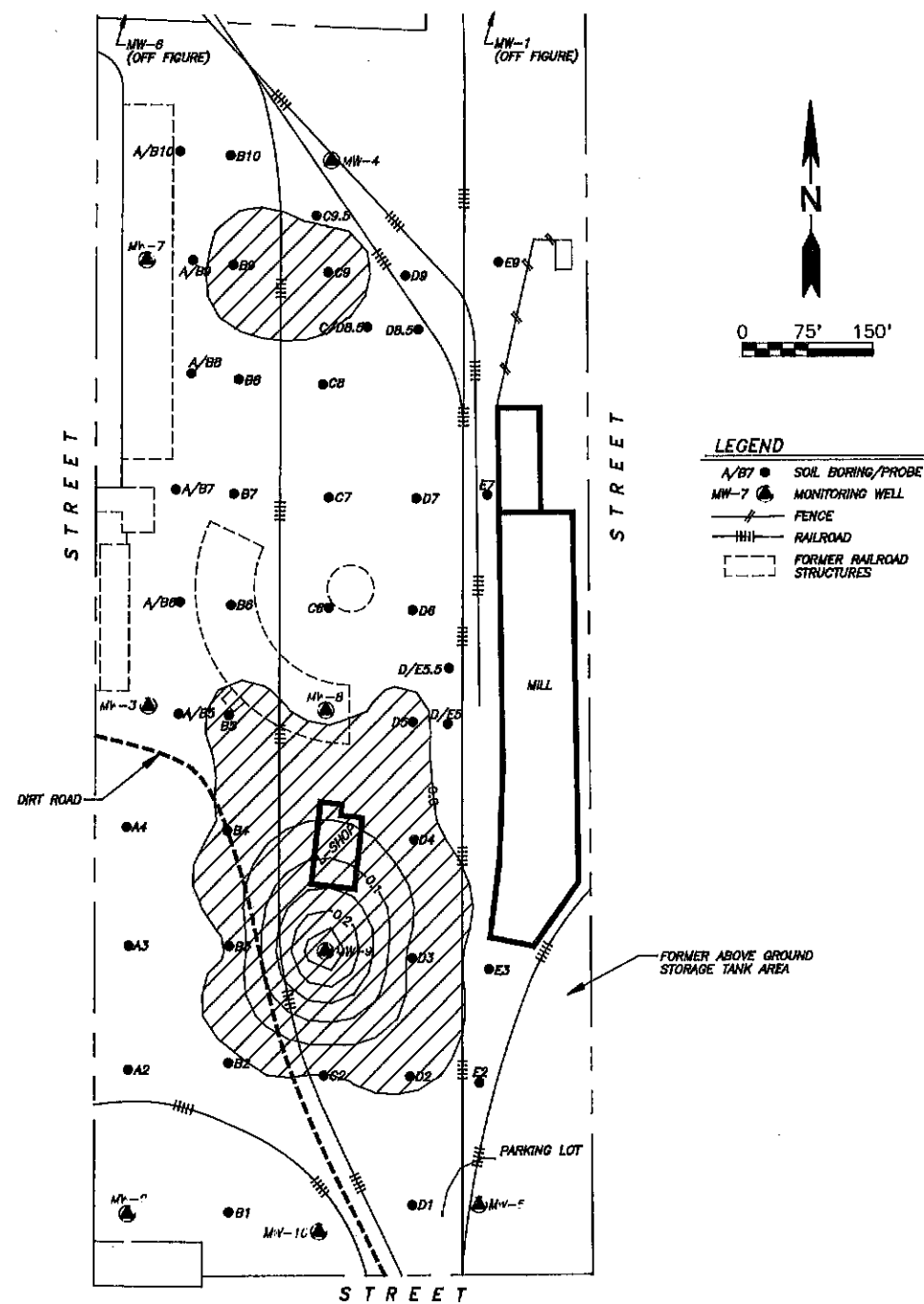


Figure 6. Hydrocarbon volume (gal/ft<sup>2</sup>).

from MW-9, which was considered an artifact of the sampling and analysis process). Anthracene was the only PAH reported in the B4 sample. The PAHs which were identified in samples from MW-9 (locations are for the 10 feet BGL sample unless otherwise indicated) were anthracene (0.370 mg/Kg), fluorene (0.300 mg/Kg), 2-methylnaphthalene (1.70 mg/Kg), naphthalene (0.330 mg/Kg), phenanthrene (4.3 mg/Kg at 5 feet BGL), and pyrene (1.3 mg/Kg at 5 feet BGL). With the exception of anthracene, all of these are included on the list of PAHs in No. 2 diesel fuel or No. 2 fuel oil presented above. Anthracene and some of these PAHs may also have come from other products previously handled on-site (e.g., coal).

Comparison of laboratory TPH data by IR (418.1) and GC (OA-2) indicates very good correlation. For the 14 data points available, IR results were marginally lower (on the order of 15%) and a 0.969 correlation coefficient ( $r$ ) was calculated. The data involved are presented in Table 1 and the linear regression plot is presented in Figure 7. Examples of laboratory GC chromatograms for samples are presented in Figure 8. When compared with standard chromatograms in Figure 1, these allow conclusive qualitative identification that the PHC contamination involved was diesel fuel No. 2. It is also noteworthy that the diesel check sample contained substantial concentrations of compounds in the gasoline range.

Comparison of laboratory TPH data by IR (418.1) with field GC screening indicates a greater degree of scatter and bias than for laboratory GC data, but reasonably good correlation ( $r = 0.854$ ). There were 23 pairs of IR and field GC screening results for split samples. One of these was for the 5 feet BGL depth at location C10 and is not presented in Table 1. The other 22 pairs are listed in Table 1. For one of these (location D5), the field GC screening result appeared to be an outlier. It was inconsistent with other information regarding site conditions, was not supported by field observations, was a factor of three greater than any other field GC result, was more than an order of magnitude greater than the laboratory IR result, and was found to be "discordant" using the generalized distance test module of USEPA's computer program for outlier analysis SCOUT (Version 1.33). Therefore, it was dropped from the linear regression analysis. For the 22 data points analyzed, GC results were substantially higher (by a factor of 2.5). The linear regression plot for this comparison is presented in Figure 7. There were only eight sample locations for which both laboratory and field GC sample data exist. As would be expected due to the very good laboratory IR and GC data correlation, a slightly better but similar correlation was found between field and laboratory GC data ( $r = 0.870$ ). An example of a field GC chromatogram for the diesel check sample is presented as Figure 9.

All TPH data for samples from the 10 feet BGL depth are presented in Table 1. In addition to analytical data, field observations of PHC contamination during soil sampling (e.g., PHC odors or oil sheens) are also indicated in that table. A combined data set was prepared from Table 1 for geostatistical analysis (i.e., contouring). Where available, laboratory IR data were preferentially utilized for this purpose. Otherwise, these were supplemented with field GC screening data. Where field GC screening data were less than 100 mg/Kg and field observations did not indicate PHC contamination, the result was considered de minimis and the laboratory IR detection limit was used for contouring. Where field GC screening results exceeded 100 mg/Kg,

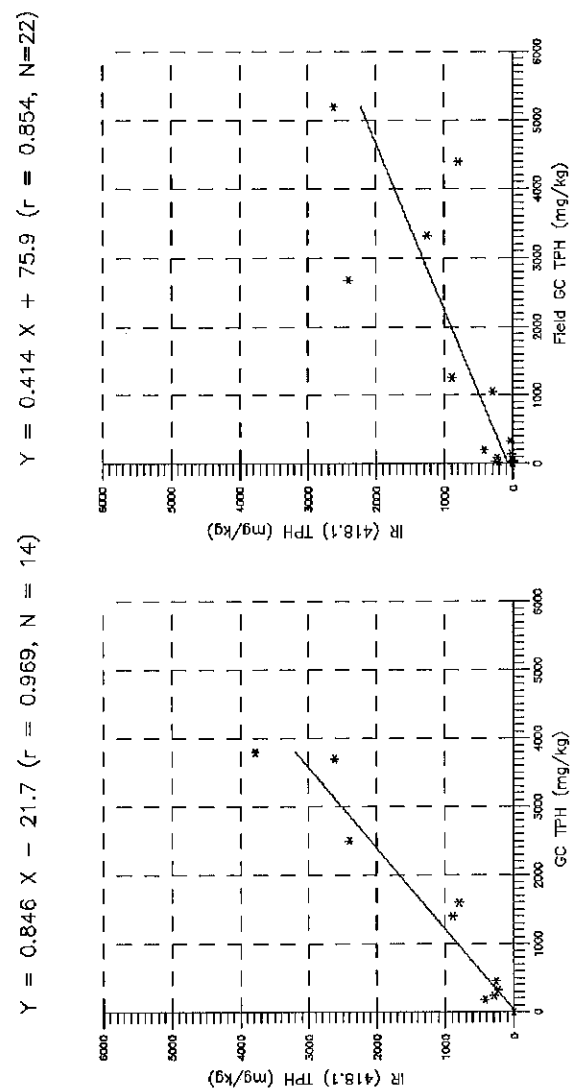


Figure 7. Linear regression analysis plots/results.

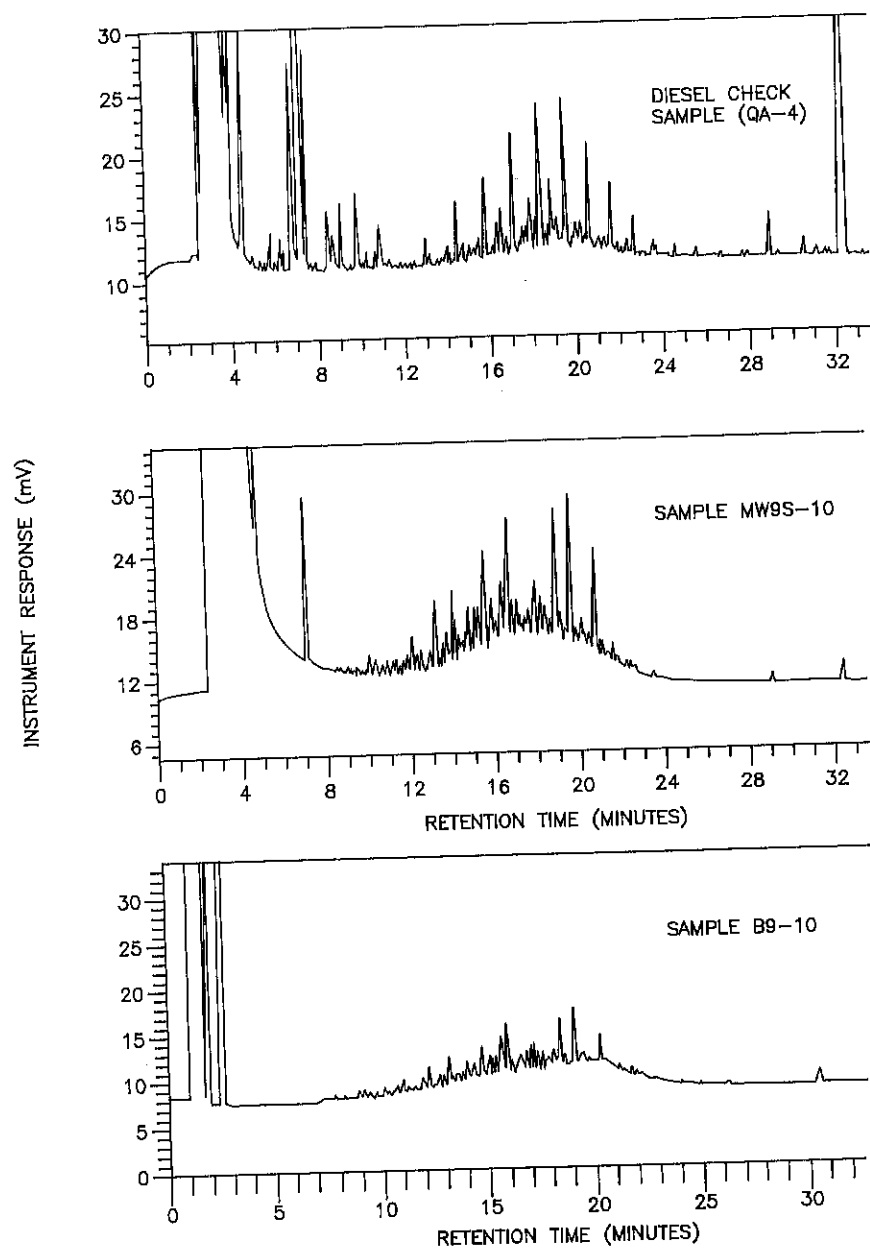


Figure 8. Laboratory GC chromatograms.

Table 1. 10 Feet BGL Soil TPH Data (mg/Kg)<sup>a</sup>

Location	Lab IR	Lab GC	Field GC	Location	Lab IR	Lab GC	Field GC
A1 (MW-2)	<10	<5	-	C6	-	-	199
A2	-	-	56	C7	22.9	-	29
A3	297	-	1,050	C8	-	-	146
A4	-	-	<1	C9	-	-	6
A5 (MW-3)	<10	-	-	C9.5	-	-	1,360
A9 (MW-7)	<10	-	-	C10 (MW-4)	<10	-	<1
A12 (MW-6)	<10	<5	-	C/D8.5	-	-	1,010
A/B5	<10	-	3	D1	43.9	-	330
A/B6	-	-	7	D2	-	-	690
A/B7	<10	-	<1	D3	2,410	2,500	2,680
A/B8	-	-	8	D4	-	-	668
A/B9	<10	-	12	D5	1,300	-	15,600
A/B10	-	-	<1	D6	-	-	5
B1	<10	-	20	D7	<10	-	4
B2	-	-	6	D8.5	-	-	2
B3	231	320	83	D9	<10	<20	47
B4	892	1,400	1,260	D/E5	260	450	31
B5	1,250	-	3,320	D/E5.5	-	-	10
B6	-	-	77	E1 (MW-5)	293	240	-
B7	<10	-	10	E2	-	-	123
B8	-	-	20	E3	209	-	26
B9	798	1,600	4,390	E7	10	-	32
B10	-	-	96	E9	-	-	11
C1 (MW-10)	<10	<5	-	E17 (MW-1)	<10	<5	-
C2	2,620	3,700	5,190				
C3 (MW-9)	3,780	3,800	-				
C5 (MW-8)	421	180	5,420				

<sup>a</sup>. Results columns "Lab IR", "Lab GC", and "Field GC" are for samples analyzed by PACE using methods 418.1 and OA-2 and field GC screening, respectively. Locations where field observations (e.g., PHC odor or oil sheen) indicated PHC contamination are bolded. Results for these locations are also bolded.



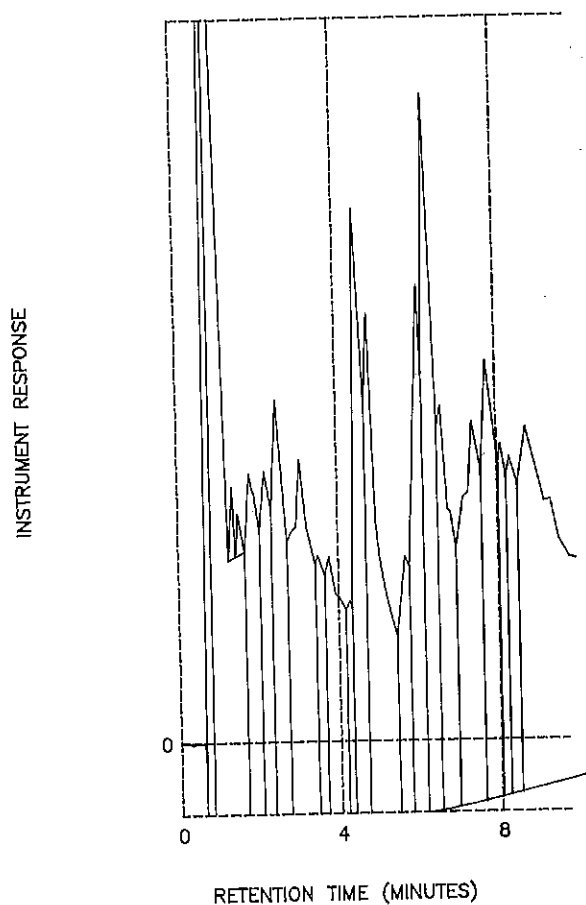


Figure 9. Field GC chromatograms (diesel check sample).

they were converted to an equivalent IR value by use of the appropriate linear regression equation in Figure 7. This was done in six cases. The locations for them and converted values obtained and used were:

1. C9	2,320 mg/Kg
2. C9.5	639 mg/Kg
3. C/D8.5	494 mg/Kg
4. D2	362 mg/Kg
5. D4	352 mg/Kg
6. E2	127 mg/Kg

The combined set of 50 data points was used with a computer contouring program to delineate the horizontal extent (measured by soil concentration) of PHC contamination at the 10 feet BGL depth. The resulting plot is presented as Figure 5. The separate zones in Figure 5 exceeding 500 mg/Kg TPH amount to a total of approximately 162,000 ft<sup>2</sup> (3.72 acres). A somewhat similar plot was produced using data for all depths and the computer program SpillCAD (Version 3.12)<sup>5</sup> to indicate the volumetric distribution of PHC contamination in gallons/feet<sup>2</sup>. The SpillCAD estimate of total remaining volume, based on this combined data set for TPH in soil, was approximately 9,000 gallons. The fluid and soil properties used to arrive at this estimate were:

#### Fluid

a. Oil/water density ratio (Pro)	0.83
b. Oil/water dynamic viscosity ratio ( $\mu_{ro}$ )	2.70
c. Water/oil surface tension ratio ( $\beta_{ao}$ )	2.80
d. Water surface tension/interfacial tension ratio ( $\beta_{ow}$ )	1.40

#### Soil

a. Total porosity ( $\phi$ )	0.530
b. Effective porosity ( $\phi_e$ )	0.063
c. Saturated hydraulic conductivity ( $K_{sw}$ )	$3.5 \times 10^{-4}$ cm/sec
d. Min water saturation ( $S_m$ )	0.881
e. Max saturated zone residual oil saturation ( $S_{or}$ )	0.096
f. Max unsaturated zone residual oil saturation ( $S_{og}$ )	0.065
g. van Genuchten (VG) mean pore size parameter ( $\alpha$ )	1
h. VG pore size distribution exponent ( $n$ )	2

Fluid properties were estimated from literature values for diesel fuel, while soil properties were estimated from site data, to the extent possible, or literature values for similar materials. Obviously, the accuracy of this analysis is dependent on the validity of assumptions made regarding fluid and soil properties. However, limited sensitivity testing indicated that this volume estimate was relatively insensitive to major changes in values used for those properties having the greatest level of uncertainty.

### Ground water Quality Data

Ground water quality data were consistent with soil quality data. Samples from all monitoring wells were analyzed for TPH by IR (418.1) and samples from all shallow monitoring wells were analyzed either for VOCs (8240) or benzene, toluene, ethylbenzene, and xylenes (BTEX) by USEPA Method 8020. Samples from selected wells were also analyzed for TPH by GC (OA-2) and SVOCs. Field observations or analytical results indicated PHC contamination in three of the shallow monitoring wells. There were no indications of such contamination in the other seven shallow monitoring wells or any of the deep monitoring wells. These three shallow wells were:

- MW-5 - PHC odors were observed and toluene was reported at 18 µg/l (this sample was not analyzed for SVOCs).
- MW-8 - PHC odors were observed (VOC and PAH concentrations were reported to be less than their respective detection limits).
- MW-9 - there was an intermittent layer of light nonaqueous phase liquid (LNAPL) having a maximum thickness of 0.01 foot, PHC odors were observed, TPH was reported at 29.6 mg/l (418.1) and 13 mg/l (OA-2) and benzene was reported at 40 µg/l (this sample was not analyzed for SVOCs).

### QA Data

Both field and laboratory QA data generally supported the quality of analytical results. There was greater variability for field GC screening than laboratory results and greater variability for analysis of replicate samples than replicate analysis of the same sample. Laboratory performance on field replicate samples was judged acceptable, particularly in view of apparent sample variation over short vertical distances, and the check sample result was within the advisory range specified by the supplier. For the four ground water samples where there was sufficient data to calculate ion and dissolved solids balances, results were judged acceptable (i.e., 10% or less).

## DISCUSSION AND CONCLUSIONS

These data indicate very good correlation between analysis of the soil samples at this site for TPH by IR (418.1) and GC (OA-2). Results were similar in magnitude but IR results were generally biased about 15% low. This would indicate that factors with the potential to result in a high bias for IR results (such as the use of "reference oil" calibration and clay particle dispersion) were outweighed by those having low bias potential (such as relatively poor Freon extraction efficiency). Variation in soil quality within the sample container would be an additional factor that would be expected to cause random rather than systematic bias.

These data also indicate a reasonably good correlation between field GC screening and laboratory results by either IR or GC. The degree of correlation was sufficient to make field GC screening effective in this case. However, field GC screening results appeared to be biased high by a factor of 2.5. Approximately half of this bias may have

been associated with the calibration standard used for the field GC. The check sample used for this purpose had a certified value of 1,940 mg/Kg and an advisory range of 870 to 2,620 mg/Kg. This certified value was used for field GC calibration. PACE results on this sample using IR and GC were 1,110 and 1,300 mg/Kg, respectively. Greater random bias would also be expected in this comparison than was seen for laboratory generated data, as a result of soil quality differences from split sample preparation and the use of single (field) versus five point (lab) calibration.

Soil TPH data were satisfactory for delineation of the nature and extent of diesel fuel soil contamination at this site. Although data for specific compounds in soil were consistent with soil TPH data, they would have been inadequate for reasonably precise site characterization. Similarly, ground water quality data were consistent with soil TPH data but inadequate to precisely characterize site conditions. Soil TPH data show two zones and probably two separate sources of contamination: (1) the primary zone centered on the former locomotive shop, and (2) a secondary zone 600 feet north of the shop in the vicinity of tracks immediately east of the former terminal. These zones are not connected. Maintenance and/or fueling activities associated with these locations most likely resulted in existing conditions. Soil contamination in substantial portions of both of these zones exceeded 500 mg/Kg TPH, a level greater than generic cleanup standards in many jurisdictions.<sup>6</sup> However, hydrogeologic and contaminant data indicate that despite the time which has elapsed since contamination occurred (greater than 30 years) and the volume of contamination involved (possibly 9,000 gallons), site conditions are not conducive to contaminant transport and contamination has been largely contained within site boundaries. In view of these circumstances and the lack of downgradient uses (i.e., water supply wells or close surface waters), remedial action was not required. The process leading to this decision amounted to a qualitative risk assessment with selection of natural attenuation as the remedial option.

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## **CHAPTER 3**

### **Soil Recycling: From Problem to Product**

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As landfill space is becoming more and more precious, alternatives to disposing of petroleum containing soils (PCS) are needed. In response to these needs, Union Pacific Railroad and Radian Corporation performed a study to determine the effectiveness of using PCS as a raw material substitute in pavement products. The PCS used in the study was collected from railroad facilities (rail yards, tracks, refueling facilities, and ballasts) which had been affected by the past use of No. 2 and No. 6 diesel fuel for typical railroad operations. The study showed that the PCS could be successfully used to replace typical pavement raw materials used in hot mix and cold mix asphalt concrete, and in road base.

Many state agencies are permitting the use of PCS in pavement products since the PCS may be designated as a "recycled" material and not as a "solid waste." A recycled material is one which may be used or reused as an effective substitute for commercial products. Materials are considered to be solid wastes when they are: 1) applied to or placed on the land in a manner that constitutes disposal, or 2) used to produce products that are applied to or placed on the land or are otherwise contained in products that are applied to or placed on the land.<sup>1</sup> Pavements involve multiple layers of construction materials, typically a wearing course, a base, a subbase, and the subgrade. The paving products with the PCS would be placed on prepared subgrade, not directly on the land. Therefore, the use of PCS as proposed in this study would meet the definition of a recycled material, and would be used in accordance with applicable regulations.

#### **DESCRIPTION OF PAVEMENTS**

Pavement can be defined as "a structure that maintains intimate contact with and distributes loads to the subgrade and depends on aggregate interlock, particle friction, and cohesion for stability".<sup>2</sup> Figure 1 presents the various components of a typical pavement. The principal elements of a pavement are a "wearing surface," base, subbase

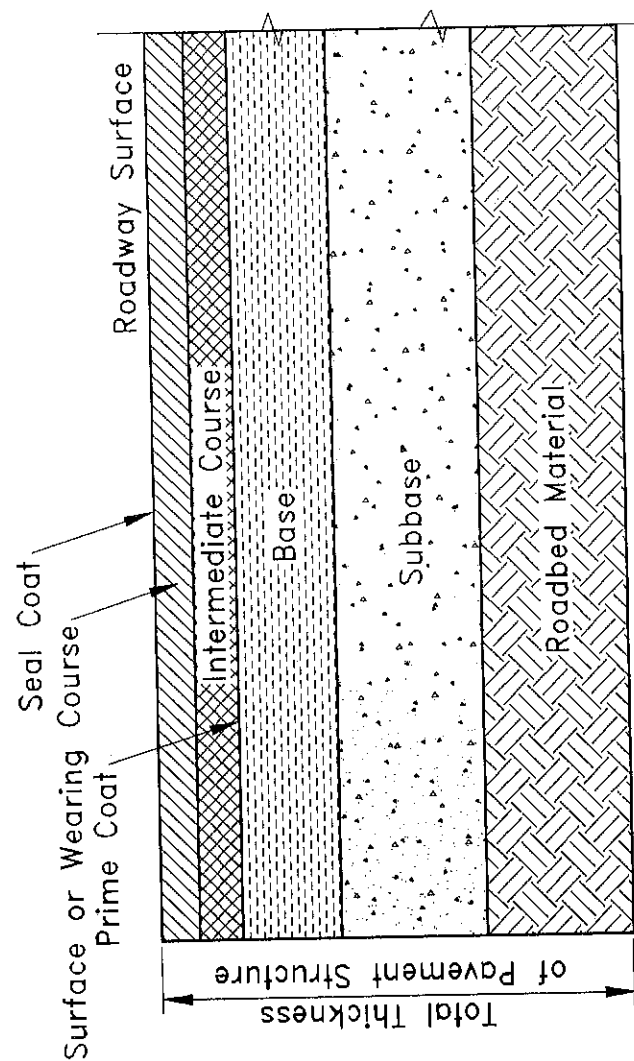


Figure 1. Typical pavement structure.

(not always used), and a subgrade. Depending on the service requirements of the pavement, an intermediate course may be required as part of the wearing surface. This wearing surface may range in thickness from 1 to 6 inches or more, and will typically be an asphalt concrete mix (hot or cold mix) or a cement-concrete mix. The base is a layer of high stability and is typically composed of gravel or crushed rock, or it may be granular material treated with asphalt, cement, or lime-fly ash stabilizing agents. A subbase is used in areas where frost action is severe or in locations where the subgrade soil is excessively weak. The composition of a subbase is similar to a base. The subgrade is the foundation layer for the pavement. The subgrade is typically a compacted soil layer, but may sometimes be the natural earth surface.

#### Description of Typical Raw Materials

The raw products typically used to make the pavement products are aggregate and asphalt cement. Aggregate is any hard, inert material used in graduated sized particles or fragments. Typical aggregates include sand, gravel, crushed stone, slag, and rock dust. The key properties necessary for an aggregate to be used in paving are maximum particle size and gradation, cleanliness, toughness, particle shape, surface texture, absorptive capacity, and affinity for asphalt (when used in asphaltic concrete).

The aggregate gradation refers to the percentage of aggregate (by weight) retained on different sized sieves compared with the total amount of aggregate. The aggregate must be clean so the asphalt will adhere to the particles. The aggregate's ability to resist abrasion and degradation is its toughness. The particle shape is important because angular particles tend to interlock and resist displacement better than round, smooth particles. However, round and smooth particles are required for filling air voids. A rough surface texture will allow asphalt cement to cling to the aggregate. Porous aggregates will absorb asphalt cement, leaving less of the cement on the surface. Certain types of aggregate have a high affinity for asphalt which resists the efforts of water to strip the asphalt from them.

Paving asphalts are typically classified into three general types: asphalt cement, cutback asphalt, and emulsified asphalt. Asphalt cement is specially prepared with regard to quality and consistency for direct use in paving products. Cutback asphalt is asphalt cement which has been liquefied by blending with petroleum solvents and is typically used in cold mix asphalt concrete. The emulsified asphalt is asphalt cement combined with water (emulsifying agents are used to make the asphalt cement miscible). The viscosity of the cutback and emulsified asphalts are reduced, allowing the mixture to surround the aggregate; upon exposure to the atmosphere, the solvents or water evaporate, leaving the asphalt cement to bond with the aggregate.

#### Description of Pavement Products

The base or subbase course is generally composed of a component referred to as road base. Road base may be composed of gravel or crushed rock, or it may be a granular material treated with asphalt, cement, or lime-fly ash stabilizing agent. Locally available materials are usually used for the base if they meet specified requirements. The base is a layer (or layers) of very high stability and density and is usually composed of well-graded aggregates. Its principal purpose is to distribute the stresses created by wheel loads acting on the wearing surface.

A "hot mix" asphalt is typically used as the wearing course and consists of liquid asphaltic products, asphalt emulsions or road tars, and a soil-aggregate mixture prepared in a central plant and transported to the project site for placement. The primary characteristics which influence hot mix are the mix density, air voids, and the asphalt content. The density of the finished pavement is essential to the performance of the pavement and is controlled by aggregate size and shape, mixing, and final compaction. Air voids in the hot mix allow for expansion and contraction of asphalt without flushing the asphalt to the surface. The asphalt content is critical to a pavement's service life.

The wearing surface or the base course may also consist of a "cold mix" asphalt concrete. Cold mix asphalt concrete consists of emulsified or cutback asphalt and a soil-aggregate mixture. The concrete mixture may be prepared at a central plant or in place. The characteristics which influence cold mix are similar to that of hot mix asphalt.

## EXPERIMENTAL DESIGN

A comparison of road base and asphalt products made without PCS (the control sample) and with varying amounts of PCS was conducted to show that PCS is an effective substitute for the aggregate raw materials that are typically used in pavement products. The structural properties of the pavement products with and without PCS were tested to determine if there were any effects due to the addition of PCS to the raw materials. This section discusses the preparation of samples and the test procedures used to compare the different pavement products.

Similar analyses were performed on hot mix and cold mix samples. Both hot mix and cold mix designs received a complete Marshall mix design, extraction, and gradation analyses. The Marshall mix design analysis consists of bulk specific gravity for density determinations, theoretical maximum specific gravity and density, percent air voids, stability, and flow. The cold mix design was also analyzed for volatile hydrocarbons. The raw materials for the hot and cold mixes were analyzed for total recoverable petroleum hydrocarbons (TRPH).

### Sample Preparation

The hot mix, cold mix, and road base aggregate materials were prepared by performing large-scale sieve breakdowns on all of the aggregates and PCS, and then recombining the graded aggregates and PCS to meet a target gradation for each mix. The large-scale sieve breakdowns allowed the soils testing laboratory to generate samples which were within tolerances of the target gradations, and to accurately blend specific percentages of the PCS with the aggregate samples. Target gradations are the ideal gradations at which aggregate materials will reach optimum performance characteristics such as shear strength, stability, and density.

A complete Marshall mix design analysis was performed on each of the hot mix and cold mix samples. This mix design involves the preparation of three briquette specimens (4 inch diameter and 3 inch height). The aggregates were combined with the PCS to the target gradations for each of the hot mix and cold mix designs. The hot mix samples were prepared by blending aggregate (at 325°F) and the asphalt oil (at 275°F) and molding and compacting approximately 1,280 grams of the mix into a

briquette. The cold mix samples were prepared by blending aggregate (at 190°F) and the asphalt oil (at 140°F). The mix was cured for 56 hours at 140°F. Approximately 1,260 grams of the mix was then molded and compacted into a briquette. The analyses were performed on three briquettes, and the results were averaged.

The road base mix samples were prepared by molding the PCS and soil mixes into cylinders of 2.416 inch diameter by 5 inch height. The cylinders were molded by placing the soils (at specified moisture contents) in five layers and compacting each layer with 40 blows using a 10-lb hammer and 18-inch drop.

### Sample Analysis

The hot mix, cold mix, road base and PCS were each analyzed for specific parameters. The test methods, brief testing procedures, and the purposes of the tests are shown in Table 1.

## DISCUSSION OF TEST RESULTS

This section summarizes the results of the tests performed on the hot mix, cold mix, road base, and PCS. Because of the inherent nature of the materials used, it is difficult to achieve truly homogeneous samples of hot mix, cold mix, or road base. The lack of homogeneity can result in material variation among multiple samples. Analytical error associated with test methods can increase variability, and inconsistent results are not uncommon when testing these pavement products. These inconsistencies were taken into consideration for this study. The raw materials used in the study were collected from a facility in Utah which had aggregate target gradations of existing mixes corresponding to the state of Utah Department of Transportation (DOT) requirements. Therefore, the results of the tests were compared to state of Utah DOT standards when standards were available.

### Petroleum Containing Soils

PCS was tested for particle size and TRPH. The PCS consisted of approximately 30% fine gravel, 12% coarse sand, 21% medium sand, 22% fine sand, and 15% fines (minus #200 sieve) and contained approximately 10,000 ppm TRPH. The gradation (average of 4 samples) of the PCS is shown in Table 2.

### Hot Mix

Analyses were performed on six hot mix samples containing 0, 1, 2, 3, 4, and 5% PCS (by weight). The sample with 0% PCS was the control sample. The results of the sieve analyses after oil extraction are shown in Table 2. The particle-size analyses and oil extractions show that the hot mixes were accurately mixed and graded, and were well within the  $\pm 3\%$  tolerance of the target aggregate gradation. These results show that any inconsistencies in results for other analyses should not be attributed to the gradation of the hot mix samples.

The results of the Marshall mix design analysis on the hot mix designs are shown in Table 3. Density, percent air voids, stability and flow are the most critical properties required in making an acceptable hot mix. The densities of the hot mix samples varied less than 0.4%, and the percent air voids varied less than 10% from the control mix (0% PCS), which are negligible variances.

Table 1. Sample Analyses

Matrix	Parameter	Purpose	Test Method
Hot Mix/Cold Mix	Bulk specific gravity (MMD)	Determine the unit weight and percent air voids in compacted specimens.	ASTM Method D 2726
Hot Mix/Cold Mix	Theoretical bulk specific gravity (MMD)	Determine maximum density and percent air voids in compacted mix.	ASTM Method D 2041
Hot Mix/Cold Mix	Stability and flow (MMD)	Measure the resistance to plastic flow of cylindrical specimens. Maximum load is the stability (1h-force). Displacement between no load and maximum load is flow (0.01").	ASTM Method D 1559
Hot Mix/Cold Mix	Void in mineral aggregates (VMA)	Determine the amount of void space in the aggregates available to be filled by asphalt.	Determined in ASTM Method D 2041
Cold Mix	Hydrocarbon volatile content	Determine hydrocarbon volatile fraction present in a bituminous mixture.	ASTM Method D 1461
Hot Mix/Cold Mix /Road Base	Maximum density	Determine maximum density of a molded specimen. Used to compare control samples to PCS mixes.	Determined in ASTM Method 2726
Hot Mix/Cold Mix /Road Base/PCS	Particle-size distribution	Verify particle size gradation in soils.	ASTM Method D 222
Road Base	Moisture-density relations of soils-aggregate mixtures	Determine the optimum moisture content for a given soil. Optimum moisture content is used to determine maximum shear strength of the soil.	ASTM Method D 1557
Road Base	Unconsolidated-undrained triaxial compression test	Determine the shear strength of soils at optimum moisture content.	ASTM Method D 2850
Hot Mix/Cold Mix /Road Base/PCS	Total recoverable petroleum hydrocarbons	Determine the total recoverable petroleum hydrocarbons in the material.	Modified EPA Method 418.1

MMD - Marshall mix design.

Table 2. Hot Mix Extraction/Gradation Results (PCS and Soil Blends)

Sample Screen Size	Petroleum Containing Soil Blended in Hot Mix							Average PCS Results
	0%	1%	2%	3%	4%	5%	Target	
3/4"	100	100	100	100	100	100	100	98
1/2"	91	88	90	90	90	88	89	90
3/8"	80	79	81	82	80	80	79	85
#4	58	56	58	59	57	57	56	70
#8	41	40	42	42	40	40	40	60
#16	27	26	28	28	26	27	28	53
#30	21	20	21	22	20	21	21	45
#50	17	17	18	18	16	17	17	32
#100	12	12	13	13	11	12	12	28
#200	7.1	7.0	7.9	7.7	6.8	7.0	7.5	18
Extracted Oil Content	4.80	4.63	4.62	4.56	4.63	4.66		NA
Factored Oil Content*	4.95	4.78	4.77	4.71	4.78	4.81		NA

\*Average retention factor of 0.15% added for asphalt retained in soil.

Table 3. Marshall Mix Design Analysis Results - Hot Mix

Analysis	Percent Petroleum Containing Soil Blended in Hot Mix					
	0%	1%	2%	3%	4%	5%
Specific Gravity	2.246	2.243	2.243	2.246	2.254	2.249
Density (pcf)	140.1	139.9	140.1	140.2	140.6	140.4
Stability (psf)	2,116	1,981	2,036	1,858	2,006	1,864
Flow (0.01")	11	10	11	12	13	11
Voids (%)	6.06	5.44	5.71	5.43	5.65	5.82
VMA (%)	16.6	15.96	16.23	15.97	16.22	16.37
Max Spec. Gravity	2.391	2.372	2.379	2.375	2.389	2.388
Max Density (pcf)	149.2	148.0	148.4	148.2	149.1	149.0

VMA = Voids in Mineral Aggregate.

The stabilities of the hot mix samples showed more variability but were within 12% of the control mix. The results show that as the percentage of PCS is increased in the hot mix samples, the stability is not substantially affected. All of the stability results surpassed the state of Utah minimum requirement of 1,200 lb. Flow for the hot mix samples with PCS remained fairly consistent in the 0.11- to 0.13-in. range.

#### Cold Mix

Analyses were performed on cold mix containing 0, 10, 20, 25, 30, and 50% PCS (by weight). The sample with 0% PCS was the control sample. Analyses performed on the cold mix samples included particle-size analysis on aggregate after extraction of asphalt oil, determination of hydrocarbon volatile content, and a complete Marshall mix design analysis.

The results of the particle-size analyses and oil extractions are shown in Table 4. The particle-size analyses and oil extractions reveal that the cold mix samples had a range of  $\pm 4\%$  of the target gradation. This  $\pm 4\%$  tolerance is slightly higher than the standard tolerance of  $\pm 3\%$  specified for the aggregate pit from which the raw materials were received. The higher range is due to the high percentage of PCS used in the mix and the high content of fine material (minus #16 sieve) in the PCS.

**Table 4. Cold Mix Extraction/Gradation Results**

Sample	Percent Petroleum Containing Soil Blended in Cold Mix						Target
	0%	10%	20%	25%	30%	50%	
Screen Size	% Passing						
1"	100	100	100	100	100	100	100
3/4"	100	99	99	98	99	99	99
1/2"	92	89	90	90	90	91	91
3/8"	81	78	78	78	77	79	80
#4	48	48	49	47	46	46	50
#8	32	31	32	31	30	33	34
#16	26	25	26	24	23	28	27
#30	20	19	19	18	17	24	21
#50	15	15	15	14	13	18	16
#100	9	10	11	11	10	14	13
#200	6.6	7.2	8.7	8.5	8.1	11	8.0
% MC-800 Added	6.24	6.24	6.24	6.24	6.24	6.24	
% Asphalt Target	5.25	5.25	5.25	5.25	5.25	5.25	
% Extracted Asphalt	5.45	5.66	5.70	5.39	5.63	6.05	
% Volatile Loss	12.66	9.29	8.65	13.62	9.78	3.04	

The target percent asphalt oil after curing was 5.25%. Literature from Phillips 66, the supplier of the MC-800 asphalt, indicated that the petroleum distillate in the asphalt ranged between 11 and 27%.<sup>3</sup> To reach the target of 5.25% asphalt after curing, 18% of the asphalt was assumed to be petroleum distillate that would evaporate during curing. The results show that the amount of evaporated asphalt varied from 3.04 to 13.62%. The average amount of evaporated asphalt was 9.51%. Therefore, the average amount of asphalt in the mixes after curing was 5.65%. Because the average percent asphalt after curing exceeds the target value of 5.25%, it is possible that the 18% average for petroleum distillate may be high.

Percent asphalt is determined by weighing the cold mix sample after curing, then extracting the asphalt from the mix by applying citric acid to the mix until no asphalt oil was visible. The sample is weighed again and the difference in weight is considered to be the amount of asphalt in the original mix, and a percentage of the total weight is determined. The differences between the amounts of evaporated asphalt in the various samples may be a result of inconsistent curing times (laboratory error) and/or the retention of asphalt on the aggregate after extraction. It is also possible that the mass of petroleum hydrocarbons contributed by the PCS was removed during the extraction, thereby making the "extracted asphalt" value artificially high. However, this amount would be very small (less than 0.05% of the mass) and would, therefore, have little effect on the results. The percent asphalt is important to the cold mix because it may affect the percent air voids and flow (discussed below).

The results of the Marshall mix design analysis on cold mix designs are shown in Table 5. Stability, percent air voids, and densities are the most critical properties required in making suitable cold mix. The stability criterion for cold mix paving mixtures is 750 lb (Asphalt Institute recommendation). The stability of the control mix was 2,627 lb. The stability of the samples containing PCS varied from 2,191 lb to 2,604 lb. The variance in stability of the mixes was not proportional to amount of PCS in the mix. Therefore, it is believed that the amount of PCS in the mix does not significantly affect the stability of the mix.

**Table 5. Marshall Mix Design Analysis Results - Cold Mix**

Analysis	Percent Petroleum Containing Soil Blended in Cold Mix					
	0%	10%	20%	25%	30%	50%
Specific Gravity	2.228	2.308	2.348	2.319	2.344	2.363
Density (pcf)	142.8	144.0	146.5	144.7	146.3	147.4
Stability (psf)	2,627	2,191	2,604	2,340	2,577	2,487
Flow (0.01")	19	16	15	15	15	16
Voids (%)	4.59	3.02	2.65	3.40	2.50	0.59
VMA (%)	17.44	16.49	16.45	16.14	16.10	15.33
Max Spec. Gravity	2.398	2.380	2.412	2.397	2.404	2.377
Max Density (pcf)	149.6	148.5	150.5	149.6	150.0	148.3

VMA = Voids in Mineral Aggregate

The percent air voids and the density in the cold mix samples were affected by the amount of PCS used. The percent air voids in the 0% PCS mix was 4.59%. The percent air voids in the samples containing PCS ranged from 0.59 to 3.40%. The criteria for percent air voids is 3 to 5% in compacted cold mix. The density increased from 142.8 lb/ft<sup>3</sup> (pcf) with 0% PCS, to 147.4 pcf for the sample with 50% PCS. Although density will increase when the percent air voids decreases, the percent air voids must be maintained above the minimum level to allow for the expansion and contraction of the pavement products that is a direct result of freeze/thaw conditions. The decrease in percent air voids and the increase in density of the mixes containing high percentages of PCS may be due to the asphalt content exceeding the target quantity, and may also be attributed to deficient or excessive compaction causing high or low percent air voids, respectively.

The flow was also affected by the addition of PCS to the cold mix. The flow for the control sample was 0.19 in.; the flow for mixes containing PCS ranged from 0.15 to 0.16 in. The criterion for flow of a cold mix is 0.08 to 0.16 in. In this case, the addition of PCS to the cold mix design brought the mix into the acceptable range.

#### Road Base

Road base was tested using 0, 5, 10, 15, 20, and 25% blends of PCS (by weight), with the sample containing 0% PCS being the control sample. The road base was analyzed for particle-size distribution, optimum moisture content, shear strength, and TRPH. The results of the particle-size analyses are shown in Table 6. The results show a variance of  $\pm 2\%$  in the actual and target gradation for the road base and PCS blends. This tight variance implies that results in additional tests (i.e., optimum moisture content, maximum shear strength, etc.) should not be attributed to the gradation of the mixes.

Table 7 presents the results of the maximum dry density, optimum moisture content, and maximum shear strength. These results reveal that the physical properties of the mixes are significantly changed by increasing the percentage of PCS. As the quantity of PCS is adjusted from 20 to 25%, the optimum moisture content and shear strength are affected. The optimum moisture content decreased from 7.1 to 5.2%, and the shear strength decreased from 4,342 psf to 2,651 psf in the 20 and 25% PCS blends, respectively. The optimum moisture content of the mixes with 15 and 20% PCS was not affected; however, the shear strength declined from 5,120 to 4,342 psf, respectively. The maximum dry density in all of the road base mixes ranged from 136.6 to 138.6 pcf, which is an acceptable variance.

One explanation for the decrease in moisture content may be that the petroleum hydrocarbons in the mixes with higher percentages of PCS prevented the soil from absorbing the additional moisture, thereby decreasing the optimum moisture content, but this effect would be minimal. It is more likely that the reduction in optimum moisture content and shear strength is due to the variability of the test method for optimum moisture content, which is highly variable in standard testing. This variability may affect the testing of optimum shear strength, making the shear strengths test results lower than the actual value. These results indicate that 15% PCS may be the maximum amount of PCS that can be blended in this type of road base. Further studies of the road base containing greater than 15% PCS would be necessary to determine the maximum amount of PCS which could be used without affecting the shear strength of the road base mix.

**Table 6. Road Base Gradation Results**

Sample	Percent Petroleum Containing Soil Blended in Road Base						Target
	0%	10%	20%	25%	30%	50%	
Screen Size	% Passing						
1"	100	100	100	100	100	100	100
3/4"	99	99	99	99	99	99	99
1/2"	91	90	91	91	90	91	91
3/8"	81	80	80	80	80	80	80
#4	49	52	50	50	50	50	50
#8	33	33	32	33	32	33	34
#16	27	27	27	27	28	27	27
#30	20	20	20	20	20	19	21
#50	15	16	15	15	15	14	16
#100	13	12	12	12	12	12	13
#200	9.0	8.8	8.8	8.8	8.8	8.9	9

**Table 7. Road Base Analysis Results**

Analysis	Percent Petroleum Containing Soil Mixed with Road Base					
	0%	5%	10%	15%	20%	25%
Max. Dry Density	138.6	137.8	136.6	137.5	137.4	137.3
Opt. Moisture Content	7.0	7.2	6.7	7.0	7.1	5.2
Plasticity	NP	NP	NP	NP	NP	NP
Max. Shear Stress (psf) with 3.5 psi confining pressure	5,743	5,466	5,741	5,120	4,342	2,651

NP = Non-Plastic



### Results of TRPH Analyses

Results of the TRPH analyses on the PCS and the raw materials are presented in Table 8. The TRPH analyses were performed to determine the concentration of TRPH in the PCS, and to determine if the raw materials for the pavement products contained any petroleum hydrocarbons. The PCS which was used in each of the pavement components was analyzed before being blended with the aggregates. The results of these analyses show that a "typical" (representative) sample of PCS has a TRPH concentration ranging from 9,500 to 10,000 ppm.

The TRPH analysis performed on the raw materials for the hot mix revealed a concentration of 360 ppm, but this contamination is likely the result of improper sampling procedures. The raw materials for the hot mix were placed in a sample jar which previously contained PCS. The sample jar was found to have not been properly decontaminated with a solvent, thus cross-contamination may have occurred. This error does not affect any other analyses performed on the hot mixes—the raw materials for the hot mix were assumed to contain no petroleum hydrocarbons. The TRPH analyses performed on the raw materials for cold mix and road base showed that the TRPH concentration was below the detection limit of 10 ppm.

TRPH analyses were also performed on each of the road base mixes with increasing amounts of PCS. The results revealed that the TRPH concentrations in the mix increased relative to the PCS blended in the mix. These results indicate that the PCS used in all of the road base mixes was relatively consistent.

**Table 8. Total Recoverable Petroleum Hydrocarbons in PCS Mix Results**

Matrix	% PCS	TRPH ( $\mu\text{g/g}$ )	Detection Limit ( $\mu\text{g/g}$ )
Hot Mix	0	360*	20
PCS Used in Hot Mix	100	10,000	20
PCS Used in Cold Mix	100	9,500	20
Cold Mix/Road Base	0	10	10
Road Base	5	290	10
Road Base	10	440	10
Road Base	15	890	10
Road Base	20	1,300	10
Road Base	25	1,700	10
PCS Used in Road Base	100	9,500	10

\* Attributed to cross-contamination in the soil laboratory.

### CONCLUSIONS

The general conclusion from the study is that petroleum containing soil (PCS) is an effective commercial substitute for typical raw aggregate materials used in pavement products.

The PCS in the hot mix samples was varied from 0 to 5%. The densities of the hot mix samples varied less than 0.4%. The percent air voids in the hot mix samples varied less than 10%, and the stabilities of the samples varied less than 12% from the control mix. The conclusions from the hot mix test results include:

- Densities, percent air voids, and flow were essentially consistent for all hot mix samples.
- Stabilities varied slightly, but results for all samples surpassed the state of Utah minimum requirement.

The cold mix samples were prepared and tested with PCS contents between 0 and 50%. The stabilities of the cold mix varied less than 17% from the control mix and significantly surpassed the standard criteria. The flow of the mixes decreased when the amount of PCS in the mixes was increased. The percent air voids significantly decreased with the higher PCS contents, and densities increased slightly with the increased PCS content. The conclusions from the cold mix test results include:

- The stabilities of the cold mixes were not significantly affected by the increase in PCS. Stabilities exceeded the minimum criterion set by the state of Utah DOT.
- The flows decreased for the cold mix samples with increased PCS content and brought the mix into the acceptable range of flow criteria.
- The percent air voids were affected by the increased PCS content and the minimum criterion set by the state of Utah DOT was not met.
- PCS can be blended with aggregates in quantities up to 30% in cold mix without significant detrimental effects.

The PCS in the road base samples was varied between 0 and 25%. The particle-size analysis varied less than 2%, the optimum moisture content remained consistent up to the addition of 20% PCS and decreased significantly for the 25% PCS sample, and the shear strengths decreased significantly in the mixes with more than 15% PCS. The conclusions from the road base results include:

- The results for the optimum moisture content may be in error due to the significant variability in the test method, therefore the results for the shear strength may be in error. Further studies are required to obtain additional data on the effect of PCS on the shear strength of road base.
- PCS can be used in road base up to 15% without significantly affecting the physical properties of the road base.

The physical properties of pavement products made with PCS are consistent with the properties of products made without PCS within the range of substitutions tested in this study. In most cases, the PCS products exceeded the criteria set by the state of Utah DOT, when criteria were available for comparison. This study shows that the PCS can be used in hot mix, cold mix, and road base to make pavement products that are equivalent to the products made without PCS.

### PCS PRODUCT USE

Pavement products manufactured with recycled PCS may be used for commercial or state department of transportation applications. Utah, California, Nevada, and Texas solid waste and transportation agencies currently approve the use of recycled PCS in pavement products and construction. The state of Texas requires contractors working on pavement projects to salvage any asphalt pavement that is removed rather than disposing of the materials. This removed asphalt is typically recycled in new asphalt pavement, which is similar in concept to recycling PCS in pavement products.

Existing pavement product facilities can be easily modified to incorporate PCS as a raw material substitute. General facility management requirements include: storing PCS on an impervious liner within a bermed area to prevent migration of the petroleum constituents and to control run-on and run-off from the area; handling and processing PCS to prevent loss of material through loading/unloading and wind dispersion; weighing and controlling use of the PCS to ensure it is used appropriately; random sampling and analysis of the PCS to ensure consistency with the generator's analyses; and documentation of the receipt of PCS from the generator and reuse of the PCS as a pavement product.

In the state of Texas, Standard Exemption Number 99 exempts asphalt concrete facilities from needing an air permit for hot mix asphalt production; the exemption does not specifically prohibit the incorporation of PCS into asphalt paving materials. Prior to the production of PCS containing pavement products the facility chosen to manufacture the products should prepare general facility specifications for the use of the PCS. This document will define the procedures the facility is to follow for the management and use of the PCS. The facility and generator must also obtain state approval for the process.

### References

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3. Material Safety Data Sheet, Asphalt MC-250, MC-800, MC-3000, Phillips Petroleum 66, December 14, 1988.

### Questions and Answers:

Q. Have you tried any soils that had clay in them?

A. No we have not. It's very likely that if the amount of fines in the clays are high, it won't be an effective substitute in the hot mix/cold mix of the road base. We are discussing with the State of Texas using clay soils in embankments. Lining the embankments with clay is a very effective utilization. We're working with them now to see what else can be done.

Q. You had said that in the cold mix test you heated the soil to about 225 degrees. Typically cold mixes are done on site by mobil units, at least in New York. Did you do any testing without heating the soil and do you think that would have any effect?

A. I personally don't think it will have any effect, but, no we did not do any tests without heating the soils. The heating was performed in accordance with the State of Texas's DOT regulations, to show how this would effectively be done. Usually cold mix is stored on site for months at a time and heating shows the typical breakdown effects of the petroleum distillate. It enhances and increases the speed of that.

Q. Have there been any studies performed to determine the breakdown of pyrenes or other compounds in the cold mix which may potentially effect groundwater?

A. We have not performed any of those studies. Health assessments have been performed to show that by adding the PCS, the likelihood for this contamination is less, or is similar to that caused by strictly using typical cold mix.

## CHAPTER 4

### Regulatory Permitting for In Situ Bioremediation Treatment: Case History

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#### INTRODUCTION

Over the past decade, bioremediation has gained a reputation as a cost-effective innovative technology for hydrocarbon remediation.<sup>1-7</sup> In particular, the term bioremediation frequently denotes *in situ* applications of the technology, usually by recovery of contaminated groundwater that is amended with oxygen and nutrients prior to reintroduction back into the subsurface<sup>8-9</sup>. The recovered groundwater can be reinjected or reinfiltred into contaminated soil locations to promote soil flushing of contaminants, and to accelerate *in situ* biodegradation of dissolved-phase constituents<sup>10-12</sup>.

*In situ* bioremediation likely employs hydraulic capture of reinfiltred groundwater to ensure that contaminated or nutrient-amended groundwater is kept within a closed-loop maintained by pumping wells for adequate treatment of hazardous constituents prior to flow dispersion from the affected site<sup>13-15</sup>. In this case history, closed-loop *in situ* bioremediation is defined as hydraulic capture of the plume and reinfiltred of recovered groundwater following oxygen and inorganic nutrient amendments. The hydraulic containment provided by five high capacity recovery wells is designed to minimize losses of impacted groundwater from the treatment area. A small portion of the recovered groundwater is diverted to the sanitary sewer for maintenance of hydraulic capture.

While the closed-loop design for *in situ* bioremediation promises an engineered solution integrating pumping and bioremediation technologies, regulatory permitting of this remediation approach is not trivial.<sup>14</sup> Regulatory approval of closed-loop *in situ* bioremediation cited in this case history required approvals at the state and local level for over a half-dozen specific permits that allowed variances from existing regulations.



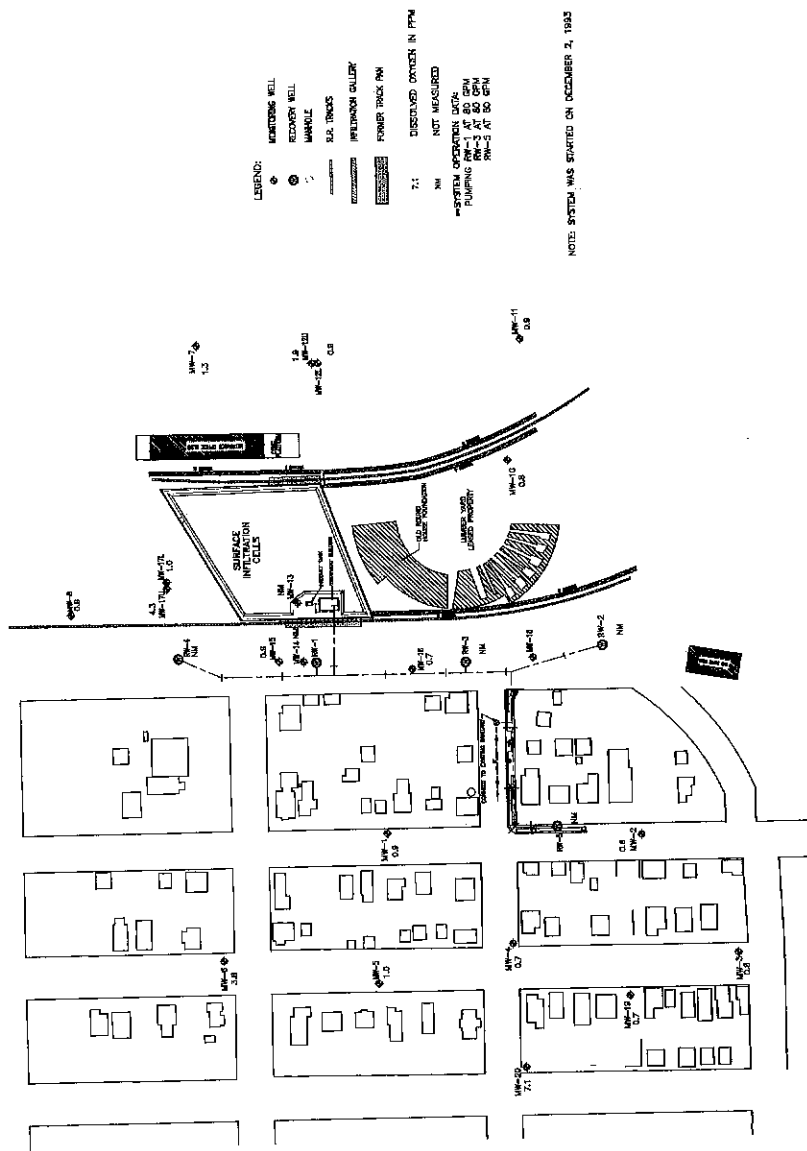


Figure 2. Site map with in-situ bioremediation system.

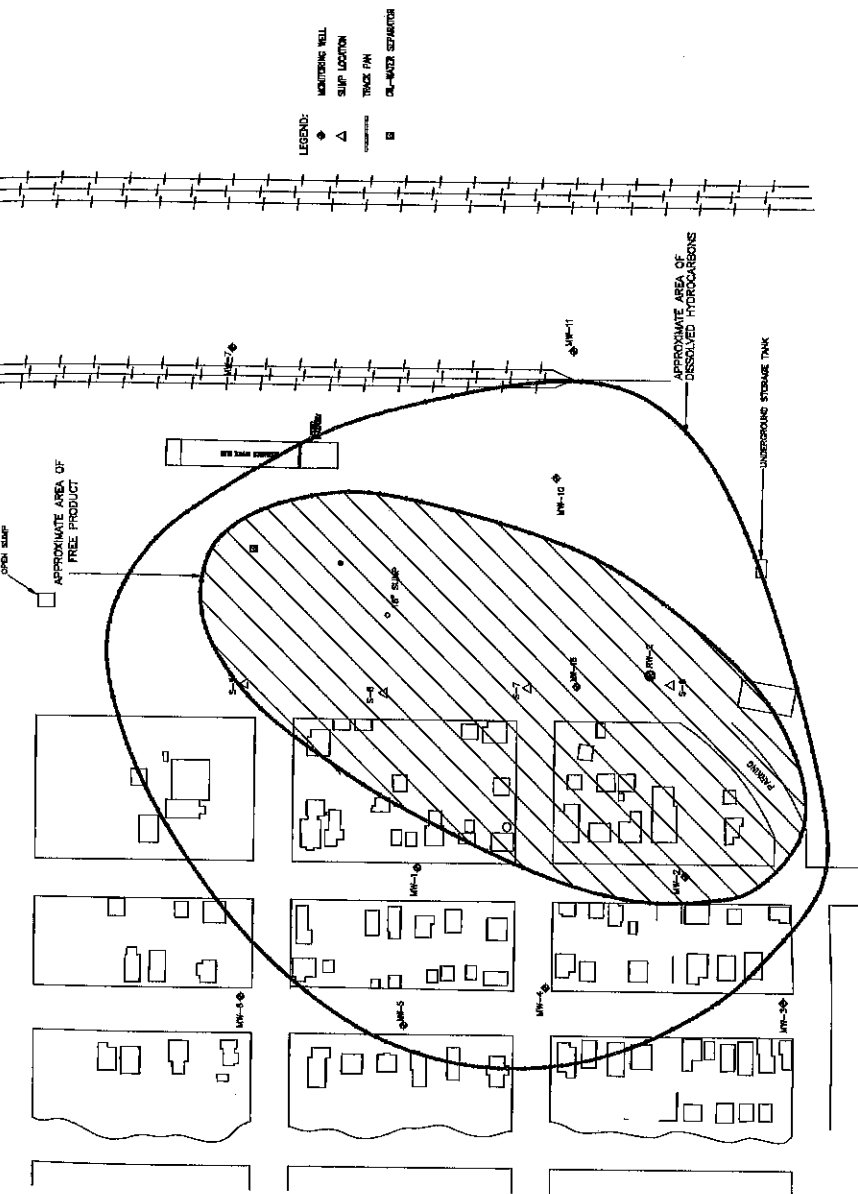


Figure 3. Approximate extent of ground water contamination.

Six potential alternatives were identified for site remediation. Alternatives considered were:

1. Groundwater extraction in combination with *in situ* biological treatment,
2. Groundwater extraction and treatment by air stripping,
3. Groundwater extraction and treatment by activated carbon,
4. Soil venting,
5. Air sparging,
6. No action.

These alternatives were evaluated on the basis of the following criteria:

- Life cycle costs,
- Permits required,
- Emission rates,
- Other factors including site hydrogeologic conditions, public image, flexibility, risk of permit violations, vendor confidence, simplicity, risk of increased costs, and potential schedule problems.

Due to legal and regulatory ramifications involving off-site hydrocarbon concentrations, no action was not considered feasible. Given the physical and chemical properties of fuel oil hydrocarbons, volatilization mechanisms employed with air sparging and soil vapor extraction (AS/SVE) are less effective when compared to AS/SVE remediation strategies for gasoline-type constituents.<sup>16</sup> However, AS/SVE offers increased bioremediation of both contaminated groundwater and soil by oxygen enhancement. Groundwater extraction is an effective method to provide hydraulic containment,<sup>17-18</sup> but has been demonstrated to rarely achieve cleanup goals for groundwater.<sup>19-21</sup> Thus, the groundwater extraction options employing either activated carbon or air stripping aboveground treatments prior to discharge would mitigate plume migration with expensive and prolonged remediation treatment time that would never achieve aquifer cleanup goals. In addition, surface treatment and disposal to sanitary or storm sewer would not address the vadose zone contamination associated with the source area.

In contrast, *in situ* bioremediation integrates hydraulic containment as necessary to prevent further contaminant migration. Biodegradation serves as the primary hydrocarbon removal mechanism for saturated and unsaturated soils impacted with hydrocarbons. Groundwater is hydraulically captured and recirculated in a closed-loop circuit following amendments with oxygen and inorganic nutrients. In addition, the groundwater resource is conserved through the closed-loop recirculation strategy. Since aboveground treatment is not employed with this option, contaminant transfer to other media (air or carbon) is not a consideration. While conceptually the *in situ* bioremediation program as outlined makes sense, regulatory permitting issues were more intensive given the innovations employed in the system including:

- High capacity recovery wells totaling 625 gpm,
- Access to install one high capacity recovery well and utility trench in downgradient residential area,
- No aboveground treatment other than free product separation, to reduce hydrocarbon concentrations prior to discharge,
- Negotiation for minimal flow diversion to the sanitary sewer for purposes of maintaining hydraulic capture of the plume and reinfiltreated inorganic nutrients,
- Introduction of bromide/chloride tracers into the subsurface to verify hydraulic capture and evaluate travel times,
- Permit for discharge to local Publicly Owned Treatment Works of sewer flow without pretreatment,
- Negotiating a comprehensive monitoring program including target hydrocarbon constituents, DO, nutrients and key inorganics,
- On-site discharge into the one-acre infiltration pond and six below-grade galleries under Wisconsin Pollutant Discharge Elimination System (WPDES) permit (Table 1), without hydrocarbon pretreatment and with nutrient addition prior to discharge.

Table 1. WPDES Permit Conditions

Parameters	Effluent Limit	Sample Type
Flow	Initially 100 GPM; Currently 340 GPM Up to 625 GPM with WDNR Approval	Total Grab
BETX	Wisconsin Statutes 144.76 <sup>a</sup>	Grab
Polynuclear Aromatic Hydrocarbons	Wisconsin Statutes 144.76 <sup>a</sup>	Grab
Diesel Range Organics	Wisconsin Statutes 144.76 <sup>a</sup>	Grab
pH	Within 6 - 9 S.U.	Grab
Dissolved Oxygen	-	Grab
Phosphorus	-	Grab
NO <sub>2</sub> + NO <sub>3</sub> -Nitrogen	-	Grab
Total Kjeldahl Nitrogen	-	Grab
Ammonia-Nitrogen	-	Grab
Total Nitrogen	10 mg/L, Monthly Average <sup>b</sup>	Calculated

<sup>a</sup> The discharge of BETX (benzene, ethylbenzene, toluene, and total xylenes) and polynuclear aromatic hydrocarbons (including naphthalene) in the water carrying the oxidant and nutrients back to the contaminated soil zone shall be regulated as specified by the DNR remediation project manager under the approval issued pursuant to §. 144.76, Wisconsin Statutes. This *in situ* bioremediation process will be monitored with groundwater elevation measurements, and contaminant test results from the seepage water and groundwater monitoring wells. The discharge to seepage (i.e., reinfiltation) will be regulated to facilitate continued cleanup of this site with the goal of regaining compliance with the groundwater standards contained in Ch. NR 140, Wisconsin Administrative Code.

<sup>b</sup> Total nitrogen is calculated as the sum of total Kjeldahl nitrogen and NO<sub>2</sub>+NO<sub>3</sub>-nitrogen.

### IN SITU BIOREMEDIATION SYSTEM: DESIGN

To verify the effectiveness of using the closed-loop *in situ* bioremediation strategy, several elements of the design were further assessed during pre-design activities. Several of the more important elements that were assessed are listed as follows:

- Assessment of passive biodegradation by evaluating aerobic and denitrifying electron acceptor systems and inorganic nutrient concentrations,
- Effectiveness of soil flushing for fuel oil constituents,
- Biological microcosm testing for effects of oxygen, nitrate, and inorganic nutrient amendments for site groundwater bioremediation,
- Twenty-six monitoring wells to evaluate hydrogeologic conditions and extent of contamination,
- Numerous soil borings (39) to assess soil stratigraphy and extent of contamination,
- Aquifer testing to evaluate aquifer properties,
- On-site infiltration testing to evaluate infiltration rates and plugging potential,
- Geochemical evaluation to determine the potential for precipitation subsequent to oxygen and nutrient addition.
- Sieve analysis (10), falling head permeability tests (2), and hydraulic conductivity tests for aquifer properties evaluations,
- Design of bromide and chloride tracer study to demonstrate hydraulic capture and evaluate breakthrough times as specified by the WPDES permit conditions,
- Modeling of groundwater flow under various pumping and reinfiltration scenarios using a two-dimensional, analytical simulation model, Single Layer Analytical Element Model (SLAEM).

Figure 4 depicts the SLAEM modeling superimposed over the approximate extent of groundwater contamination. Additional regulatory-specified reporting to complement the above elements for the site remediation program were the Corrective Action Plan (CAP), plans and specifications, and operation/maintenance plans.

#### Treatability Testing

Additional site data was acquired to more completely evaluate the groundwater environment with respect to passive biodegradation. Field measurements for DO, pH, and conductivity were obtained. Groundwater samples were collected and analyzed for inorganic nutrients, anaerobic electron acceptors, total organic carbon, and determinations for oxygen demand (i.e., chemical oxygen demand and biochemical oxygen demand). Based on the collected data, the groundwater at this site was judged conducive for bioremediation. Extensive natural passive biodegradation in the site groundwater was noted, explaining why the dissolved-phase plume of hydrocarbons was limited to a short distance downgradient the site.

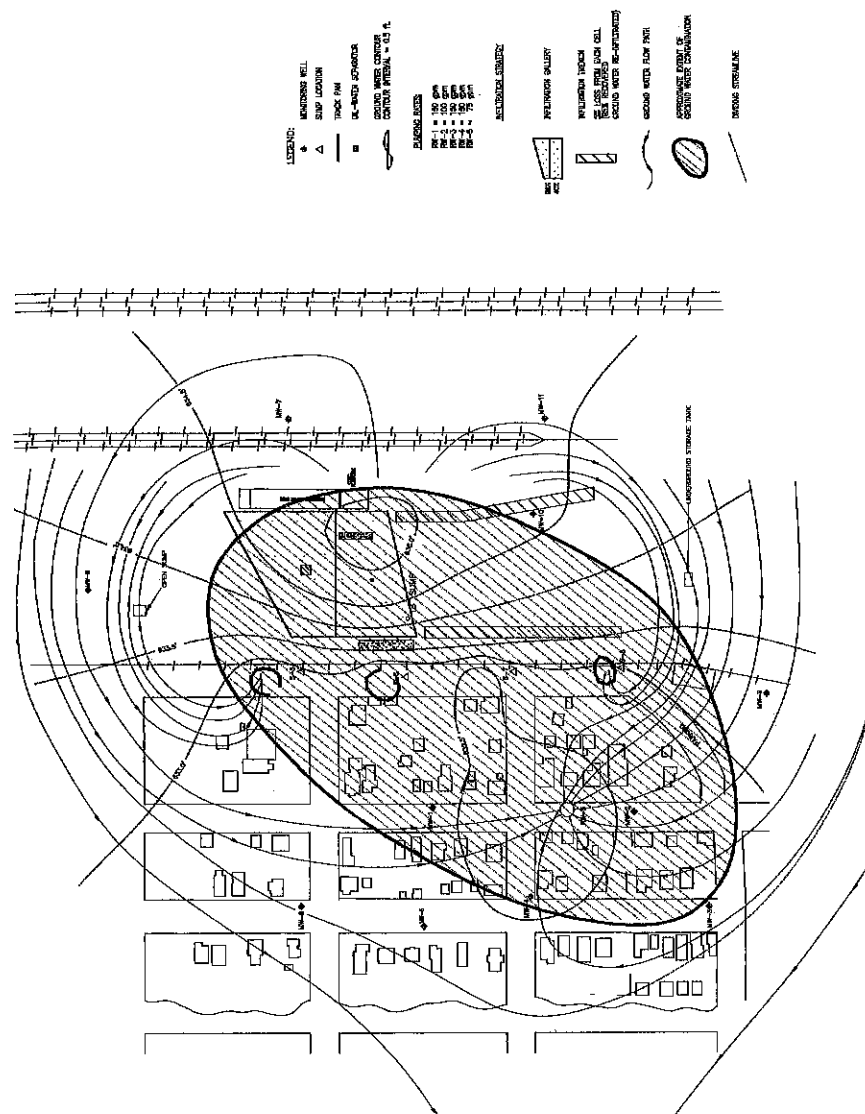


Figure 4. Groundwater modeling results.

Since much of the source fuel oil contamination exists in the unsaturated zone, reinfiltration of recovered groundwater through contaminated zones was assessed with soil column studies. The studies utilized contaminated soil packed into columns and site groundwater to flush through the soil column for up to 300 pore volumes. Based on the soil flushing tests, 300 pore volumes of water yielded nondetectable benzene, toluene, ethylbenzene, xylenes (BTEX), and naphthalene with significantly reduced total alkylbenzenes in the resulting leachate (Figure 5). Soil flushing using 300 pore volumes of groundwater corresponds to a three to five year treatment duration based on the recovery well pumping rates and the majority of recovered groundwater reinfiltrated on site.

Microcosms containing groundwater and saturated soil were evaluated for amendments including DO (aerobic electron acceptor), nitrate (anaerobic electron acceptor), and inorganic nutrients (nitrogen and phosphorus). Passive biodegradation was known to be effective for removal of BTEX and naphthalene in the site groundwater, and microcosm testing confirmed that target compounds were reduced without any amendments to the recovered groundwater. However, target compound removal rates were optimized by using additional amendments of DO and inorganic nutrients as shown in Figure 6.

#### *In Situ* Bioremediation System Design

The remedial program consists of five high-capacity recovery wells having a potential extraction rate of 625 gpm. The recovery wells control the site hydraulic gradient, recover residual free-phase product, and provide the water for reinfiltration used to flush soil contamination and deliver amendments to the subsurface as depicted in the simplified process flow diagram shown in Figure 7. Recovered groundwater is not treated (e.g. air stripping) prior to reinfiltration. Amendments to the groundwater prior to reinfiltration include DO and inorganic nutrients consisting of ammonia-nitrogen and reactive phosphorus (Figures 8 and 9). Gas-liquid contactors are used to add DO from a high-purity oxygen source that is generated on site. Amended groundwater is discharged into on-site ponds and/or buried infiltration trench locations noted in Figure 10.

Design activities for the treatment system were initiated in 1991. Preliminary approval of the conceptual design was received in late 1992 following extensive interaction with various sections of the Wisconsin Department of Natural Resources (WDNR), with formal permit approval given in June 1993.

#### Treatment System Construction and Startup

The *in situ* remediation system was constructed in the last half of 1993, and the site became operational on December 3, 1993. Initially, the system operated with a total flow rate of 100 gpm extracted from a single recovery well. Two recovery wells were on-line pumping 160 gpm by the end of December 1993 with approximately 10 gpm diverted to the sanitary sewer. In March 1994 the extraction rate was increased to 240 gpm by activating the most downgradient recovery well, RW-5. Measured groundwater contours resulting from the operation of three recovery wells is depicted in Figure 11. The groundwater extraction rate was further increased to 340 gpm in July 1994.

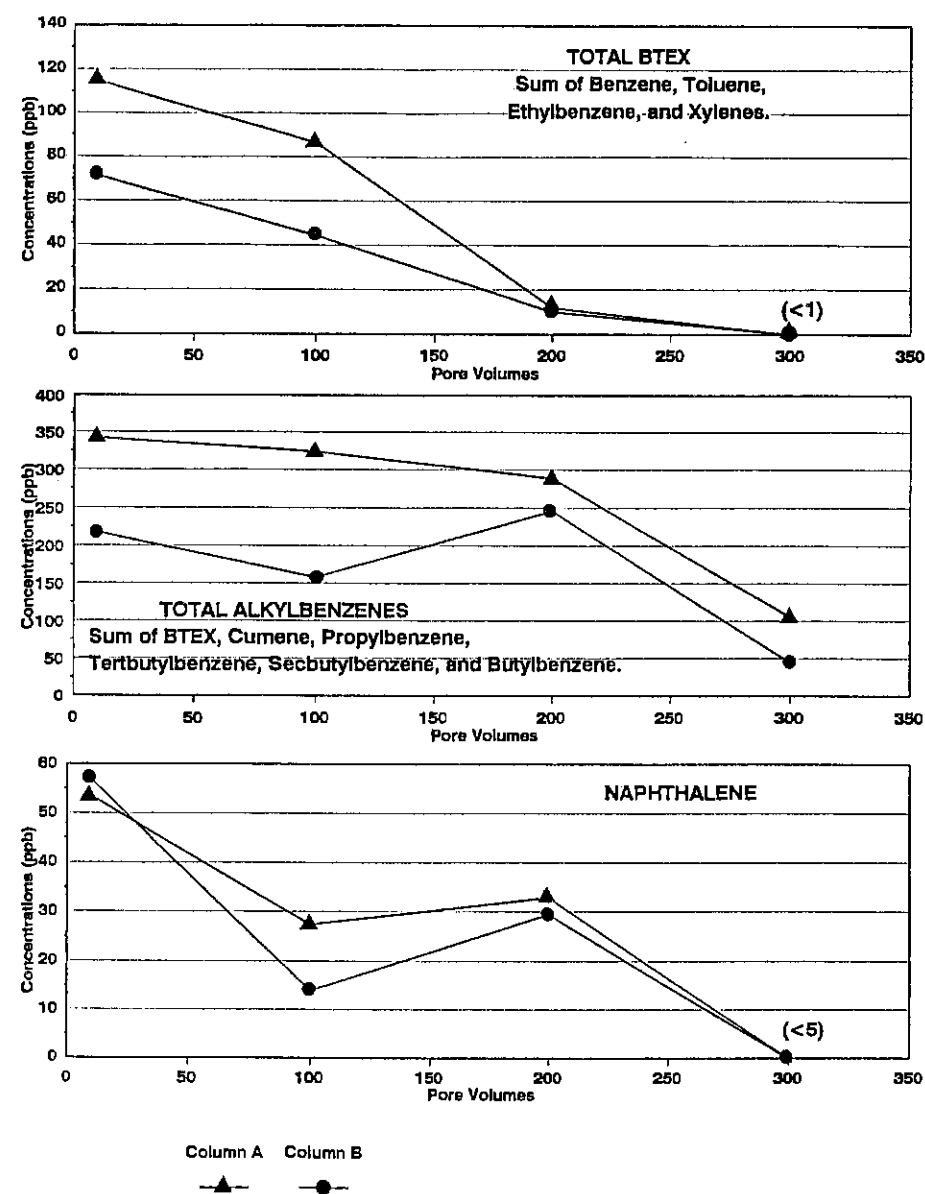


Figure 5. Soil column flushing tests.



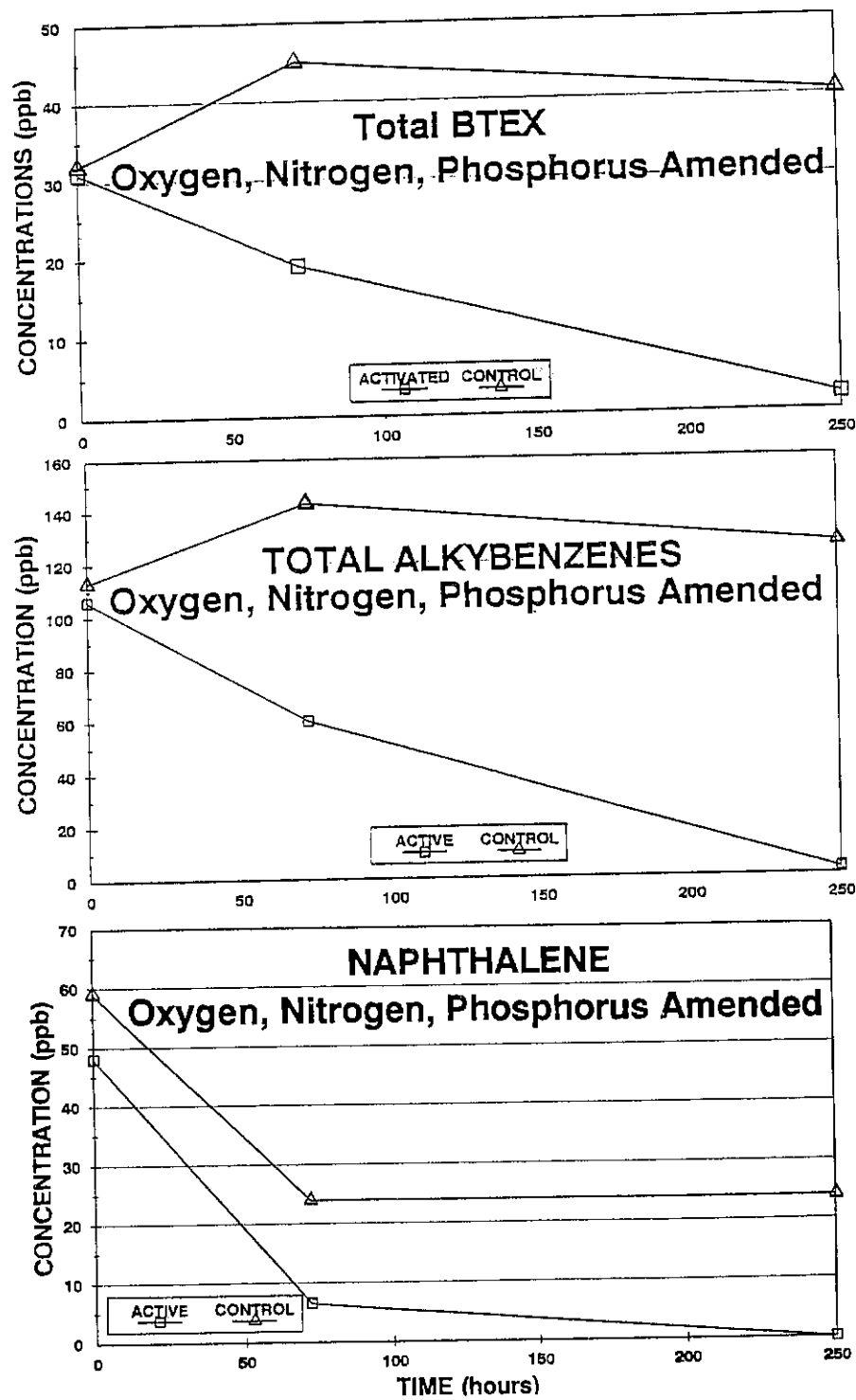


Figure 6. Microcosm optimization tests.

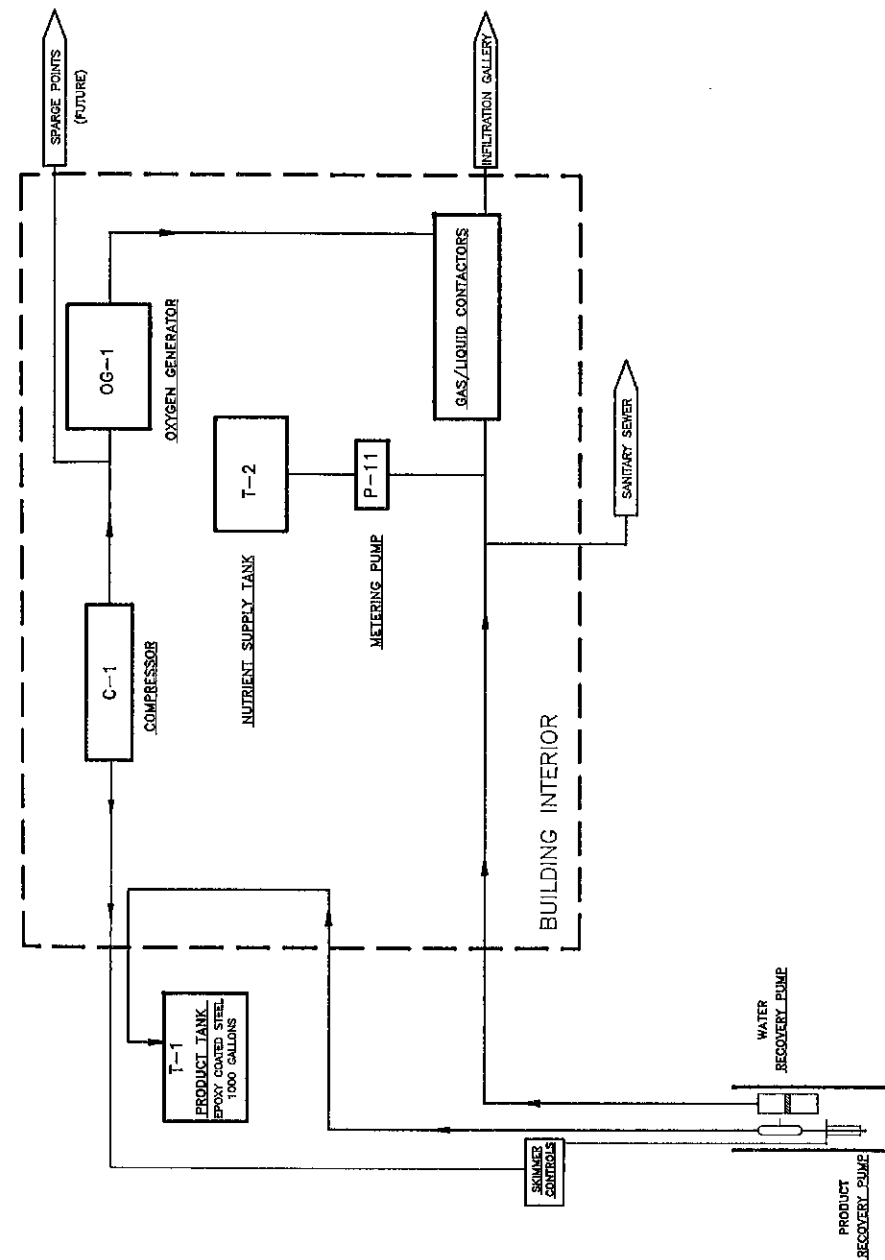
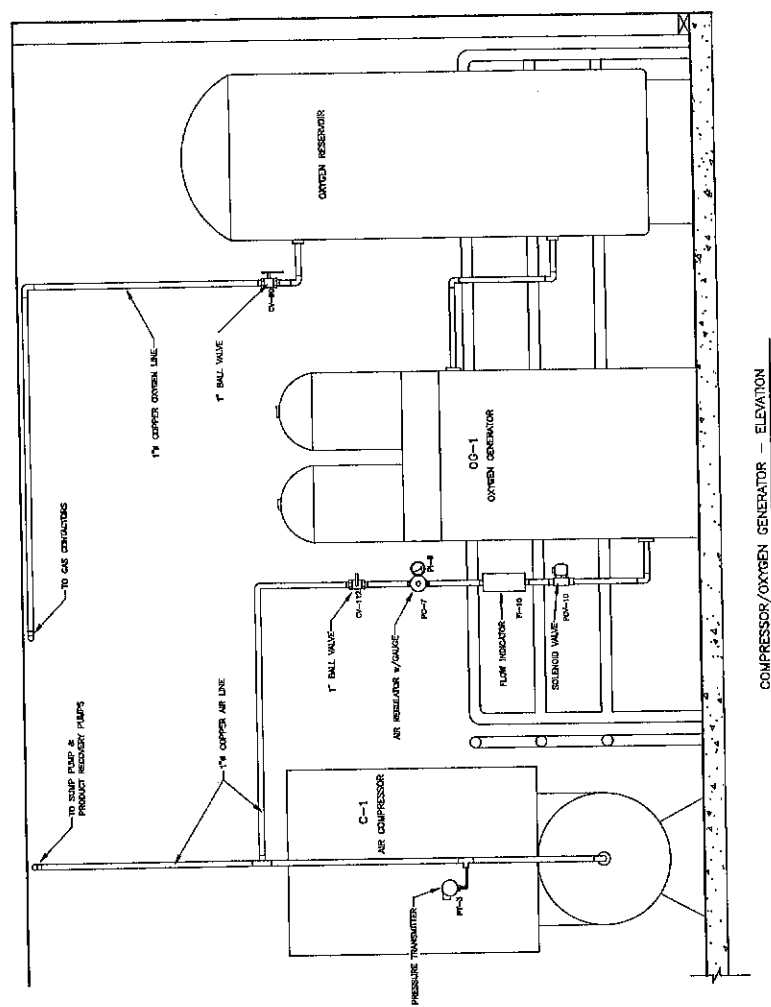
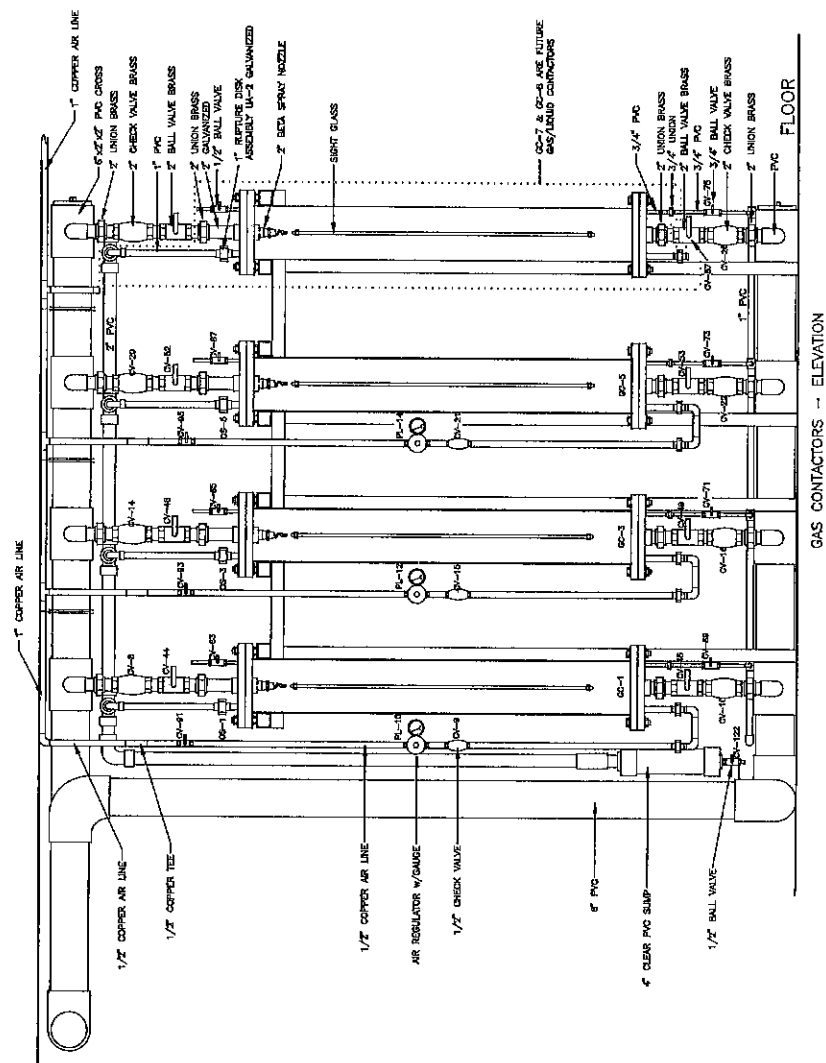


Figure 7. Simplified process flow diagram



COMPRESSOR/OXYGEN GENERATOR - ELEVATION

Figure 8. High-purity oxygen source.



GAS CONTRACTORS - ELEVATION

Figure 9. Oxygen transfer via gas-liquid contractors.

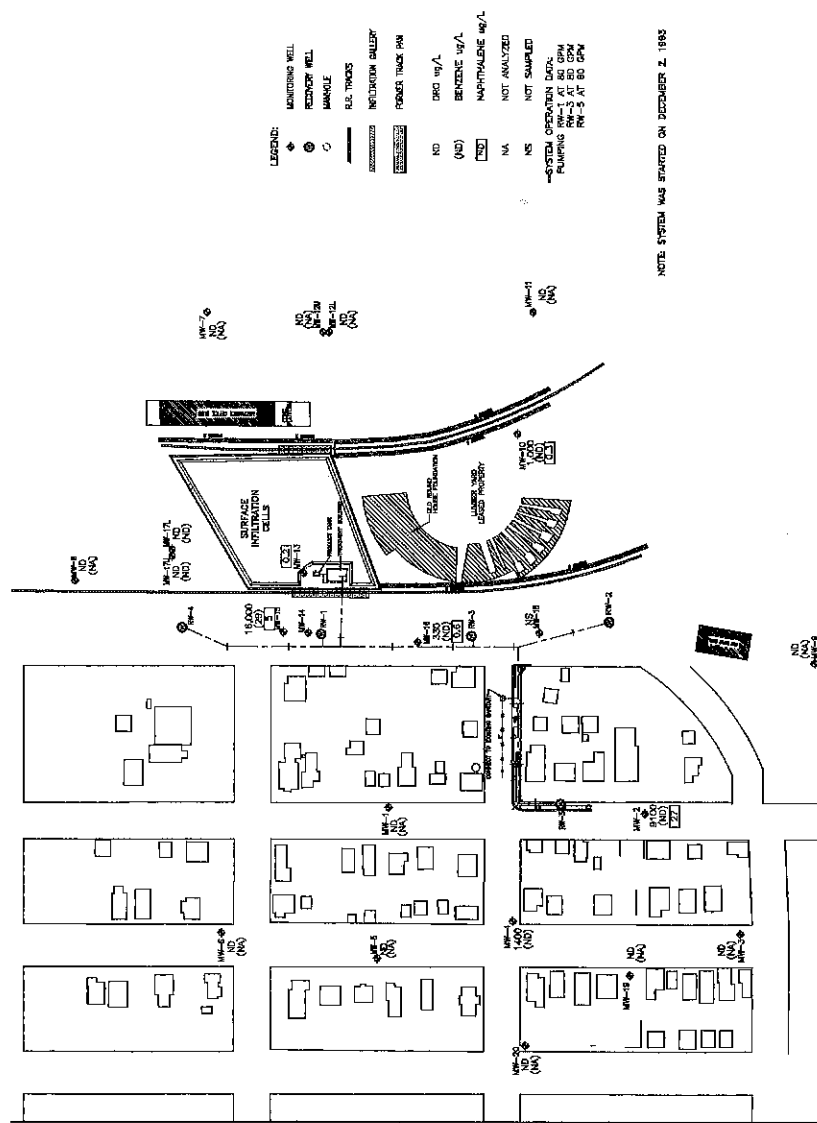


Figure 10. Groundwater discharge locations.

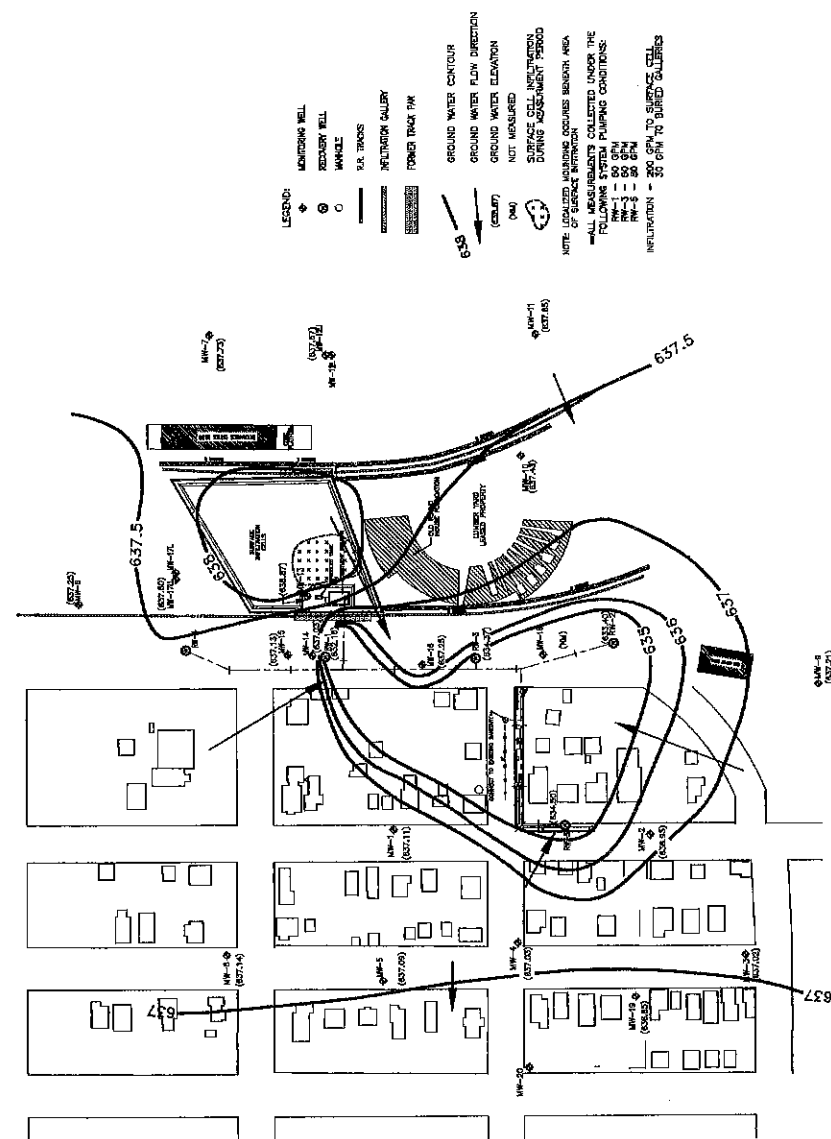


Figure 11. Recovery wells' influence on groundwater contours.

### Treatment Effectiveness

Since the system went into operation through August 1994, approximately 60 million gallons of groundwater have been extracted. Of this, 4 million gallons have been discharged to the sanitary sewer, and 56 million gallons have been reinfilted after oxygen and nutrient additions. Reinfiltation has occurred in both the on-site ponds and below-grade galleries. A tracer study and extensive groundwater monitoring have demonstrated hydraulic capture.

Seven monitoring wells nearest the infiltration zones have noted increased DO levels due to the influence of system operation. Inorganic nutrient concentrations have increased immediately downgradient to the zones of reinfiltation. System operation, which is largely automated and linked via modem to the office, has been mostly uninterrupted except for periods of maintenance and system upgrades.

During the period from startup to the present, all permit conditions governing discharge groundwater quality and *in situ* concentrations of inorganic nutrients have been maintained.

### CONCLUSIONS

*In situ* bioremediation offers significant benefits to conventional pump and treat remedial strategies. In this site case history, pumping of recovery wells provides the needed hydraulic containment to prevent spread of the dissolved-phase plume and to ensure capture of infiltrated groundwater amendments. Significant permitting concessions gained from the regulatory community allows recovered groundwater to be conserved and utilized as the carrier to deliver the subsurface biological enhancements needed to optimize *in situ* bioremediation.

Regulatory permitting for the site remedial operation included authorization for high capacity recovery wells, no pre-treatment required prior to discharge from the system, low percent diversion to the sanitary sewer, and reasonable discharge permit levels for on-site reinfiltation through surface ponds or subsurface infiltration trenches. Cooperative client-consultant-regulatory relations were established early in the project design phase, yielding a sound regulatory understanding of the permitting issues that had to be addressed with this project. Despite specific WDNR guidance that prohibited many of the aspects designed into this *in situ* bioremediation system, sound technical pre-design activities (assessment of passive biodegradation, soil flushing and microcosm studies) complemented the design efforts, leading to reasonable system permits and successful implementation of the remedial program.

The treatment system that was implemented incorporates the best features of several key elements of the various remedial approaches that were evaluated, including hydraulic containment, source soil cleanup, and *in situ* bioremediation of groundwater and soil. Gaining the cooperation and valuable input from the regulatory community gave this project the best treatment options integrated into a single treatment system.

This project has demonstrated that a cooperative relationship between industry, regulatory agency and environmental consultant can work effectively to implement innovative technologies which, in this case, was the most effective remedial strategy. Without the flexibility of the regulatory agency, a suboptimal remedial program would have been established.

### ACKNOWLEDGMENTS

Burlington Northern Railroad and Delta Environmental Consultants, Inc. (Delta) thank Steve Olson of Delta for his valuable drafting support to prepare this presentation.

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#### Questions and Answers:

**Q.** At the beginning of your talk you talked about the groundwater plume actually being in equilibrium. I think that you said there was no further migration of petroleum downgradient. Why didn't you choose passive remediation as a possible methodology for cleanup? Also, did the community have any concerns about the cleanup at the site?

**A.** I will start with the more difficult question, the second part. The client in this case had tremendous problems with the neighborhood. They're now a property owner in many instances where they didn't intend to be. The people also were uninformed about what *in-situ* bioremediation was and it required a significant education effort on the part of the Wisconsin DNR and us on behalf of the client. It is not a trivial exercise to get this kind of technical information across to lay people. Back to your first question. Why wasn't natural bioremediation or passive bioremediation employed or considered as an option? The presence of the free product really precluded just using that as the treatment for groundwater. As long as a significant source of free product existed there, the amount of contaminants that could mobilize into the water and move downgradient was still fairly high. As long as there was some means to capture the free product and then also utilize the excess water contained along with the free product, it was felt that it was a sound engineering decision to take advantage of that water source. We are hoping that natural or passive bioremediation will be an effective arm of the whole remediation strategy in that whatever happens to get out of the zone of capture, will have a better chance of being naturally biodegraded as it moves downgradient.

## CHAPTER 5

### Soil Respirometry Used for Biotreatability Testing of Petroleum Contaminated Soil

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#### INTRODUCTION

Biological treatment is often a low-cost alternative to other technologies because bioremediation processes, when applicable, can be implemented at lower capital and operations expense than competing technologies, such as incineration. Bioremediation minimizes worker health and safety concerns because biological processes usually do not involve operation of equipment under hazardous conditions (e.g., elevated temperatures or pressures). The principal shortcomings to biotreatment are that the processes tend to take longer, typically months to years instead of hours to weeks; very low treatment endpoints are often not achieved; and treatment often takes large amounts of space, which may not be readily available without interfering with ongoing operations. Some have also argued that bioremediation tends to be applicable only when wastes exist at relatively low concentrations (e.g., <1%); however, with proper technical management and technology selection, treatment of organic pollutants in the 1-5% range is possible.

Petroleum hydrocarbons are often encountered as contaminants of soil. There are a number of factors which can influence the rate and extent of petroleum hydrocarbon biodegradation. These include chemical composition of the hydrocarbons; physical state of the hydrocarbons; concentration of the hydrocarbons; temperature, oxygen, and nutrients; salinity; pressure; water activity; and pH, and have been reviewed.<sup>1</sup> Other factors, directly related to the interaction of microorganisms and the hydrocarbon pollutant, affect ultimate destruction.

Hydrocarbons are segregated into general classes that include saturates, aromatics, asphaltenes, and resins. The extent of biodegradation of various hydrocarbons has been reported to be: n-alkanes > branched alkanes > low molecular weight aromatics > cyclic alkanes.<sup>1-2</sup> This relationship varies, based on prior exposure of natural microbial populations to the contaminants, a phenomenon which has been widely observed in the environmental remediation industry.

The metabolic capacity among soil microorganisms for degrading normal alkanes is widely distributed in the soil environment, but less widely distributed for branched alkanes.<sup>3</sup> The normal aerobic oxidation pathway for n-alkanes involves a series of steps, which has been described in detail previously.<sup>4</sup>

Biodegradation of branched alkanes is similar to that of normal alkanes, but is strongly influenced by the location within the hydrocarbon molecules of the branching points.<sup>5</sup> Most of the bacteria that are able to attack branched hydrocarbons are actinomycetes and include the genera: *Corynebacterium*, *Brevibacterium*, *Mycobacterium*, *Nocardia*, and *Rhodococcus*.<sup>6</sup> Alkyl side chains present on branched alkanes are metabolized in the same manner as they are for normal alkanes (i.e., a terminal methyl carbon is oxidized first to an alcohol, then to an aldehyde, and ultimately to an organic acid). The resulting organic acid is called a branched alkanic acid and is usually metabolized further by way of  $\beta$ -oxidation.<sup>5,7</sup> The extent to which  $\beta$ -oxidation is effective depends on where the branching occurs, but can be ranked as 4-methylalkanoic acid > 2-methylalkanoic acid > 3-methylalkanoic acid. In the latter,  $\beta$ -oxidation is blocked.<sup>6</sup> When degradation of alkyl side chains results in the formation of a quaternary carbon atom (i.e., a neopentyl group) the resulting molecule can be resistant to further microbial degradation.<sup>8</sup>

Enhancements are often advocated to increase the rate or extent of petroleum hydrocarbon biodegradation. It is not always clear whether or not such bioenhancements are effective or meet vendor claims for commercial products, but this can be determined at relatively low cost by performing treatability tests. This chapter presents two case histories involving biotreatability testing of a soil contaminated with diesel fuel, and a soil contaminated with non-PCB transformer oil called mineral oil dielectric fluid (MODF). The treatability tests were conducted using soil respirometry under various amendment conditions.

## BIOTREATABILITY TESTING

Biotreatability tests are investigations conducted in the laboratory, at a bench-scale, or on a pilot-scale to assess the effectiveness of a technology for treating contaminants of concern. These tests are also conducted to determine if lower treatment targets or more rapid rates of pollutant destruction can be achieved through the use of enhancement techniques.

For aerobic biological processes the presence of metabolically functioning microbial populations can be assessed by measuring microbial activity. Microbial activity is different from microbial enumeration (microbial counts). Microbial enumeration is an indication of the number of viable microorganisms that are present in soil. Enumeration of these microorganisms does not indicate if the microbes are engaged in the metabolic activity of hydrocarbon degradation and generally underestimates actual population numbers. In contrast, microbial activity measurements indicate whether or not microorganisms are metabolically active in a soil.

## Soil Respirometry

Soil respirometry is an efficient method to quantitatively determine the activity of hydrocarbon degrading microorganisms as they metabolize soils laden with petroleum hydrocarbons. It has been used for biotreatment screening to assess the suitability of bioremediation as a treatment option.<sup>9</sup> This chapter describes its use to assess the effectiveness of biological treatment enhancements.

The procedure consists of adding a known amount of hydrocarbon-contaminated soil (typically 1 Kg) to a respirometer flask of known volume. Oxygen uptake and carbon dioxide evolution in the closed flask are measured over an incubation period as a direct measure of microbial activity. Companion soil pans can be tested under the same conditions to measure pollutant degradation without disturbing the contents of the respirometer. Rates of microbial activity are determined directly from cumulative oxygen consumption or carbon dioxide evolution.

The schematic arrangement of the respirometry apparatus used in the studies described in this chapter is depicted in Figure 1. The respirometer flask is modified from the Gledhill design used for determining CO<sub>2</sub> evolution to assess biodegradability by soil microorganisms.<sup>10</sup> The flask is a closed system to which air is added as needed. The entire system is attached to a manometer.

### Establishment of Respirometers

For the investigations presented in this chapter, each respirometer flask received between 950-1050 grams of soil on a dry-weight basis. In addition to treatment respirometers, replicate barometric control respirometers were established with glass beads instead of soil, to correct microbial activity measured in the treatment vessels for daily atmospheric pressure. Major nutrients (N and P) and moisture requirements were determined based on an initial soil characterization. Other amendments, such as surfactants or bioaugmentation cultures, were added according to manufacturer recommendations. Often these products contain separate nutrients mixtures which need to be added as separate treatments to determine whether the nutrients are effecting enhanced biodegradation, or whether the surfactant or bioaugmentation culture is enhancing TPH biodegradation. During the investigations presented in this chapter, major nutrients were added at C:N and C:P ratios of 12:1 and 120:1, respectively (i.e., C:N:P of 120:10:1). Nutrients did not become limiting during these studies. Where tested, a bioaugmentation product (and vendor nutrients) were added weekly and a surfactant (an anionic polyacrylamide) was added once at the beginning of the study at a rate of 0.1% (w/w).

### Measurement of O<sub>2</sub> Uptake

Oxygen uptake was measured for each respirometer flask on a daily basis using U-tube manometers. As O<sub>2</sub> was consumed by aerobic metabolism, a negative pressure developed within the closed flasks which is related to the O<sub>2</sub> partial pressure.<sup>11</sup> The time and date were recorded, as were manometer readings (as mm H<sub>2</sub>O) for each of the respirometers, on a daily basis. Following this, each respirometer, including the barometric controls, was opened and sparged with breathing air from a gas cylinder to ensure that fresh oxygen was added to the headspace so that O<sub>2</sub> did not become limiting to the microorganisms and

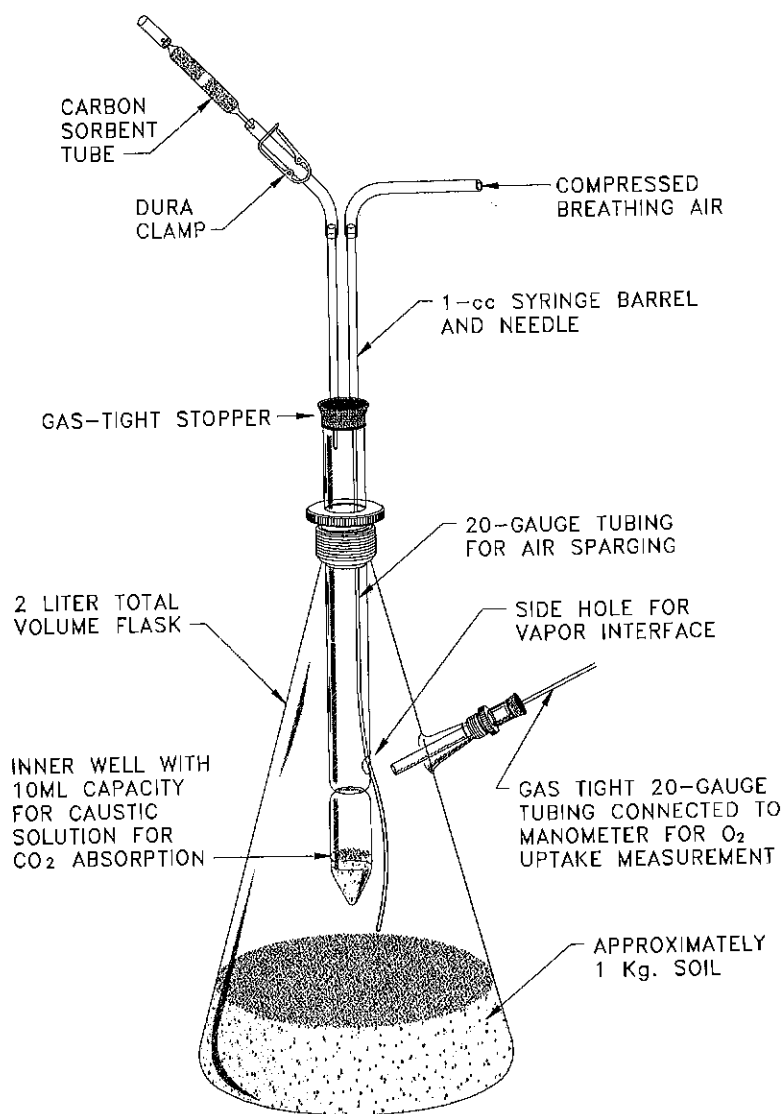


Figure 1. Respirometry flask assembly.

reduce their metabolic activity. The logged manometric data were entered into a computer database to calculate daily and cumulative oxygen uptake.

#### Measurement of CO<sub>2</sub> Evolution

The amount of petroleum hydrocarbon that was mineralized was determined by monitoring CO<sub>2</sub> production in each flask. The CO<sub>2</sub> was trapped in an aqueous alkaline solution (usually 1 N KOH) within each of the respirometers and measured by titrimetric analysis. Absorbed CO<sub>2</sub> in the KOH exists as CO<sub>3</sub><sup>2-</sup>. Carbonate ion was precipitated as BaCO<sub>3</sub> by adding BaCl<sub>2</sub> prior to titration. Residual base was then titrated using a standard solution of HCl and the amount of CO<sub>2</sub> absorbed was calculated based on the amount of KOH that had been neutralized. All treatments were corrected for any carbon dioxide levels detected in the barometric control respirometer flasks.

#### Petroleum Hydrocarbon Determinations

Soil pans were established adjacent to the respirometers to enable easy access to the soil for sampling on a periodic basis. All soil pans were lightly covered with aluminum foil to prevent photooxidation and to facilitate air exchange. The soil pans were weighed weekly, distilled water was added as needed to minimize moisture losses, and soils were mixed with a spatula to simulate tilling during an *ex situ* treatment process.

Petroleum hydrocarbon removal rates were determined by periodic sampling and Total Petroleum Hydrocarbon (TPH) analysis of samples taken from similarly treated soils added to soil pans. TPH levels were measured using either the Modified EPA 8015 Method (8015M) or ASTM D2887-89 modified to measure hydrocarbons from C<sub>12</sub> to C<sub>44</sub>. Both of these are capillary gas chromatography (GC) methods that involve analysis of petroleum hydrocarbons extracted from soil. Methylene chloride was used to extract the TPH using either Soxhlet (EPA 3540) or sonication (EPA 3550) methods. The extract was injected onto the GC column where constituents were separated and then detected by a flame ionization detector (FID) as they eluted off of the column.

The 8015M method provides a single TPH number based on integration of the chromatogram over an elution time window selected for the contaminant being measured. The ASTM D2887-89 method also involves GC-FID, but segregates hydrocarbon constituents based on their boiling point ranges, which are related to carbon chain lengths. Boiling point ranges were determined for the percent of carbons ranging in chain length from C<sub>12</sub> to C<sub>44</sub>. This resulted in a total of 10 separate fractions. A total TPH number was derived by integrating the chromatogram over the entire C<sub>12</sub> to C<sub>44</sub> range. The percent of TPH measured within each fraction was used to calculate the concentration of TPH within individual fractions.

#### CASE HISTORIES

Examples of the use of biotreatability tests used to measure microbial activity under various amendment conditions, and the use of this information to select remediation alternatives for full-scale operation, are presented in the following discussion.

### Diesel Contaminated Soil

The first case describes testing performed on a soil that had been contaminated with diesel fuel during fuel delivery operations. The contaminated area was a plume that covered a roughly rectangular area, approximately 150 ft in length by 120 ft in width, from the ground surface to groundwater which ranged from 9 to 12 ft in depth. This constituted about 12,000 tons of contaminated soil. Soil samples were collected for use in biotreatability tests by making 5 soil bores within the entire contaminated area and taking samples from various depths. These were composited prior to treatability testing.

#### Chemical and Physical Characteristics of the Composite Soil

Chemical measurements and physical tests were performed to determine if any soil-specific problems might be apparent that could affect biotreatment of the TPH. Organic analyses indicated that initial TPH level was nearly 14,000 mg/Kg. Inorganic analyses indicated that available nitrogen was not present in sufficient amounts and that nutrient amendment would be required. Available phosphorus was present but at relatively low levels, and potassium concentrations were considered to be adequate. Soil moisture and pH (6.5) were suitable for supporting microbial activity and adequate solubility of major nutrients. Particle size analysis revealed a particle distribution of 87.8% sand, 2.8% silt, and 9.9% clay which corresponds to a sand or loamy sand.

#### Respirometry Test

A respirometry test was conducted for a 60-day incubation period under various control conditions that included: 1) an unamended contaminated soil control, and 2) a nutrient-amended uncontaminated soil control to assess the level of microbial degradation in unamended soil and uncontaminated soil, respectively. Treatment conditions evaluated were: 1) biostimulation of indigenous microorganisms by nutrient amendment, and 2) bioaugmentation using a commercial inoculum. Figure 2 depicts microbial activity, measured by CO<sub>2</sub> evolution, observed in the various respirometer vessels.

During this biotreatability test, TPH determinations (8015M method) were performed initially and at the end of the 60-day incubation period. Figure 3 summarizes TPH data for the various treatments and compares it with initial levels.

#### Case 1 Results

The greatest microbial activity was observed in the treatment inoculated with a bioaugmentation culture; however, the most effective TPH reduction occurred in the treatment to which nitrogen and phosphorus had been added to stimulate indigenous microorganisms. The increased CO<sub>2</sub> evolution was associated with the weekly inoculum additions, not to enhanced TPH destruction. It is probable that the inoculum biomass was mineralized instead.

The nutrients, described as "Vendor Nutrients" and used in conjunction with the bioaugmentation inoculum, generated about the same level of microbial activity as was seen for the indigenous microbial populations amended with nitrogen and phosphorus, but this treatment condition was not as effective in biodegradation of TPH present in the contaminated soil as was simple addition of nitrogen and phosphorus.

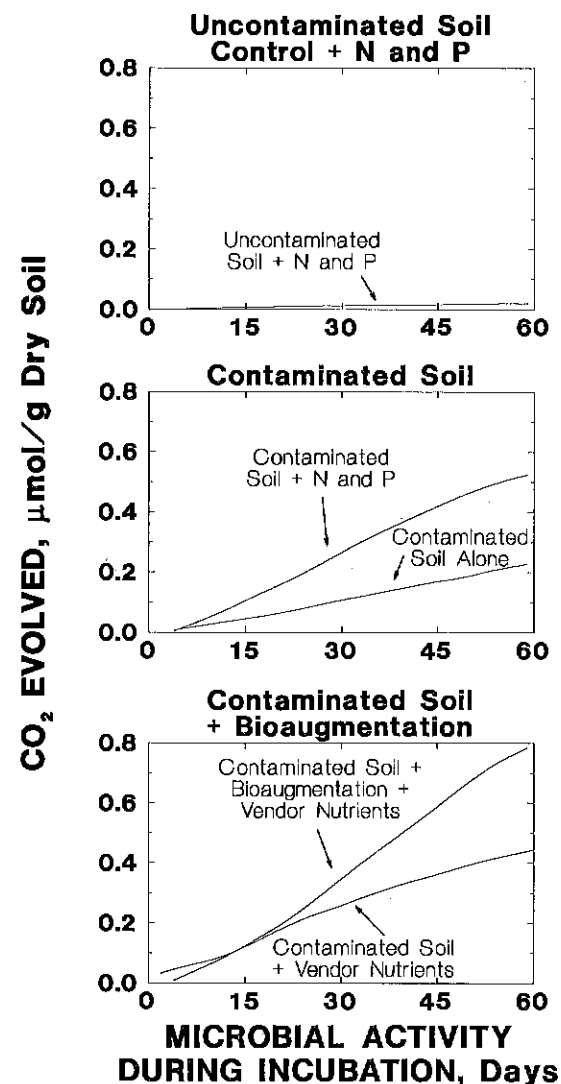
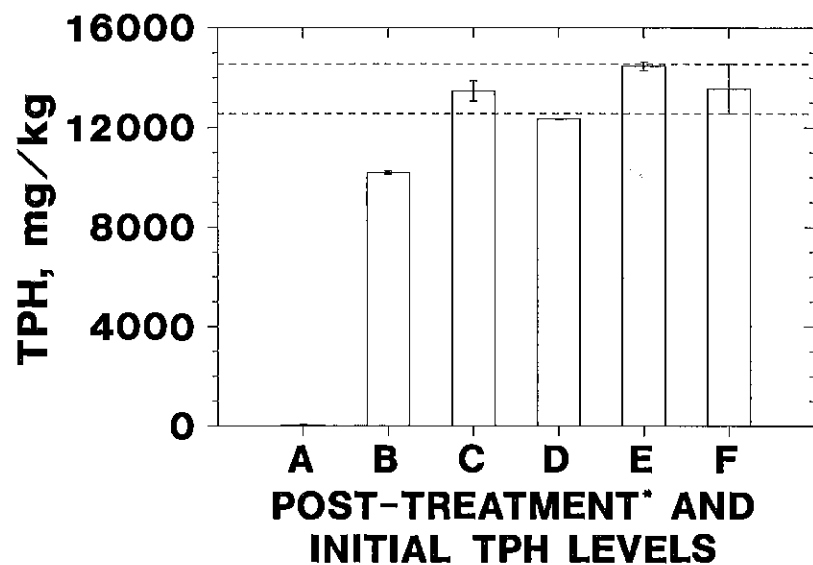


Figure 2. Microbial activity measured by CO<sub>2</sub> evolution in diesel contaminated soil.





#### TREATMENT CONDITION

- A = Uncontaminated Soil Control + N and P
- B = Contaminated Soil + N and P
- C = Contaminated Soil Alone
- D = Contaminated Soil + Bioaugmentation + Vendor Nutrients
- E = Contaminated Soil + Vendor Nutrients but no Bioaugmentation
- F = Average Initial Soil TPH Level

\* Post-treatment TPH levels measured after 60 days of incubation.

Figure 3. TPH Biodegradation in diesel contaminated soil.

TPH reduction among the various treatment conditions was statistically compared with initial TPH levels and among the various treatments by analysis of variance (ANOVA). Differences among group means were then compared using Tukey's HSD *post hoc* analysis to measure the significance of any differences between these treatments. These results indicate that TPH levels present in the uncontaminated soil control (Treatment A in Figure 3) were significantly different ( $p < 0.001$ ) from the remaining treatments and the initial TPH levels. This indicates that the uncontaminated soil, which had very low TPH levels, was significantly different from the contaminated soil treatments with respect to TPH levels. This information, taken with the microbial activity data presented in Figure 2 indicate that very little of the observed microbial activity could be attributed to sources of carbon present in the soil other than TPH.

The contaminated soil amended with major nutrients to stimulate indigenous microorganisms (Treatment B in Figure 3) was significantly different ( $p < 0.05$ ) from the contaminated soil control (Treatment C in Figure 3) and all of the other treatments. These results indicate that, under the conditions present in this experiment, amendment with nitrogen and phosphorus was more effective in reducing TPH levels than any other treatment. The remaining treatments (i.e., C, D, E, and F) were not found to be significantly different from one another.

This case history indicated that bioaugmentation would not enhance diesel biodegradation, and that nutrient amendment for biostimulation of indigenous microbial populations would be a beneficial enhancement. During full-scale site cleanup, nutrient amendment is the only treatment other than aeration which is being undertaken.

#### Mineral Oil Dielectric Fluid

The second case involves biotreatability testing for MODF petroleum hydrocarbons. MODF is a non-PCB dielectric fluid used in transformers. MODF is a petroleum-derived oil free of acid, alkali, and corrosive sulfur, with a high oxidation stability, a high flash point, and a low viscosity. It is prepared from a naphthenic petroleum fraction containing branched and cyclic (but nonaromatic) hydrocarbons, with chain lengths primarily in the range of 14 to 24 carbons. The average chain length of MODF is characteristically 19 carbons, which is a heavier hydrocarbon than gasoline, diesel, or jet fuels.

Soils can become contaminated with MODF during routine maintenance operations and through episodic spills. Usually contamination volumes are relatively small. It is desirable to find alternatives to landfilling for these materials which was the basis for considering bioremediation as a potential treatment alternative.

#### Chemical and Physical Characteristics of the Composite Soil

A composite sandy clay loam soil (59.9% sand, 16.3% silt, and 29.3% clay) contaminated with MODF at initial TPH (ASTM GC-FID analysis) concentrations of about 22,000 mg/Kg was used for these investigations. The soil contained adequate initial amounts of nitrogen (55 mg/Kg) and phosphorus (189 mg/Kg), and the pH (6.3) was suitable for supporting microbial activity and adequate solubility of major nutrients. The moisture holding capacity (field capacity) for this soil was about 29% moisture. Biotreatability tests were performed

using soil maintained between 80% and 90% of field capacity to avoid developing anaerobic conditions within the respirometers.

#### Respirometry Test

A respirometry test was conducted for a 180-day incubation period under various treatment conditions that included: 1) an unamended contaminated soil control, 2) a nutrient-amended contaminated soil treatment, and 3) a nutrient and surfactant-amended contaminated soil treatment. The unamended treatment was included to assess the microbial activity of indigenous soil microorganisms without any additions, in view of the fact that initial nitrogen and phosphorus levels appeared to be adequate. The nutrient-amended treatment was included to determine if any enhanced TPH biodegradation could be attained by addition of major nutrients. A surfactant amendment using an anionic polyacrylamide surfactant (Cyanamer P70®) was applied initially at a 0.1% (w/w) application rate. This surfactant was selected based on literature references that had indicated its effectiveness in enhancing biotreatment of heavy organic hydrocarbons. All respirometers were established in triplicate, as were similarly amended soil pans.

#### Case 2 Results

Figure 4 depicts respiration, as measured by oxygen consumption and carbon dioxide evolution, that was observed during the study period. A random subset of error bars (as standard deviations) is presented to indicate the variability that was observed among the treatment vessels. The error bars reveal good agreement among replicate treatments for both oxygen consumption and carbon dioxide evolution. Although the microbial activity was similar among all treatment conditions, the most extensive microbial activity was measured in the unamended control soil. Microbial activity in the nutrient-amended and the surfactant-amended soils was about the same. The finding that the level of activity in the unamended control soil would exceed the other treatments was not expected.

Nutrient analyses indicated that nitrogen levels in the unamended control were below detection limits soon after the beginning of the experiment. A microbial culture enrichment was performed to determine if microbial populations in the unamended control existed that were capable of growth on a culture medium containing MODF as the sole carbon source and nitrogen available only as atmospheric nitrogen (i.e., free-living nitrogen fixation). Results from these enrichments indicated that such organisms did exist in the unamended soil. Although free-living nitrogen fixation was not confirmed by use of a nitrogenase assay, the organisms derived from this enrichment were identified by analysis of membrane fatty acids and found to have high similarity with organisms for which free-living nitrogen-fixation has been demonstrated. Thus it is believed that the high level of activity in the unamended control was attributed, in part, to these organisms. This is significant because it may be possible to enhance *in situ* TPH biodegradation during a bioventing process that involves biostimulation through the addition of nitrogen and oxygen in air.

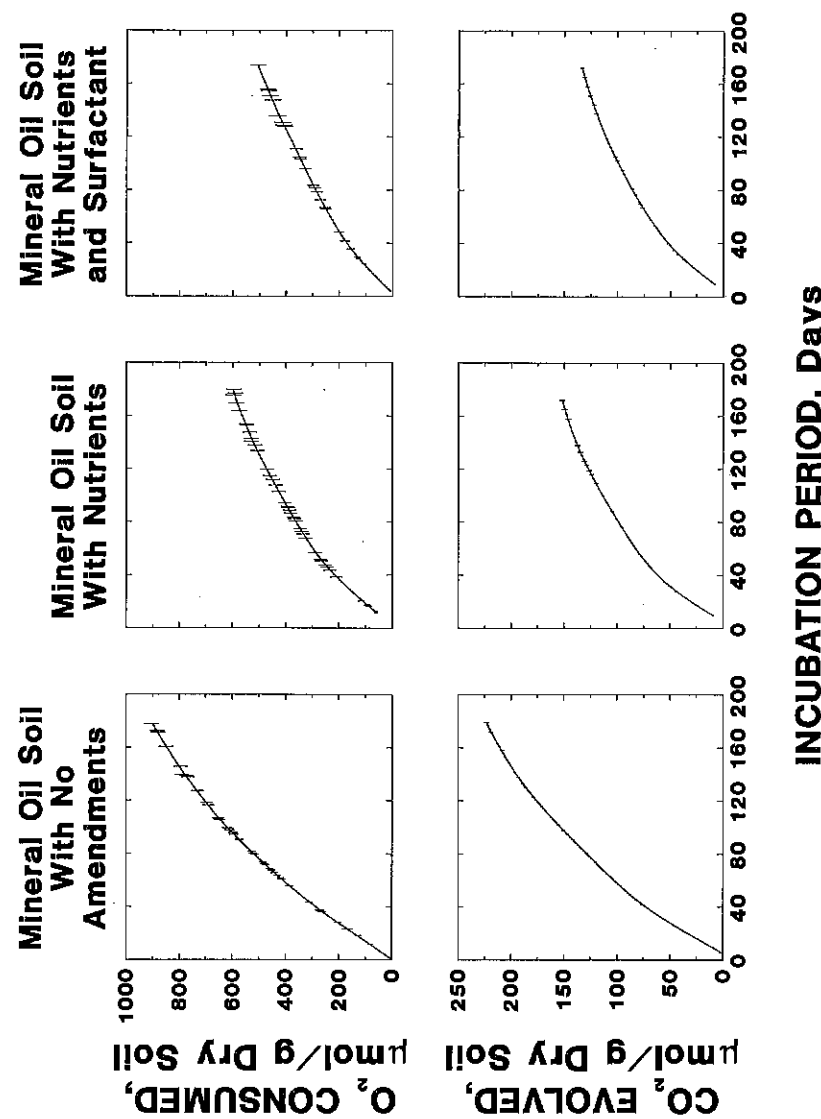


Figure 4. Microbial activity measured by O<sub>2</sub> consumption and CO<sub>2</sub> evolution in mineral oil contaminated soil.

TPH results for the various treatments are presented in Figure 5 where it can be seen that the most extensive MODF biodegradation occurred in the unamended control. Periodically samples were taken to measure TPH levels at the times indicated to assess TPH biodegradation rates. These data suggest that no benefit was gained through the use of the surfactant tested and that enhanced biodegradation did not occur by nutrient amendment.

TPH biodegradation rates were determined by fitting data to zero order (i.e., linear regression) and first order models. Both types of kinetics were evaluated because visual observation of the data presented in Figure 5 indicated that either model might be appropriate. Plots of these kinetic models are presented in Figure 6 for all of the treatments tested. Consistent with the microbial activity data, TPH rate determinations revealed that the most rapid biodegradation occurred in the unamended control ( $\approx 51$  mg/Kg/day; 192 day half-life). The surfactant treatment demonstrated the next most rapid biodegradation ( $\approx 44$  mg/Kg/day; 239 day half-life) and was followed by the nutrient amended treatment ( $\approx 25$  mg/Kg/day; 462 day half-life).

These findings have been used to select treatment conditions to be evaluated on a large scale at a pilot-scale treatment facility. Among the conditions that will be evaluated will be control measures to shorten the treatment times.

## SUMMARY

Soil respirometry, coupled with analyte measurements, is a rational approach for selecting treatment alternatives and/or process enhancements. In the case histories presented in this chapter, soil respirometers were used to assess the effectiveness of various amendments to enhance the bioremediation of petroleum contaminated soils. In one case, nutrient amendment used to stimulate indigenous soil microorganisms was effective in attaining the most extensive TPH biodegradation. In the second case, the greatest biodegradation was attained by unamended indigenous soil microorganisms. It was postulated that this was the result of hydrocarbon-degrading bacteria that were able to fix atmospheric nitrogen.

The soil respirometry approach for measuring microbial activity described in this chapter has been successfully used for soils contaminated with fuels (e.g., diesel, gasoline, and jet fuel), heavy organic hydrocarbons (e.g., MODF) and for determining hydrocarbon treatment endpoints. It is appropriate for simulating land treatment, composting, and bioslurry remediation configurations, and could easily be modified to measure *in situ* microbial activity under conditions that simulate a bioventing or air sparging technology.

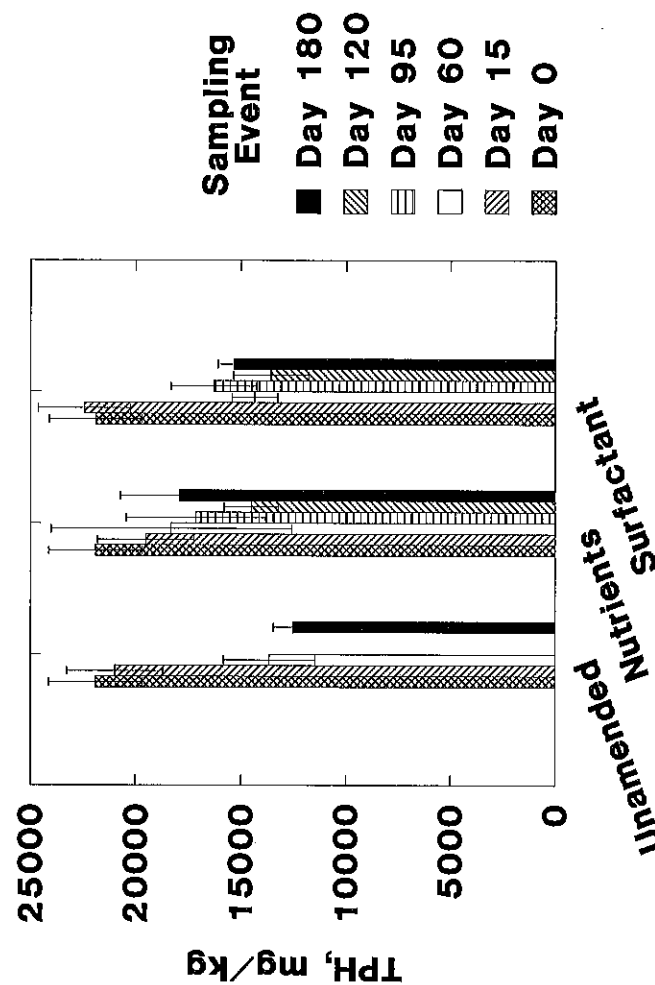


Figure 5. TPH biodegradation in mineral oil contaminated soil.

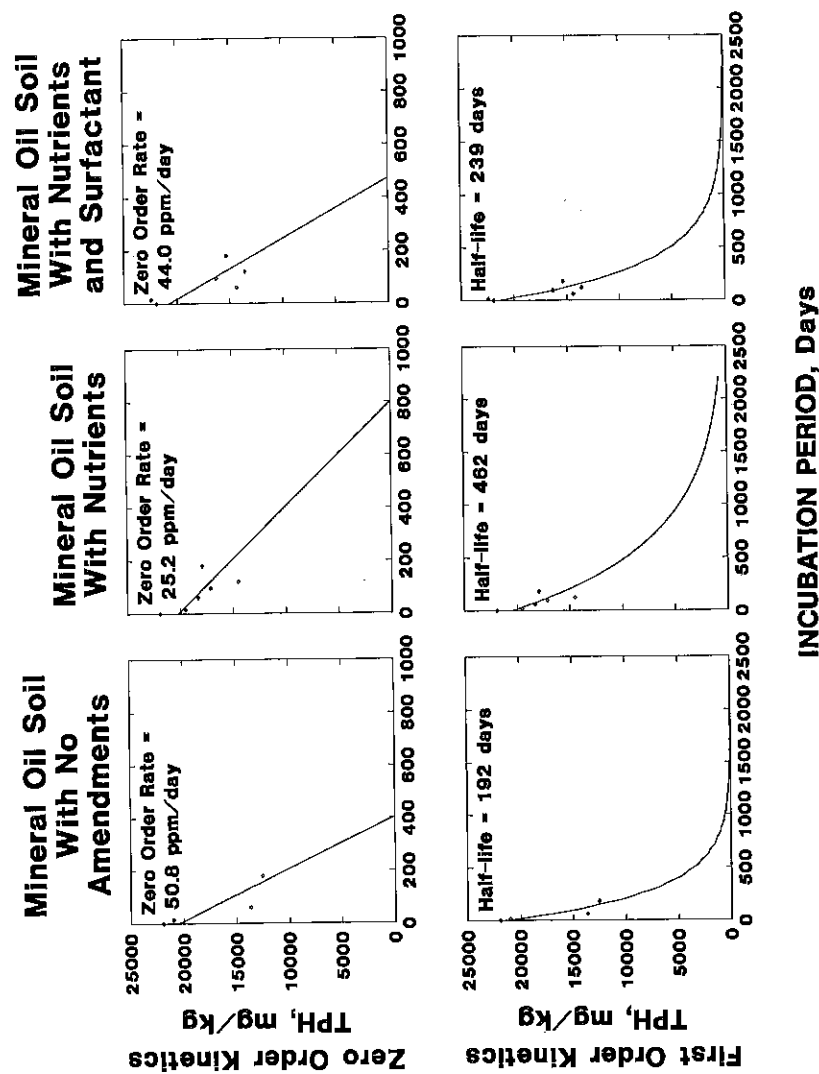


Figure 6. TPH biodegradation rates measured in mineral oil contaminated soil.

### Acknowledgments

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**Questions and Answers:**

Q. I was wondering who might be doing bench scale treatability testing on bio. I found the data on the oxygen uptake studies vs. the TPH reduction to be pretty interesting. Clearly the bioaugmented and fertilized sample showed a lot of biological activity as measured by CO<sub>2</sub> but then when you looked at the TPH numbers it really did not seem to work out. We have used oxygen uptake studies in the same sort of way to try to measure biological activity and have had the same problem in trying to correlate what appears to be a lot of biological activity and not necessarily a lot of contaminant reduction. I'm just throwing it out here to the people at the table or to anyone in the audience. What's going on there? I don't understand it. Are we simply getting a lot of the induced bugs eating each other, creating a lot of CO<sub>2</sub> because there's not a lot of contaminant but a lot of nutrient base there? Is there anybody in the audience who can enlighten us?

Audience comment. It's fairly common in doing respirometry studies to find that sort of thing resulting from degradation of a lot of non-target organics which may be more predominant than the target TPH compounds.

Q. And do you speculate that those non-target organics are soil organics or petroleum contaminant organics?

Audience comment. Well they could be both. It certainly depends upon the nature of the soil. Topsoil, for example, very often has a much larger concentration of non-target organics than TPH organics, even if it's been subject to contamination. In subsoil, it may well be you could still get that kind of result because certain fractions of the TPH, or I should say certain fractions associated with the contamination, may not be measured as TPH.

Q. Again, that goes back to the issue that what we probably need is some chromatograms to really understand what's really being degraded, as opposed to simply running TPH. We have seen poor correlation between some of those oxygen uptake studies and CO<sub>2</sub> development. I don't know if it's a measurement issue or if the bugs are themselves a carbon source and they're eating themselves and creating CO<sub>2</sub>.

Audience comment. I work for a firm and we do a lot of testing for other companies that are doing bioremediation. I have done a lot of GC/MS work for some clients and we have found that often what is being extracted will contain large amounts of carboxylic acid, ketones and alcohols. Even when the sample is passed through a silica gel for cleanup, a lot of these compounds still come through. I believe that they are originally the parent compound from a petroleum source and they are being oxidized, become recalcitrant, and can not be further oxidized. Either that or they are extracted as TPH even with the cleanup procedures. That's what we have been seeing over and over again.

**CHAPTER 6****Bioremediation of Diesel Fuel and Bunker C Fuel Oil at Multiple Railroad Sites**

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**INTRODUCTION**

Enhanced degradation of fuel hydrocarbons in soils by bacteria and other microorganisms has been used extensively as a remediation technique and is well documented in the technical literature. Hydrocarbon-degrading bacteria have been found in almost all soil environments, and typically occur in high numbers when petroleum products are present.<sup>1</sup> Many successful field demonstrations of enhanced biodegradation of gasoline, diesel, and jet fuels in soil using *in situ* and *ex situ* methods have been reported. Both forms of bioremediation utilize naturally-occurring microorganisms in the soil to biodegrade petroleum hydrocarbons in the presence of an adequate supply of oxygen, moisture, and nutrients.

Hydrocarbon-degrading soil bacteria require sufficient oxygen, nutrients, and moisture to attain the activity levels required for effective soil treatment. Because insufficient oxygen is often the primary limiting factor for petroleum biodegradation, aeration of contaminated soil is performed to provide sufficient oxygen for soil bacteria. For *ex situ* remediation, this is generally accomplished through aboveground spreading and tilling of excavated contaminated soils (i.e., landfarming), which supplies oxygen to the soil microorganisms and produces a homogeneous mixture of soil. Periodic moisture and nutrient addition may also be required. Once sufficient oxygen, nutrients, and moisture are provided, natural bacteria in the soil multiply and thrive using fuel hydrocarbons as their primary carbon source.<sup>2</sup> Optimal temperatures for petroleum biodegradation have been reported as 68 degrees Fahrenheit (°F) to 104°F. Biodegradation can continue at temperatures above freezing; however, the rates of degradation can decrease significantly with decreasing temperatures.<sup>2</sup>

Another factor influencing hydrocarbon biodegradation is the availability of nutrients, such as nitrogen and phosphorus, to soil microbes. A carbon-to-nitrogen

(C:N) ratio of 20:1 is considered optimum for fuel biodegradation in soils.<sup>3</sup> Lack of adequate phosphorus may also limit biodegradation. Recent research on jet fuel contamination at Tyndall Air Force Base (AFB) suggests that soil bacteria recycle nutrients, and may rely on nitrogenase bacteria to fix atmospheric nitrogen, thereby introducing useful forms of nitrogen for fuel-degrading microbes.<sup>4</sup>

Adequate soil moisture is also required to sustain growth of hydrocarbon-degrading microbes. However, excessive saturation of soil with water will reduce air permeability in soil, resulting in a lower oxygen supply, and consequently inhibiting aerobic biodegradation. Saturation between 50% and 80% of the water-holding capacity of a soil is considered optimal for aerobic microbial activities.<sup>2</sup>

Aboveground treatment of hydrocarbon-contaminated soils has several advantages over *in situ* treatment. Landfarming of excavated soils produces a more homogeneous mixture of sands, silts, and clays. In the *in situ* environment, sand and clay lenses frequently result in a nonuniform distribution of fuels, making uniform treatment more difficult. Oxygen, nutrients, and moisture can be evenly distributed in aboveground operations, and hydrocarbon treatment is more rapid and uniform. Finally, the sampling of soils in aboveground operations is comparatively simple and more reliable than sampling in soil borings, which are subject to subsurface nonuniformities.

Numerous studies have demonstrated petroleum degradation in soils by indigenous microbes.<sup>1,5,6</sup> Generally, the rate of petroleum degradation is increased when increased oxygen and nutrients are supplied to indigenous soil bacteria (a process referred to as biostimulation).<sup>7</sup> The three bioremediation sites described below illustrate the effectiveness of biostimulation to increase biodegradation rates of fuel hydrocarbons in soils at railroad sites. A discussion of each site background, details of bioremediation cell construction, and full-scale landfarm operations, sampling results, and costs are presented in this chapter.

## SITE 1: RAILROAD FACILITY - AMARILLO, TEXAS

### Background

This site was established in July 1992 to provide bioremediation of petroleum hydrocarbon contaminated soils resulting from several remedial projects. Soil was contaminated with No. 2 diesel fuel used in railroad fueling operations. The contaminated soils (approximately 900 cubic yards) were excavated and transferred to a prepared and lined treatment cell consisting of two distinct treatment rows. Soils were segregated by row based on differences in initial total recoverable petroleum hydrocarbon (TRPH) levels. Row 1 contained soil from previous yard cleanup work and an underground storage tank (UST) removal. Row 2 contained contaminated soils accumulated from a construction project which included the removal of a UST (found not to be leaking) and an old diesel pump house and piping system which was heavily contaminated. The cleanup goal established by the Texas Natural Resource Conservation Commission (TNRCC) for this site was less than 600 milligrams per kilogram (mg/Kg) TRPH. The details of the construction of the bioremediation cell are discussed below.

### Bioremediation Cell Construction

The bioremediation cell was constructed to meet the guidelines of the TNRCC. These guidelines contain specific requirements for the construction of bioremediation cells that take into consideration such factors as proximity of the site to water supply wells, surface topography constraints, and physical design parameters (such as containment berms, cell liners, etc.). Applicable requirements vary greatly among states where bioremediation of soils is regulated, and must be considered prior to use of this remedial alternative. The construction of the bioremediation cell is a minor effort consisting of site clearing, grading, berm construction, liner installation, and installation of a liner protector, which at this site consisted of 6 inches of native soils. Plans for construction and operation of the bioremediation cell were approved by the TNRCC prior to its construction. The overall treatment cell dimensions were 300 feet long by 100 feet wide by 18 inches deep, with a 20-foot-wide access road separating the rows along the entire length of the cell. The liner material consisted of two layers of 10-millimeter polyethylene which was approved by TNRCC instead of a single layer of 40-millimeter polyethylene. A field fence with appropriate signage was installed to denote the treatment site boundary and to prevent unauthorized traffic and dumping. Access to the site was limited to cell bioremediation maintenance personnel.

### Full-Scale Operations

A local environmental subcontractor was employed to provide all cell maintenance on a monthly schedule. To monitor the subcontractor's performance, all maintenance work was verified by site railroad personnel. The subcontractor was required to use a high-speed mixer (Bow Mag) to turn the soils once per month. To minimize the risk of liner damage, discing of the soils was not permitted.

Commercial (liquid) nutrients and water were applied monthly when the soils were mixed. Nutrient and soil moisture content were predetermined at the initiation of the project, and were based on representative samples from operational bioremediation facilities treating similar soils and contaminants in the area. The optimal soil moisture for this soil type was determined to be 10 to 15% by weight. A commercial spray unit was used to apply the predetermined nutrient mixture which consisted of carbon:nitrogen:phosphorous at the ratio of 20:1:0.1. The nutrient was mixed at the rate of 2.5 gallons nutrient to 0.5 gallon nutrient activator to 550 gallons of water per treatment row. The activator was used to expedite the biological startup action of the nutrient. Raw material costs averaged \$600 per row per application. Labor and equipment for maintenance and application added an additional \$600 per row per application, including costs for soil sample analysis. The total monthly site operating expense for both rows (\$1,200 per row) was \$2,400.

Soil sampling involved collection of composite samples from consistent, controlled locations on a predetermined quarterly (approximately) schedule. Soils were tested for TRPH using analytical method SW3550/E418.1. There was no deviation in the nature or schedule of routine maintenance activities during the treatment period.

### Sampling Results

Collection of composite soil samples and completion of laboratory analyses were performed five times, including the initial baseline sampling event, over the

remediation periods of 18 months (Row 1) and 15 months (Row 2). The TRPH results from these analyses for Rows 1 and 2 are summarized in Tables 1 and 2, respectively.

Figures 1 and 2 illustrate the TRPH sampling results over the periods during which monthly maintenance was conducted for Rows 1 and 2, respectively. The TRPH reduction rates substantially decrease after approximately 1 year as a result of decreasing substrate availability and the lower rates of degradation associated with polynuclear aromatic hydrocarbons and other more recalcitrant hydrocarbons. Although the TNRCC TRPH action level of 600 mg/Kg for site closure was met in the June 6, 1993 sampling round (an average of 500 mg/Kg TRPH for Row 1 and 354 mg/Kg TRPH for Row 2), monthly maintenance was continued for approximately 4 additional months. The final round of soil sampling showed average TRPH concentrations of 260 mg/Kg for Row 1 and 325 mg/Kg for Row 2, both of which were significantly below the cleanup goal. Closure of the bioremediation cell for Site 1 has been approved by TNRCC.

#### Costs

The following cost comparisons are given for Site 1 for bioremediation to reach the cleanup goal in both bioremediation cells, and for thermal treatment of these soils based on contractor bid pricing. Bioremediation cell construction and decommissioning costs, costs associated with thermal treatment permit approvals, and pre-treatment analytical costs were not included. The costs for these items are approximately equivalent for this site.

#### Bioremediation:

14 months at \$2,400 per month = \$33,600.\*

\$33,600/900 cubic yards = \$37 per cubic yard \*

#### Thermal Treatment:

Includes mobilization, burner fuel, site electrical, prescreening, acceptable moisture content, and material handling:

900 cubic yards @ \$74 per cubic yard = \$66,600\*\*

Net project savings by using bioremediation \$33,000.

\* Actual Cost

\*\* Estimated Costs

## SITE 2: RAILROAD FACILITY - EASTERN AMARILLO, TEXAS

#### Background

This bioremediation project was initiated in March 1992 to provide bioremediation of petroleum hydrocarbon contaminated soils resulting from remediation of two clay-lined, diesel fuel spill-containment and storage lagoons and stockpiled soil from a UST removal. The primary contaminant was No. 2 diesel fuel. After the lagoons were drained, the contaminated sidewalls, bottom sludges, and subsurface soils of the

Table 1. Comparison of Full-Scale Soil Treatment - Railroad Facility - Amarillo, Texas - Site 1, Row 1

TRPH Level	High	Low	Number of Samples	TRPH Average	Date of Sample	Days from Last Sample	Reduction Rate (mg/Kg/day)	TRPH Percent Reduction
38,644	1,685		12	15,754	April 16, 1992 <sup>a</sup>	Baseline	0	0
10,955	4,681		2	7,818	October 12, 1992	179 (179) <sup>b</sup>	44	50
3,814	2,441		2	3,127	February 12, 1993	123 (302)	38	80
580	420		2	500	June 6, 1993	114 (416)	23	97
260	260		1	260	October 11, 1993	126 (542)	1.9	98

<sup>a</sup> April 16, 1992 samples from stockpile prior to landfarm construction on July 30, 1992.

<sup>b</sup> The total number of days since the bioremediation cell began operation (179).

Table 2. Comparison of Full-Scale Soil Treatment Data - Railroad Facility - Amarillo, Texas - Site 1, Row 2

TRPH Level	Low	High	Number of Samples	TRPH Average	Date of Sample	Days from Last Sample	Reduction Rate (mg/Kg/day)	TRPH Percent Reduction
14,756	3,170		6	7,599	July 30, 1992	Baseline	0	0
4,851	2,026		2	3,439	October 12, 1992	75	55.5	55
1,196	1,022		2	1,109	February 12, 1993	123 (198) <sup>a</sup>	19	85
650	57		2	353	June 6, 1993	114 (312)	6.6	95
470	80		2	325	October 11, 1993	126 (438)	0.22	96

<sup>a</sup> The total number of days since the bioremediation cell began operation (198).

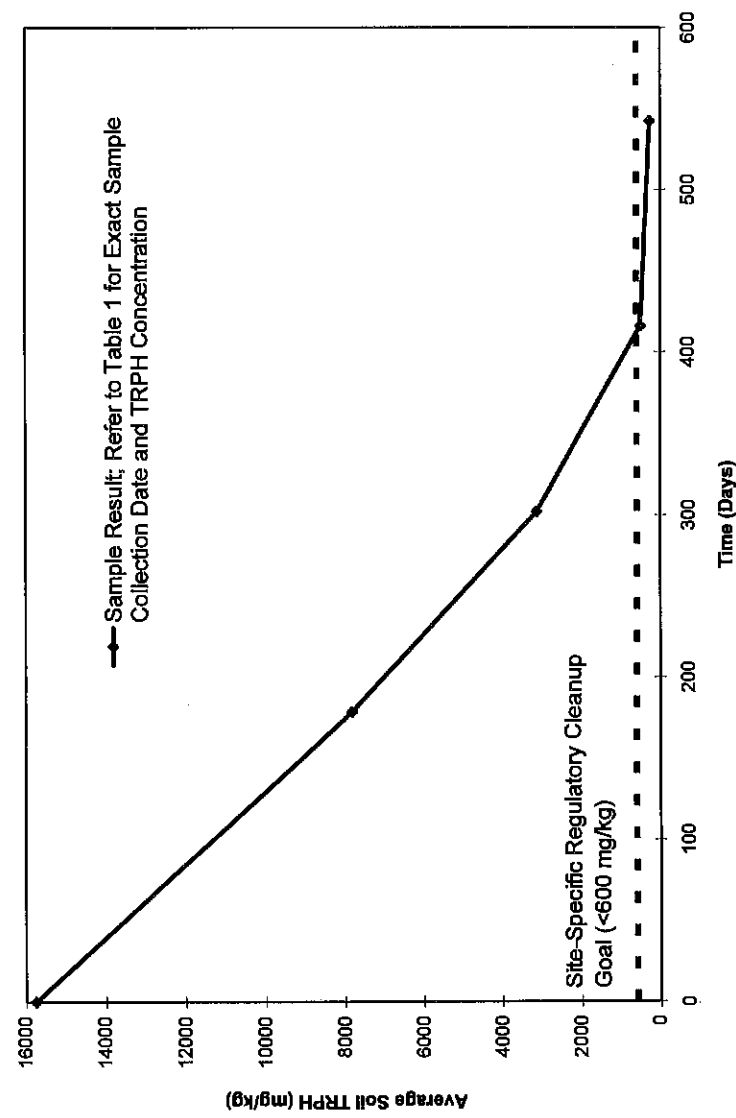


Figure 1. Total Recoverable Petroleum Hydrocarbon Soil Results, Site 1, Row 1 (492 cubic yards).



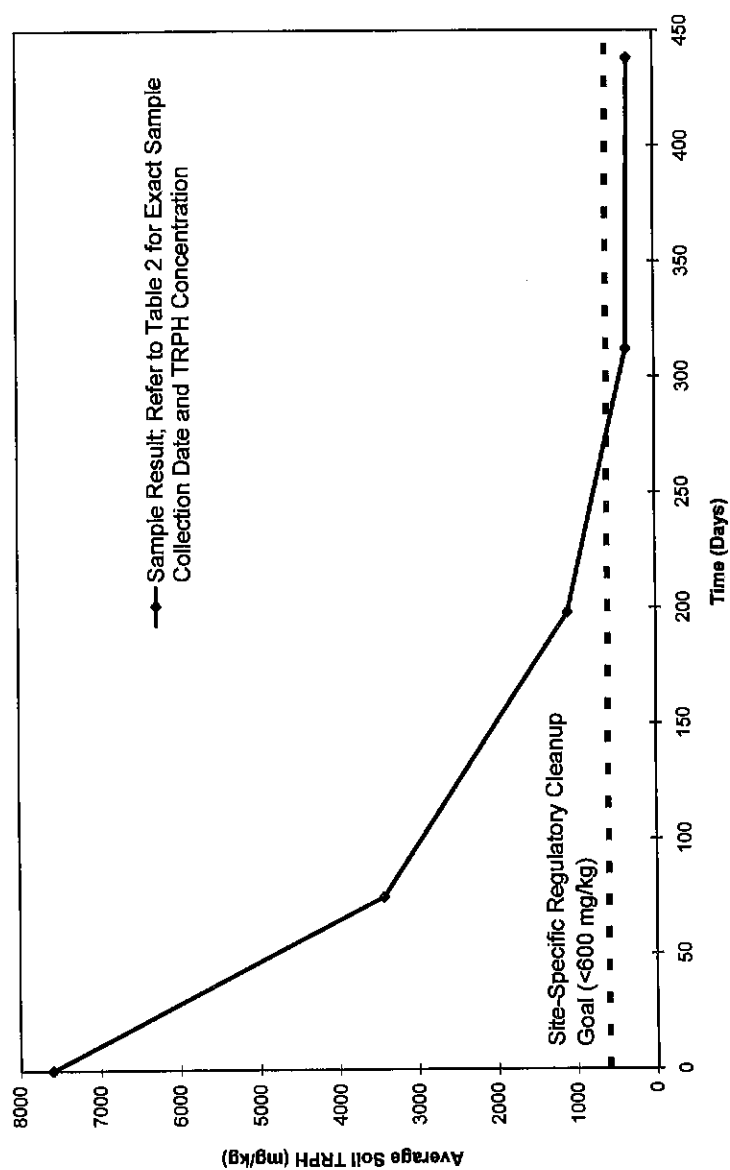


Figure 2. Total Recoverable Petroleum Hydrocarbon Soil Results, Site 1, Row 2 (408 cubic yards).

earthen lagoons (approximately 4,800 cubic yards) were removed and transferred to the bioremediation cell. The UST remedial project, located adjacent to the lagoons, contributed approximately 200 cubic yards of additional contaminated material.

Soils from both projects (approximately 5,000 cubic yards) were placed into a single prepared cell for treatment. The cleanup goal established by TNRCC was less than 600 mg/Kg TRPH.

#### Bioremediation Cell Construction

The construction of the cell (also approved by TNRCC prior to construction) was similar to that of Site 1, but soil was not segregated into rows. Location of the cell was selected by railroad officials. The site was triangular in shape (300 feet by 300 feet by 300 feet) and bordered by railroad tracks on all sides. The limited working space available, plus the large volume of material placed in the cell, resulted in a working soil treatment depth that exceeded 24 inches. Initial maintenance of the cell was hampered by the soil depth and the silty, unstable nature of the lagoon sludges.

#### Full-Scale Operations

As discussed for Site 1, a scheduled monthly maintenance program was established and a local environmental subcontractor was employed to provide all maintenance at this site. Commercial nutrients were also applied in the same manner as described for Site 1. The nutrient was mixed at the rate of 6 gallons nutrient to 1 gallon nutrient activator to 1,100 gallons of water per application. Due to the high clay content of the soil, cow manure was used as an antibinding matrix to promote aeration of the soils. Cow manure was chosen because of its high nitrogen content. An additional 1,000 cubic yards of manure brought the total treatment cell volume to 6,000 cubic yards. Samples for TRPH levels were not initially collected at the bioremediation cell due to the known (high) initial baseline results and the reduction rate of TRPH estimated from operation of the Site 1 facility. Raw material costs for this site averaged \$1,100 per application. Labor and equipment for maintenance and application added another \$1,100 per application including costs for soil sample analysis. The total monthly site operational expense was \$2,200.

Soil samples were collected on a quarterly schedule. Composite soil samples were collected at controlled locations for consistency. Soils were tested for TRPH using analytical method SW3550/E418.1.

#### Sampling Results

Collection of composite samples and completion of laboratory analyses were performed six times during the 25-month remediation period. The results of TRPH analyses are summarized in Table 3.

Figure 3 illustrates the TRPH sampling results over the period during which monthly maintenance was conducted. The irregularity in TRPH results is believed to be related to the potential for stratification of TRPH in the soil cells, and to the field sampling and analytical variability that is inherent in soil sampling. As discussed for Site 1, the TRPH reduction rate appeared to decrease with time. Reductions in biodegradation rates are common in landfarming applications and are generally the result of decreasing substrate availability and the lower rates of degradation associated with more recalcitrant hydrocarbons. Seasonal temperature fluctuations can also

Table 3. Comparison of Full-Scale Soil Treatment Data - Railroad Facility - Eastern Amarillo, Texas - Site 2

TRPH Level	Low	High	Number of Samples	TRPH Average	Date of Sample	Days from Last Sample	Reduction Rate (mg/Kg/day)	TRPH Percent Reduction
30,908	7,901	11	16,285	March 12, 1992	Baseline	0	0	
5,920	2,081	2	4,001	October 12, 1992	215 (215) <sup>a</sup>	57	75	
8,826	2,581	2	5,703	February 12, 1993	124 (339)	NA <sup>b</sup>	NA	
7,800	2,700	2	5,250	June 6, 1993	114 (453)	4	NA	
1,500	1,200	2	1,350	January 7, 1994	160 (613)	24	92	
490	300	2	395	May 20, 1994	132 (745)	7	98	
300	85	4	190	August 17, 1994	89 (834)	2	99	

<sup>a</sup> The total number of days since the bioremediation cell began operation (215).

<sup>b</sup> Not applicable because preceding TRPH concentration is less than TRPH concentration in this sampling event due to field sampling and analytical variability that is inherent in soil sampling.

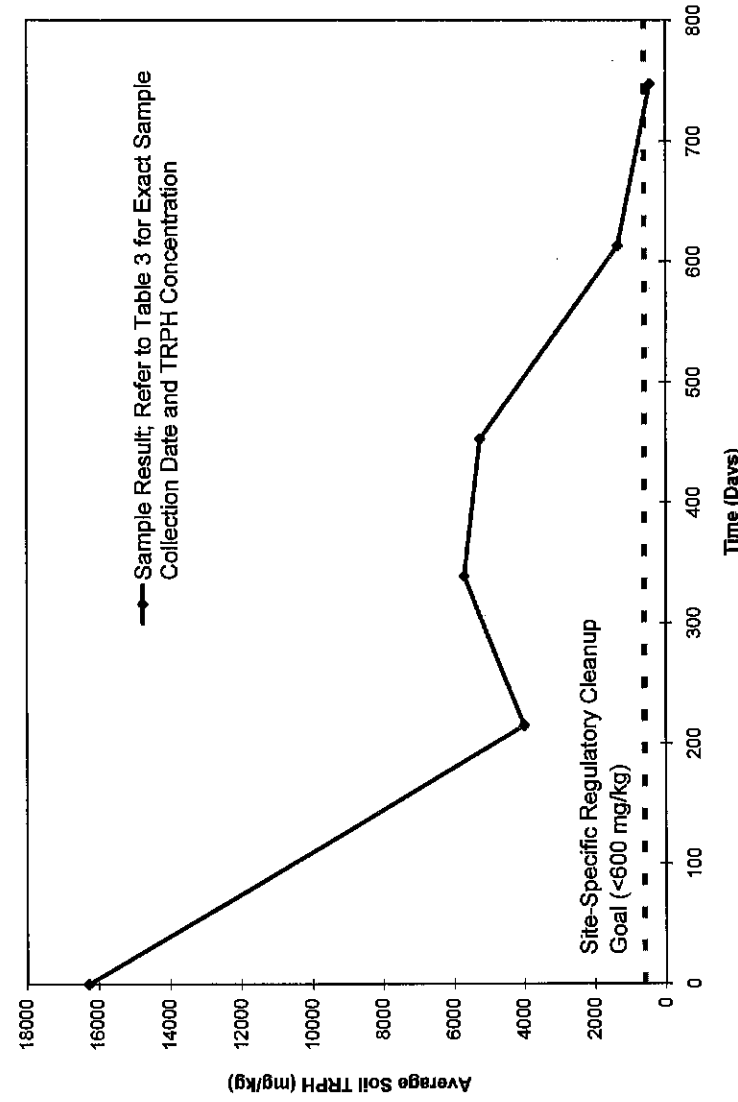


Figure 3. Total Recoverable Petroleum Hydrocarbon Soil Results, Site 2 (6000 cubic yards).

significantly affect the biodegradation process. Sampling variability also may create short-term deviations from long-term trends in TRPH reduction.

Although the TNRCC TRPH cleanup level of 600 mg/Kg for closure was met in the May 20, 1994 sampling round (395 mg/Kg), monthly maintenance continued for 3 months. The final round of sampling showed an average TRPH concentration of 190 mg/Kg, which was significantly below the cleanup goal. Based on these results, closure of the bioremediation cell has been approved by TNRCC.

#### Costs

The following cost comparison is given for Site 2 for bioremediation to reach the cleanup goal and for thermal treatment of these soils based on contractor bid pricing:

##### Bioremediation:

25 months @ \$2,200 per month = \$55,000\*

\$55,000/6,000 cubic yards = \$9 per cubic yard

##### Thermal Treatment:

Includes mobilization, burner fuel, site electrical, prescreening, acceptable moisture content, and material handling.

6,000 cubic yards @ \$74 = \$444,000\*\*

Net project savings by using bioremediation \$389,000.

\* Actual Cost

\*\* Estimated Cost

### SITE 3: STOCKPILED SOIL FROM UST REMOVALS - STAMFORD, TEXAS

#### Background

This project was initiated in October 1991 to provide bioremediation of petroleum-(Bunker C fuel oil) contaminated soils. These soils (approximately 480 cubic yards) resulted from previous remedial activities conducted during two 10,000-gallon UST removal operations. Soils removed from the two UST sites were segregated and placed in bioremediation cell 1 (130 cubic yards) and bioremediation cell 2 (350 cubic yards) based on TRPH concentration differences at the sites.

The initial cleanup level for these soils was set at 100 mg/Kg TRPH by TNRCC. However, this was later increased to 500 mg/Kg in 1993 based on TNRCC's risk-reduction guideline for the Bunker C fuel oil classification.

#### Biotreatment Cell Construction

A site on the railroad's property was designated for construction of the bioremediation cells. Two bioremediation cells were constructed to contain contaminated soils from the two sites after TNRCC approval had been obtained. Both cells were lined with 6-millimeter polyethylene, and a 6-inch protective layer of clean

soil was placed on top of the liner. Bioremediation cell 1 and bioremediation cell 2 measured approximately 90 feet long by 40 feet wide by 15 inches deep and 80 feet by 80 feet by 18 inches deep, respectively.

#### Full-Scale Operations

A local environmental contractor was hired to perform all maintenance operations on a monthly cycle on the bioremediation cells. Nutrients and soil mixing operations, and soil analysis were included in the contract. Monthly operating expenses for the two bioremediation cells were \$1,500 which also includes composite soil samples that were collected quarterly over the 17-month period of operation of the bioremediation cells.

#### Sampling Results

Quarterly sampling and analysis were performed six times during the 17-month bioremediation period. The analytical results for bioremediation cells 1 and 2 are summarized in Tables 4 and 5, respectively:

Initial composite soil sampling for TRPH used Method E418.1 with Soxhlet extraction (Method 3540). This method was later changed due to inconsistencies in test results. It was identified that the soils in both cells contained asphalt pavement fragments excavated during the UST removals. The composite soil samples also apparently contained asphalt, resulting in higher than expected TRPH concentrations. Changing the extraction method to sonication (Method 3550) for the final round of quarterly sampling eliminated this matrix interference problem.

Figures 4 and 5 illustrate the TRPH sampling results over the cell maintenance period of 17 months. The irregularity in TRPH results is believed to be related to the potential for stratification of TRPH in the soil cells, and to the field sampling and analytical variability that is inherent in soil sampling. As noted for Sites 1 and 2, biological degradation rates decreased between the first and second quarterly sampling events. Because the cleanup goal of 500 mg/Kg has been achieved, TNRCC has authorized closure for this site.

#### Costs

The following cost comparisons are given for Site 3 for bioremediation to meet the cleanup goal and for thermal treatment of these soils based on contractor bid pricing:

##### Bioremediation:

17 months @ \$1,500 per month = \$12,075\*

\$12,075/480 cubic yards = \$25 per cubic yard

##### Thermal Treatment:

480 yards @ \$74 = \$35,520\*\*

Net project savings by using bioremediation \$23,445.

\* Actual Cost

\*\* Estimated Cost

Table 4. Comparison of Full-Scale Soil Treatment Data - Railroad Facility - Stamford, Texas - Site 3a

TRPH Level	Low	Number of Samples	TRPH Average	Date of Sample	Days from Last Sample	Reduction Rate (mg/kg/day)	TRPH Percent Reduction
NA <sup>a</sup>	NA	1	30,624 <sup>b</sup>	October 25, 1991	Baseline	0	0
NA	NA	1	619.6 <sup>b</sup>	February 4, 1992	102 (102) <sup>c</sup>	294	98
NA	NA	1	4572 <sup>b</sup>	May 6, 1992	92 (194)	NA <sup>d</sup>	NA
NA	NA	1	3120 <sup>b</sup>	September 14, 1992	131 (325)	11	NA
NA	NA	1	1039 <sup>b</sup>	December 18, 1992	95 (420)	22	NA
187.2	36.6	4	87.0	March 19, 1993	91 (511)	11	99.7

<sup>a</sup>Not applicable.

<sup>b</sup>Represents a composite of 6 sample locations consisting of grab samples at the surface, at 6 inches below ground surface (bgs), and at 12 inches bgs from each sample location.

<sup>c</sup>The total number of days since the bioremediation cell began operation. <sup>d</sup>Not applicable because preceding TRPH concentration is less than TRPH concentration in this sampling event due to field sampling and analytical variability that is inherent in soil sampling (102).

Table 5. Comparison of Full-Scale Soil Treatment Data - Railroad Facility - Stamford, Texas - Site 3b

TRPH Level	Low	Number of Samples	TRPH Average	Date of Sample	Days from Last Sample	Reduction Rate (mg/kg/day)	TRPH Percent Reduction
NA <sup>a</sup>	NA	1	134.5 <sup>b</sup>	October 25, 1991	Baseline	0	0
NA	NA	1	46.0 <sup>b</sup>	February 4, 1992	102 (102) <sup>c</sup>	0.87	66
NA	NA	1	84.7 <sup>b</sup>	May 6, 1992	92 (194)	NA <sup>d</sup>	NA
NA	NA	1	68.7 <sup>b</sup>	September 14, 1992	131 (325)	0.12	NA
NA	NA	1	57.2 <sup>b</sup>	December 18, 1992	95 (420)	0.12	NA
7.4	2.6	4	4.7	March 19, 1993	91 (511)	0.58	97

<sup>a</sup>Not applicable.

<sup>b</sup>Represents a composite of 6 sample locations consisting of grab samples at the surface, at 6 inches below ground surface (bgs), and at 12 inches bgs from each sample location.

<sup>c</sup>The total number of days since the bioremediation cell began operation. <sup>d</sup>Not applicable because preceding TRPH concentration is less than TRPH concentration in this sampling event due to field sampling and analytical variability that is inherent in soil sampling (102).

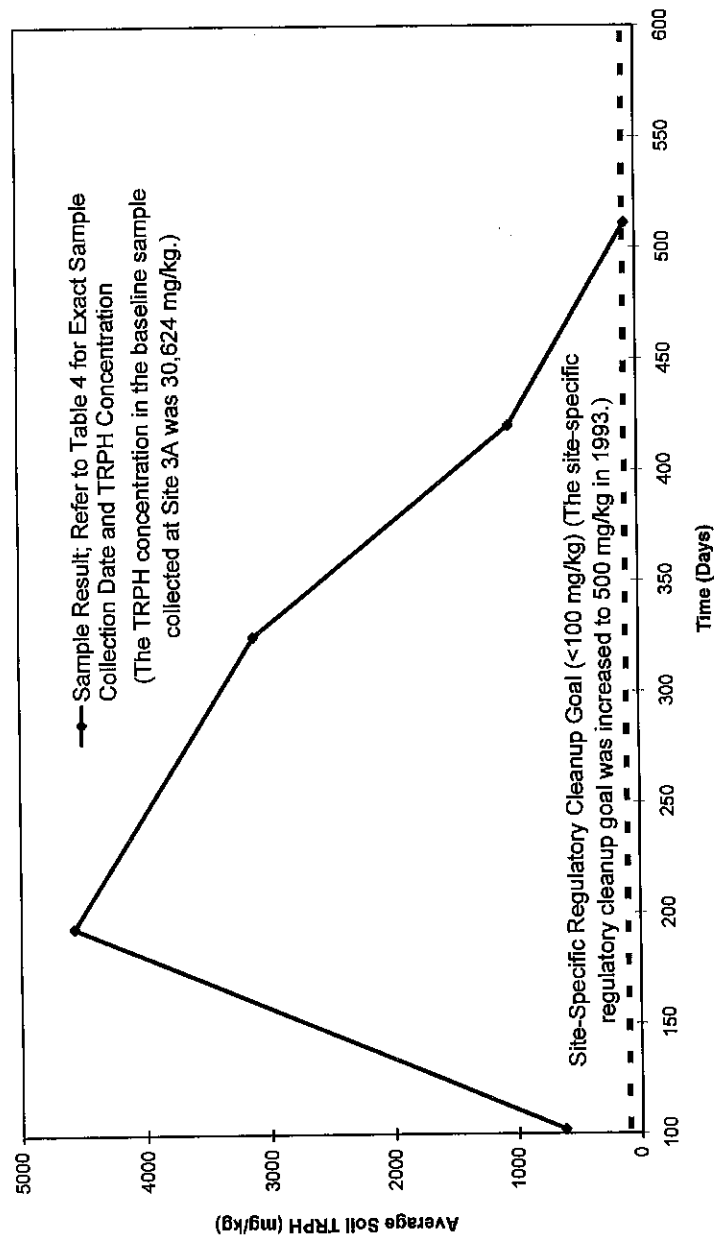


Figure 4. Total Recoverable Petroleum Hydrocarbon Soil Results, Site 3A, Bioremediation Cell 1 (130 cubic yards).

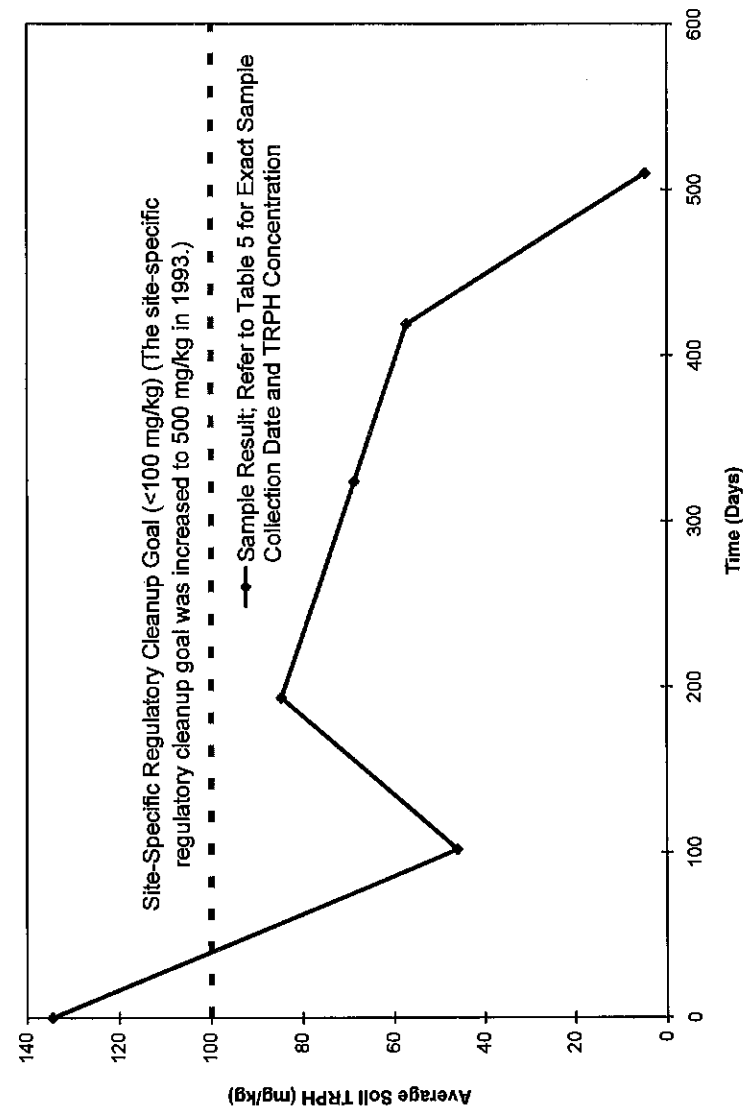


Figure 5. Total Recoverable Petroleum Hydrocarbon Soil Results, Site 3A, Bioremediation Cell 2 (350 cubic yards).

## SUMMARY

The analytical results and actual project costs for the three sites provide evidence to support the consideration of bioremediation of petroleum hydrocarbon contaminated soils as a viable option for certain remediation projects. Although fuels such as diesel fuel and Bunker C fuel oil are more resistant to biodegradation than lighter fuels such as gasoline, bioremediation has been shown to be a cost-effective remedial alternative. The use of a high-speed mixer to turn soils was very effective in aerating the soils.

The TRPH concentrations at these three sites were reduced below state regulatory levels for closure (ranging between 500 and 600 mg/Kg TRPH) within 14 to 25 months and TRPH percent reduction ranged from 96 to 99.7. The actual cost per cubic yard for bioremediation of the petroleum contaminated soils ranged from \$9 to \$37. Potential problems that were identified from the studies at these sites include selecting proper analytical extraction methods for soils containing asphalt material and decreased TRPH reduction rates with time as a result of decreasing substrate availability and the lower rates of degradation associated with more recalcitrant hydrocarbons.

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## Questions and Answers:

Q. I was curious about the costs of the bioremediation land farming activities. The costs, if I recall, were between \$9 and \$37. Is that correct?

A. Yes.

Q. Did those costs include construction of the actual cell itself? I know you mentioned that they did not include any excavation.

A. Right. The cost was strictly the treatment and application of the nutrients, maintenance and soil mixing and ranged from \$1500 to \$2200 per event, which is about on a monthly basis.

Q. OK. So they did not include the costs for construction of the actual cell?

A. No they did not.

Q. I saw that you had put in a 45 millimeter liner. Was that put in for the treatment cell or was that put back in when you reconstructed the lagoon?

A. The 45 millimeter oil and gas resistant liner was for the storage lagoon once we had reconstructed it.

Q. So there was not a liner used for the bioremediation cell?

A. For the bioremediation cell it was two 10 millimeter liners

Q. That would have been an unsealed situation?

A. Yes

Q. I think you said the objectives for cleanup levels on three of the four sites were 600ppm.

A. Correct

Q. Were you permitted to leave those soils in place, once they were below the 600?

A. Yes

Q. So there was no further remedial activity?

A. They could use that soil on the site somewhere for backfill, if they liked.

Q. As long as it stayed on their own property?

A. Yes.

Q. Do you feel like a more aggressive aeration schedule during peak degradation times could have lessened your remediation time? I saw some of your timeframes were 450 to 800 days, that's a year and a half to 3 years.

A. It's possible but we didn't assess this. We didn't do any kind of respiration testing to see if the soils remained oxygenated between soil mixing cycles.

## CHAPTER 7

### **Full-Scale Bioventing System Installed as Part of UST Closure Project Results in Rapid, Cost-Effective Remediation of Diesel Contaminated Soils**

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#### INTRODUCTION

A full scale bioventing system was installed at a leaking underground storage tank (UST) site in Seattle, Washington to remediate an estimated 6,800 cubic yards of residual diesel fuel contaminated soils. A horizontal air injection system was designed and installed at the bottom of two separate tank pit excavations during UST closure activities at the site, resulting in significant cost-savings. The system design allows a large subsurface area to be affected by creating oxygen-enriched beds through which oxygen is dispersed out into contaminated soils beneath and surrounding the former tank pits. The presence of the supplied oxygen into the subsurface enhances the natural biodegradation of total petroleum hydrocarbons (TPH) by indigenous microorganisms in the soil.

A free product recovery system previously installed at the site was modified to increase the average pumping rate to approximately 30 gallons per day. As a result, the water table was lowered and residual product allowed to form a "smear" zone at the capillary fringe. Injected air into the smear zone then allowed the biodegradation of the remaining contaminants to occur.

Results of two years of full-scale system operation and testing show average TPH biodegradation rates of up to 2,582 mg/Kg TPH per year were reached. Analytical results for soil samples collected after the first year of system operation indicate that even higher biodegradation rates were achieved.

#### Background

The project site is located in King County in the Puget Lowland geomorphic region of western Washington. This area is characterized by a relatively mild climate with an average annual precipitation of 35 inches. The area surrounding the facility is urban/residential, consisting of small businesses and apartments.

Surficial geology near the facility consists of the Vashon Drift, composed primarily of glacial outwash sands and gravels interlayered with till. The till contains a dense, compact mixture of clay, silt, sand and gravel with a soil moisture content ranging from 15 to 28%. Regionally, groundwater occurs within the outwash sand and gravel deposits as perched water above the till and as confined water beneath the till. At the study location, groundwater occurs at a depth of 15 to 17 feet under unconfined conditions with seasonal fluctuations of four feet.

Initial investigations to determine the nature and extent of petroleum hydrocarbon contamination present at the site were conducted in 1989 and 1991. As a result, TPH concentrations up to 9,100 mg/Kg were detected in soil samples collected from the immediate vicinity of seven diesel fuel USTs.

#### Remediation of Fuel Contaminated Soils

Residual diesel fuel contaminated soils at the site presented a long-term source of groundwater contamination. Due to space limitations and the depth of contamination (up to 17 feet), only *in situ* remediation methods were considered to remediate the contaminated soil. Bioventing was selected as the most viable *in situ* technology for pilot study evaluation.

The use of air as a medium to contact and remove volatile hydrocarbons has been implemented extensively in soil vapor extraction systems. Due to the tremendous viscosity and diffusion advantages of air, soil vapor extraction has been more successful than soil flushing in contacting fuel residuals trapped in soil micropores. A full-scale soil venting project which reduced fuel residuals from an average TPH concentration of 900 mg/Kg to less than 10 mg/Kg was completed at Hill Air Force Base, Utah.<sup>1</sup> Monitoring of vented soil gas indicated that volatilization accounted for 60% of the removal, and biodegradation accounted for the remaining 40%.<sup>2</sup>

A lack of oxygen generally limits the natural biodegradation of hydrocarbons by indigenous soil bacteria. Once oxygen is supplied by soil venting, indigenous bacteria multiply and thrive, using fuel hydrocarbons as their primary carbon source. For sites with diesel fuel or heavier hydrocarbon contaminants, volatilization plays a less significant role in the soil venting system as compared to biodegradation.

Soil permeability to air is an important consideration in bioventing design. Adequate air permeability is important in supplying indigenous bacteria with oxygen. The bioventing technology has been applied with success to a variety of soil types including soils consisting of 80% clay.<sup>3</sup> Other factors influencing the fuel biodegradation rate are average soil temperature and the availability of basic nutrients such as nitrogen and phosphorous. Based on these considerations, a pilot study was implemented six months prior to scheduled UST system closures at the site with the goal of defining the parameters for design, installation, and operation of a full-scale bioventing system.

#### METHODOLOGY

The bioventing pilot study consisted of a series of preliminary tests designed to define the scope for the full-scale installation of an *in situ* bioventing system. The

objective of the pilot test was to better define the volatilization/biodegradation potential at the site, to determine the venting rate required to uniformly distribute air (oxygen) through the unsaturated zone, and to measure the natural levels of hydrocarbon biodegradation under oxygen-enhanced conditions.

A site plan showing the facility layout, including the former UST areas on the north and northwest sides of the building is shown on Figure 1. Pilot testing activities consisted of the installation of a central air injection well (VIW) and two vapor monitoring points (VMPs), followed by air injection tests and an *in situ* respiration test in which oxygen uptake in the soils due to biodegradation was measured over time. Air injection, rather than vapor extraction, was selected as the test method because diesel fuel contamination in soils is more susceptible to natural biodegradation by supplying the subsurface with additional oxygen than volatilization associated with conventional vapor extraction techniques. Additionally, low flow air-injection did not require costly off-gas treatment or air-permitting.

#### Pilot Study Results

Three distinct tests were conducted to fulfill the objectives of the pilot study. The first test was a 70 minute preliminary system check to ensure proper operation of the 5-horsepower positive displacement blower unit, pressure gauges, and vapor monitoring equipment, and to measure the initial pressure responses at the vapor monitoring points and air flow rate.

#### Air Injection Test

After initial system adjustments were made, a second test was performed for approximately 24 hours. During this test, air was injected into the subsurface at the injection well and pressure responses were measured to evaluate steady state operating conditions, the air permeability of the soil layer within the screened intervals of the VMPs, and the radius of influence of the VIW.

Soil permeability (k) values for VMP-1 and VMP-2 were 9.8 and 6.8 darcy, respectively. A k value on the order of 1 to 10 darcy corresponds to fine to medium grained soils.<sup>4</sup> These k values were slightly higher than expected, based on the high pressure required to induce flow through the soils. However, they were consistent with grain-size distribution results from independent sieve analyses which indicated a composition of 88% sand at a depth of 13 to 14.5 feet in the vapor injection well.

Changes in oxygen levels, carbon dioxide levels, and hydrocarbon vapors at the VMPs were also measured during the air injection test. Oxygen concentrations are an excellent indicator of soil gas movement through the contaminated zone. In the absence of vacuum extraction or air injection, soil gases in contaminated areas are depleted of oxygen and accumulate high levels of carbon dioxide as a result of biological fuel consumption. As air is injected into the subsurface through the injection well, stagnant soil gas is replaced by fresh soil gas. The result is an increase in oxygen and a decrease in carbon dioxide.

The ability of air injection to promote oxygen flow through the entire contaminated soil column was demonstrated by the air injection test. Initial oxygen readings confirmed that in the absence of active air injection, indigenous bacteria had consumed virtually all of the available oxygen in areas where fuel contamination was



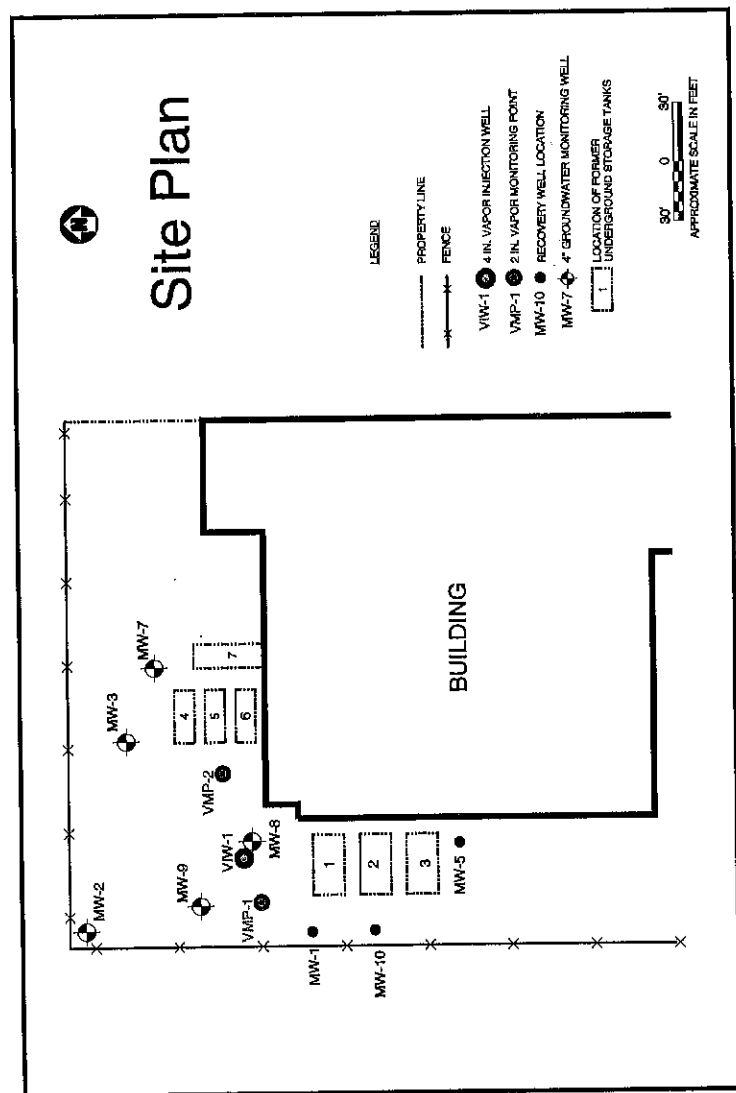


Figure 1. Site plan.

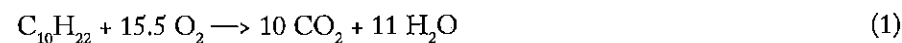
the primary carbon source. During the test, several oxygen measurements were taken at VMP-1 and VMP-2 to confirm the accuracy of the data. The results showed that oxygen concentrations increased from 4.1 to 10.5% at VMP-1 and from 5.0 to 17.2% at VMP-2. These results confirmed that air injection would be an effective method for increasing soil gas oxygen levels at the site, and that the sand and silt/clay soils with moisture content of 15 to 28% did not restrict the flow of oxygen-rich air in the subsurface.

#### In Situ Respiration Test

As indigenous bacteria consume fuel hydrocarbons, they utilize oxygen and produce carbon dioxide. Research has shown that oxygen consumption provides the most accurate estimation of hydrocarbon degradation.<sup>5</sup>

At the completion of the air injection test, the system was shut down and an *in situ* respiration test was initiated. Oxygen consumption and production of carbon dioxide by indigenous soil bacteria in the oxygenated test wells were measured over a two-day period. These data were used to establish the average biodegradation rate of the indigenous microorganisms and to predict the time required to biodegrade fuel hydrocarbon residuals using the bioventing technology.

The average oxygen utilization rate for VMP-1 and VMP-2 was 0.022% oxygen per minute. This oxygen utilization rate was used to estimate the rate at which diesel fuel TPH levels could be biodegraded at this site. Complete biological degradation of fuel hydrocarbons (e.g., n-decane) can be described by the equation:



Approximately 3.5 grams of oxygen is required to biodegrade one gram of fuel hydrocarbons. Based on this relationship, the average oxygen utilization rate observed in contaminated soils and the soil's air-filled porosity of 0.05 liters/kilogram, the rate of fuel biodegradation was estimated to be 2,200 milligrams of fuel per kilogram of soil per year (mg/Kg/yr). The application of these pilot-test results to full-scale remedial design is discussed in the following sections.

#### Full-Scale Bioventing System Design and Installation

A complete horizontal air injection system including a motor, blower, filters, control valves and power supply required for the operation of the system was designed and installed during UST removal activities six months after the pilot study was conducted. Key design criteria included reliability, ease of maintenance, and minimum operating cost. The entire air injection (blower) unit was skid-mounted for ease of transport and installation.

The full-scale system consists of a 5-horsepower positive displacement blower package rated at 50 cubic feet per minute (cfm) air flow rate at a pressure of 12 pounds per square inch (psi). The unit is equipped with an inlet filter, inlet and outlet silencers, discharge dilution valve (to control injection pressure/rate), pressure relief valve, outlet pressure and velocity gauges, and check valve.

The system was installed by routing a two-inch diameter galvanized steel air injection pipe from the blower unit to a four-inch diameter PVC manifold pipe located below grade. The manifold pipe connects two four-inch diameter vertical PVC air injection pipes installed at the corners of the former UST excavation pits. The vertical injection pipes were installed during the UST closure activities and manifolded to a horizontal arrangement of four-inch diameter perforated PVC piping in each tank pit as illustrated in Figure 2.

The horizontal piping arrangements were installed at a depth of 10 to 12 feet below grade at the bottom of the excavated tank pits. The piping was placed on top of a six-inch layer of pea gravel, and then completely covered with another 12 inches of pea gravel to provide a permeable medium across the entire bottom of each tank pit excavation. A six-millimeter polyethylene membrane was then installed on top of the pea gravel and overlain by a six-inch thick impermeable layer composed of a mixture of portland cement, sand, and potash to impede any vertical migration of injected air back through the clean backfill of the tank pit cavity, thereby minimizing the potential for short-circuiting the system. The tank pit excavations were then backfilled with clean bank-run gravel (1/4 to 1 1/2-inch aggregate) compacted in 12-inch lifts to six inches below grade. Square, flush-mounted steel street boxes were installed around the vertical injection riser pipes located in the corners of the two former tank pits prior to installation of the final covers. Final cover consisted of six inches of concrete over the north tank pit and six inches of asphalt over the western tank pit. An isometric view of the horizontal air injection system is included as Figure 3.

A horizontal air dispersion system, rather than a series of vertical injection wells, was selected for two reasons. First, a horizontal arrangement of perforated PVC piping could be constructed and installed in the tank pit excavations on the north and west sides of the facility during UST closure activities, resulting in reduced installation costs. The complete installation of the system added only approximately 1/2-day to the fuel system closure construction activities. Secondly, this system design allows a greater surface area to be affected by creating an oxygen-enriched bed through which oxygen is dispersed out into residual TPH contaminated soils beneath and surrounding the former tank pits.

The full-scale bioventing system has been operated in conjunction with the existing on-site groundwater recovery system. Operation of both systems has resulted in lowering of the water table, exposing the smear zone at the capillary fringe to air injection which enhances the natural biodegradation of residual petroleum hydrocarbons. A cross-section illustrating the effects of this dual remediation system is shown in Figure 4.

#### Vapor Monitoring Point Installations

Prior to full-scale system start-up, ten additional VMPs (VMP-3 through VMP-12) were installed along the perimeter of the air injection system and property boundaries (Figure 2). The additional VMPs serve several purposes. First, they are used as passive venting or release points for hydrocarbon vapors which may accumulate in the subsurface as a result of air injection. Secondly, they serve as an early warning system for vapors migrating off-site. Finally, they are used to monitor the effectiveness

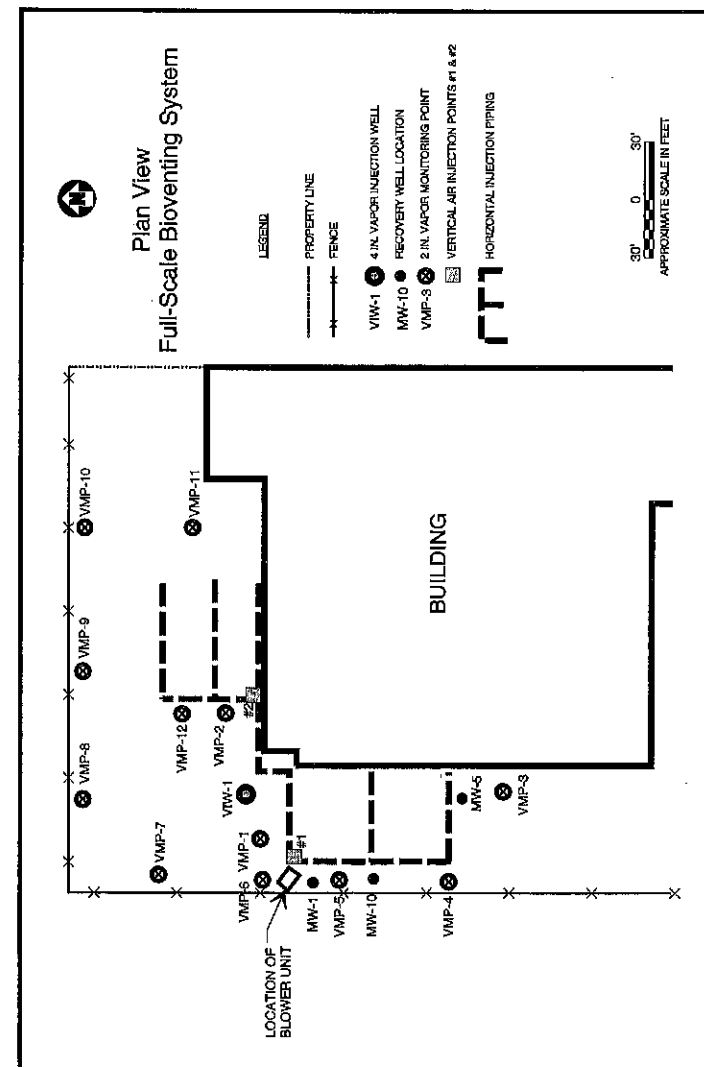


Figure 2. Full-scale bioventing system (plan view).

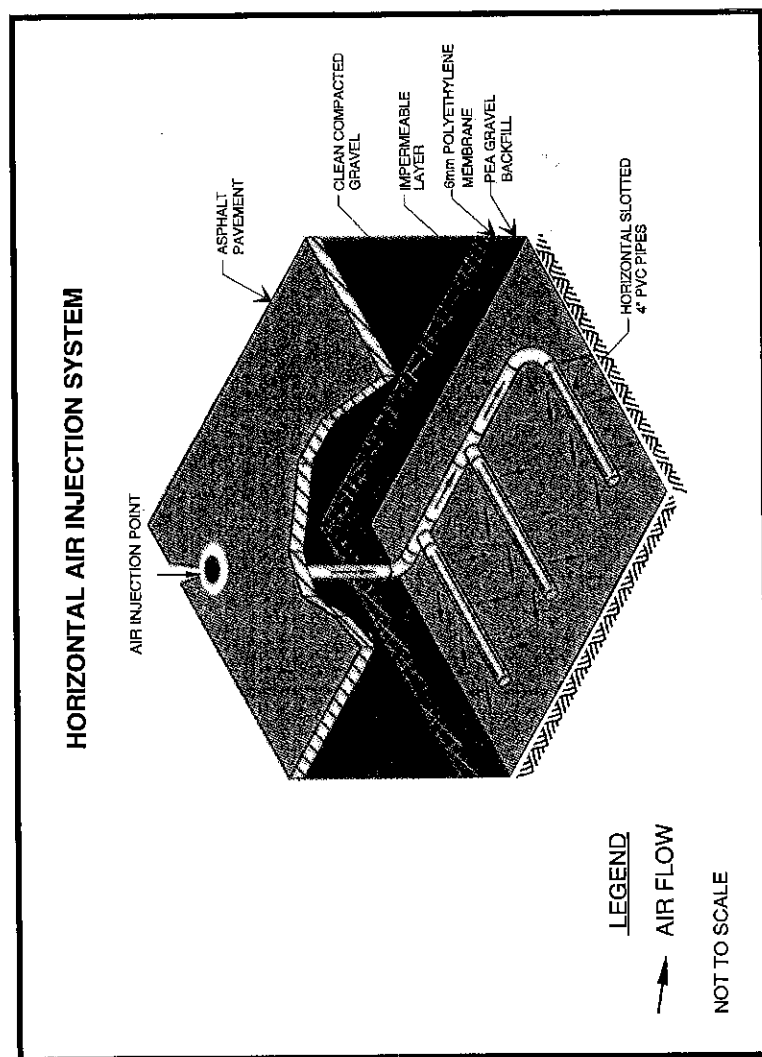


Figure 3. Horizontal air injection system (isometric view).

of the bioventing system by measuring changes in oxygen and carbon dioxide levels in the surrounding soils during routine monitoring and *in situ* respiration tests.

The VMPs were installed using hollow stem auger drilling techniques and were constructed of two-inch diameter slotted PVC screen and riser. Each 10 foot length of well screen was installed to a depth of 15 feet, or approximately two feet above the water table at the time of installation.

#### Baseline Monitoring and System Start-up

Prior to system start-up, oxygen, carbon dioxide, and hydrocarbon levels were monitored in each of the 12 monitoring points (VMP-1 through VMP-12) using portable gas analyzers to establish baseline concentrations to be referenced during subsequent bioventing system monitoring and *in situ* respiration tests.

#### Air Injection System Monitoring

During the course of the first 24 months of system operation, changes in oxygen and carbon dioxide concentrations and pressure responses have been observed in monitoring points more than 80 feet from the air injection system. This indicates that the horizontal system has created a wider radius of influence than the original pilot study estimate of 30 feet, which was based on a 24-hour period of air injection into the vertical injection well VIW-1.

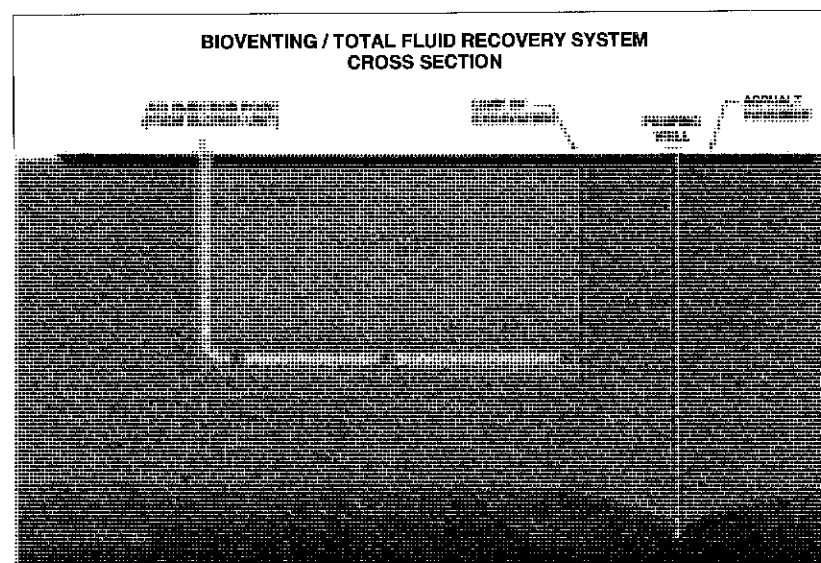


Figure 4. Bioventing/total fluid recovery system (cross-section).

## RESULTS

### Respiration Test Results

Five *in situ* respiration tests have been conducted during the first 24 months of bioventing system operation. A sixth and final respiration test has been scheduled. The objective of these tests was to determine if oxygen utilization rates were remaining constant, increasing, or decreasing with time. The tests were conducted after 60 days, 180 days, 270 days, 400 days and 600 days of operation.

A minimum of three VMPs were selected from the areas of greatest contamination to conduct each of the respiration tests. Data collected from the respiration tests were evaluated in the same manner as the initial pilot test data to determine the average biodegradation rates shown on Figure 5.

After 60 days of operation, the average calculated biodegradation rate was 440 mg/Kg/yr. An increase in the average biodegradation rate to 1,610 mg/Kg/yr was observed based on the 180 day respiration test data, and the 270 day respiration test data showed an increase in the average biodegradation rate to 2,582 mg/Kg/yr, exceeding the pilot test predicted rate of 2,200 mg/Kg/yr. Increases in biodegradation rates by as much as one and one-half times have been observed at other bioventing sites. These increases may be attributed to establishment and growth of the microbial population as oxygen is supplied to the subsurface.

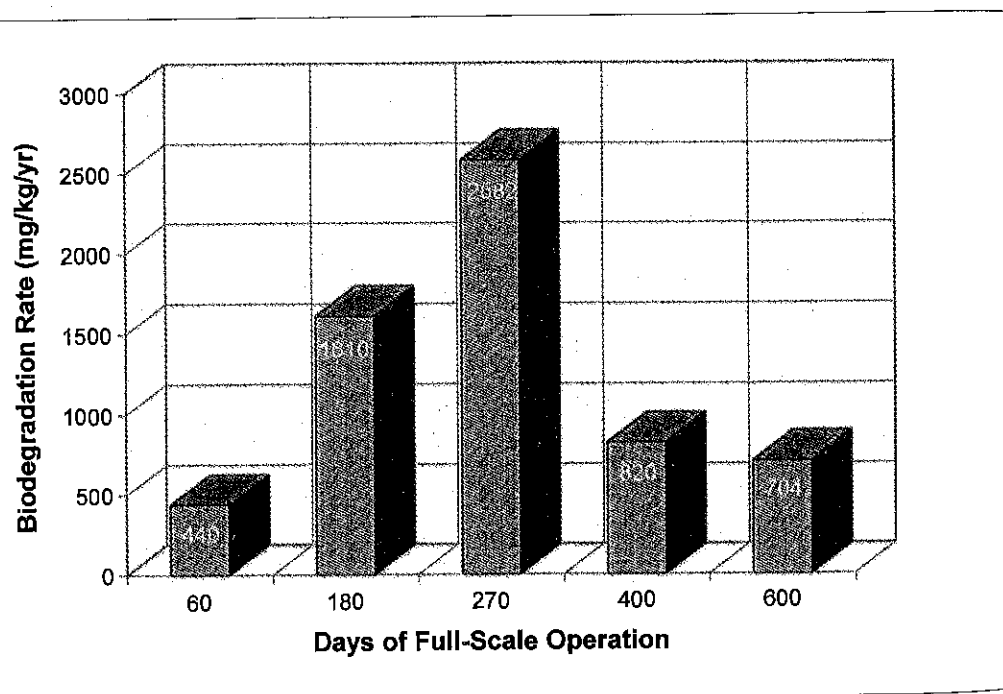


Figure 5. Average biodegradation rates.

The average biodegradation rate calculated based on the 400 day respiration test data was 820 mg/Kg/yr and the most recent test conducted (600 day) indicated an average biodegradation rate of 704 mg/Kg/yr. This marked decrease in the average biodegradation rate has been attributed to a decrease in available hydrocarbon contamination used as a carbon source for the microbial population.

### Confirmatory Soil Sampling

To independently confirm the TPH reduction predicted by the respiration test results, six soil borings were advanced to depths ranging from 5.5 to 18 feet after one year of bioventing. Soil samples were collected continuously in accordance with established ASTM Standard D-1586. The soil boring locations were selected to coincide with previous drilling locations so that analytical results could be directly compared to measure the success of the remediation system.

All samples retrieved from the borings were visually inspected for signs of staining and screened for the presence of hydrocarbon odors and organic vapors with a photoionization detector (PID). At each drilling location, one soil sample was collected from the interval previously sampled. At four of the six soil boring locations, field screening methods indicated a zone of contaminant concentrations greater than the interval previously sampled. In these cases, a second soil sample was collected from the interval corresponding to the highest PID readings to obtain a "worst case" sample to account for the effect of groundwater table fluctuations. To allow for direct comparison of analytical data, the analytical methods used in the initial sample analysis were used in the confirmatory analysis.

A comparison of analytical results from previous site investigations (before bioventing) with the results from the confirmatory soil samples collected after one year of bioventing indicates that a significant reduction of TPH concentrations has occurred. Original TPH data and "worst case" data (highest TPH concentration of the samples collected at each of the confirmatory soil sampling locations) are depicted on Figure 6. Based on these data, an overall average TPH reduction of 96% was observed after just one year of bioventing. Each TPH value which was lower than 1000 mg/Kg during the pre-bioventing assessments was reduced to below method detection limits, while concentrations initially over 1,000 mg/Kg were reduced by more than 90%.

The observed decreases in TPH concentrations are much greater than the reduction anticipated by the estimated biodegradation rates obtained from pre- and post-full-scale bioventing respiration tests. Other factors which likely contributed to the reduction of TPH include volatilization and operation of the free product/groundwater recovery system.

Results of the 400 and 600 day respiration tests indicate that biodegradation rates have significantly decreased. This decrease in the biodegradation rate is a reflection of the reduced TPH concentrations in the confirmatory soil samples collected.

## SUMMARY

The costs associated with this remediation project, from pilot study and full-scale system design and installation, to post-system startup monitoring are illustrated in Figure 7. An overall cost of \$23.65 per cubic yard has been estimated for bioventing

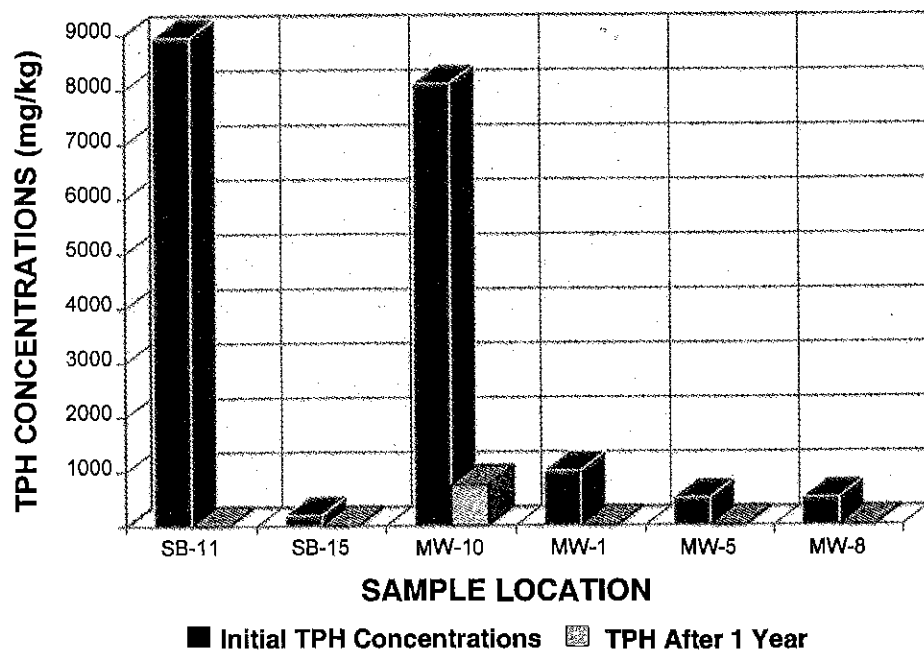
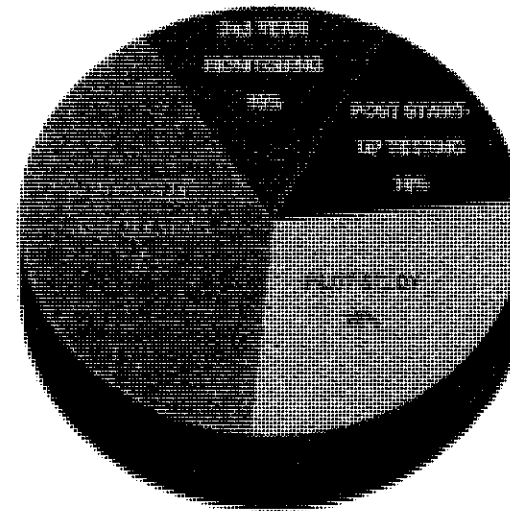
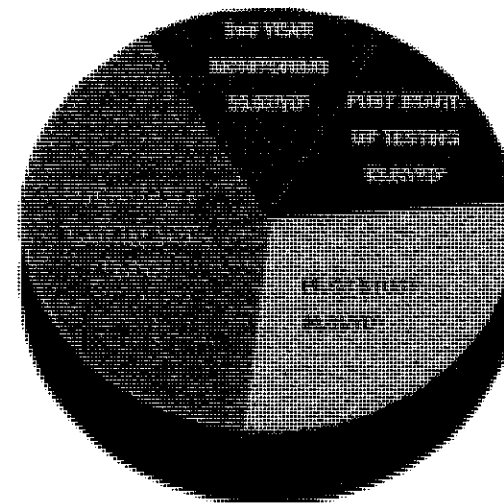


Figure 6. TPH concentrations in soil.



PERCENTAGE OF TOTAL COST  
BY ACTIVITY



COST PER CUBIC YARD  
PER ACTIVITY  
(TOTAL COST \$23.65/CUBIC YARD)

Figure 7. Bioventing cost breakdown.

operations through the end of 1994. Data collected through two years of full-scale bioventing, including the results of confirmatory soil sample analytical data, indicate that the bioventing technology can be applied as a cost-effective alternative to soil excavation and disposal. Additionally, where known fuel releases have occurred and subsurface contaminant distribution favors a horizontal system configuration, significant cost savings can be realized by installing the bioventing system during UST closure, upgrade, or other site activities that require excavation.

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## CHAPTER 8

### Biostabilization of Petroleum Hydrocarbons: Case Studies in Support of Alternate Cleanup Standards for TPH

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**Mark Larsen**

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RETEC has compiled a database summarizing the results of biotreatment demonstrations conducted on the bench-, pilot- and full-scale. Most of RETEC's projects have involved biotreatment of weathered hydrocarbons (i.e., product spills greater than 5 years old). This paper summarizes the principal conclusions which have been drawn based on the data.

Figures 1 and 2 summarize the removal efficiencies measured for diesel and oils during biotreatment. For purposes of this paper, hydrocarbons are classified as diesels if greater than 90 percent of the measurable TPH is between the boiling ranges of n-C<sub>12</sub> and n-C<sub>24</sub> alkanes. Hydrocarbons are classified as oils if greater than 20 percent of the measurable TPH has a boiling range greater than that of n-C<sub>24</sub> alkanes.

In general, the percent reductions in soil TPH concentrations decrease with increasing molecular weight. For the biotreatment projects involving diesels, biotreatment reduced soil TPH concentrations an average of 90 percent. The data set includes relatively few outlying data points, and heavily-weathered diesels (spills greater than 20 years old) behave similarly to less-weathered diesels. For oils on the other hand, biotreatment reduced TPH concentrations an average of 83 percent. The oil data were much less consistent, with wider performance ranges. The oils exhibiting the lowest removal efficiencies tended to be heavier and more-weathered than those with higher removal efficiencies.

Some RETEC projects have included measurement of soil characteristics following biotreatment. The data collected to date suggest that while biotreatment does not necessarily result in complete removal of soil TPH, the residual TPH has reduced mobility and toxicity.

TPH characterization analyses performed using gas chromatography methods indicate that biotreatment results in preferential removal of lighter hydrocarbons. Figures 3 and 4 present the data from TPH characterizations performed before and after bench-scale biotreatment tests. In both cases, the molecular weight distribution of the residual hydrocarbons is significantly shifted toward heavier compounds. Based on the known solubilities of hydrocarbon compounds, it is reasonable to expect that the heavier molecular weight distribution of the biotreated material (as well as the reduced TPH concentrations) would result in lower concentrations of leachable hydrocarbons.

Several tests have been developed by EPA and other regulatory agencies to quantify the potential for contaminant leaching in soils. Figures 5 and 6 present leachability data collected during one bench-scale demonstration of bioventing. In this test, the TPH was identified as a weathered fuel-oil. During the 10-week bioventing test, leachable PAH concentrations were measured using a water extraction procedure. The procedure was based on protocols recommended by the California Water Quality Board, and involved combining 1 part soil with 10 parts water, tumbling the mixture for 24 hours in a TCLP-type extraction tumbler, and analyzing the filtered water phase by standard EPA methods. The data obtained indicated that leachable PAH concentrations decreased more rapidly than did soil TPH concentrations. Samples tested for leachable TPH after 10 weeks of bioventing indicated low levels of leachable TPH.

Microtox bioassays have been used frequently to quantify the potential toxicity of contaminants in soil. In one bench-scale land treatment demonstration project, initial and final soil samples were tested for toxicity using a Microtox procedure. Significant toxicity (expressed 100 times the reciprocal of the  $EC_{50}$ ) was measured prior to biotreatment. Following biotreatment, no toxicity was detected (Figure 7).

The data presented in this paper support the concept of TPH biostabilization. We recommend that this concept be investigated more fully. One objective of further investigation should be the development and use of standardized leaching and toxicity tests. Figure 8 illustrates the importance of methodology in quantifying TPH leachability. TPH leachability in the residuals of a land treatment unit were measured by both the TCLP leaching procedure and the water extraction method recommended by the California Water Quality Board. In the TCLP extracts, TPH concentrations were below the method detection limit. The California method, on the other hand, resulted in low but measurable TPH concentrations.

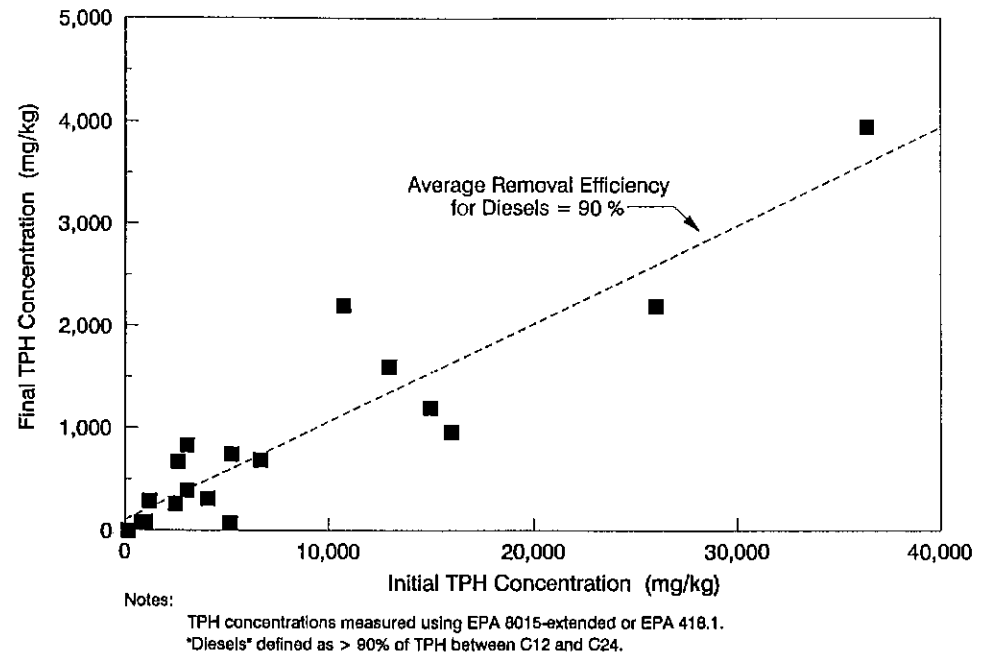


Figure 1. For biotreatment of diesel in soils TPH removal efficiency averages 90%.

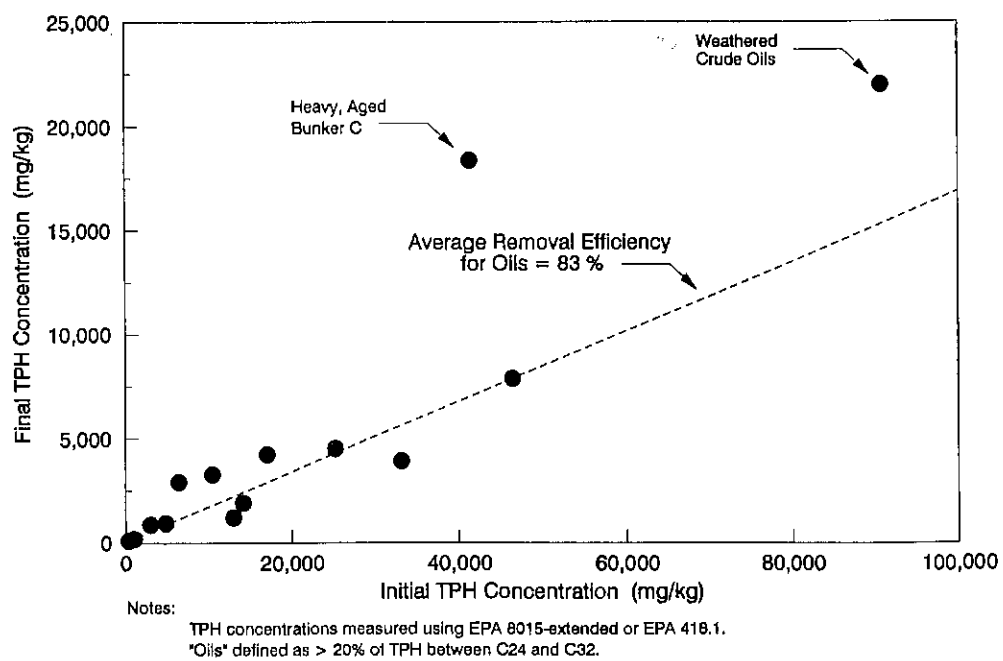


Figure 2. For biotreatment of oils in soils TPH removal efficiency averages 83%.

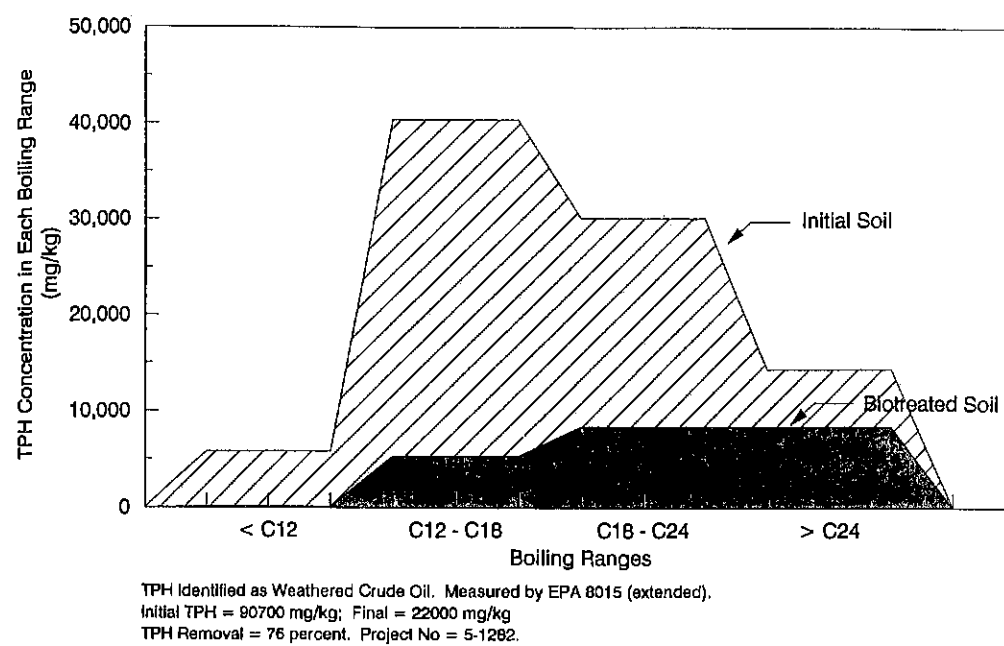
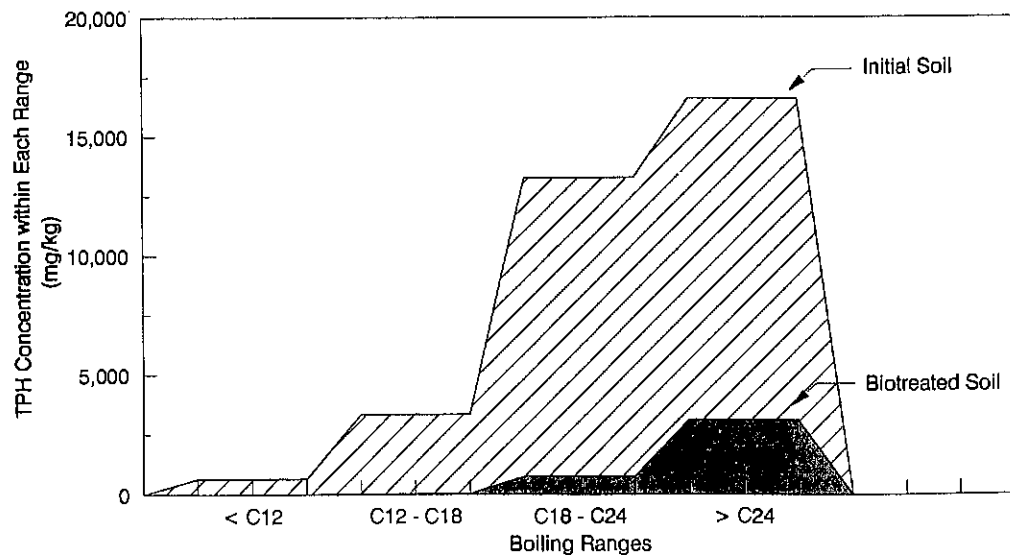


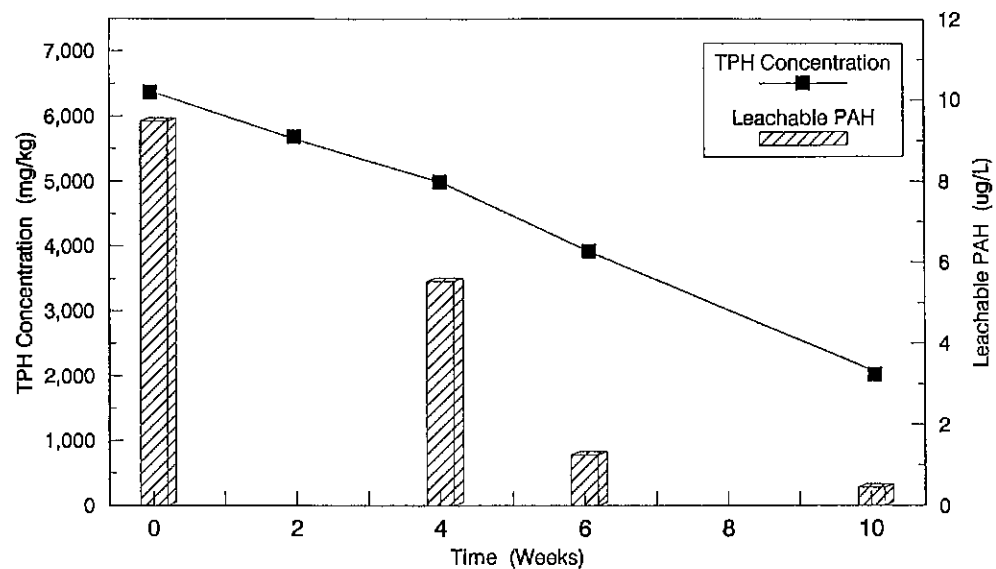
Figure 3. Bench-scale data indicate preferential removal of light-end hydrocarbons.





TPH Identified as Crude Oil. Concentrations measured by EPA 8015 (extended).  
 Initial TPH = 33,200 mg/kg; Final = 3,900 mg/kg  
 TPH Removal = 88 percent, Half-Life = 15 Days. Project No = 5-0995-100.

Figure 4. Bench-scale data indicate preferential removal of light-end hydrocarbons.



TPH Concentrations measured using EPA 418.1. TPH Identified as fuel oil.  
 Leachable PAH measured using a modification of  
 EPA's Synthetic Precipitation Leaching test and EPA 8310.

RETEC Project 3-0945 (3)

Figure 5. Significant reductions in leachable PAH during bench-scale bioventing.

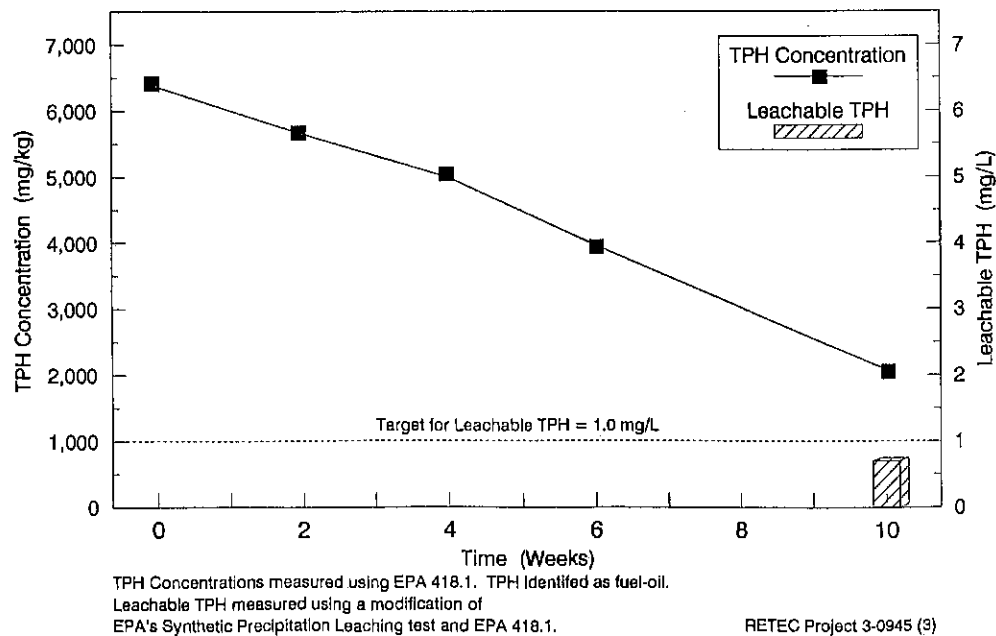


Figure 6. Low levels of leachable TPH in residuals from bench-scale bioventing tests.

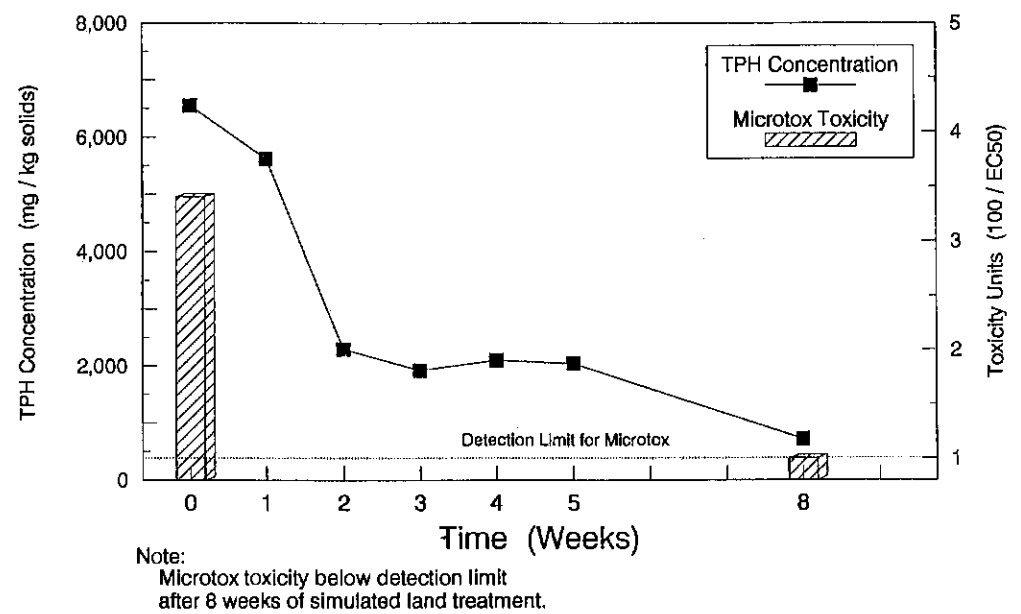


Figure 7. TPH removal and toxicity reduction during biotreatment of diesel-type hydrocarbons.

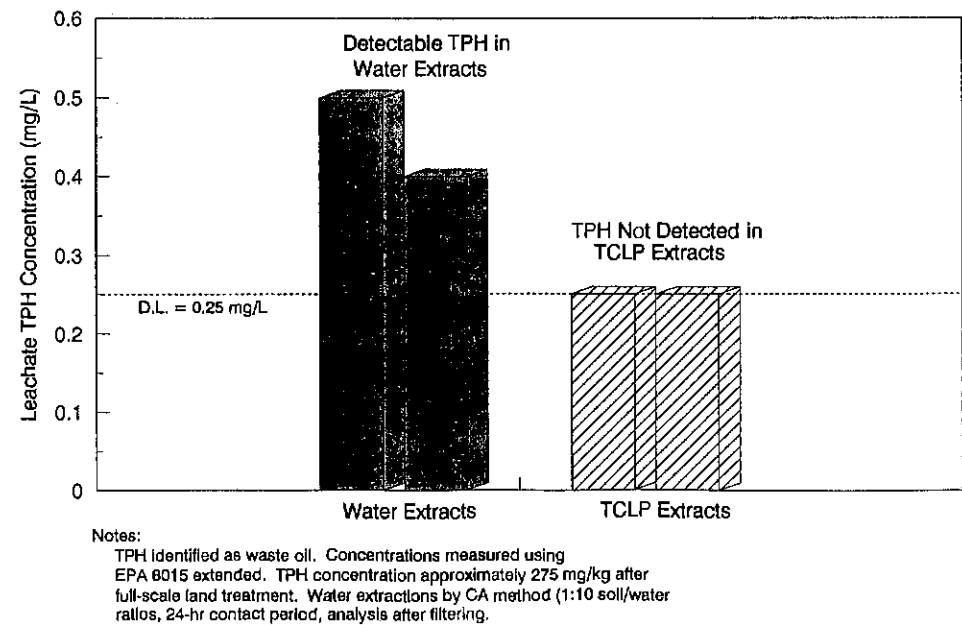


Figure 8. TCLP methods results in lower estimates of leachable TPH than alternate methods.

**Questions and Answers:**

Q. Did you try to correlate any of the data that you had on the toxicity with what might be the relevant constituents that were still left in that mass after biotreatment?

A. No. We were doing some studies for other purposes and we simply happened to run some toxicity data, so there was no correlation done that way. There really should be and that would be a very good area for some research.

Q. Also, did you do other short term toxicity testing besides Microtox, or was that the toxicity test of choice?

A. Microtox was what we were doing in that particular study. There are several other studies that I'm aware of not in the petroleum area, but in the coal tar area where people are using a much broader set of toxicological measures. They're using earthworm studies, lettuce leaf propagation and some ceriodaphnia and a much broader range. Most of that is being done on coal tar sites and former manufactured gas plant sites. There are several wood preserving facilities that are being remediated under RCRA where the performance criteria is not a chemical measure of PNAs, it's simply a toxicity reduction standard and that standard is being measured by a broader set of toxicological measures.

Q. When you extracted the soils to do the microtoxicity test, did you use supercritical fluid extraction?

A. I don't believe so but I'm not familiar with the extraction method. We used the California subset of the synthetic precipitation leaching procedure.

## CHAPTER 9

### **Anticipating Risk Assessment When Designing a Surface Soil Sampling Plan for an Active Site with Petroleum Contamination**

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#### INTRODUCTION

Historically, most sites in the U.S. with petroleum contaminated soils have been remediated without performing risk assessments. For example, since 1989, states have set cleanup targets based on total petroleum hydrocarbons (TPH) and/or benzene, toluene, ethylbenzene and xylene (BTEX) which may lead to large-scale remediation of petroleum contaminated sites. However, these cleanup targets in some states serve as jumping-off points to setting site-specific remediation goals. These policies are opportunities to use risk assessment to set reasonable, health-protective cleanup targets cost-effectively by focusing remediation on areas associated with significant risk. These developments are significant to railyards, where large quantities of diesel fuel may be the issue, and risk assessment may represent an economical way to meet state regulations.

Soil data needed for risk assessments are not always collected when assessing the nature and extent of contamination at a site. Areas where people could potentially be exposed must be sampled even if they are not the most contaminated areas. Analysis of risk also requires lower detection limits and analysis of specific parameters. Investigators are not often aware of these requirements and therefore do not take them into account when planning sampling and analysis of sites. To prepare for a risk assessment, a risk assessor must have input into the site investigation planning process to provide data needed and to avoid resampling or reanalyzing samples.

This chapter provides information needed for site investigators to anticipate and plan for risk assessment in a soil sampling program for a petroleum contaminated site. However, the information is relevant for any site that requires remediation. It includes a discussion of the issues and factors that should be considered when planning a sampling strategy, and investigates statistical methods and analytical approaches that may be helpful in assessing petroleum contamination at large active sites.

The performance of risk assessment specifically on petroleum contaminated soils requires the use of appropriate toxicity values for petroleum products or component chemicals. Many of these values are not currently available. In addition, some analytical techniques that are commonly used at many petroleum sites employ a parameter, TPH, which is not useful in health risk assessment.<sup>1</sup> The chapter briefly discusses the recent development of alternative parameters and analytical techniques that may revolutionize the whole process of risk assessment at petroleum contaminated sites.

The chapter is organized into categories of issues that should be considered when preparing a sampling plan for the risk assessment and site investigation of a site. Areas include statistical, exposure, analytical, and regulatory considerations. The paper concludes with recommendations, where possible, and suggestions for incorporating risk assessment needs into the sampling plan for petroleum contaminated site 5.

## OBJECTIVES

Most site investigators define the objectives of a study to be nature and extent of contamination, determined with the lowest number of samples, usually based on screening or professional judgment (guessing). However, four principal questions must be answered in the data collection and evaluation phase for risk assessment:<sup>2</sup>

- What contamination is present and at what levels?
- Are site concentrations really different from background?
- Are data adequate to identify and examine all exposure pathways and exposure areas?
- Are data adequate to fully characterize all exposure areas?

Answering these questions requires more than simply defining the nature and extent of contamination. Sampling for risk assessment must consider how and where human and ecological receptors might be exposed, how to represent contamination at the site, and how many samples can adequately provide the information necessary to estimate risks.

Site investigators who take into account risk assessment issues typically have to weigh the available resources against the need to locate "hot spots," to provide representative site sampling, to provide representative background samples, and to quantify sampling error. Together, site investigators and risk assessors should determine the sampling strategy or combination of strategies that best serve the data quality needs of risk assessment. A combination of statistically based and purposive sampling can often provide samples representative of a site and of the background.<sup>2</sup> Whatever sampling approach used, if it involves professional judgment, it may be subject to criticism.

## STATISTICAL CONSIDERATIONS

Risk assessment requires that the sample data be unbiased, representative, and adequate to generate meaningful statistics. The following steps should be taken to provide precision and representativeness in a soil sampling plan:<sup>3</sup>

- Identify objectives of study. They should reflect specific information required to make decisions.
- Detect components of variability in the data. Possible sources of variability include sample collection, sample preparation, analysis, and data processing.
- Choose a desired confidence level. The confidence level represents the probability that the collected data represent the average exposure conditions and extent of contamination. A confidence level of 95% or better should be attained to provide the quality of data needed for risk assessment and for future potential litigation.

The areas to be surveyed should be divided into areas of concern (stratified) and sampled according to a design that can be used to determine spatial variability of the concentration data. Areas of concern can be defined on the basis of:<sup>4</sup>

- different chemical types,
- different anticipated concentrations or hot spots,
- different release sources of concern,
- different anticipated spatial or temporal variability of contamination,
- higher or lower cost to sample, and/or
- different exposure potentials.

By stratifying the number based on exposure areas and developing a soil sampling approach that determines samples necessary to provide unbiased risk assessment data, the data collected will be representative and relatively accurate, to the level of precision needed for risk assessment.

## Soil Sampling Approaches

The soil sampling approach can focus collection of data for risk assessment. Choosing the best approach for the site and the situation can be efficient and economical by meeting statistical requirements for sample location and number of samples taken. Most site investigators only utilize judgmental (purposive) or biased sampling when there are actually two categories of soil sampling. These are purposive and statistical sampling as discussed below.

Purposive, biased or judgmental sampling is employed when samplers are confident that the location, type of pollutant, time frame of contamination and geologic characteristics are known.<sup>5</sup> This type of sampling may over- or underestimate the true conditions of exposure and extent of contamination at the site. Judgmental sampling is often biased and provides little useful information on spatial variation. Therefore, sampling locations within areas of concern only sampled purposively will not fulfill risk assessment requirements. If the sample design is purposive, the sampling error cannot be determined and estimates of the average concentrations of analytes may not represent the site.

The statistical distribution of the observed chemical data directly influences estimation of exposure point concentrations and risks. The estimation of variability and confidence intervals becomes difficult if the data are not normally distributed or do not approximate normal when subjected to a log transformation.<sup>2</sup>

Statistical sampling is based on statistical variability of the data and the confidence level, two related components. The sampling strategy should determine the number of samples needed to achieve a desired confidence level based on the variability of the data. A statistical model, which may be simple or complex, depending on the circumstances, may determine sample location in the most efficient manner.<sup>5</sup>

There are three types of statistical sampling:

Simple random sampling is a strategy where the sample locations are decided randomly. The advantages of random sampling for risk assessment are that data can be averaged and used to estimate the average concentration for a whole area of concern, the uncertainty and distribution of the data are easy to calculate; and it reduces the likelihood of sampling all high or low concentrations. However, random sampling is too resource intensive from a site investigator's point of view.

Stratified random sampling involves subdivision of the sampling universe into horizontal or vertical strata based on exposure potential or contamination, as mentioned above, and sampling randomly within those strata. Appropriate choice of strata leads to more efficient use of sampling resources compared with simple random sampling when prior knowledge is available.

Systematic sampling involves collecting samples in a regular pattern (triangular or grid) over the area of investigation. The starting point is established randomly, and samples are collected at regular intervals along transects. The spacing is determined based on variance and desired confidence levels.<sup>6</sup> Systematic sampling is preferable to other types for small areas for economic reasons. Statistical characterizations can best be done with data collected systematically. The disadvantage with systematic sampling is that special variance calculations are required to estimate confidence limits.

Table 1 summarizes sampling types described above and compares their strengths and weaknesses.

Figure 1 illustrates sampling schemes graphically.

#### Taking Enough Samples

There are two reasons to ensure that enough samples are collected and analyzed at a site and that sampling is representative. First, enough unbiased samples must be analyzed to generate a mean concentration (or several mean concentrations for different strata) to represent potential exposures to chemicals at the site (an exposure point concentration). Second, enough samples must be collected to delineate the volume of contaminated soil for remediation. Too few samples could overestimate risk, and inflate the amount of soil that exceeds the cleanup targets established for the site.

Table 1. Strengths and Weaknesses of Unbiased Sample Design

SAMPLE DESIGN	STRENGTHS	WEAKNESSES
Biased (judgmental, purposive)	<ul style="list-style-type: none"> <li>• Uses knowledge of location</li> <li>• Uses limited resources</li> <li>• Can be done quickly</li> </ul>	<ul style="list-style-type: none"> <li>• Inability to calculate uncertainty</li> <li>• Decreases representativeness</li> <li>• Increases probability of false negatives</li> </ul>
Unbiased (random, systematic grid, geostatistical)	<ul style="list-style-type: none"> <li>• Able to calculate uncertainty</li> <li>• Representativeness</li> <li>• Reduces probability of false negative</li> </ul>	<ul style="list-style-type: none"> <li>• Resource intensive</li> <li>• May require statistician</li> <li>• Time consuming</li> </ul>

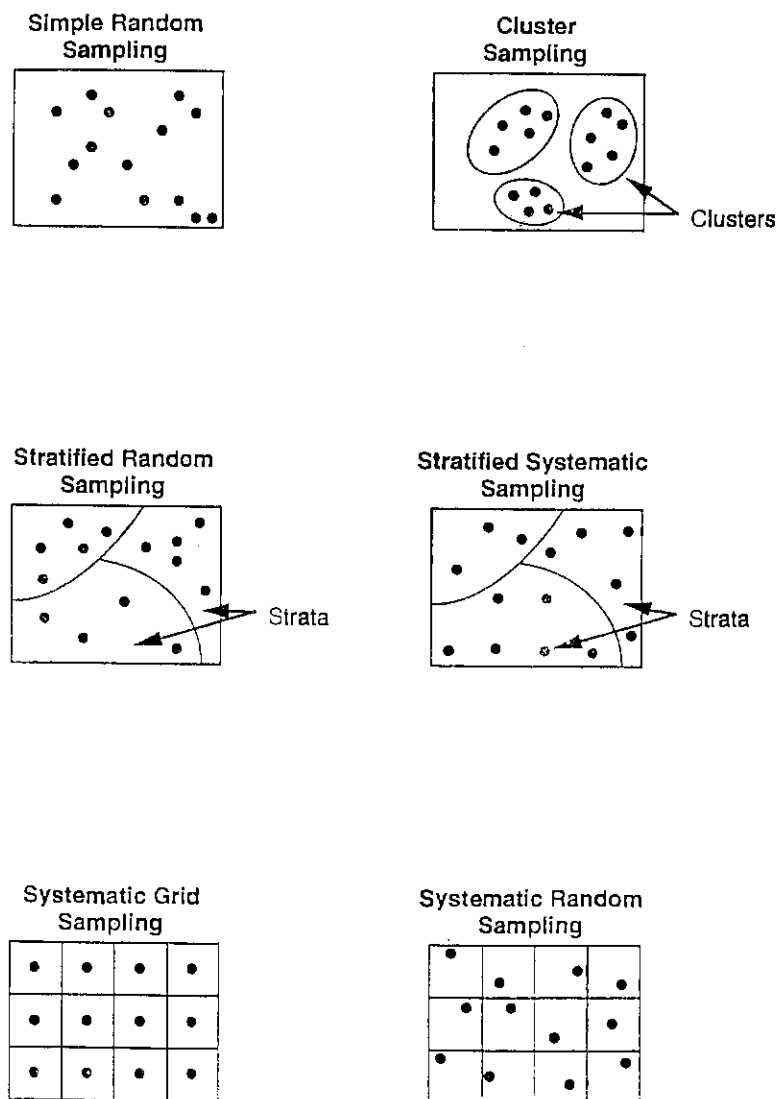


Figure 1. Common sampling designs.

Several issues should be considered when determining the appropriate number of samples necessary for a risk assessment. They include the number of exposure areas to be sampled, statistical performance of data collected, number of background samples needed and practical considerations of logistics and cost.<sup>4</sup> Of these the most critical factor is statistical performance. Which depends on the variability in the chemical concentrations reported in a medium. To reduce variability when chemical concentrations vary greatly, increase the number of samples or stratify the medium. This narrows statistical confidence intervals, thus providing more power.<sup>2</sup> Additional important considerations are the acceptable percent of false positives (Type I errors) and false negatives (Type II errors) and representativeness of potential exposures.<sup>3</sup>

The total variability in chemical concentration can be reduced substantially by subdividing the site into areas of concern. Highly variable concentrations found in only a few samples can result in uncertainty in calculating means, difficulty in defining the data distribution, and artificially high upper confidence limits (much higher than the mean). Dividing the site improves the statistical performance of the data collected to generate exposure point concentrations and results in a more accurate assessment of the site. Areas of concern do not have to account for the entire site if site-wide clean up targets do not have to be determined.<sup>4</sup>

Sampling within areas of concern should be representative and the sampling design should specifically address relevant exposure pathways. The number of samples in each zone should be proportional to the area of the zone. Take enough samples to adequately define the extent of contamination. Structure sample design to identify and characterize hot spots. Whatever sampling approach is chosen, the samples should be mapped using a grid to accurately describe and record sampling locations.<sup>2</sup> Table 2 shows relationships between the statistical performance (a gauge of the certainty that the data collected represents conditions at the site) and number of samples required. Statistical performance measures confidence level, power, and minimal detectable relative difference between site and background concentrations. The minimum recommended performance measures for risk assessment purposes are 80% confidence and 90% power. The table shows the minimum number of samples necessary to meet those requirements.

Some compositing of samples may decrease the number of analyses needed to estimate an average concentration. However, limit compositing and always supplement composite samples by several individual samples. While the average concentration can use composite data, the range of concentration cannot be determined from a composite sample. This may be appropriate if areas can be identified that are subject only to trespasser use.<sup>8</sup> Composite samples only count as one sample when generating statistics.

#### Background Samples

Enough background samples must be taken to establish that there is no difference between chemical concentrations on the site and chemical concentrations of the site at the desired confidence level. Early sampling and analysis of background samples will indicate how easy it will be to discriminate background levels from on-site contamination, and whether more sampling is needed. Background samples should be collected and analyzed prior to the final determination of the sampling design, since the number of samples necessary is significantly reduced if little background contamination is present.

Table 2. Relationships Between Measures of Statistical Performance and Number of Samples Required

Coefficient of Variation(%)	Power	Confidence Level (%)	Samples Required to Meet Minimum Detectable Relative Difference	5 %	10 %	20 %
10	95	90		36	10	3
15	95	90		78	21	6
20	95	90		138	36	10
25	95	90		216	55	15
30	95	90		310	78	21
35	95	90		421	106	28

Note: This table provides the number of samples required in a one-sided one-sample t-test to achieve a minimum detectable relative difference at confidence level and power. The coefficient of variation is based on geometric mean for transformed data.

More background samples are required when contamination exists in more than one medium. This is also true when expected variation in chemicals of concern is high and confirmed by actual data, or when relative differences between site and background are small and site concentrations of concern are low.<sup>2</sup>

Take a minimum of one background sample per medium. Small numbers of background samples increase the probability of false negative errors (i.e., that no difference exists between site and background when a difference does, in fact, exist - Type II Errors).<sup>2</sup> Rigorous statistical analyses involving background samples may be unnecessary if site and non site-related contamination clearly differ.

#### Statistics Needed

No statistics are prescribed by any guidance documents reviewed to generate mean concentrations but are strongly encouraged by all for developing a sampling plan. At a minimum, a confidence level of 95% or better around the mean is necessary for risk assessments under federal jurisdiction and for states following the EPA's lead. The goal of the sampling plan should be to obtain samples with the smallest variance and therefore the greatest precision. Because statistics should be used to determine precision, the best insurance for a good sampling plan is to rely on a professional statistician. Important statistical considerations for a sampling plan to reach these goals are Type I and II errors, accuracy and comparability, and representativeness.

Use a Student's t-distribution table to decide minimum number of samples required to achieve precision and a specified confidence level with a known coefficient of variation. Much information on this topic is provided in Data Useability for Risk Assessment Guidance.<sup>2</sup>

#### Geostatistics/Kriging

Statistics have been described that can achieve reliable and representative data for risk assessment. Statistics can also find the volume of contaminated soil and the extent of remediation necessary to achieve cleanup targets established with risk assessment. The main application of geostatistics in environmental cleanup is to estimate the concentrations of a chemical in soils to be excavated and remediated. Its most practical and beneficial application is to produce a map of soil contamination that, when used, can save significant expense at sites with high remediation costs associated with excavation of soil. Geostatistical analyses produce a map of estimated chemical concentrations and a report summarizing the volumes of clean and contaminated soil, and the volume of clean soil that has to be removed to reach contaminated soil. A geostatistical process called kriging (after "Krige") produces not only an estimated concentration map, but also a map of theoretical estimation error. These two maps can be used to produce a sampling plan optimized for the mean and the extent of contamination with or without a cost-benefit analysis. For large sites with potentially costly remediation, geostatistics can be used to design a cost-efficient sampling program and to reduce the volume of soil that must be excavated and remediated, thereby reducing sampling, and remediation costs.

Kriging generates an error map for the site after collecting and analyzing samples, showing the confidence in the data collected, and a concentration map showing locations of reported concentrations. These two maps are superimposed to show areas

of error near target concentrations, where additional sampling could better characterize an area of the site, improve confidence in the data and reduce the volume of soil needed to be remediated to achieve a cleanup goal. Kriging also allows testing the impact of additional individual samples on confidence before collecting the sample. By using kriging, a site investigator can identify areas requiring cleanup, more sampling, or no action. The area to be cleaned up is delineated by average concentrations above a risk-based soil cleanup target. Kriging can therefore be used concurrently with risk assessment.<sup>8</sup> Figure 2 shows an output map of a kriging analysis. The figure is an isomap of the lead pollution around a lead smelter. The lines are isopleths of soil lead in  $\mu\text{g}/\text{g}^{-1}$ .

Geostatistical sampling design followed by kriging analysis will calculate the fewest samples necessary for the desired precision and get the least variable average estimates from the available data. The minimum number of samples estimated in this way may still be more than expected or affordable within budget.<sup>8</sup> However, application of geostatistics to large sites where anticipated remediation costs are large may be cost effective.

Several texts and articles describe geostatistics, kriging and their application to soil sampling. Some of these are: Burgess and Webster (1980a, b, and c),<sup>9-11</sup> Burgess et al. (1981),<sup>12</sup> Journel and Huijbregts (1978),<sup>13</sup> and U.S. EPA (1988).<sup>14</sup>

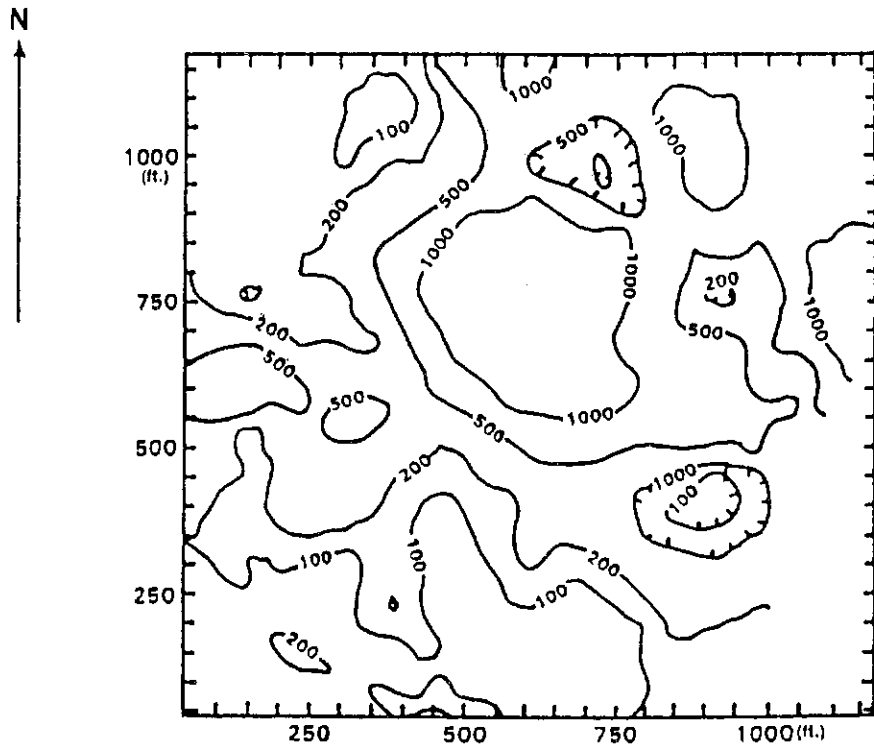


Figure 2. Example of a kriging map.

## EXPOSURE CONSIDERATIONS

Risks need only be assessed for areas actually used by people. This is often overlooked in the site investigation, and consequently, sampling efforts often do not produce the data necessary to characterize exposures at a site. Instead, data from heavily contaminated areas are often the only data available to generate exposure point concentrations. This greatly overestimates risks and makes focusing on specific exposure areas difficult. All exposure pathways and exposure areas should be identified and examined before the sampling plan is designed. Current and future exposure pathways may be limited to particular areas of the site. Focusing the sampling on these areas improves the precision and accuracy of the data supporting risk assessments. Risk assessment requires characterization of each exposure area. Data from other areas may not represent exposure conditions actually experienced by receptors. Therefore, data from areas outside exposure areas may be excluded when choosing the chemicals of potential concern and from the estimation of exposure point concentrations.<sup>2</sup> Depending on the active areas of the site, relevant exposure pathways and potential receptors, only a small subset of the total number of samples collected at the site may be used for the risk assessment. Figure 3 demonstrates what can happen if exposure pathways are not identified before designing the sampling program.

### Hot Spots

Site investigators must keep in mind that risk assessors are interested in the potential exposure of receptors to contaminated portions of the site. Hot spots must be characterized well for remediation purposes, but for risk assessment, there is no assurance that a potential receptor would go directly to a hot spot. It is more likely that exposure to the site would be random, or restricted to certain areas of the site. Therefore, for the purposes of risk assessment, less contaminated areas should be characterized in addition to hot spots if they correspond to potential exposure. Including hot spot data in calculation of the mean artificially increases the exposure concentrations and resulting risks. Health risks associated with the site as a whole will be grossly overestimated. This may affect risk-based cleanup targets and estimates of the volume of soil to be remediated to meet those targets effectively.<sup>6</sup> A strategy that stratifies the site and analyzes the areas separately can characterize hot spots. Systematic and geostatistical design approaches discussed earlier provide the best approach to hot spot identification.

### Potential Receptors

The primary receptors on a petroleum site might be employees who work there. Since this population may be present daily, for long periods, its potential for exposure to contaminants on the site is high. However, if the active areas are not the contaminated areas, an assessment of their exposure should show that. This can only be done if data are collected in active areas, even if they are not heavily contaminated.

Other potential receptors at an active petroleum contaminated site may be construction workers, utility workers, site trespassers, and nearby residents (adults and children). The site investigator and risk assessor must consider how and where these potential receptors could be exposed to contaminants associated with the site. The



characterization of potential receptors influences the exposure areas, the soil depths of interest, the exposure pathways analyzed, and the exposure factors used.

### ANALYTICAL CONSIDERATIONS

Petroleum products are complex mixtures of hundreds of thousands of chemicals, each with its individual toxic effect. For many sites the identity of the fuel product is unknown. In addition, toxicity information is only available for some pure products. However, once a petroleum product is released to the environment, changes in composition occur as a result of hydrolysis, photolysis, biodegradation, biotransformation, physical breakup and dissolution. It is therefore very difficult to know the composition of weathered products and to assess the toxicities associated with them.

It is important to choose analytical methods and detection limits appropriate for risk assessment. The quality of data obtained through the different analytical methods varies and may or may not be appropriate. Three general types of analytical procedures generate environmental data. They are analyses conducted in fixed laboratories, procedures conducted in the field using the same equipment as in fixed labs, and field screening. The appropriate method depends on the contaminants present at the site, the medium contaminated, the age of the contamination, and the budget.

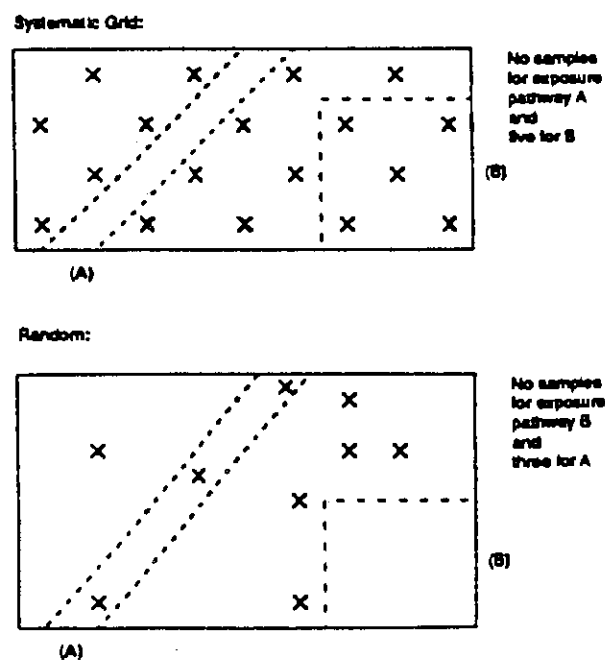


Figure 3. Examples of sample design missing exposure areas of concern.

Generally, analyte-specific methods that provide good quantitation should be used once potential chemicals of concern have been identified. Analytical method detection limits must be well below concentrations of chemicals found at the site. States prefer certain laboratory methods for detection of petroleum-related components.<sup>17</sup>

### Field Analysis vs. Fixed Laboratory Analysis

For many sites, field analyses can provide useful data for risk assessment. These analyses provide semi-quantitative results, often free of significant matrix interference, which can be confirmed by laboratory analysis. Instruments used in the field may be field GC, X-ray fluorescence (XRF), or organic vapor analyzer (OVA). With field analyses, greater numbers of samples can be analyzed with very short holding times. The precision and accuracy of field analyses may be lower than fixed laboratory analyses, but the quicker turnaround and the possibility of analyzing more samples make up for this. Fixed laboratory analyses are most appropriate for broad spectrum analysis and should also be used to confirm findings of field analyses.<sup>2</sup> Table 3 compares the strengths and weaknesses of field and fixed laboratory analysis for analyzing organic contaminants in soil. The table shows that fixed laboratory analyses are generally more precise and accurate than field screening methods.

### Sample Quantitation Limits

Choosing the analytical methods to increase detection limits is fundamental to the useability of analytical data in risk assessments. Detection limits for risk assessment must be in the low ppbs, and method-specific and sample detection limits must be documented. Risk assessment often requires a quantitation limit at or below the detection limit for routine methods for many chemicals of toxicological concern. The closer the concentration of concern is to the detection limit, the greater the possibility of false negatives (Type I) and false positives (type II) errors.<sup>2</sup>

### Identification and Aging of the Petroleum Product

Sampling alone cannot identify a petroleum product that has been subject to weathering for long periods. In cases where sites have been active for many years, historical records may record the products used. For the purposes of risk assessment, this question is not particularly important because the risk assessment is not done on historical usage of the site, instead the critical issue is the contaminants present in the soils today and potentially present in the future. If petroleum was used at the site, degradation and weathering processes have altered the components so that they no longer have the same toxicological qualities. This is important when deciding what analyses to perform because it is probable that most of the volatile components of the product have long since dissipated.

The date of contamination is relevant to risk assessment in that it provides some insight into how much weathering is likely to have taken place and, by that, how much of the aromatic or aliphatic hydrocarbons may be present. This information can be obtained through sampling for BTEX, and PAHs.

Degradation rates of different petroleum hydrocarbon classes vary, with rates decreasing as molecular mass and degree of molecular branching or substitution increases.<sup>16</sup> Regulators also prescribe analytical methods and cleanup standards based on presumed identities of contaminants.

### Choosing Analyses

Risk assessment requires testing for analyte-specific parameters. This is a problem for sites contaminated with any petroleum product. TPH does not provide data useable for risk assessment as it is not a specific parameter. TPH may be the sum of benzene, toluene, ethylbenzene and xylene (BTEX), groups of compounds (primarily aliphatics), or the entire range of petroleum hydrocarbons from C4 to C32, and petrogenic as well as phytogetic hydrocarbons.<sup>1</sup>

Testing for PAHs or BTEX may or may not result in detection, depending on the age and identity of the product in the soil. However, toxicity values are available for BTEX and PAHs and assessment of risk can be performed using these groups of chemicals if they are reported. The real problem at petroleum sites is how to characterize the mass of hydrocarbons not characterized by BTEX or PAH analyses. If these target compounds are not detected or only detected at very low levels, many other hydrocarbons may be tentatively identified, indicating a large uncharacterized mass of petroleum product with no known toxic characteristics. If the toxic components identified are removed, is the site clean? If the product has been weathered to the extent that its toxic components are no longer present, how can health-based cleanup targets be estimated? Four types of analytical parameters that show petroleum contaminations are discussed below.

Table 3. Comparison of Analytical Options for Organic Analytes in Soil

Method	MDL	Quantitative Confidence	Timeliness	Precision & Accuracy	Comparability
<b>Fixed Laboratory</b>					
CLP RAS					
VOA		✓			✓
BNA		✓			✓
Pesticides					✓
Dioxin (2,3,7,8 TCDD)		✓		✓	✓
<b>SW846</b>					
GC	✓				✓
VOA		✓			✓
BNA		✓			✓
<b>1600 Series</b>					
GC	✓			✓	✓
VOA		✓		✓	✓
BNA		✓		✓	✓
Dioxin		✓		✓	✓
<b>Field Screen</b>					
GC (PCB)	✓	✓	✓		✓
GC (Pesticides)			✓		✓
GC (VOA)	✓		✓		✓
GC (Soil Gas)	✓		✓		✓
GC (BNA)	✓		✓		✓
PHOTO VAC					
Detector			✓		

Key: ✓=Method strength

### Total Petroleum Hydrocarbons

Total Petroleum Hydrocarbons (TPH) can be quantified using several different analyses. The parameter estimates the total concentration of petroleum hydrocarbons in a sample. TPH may represent BTEX, groups of compounds or the range of petroleum hydrocarbons from C4 to C32. TPH could potentially represent combinations of chemicals with different toxicities, or chemicals with no known toxicity, and as such, the health effects associated with exposure to TPH cannot be determined. Therefore, the parameter TPH cannot be used for risk assessment. It should be supplemented with analysis for PAH and BTEX. More information has to be provided about the petroleum-related compounds present in the sample. Yet TPH standards exist in almost every state in the country. Most of these standards are not health-based.

In a petroleum contaminated site, TPH concentrations in the soil can inexpensively and effectively indicate the extent of contamination but alone will not provide useful information for the risk assessment. In addition, a recent study found an average concentration of 306 mg/Kg in a survey of urban, nonindustrial soils.<sup>17</sup> This concentration is three times higher than the commonly applied regulatory cleanup standard of 100 mg/Kg. Care should be taken when analyzing for TPH, as it may be difficult to distinguish the site-related contamination from background.

### Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are significant components of petroleum products but for a number of reasons may not be the optimal parameter to use for risk assessment. PAHs are present to a greater or lesser extent dependent on the type of petroleum product and the age of the product in the soils. Sometimes, PAHs may be the only target compounds still present in the soils. Risk assessment methods can yield risk-based cleanup levels for PAHs that range from 0.1 to 0.7 mg/Kg.<sup>17</sup> Care must be taken in sampling and analyzing for PAHs. Risk-based cleanup targets in urban areas should be compared with typical urban background levels before implementing remediation based on what may be unrealistically low cleanup targets.

Because of the conservative (health-protective) assumptions used in risk assessments, very low risk-based cleanup targets for PAHs have been set by several states. Michigan, for example, lists soil cleanup standards of 0.33 mg/Kg for carcinogenic PAHs.<sup>17</sup> New Jersey has a soil cleanup standard for benzo(a)pyrene in residential and nonresidential soil of 0.66 mg/Kg. Massachusetts' soil cleanup standard is 0.7 mg/Kg for all carcinogenic PAHs.<sup>18</sup>

A recent study sampled surficial soils in nonindustrial urban locations in New England and analyzed them for PAHs. Average concentrations of total PAH were measured at 22 ppm for samples collected within four to six feet of a road and eight ppm for samples not near the pavement. The highest concentration measured was from a street corner in Boston.<sup>16</sup> This study suggests that urban background levels of PAHs are very high.

This study also implies that sampling for PAHs at sites in urban areas may require additional sampling to distinguish the site-related contamination from background, and might inflate the volume of soil above nonsite-specific cleanup goals set by the states.

Although high background levels of PAHs may interfere with calculating health risks, with additional sampling, risks can be estimated for concentrations above background. Site-specific soil cleanup targets estimated with risk assessment would consider this.

#### *Benzene, Toluene, Ethylbenzene and Xylene*

State cleanup standards often exist for benzene, toluene, ethylbenzene and xylene (BTEX). These contaminants are constituents of petroleum products, although for many petroleum products they are minor components. BTEX can be analyzed easily and inexpensively, and toxicological values are available. Risks can therefore be estimated for BTEX reported at a site. However, BTEX is, depending on the age of the spill, most likely to degrade. BTEX left in the soil may have little relationship to the petroleum hydrocarbons still left in the soil. BTEX should be analyzed with PAHs to account for as much petroleum-related toxicity as possible.

#### *TICS*

Tentatively identified compounds (TICs) are nontarget compounds reported in the analysis of samples by GC-MS, but for which the instrument was not calibrated. TICs are identified by comparing the mass spectrum from the sample to a computerized library of mass spectra. Spectra similar to the TIC are ranked and scored for their similarity to the TIC. If TICs are reported as specific compounds, they are usually compounds whose spectra are found in the library search. Quantitation of TICs is highly uncertain because the samples were not calibrated for the specific compound tentatively identified.

The confidence in the identification of TICs can be increased if an analytical chemist reviews the computer's identification of compounds and eliminates false positive identifications. Comparison of TICs to chemicals historically used at the site, historical data, and other laboratories' data can also improve confidence.

Many classes of petroleum components will appear as TICs, such as aliphatic hydrocarbons and PAHs. In a sample known to be contaminated with diesel, analysis for organic chemicals may indicate a series of TICs as aliphatic hydrocarbons of increasing size. Identifying them to this point may be adequate if they are not carcinogenic. If PAHs are detected, they would be of greater concern and merit further analysis.<sup>2</sup> No procedure is currently recommended for assessing the risks of TICs. This is a large area of uncertainty in risk assessment of petroleum contaminated soils.

### REGULATORY CONSIDERATIONS - JURISDICTION OF THE SITE

The jurisdiction of a site dictates the options available for soil sampling, analysis, and risk assessment. Under federal jurisdiction, the guidelines for site investigations have been put forward in many guidance documents. The main differences arise when a site is under RCRA or CERCLA. The states have different rules but many of them follow the lead set by the U.S. EPA and states like California, New Jersey and Massachusetts. Most states' cleanup standards provide leeway enough so that risk assessment may be performed at individual sites.

### RCRA vs. CERCLA

The goal in RCRA corrective action is "to eliminate significant releases from solid waste management units that pose threats to human health and the environment and to clean up contaminated media to a level consistent with reasonably expected and current uses. This rule explicitly provides the EPA with authority to require source control."<sup>19</sup>

Investigations under RCRA focus on specific units, releases and exposure pathways identified by EPA to be of concern. The scope and complexity of RCRA Facility Investigations (RFIs) depend on the nature and extent of the contamination, whether releases have migrated beyond the facility boundary, the amount of existing information on the site and the likely risk at the site.<sup>19</sup>

CERCLA generally authorizes activities in situations where contamination has occurred at sites that are not under control of a RCRA owner or operator. Where contamination is related to activities at hazardous waste facilities that are currently operating or have conducted treatment, storage, or disposal of hazardous waste any time since November 19, 1980, both RCRA and CERCLA potentially apply.<sup>19</sup>

### Petroleum Policies of State Agencies

Many states have identified cleanup levels based on specific levels of TPH. In most states TPH standards are not health-based. These standards are summarized in Oliver and Kostecki.<sup>17</sup> The states often specify the detection level and laboratory method required and often provide the cleanup level as a threshold, beyond which risk assessment can be used to estimate site-specific cleanup levels.

The interim Massachusetts Petroleum Policy (WSC-94-400) identifies an alternative to the TPH parameter that can develop health-based cleanup standards or to conduct site-specific risk assessments. It also identifies dose-response values to be used with these analytical parameters. The new policy is applicable to petroleum products including gasoline, diesel fuel, no. 6 fuel, jet fuel, kerosene, (crankcase oil and waste oil are contaminated with additives and their toxicity is not addressed in the policy.)

The Massachusetts Petroleum Policy proposes to divide petroleum hydrocarbons into subgroups based on the number of carbon atoms in the molecules. For each subgroup, a "reference compound" is identified, usually chosen for well-characterized toxicity. The policy identifies an oral reference dose (RfD) or carcinogenic slope factor (CSF) for each reference compound.<sup>1</sup>

The policy recommends analyzing soil samples with gas chromatography (GC), photoionization detector (PID) and flame ionization detector (FID). The mass of petroleum hydrocarbons quantified in each segment of a chromatogram is converted to a medium-specific concentration that can then be entered into standard risk assessment equations to arrive at a risk associated with petroleum hydrocarbons. The Massachusetts approach does not address additives to fuel products (such as MTBE, EDB, etc.). The contribution of these compounds is subtracted from the total mass of hydrocarbons quantified in the chromatogram.<sup>1</sup>

The Massachusetts Petroleum Policy proposes an alternative to the TPH parameter whose associated risks can be assessed along with BTEX and PAH. In addition, the parameter also assigns toxicological values to portions of the petroleum hydrocarbons, previously unassessed. This ensures that the mass of hydrocarbons are accounted for

and their toxicity assessed. The approach also eliminates the need to know the origin and type of fuel that was spilled. It uses the petroleum products currently present in the soil and avoids the uncertainty involved in calculating the risks due to the weathering of fuel products.

## RECOMMENDATIONS

For sites with petroleum contamination, such as railyards, health risk based remediation can be less costly and less time-consuming than cleanup to state guidelines. Where state guidelines may require excavation of large quantities of soil to achieve a site-wide remediation goal, risk-based cleanup can focus specifically on areas of potential exposure. Based on extensive review of the available guidance and discussions with other risk assessment professionals, the following recommendations are provided in order to incorporate risk assessment requirements into the surface soil sampling plans for the petroleum contaminated sites. Risk assessment requires that sampling completely define contamination at the site, and that results are comparable and representative of site conditions. The following recommendations specify the most efficient and cost-effective way that this can be accomplished.

### Sampling Approach Recommendations

- Involve a risk assessor from the beginning of the site investigation to ensure that risk assessment data needs are planned for and met throughout the project.
- Use purposive sampling for the preliminary site investigation and to select areas of concern, use an unbiased approach to locate sampling points within the areas of concern.
- Consider study objectives, sources of variability, and relative costs when choosing a sampling design.
- Divide the site into areas of concern.
- Structure sample design to identify and address hot spots.
- Regardless of sampling approach chosen, establish a grid system at the site to accurately describe and record sampling locations.
- Expand the number of sampling locations to a wider area or increase sampling density where data are sparse, and add or delete specific chemicals or indicator parameters.

### Statistical Recommendations

- Take enough samples to adequately define the extent of contamination and to provide meaningful statistics on the mean.
- Take a number of samples in each zone proportional to the area of the zone.
- Take at least one background sample in each medium, more if the levels of site-contamination are low.
- Beware of high background levels of PAHs!

- Samples should be truly representative of the situation under investigation.
- Determine the acceptable levels of Type I and Type II errors.
- Attempt to take accurate and comparable samples.
- Strive for precise data (repeatable results and reliable means and low standard deviations).

### Analytical Recommendations

- Request analyte-specific testing of samples. Risk assessment requires testing for analyte-specific parameters (e.g., SVOC, VOC, and metals versus TPH, total VOC, oil and gas, etc.).
- Use limited compositing to detect contamination over an area of concern with smaller number of analyses.

### Exposure Recommendations

- Remember that even unlimited access to the site does not restrict contact by trespassers or workers to highly or obviously contaminated soils. Therefore, risks estimated using only concentrations from those areas would be gross overestimates.

### Regulatory Recommendations

- Check with the agency that has jurisdiction over the site to verify that risk assessment is approved as a means of assessing risks and setting site-specific cleanup goals based on estimated health effects.
- Suggest to the agency that they review the Massachusetts Petroleum Policy approach as a means of assessing the risks of petroleum products in soils so that it can be used at the site.

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## Questions and Answers:

**Q.** I'm one of your slightly bored risk assessors that you mentioned here. I'm glad that you mentioned background and early involvement of a risk assessor. One thing that I was rather surprised about from my own experiences was that you have been able to exclude certain areas as being not subject to human use. The regulators have let you get away with this? In my experience everything is treated as though it was a residential property.

**A.** I guess it depends on the state regulations or the agency in charge. I would say that in certain areas you can definitely prove there's never going to be a house put on the site. There are all sorts of ways to do that. I would say we have done that but I don't have any specific examples.

**Q.** As a regulator, most regulatory agencies are very understaffed and my concern about using risk assessment would be that people evaluating the risk assessments would not have sufficient time or training to do it. The risk assessment would degenerate into an opportunity to make the figures show what you want them to show. What would you say about how the regulators could properly address this to make sure the risk assessments are used properly?

**A.** I can tell you a little bit about Massachusetts. There's an office in Boston that is the main headquarters for the DEP. They have an Office of Research and Standards and they are the gurus of risk assessment in Massachusetts. I think what they have tried to do is hold seminars and go out and teach other people in the regions. I would say there's probably one person or a couple of people in each state that know what risk assessment is. When they hear that a risk assessment is happening somewhere in the state they probably want to get involved and they probably should be involved early.

## **CHAPTER 10**

### **Closure of a Diesel Fuel Contaminated Site Using The Synthetic Precipitation Leachate Procedure**

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#### **INTRODUCTION**

Diesel fuel impacted soil and groundwater were discovered during the removal of two underground storage tanks (UST) from an active railyard located in Nampa, Idaho. The residual soil impacts extend beneath active mainline tracks making remediation or removal extremely difficult and expensive. An approach for estimating the migration potential of the diesel fuel from soil to groundwater was developed. The approach is based on the composition of weathered diesel fuel and the migration characteristics and toxicity data of the diesel fuel constituents. Based on these considerations, the two elements of the approach are: 1) an evaluation of the migration potential of diesel fuel constituents in soil using the soil synthetic precipitation leaching procedure (SPLP); and 2) a health risk assessment of the diesel fuel groundwater impacts.

#### **APPROACH**

The composition of "non-weathered" - pure diesel fuel includes low molecular weight polycyclic aromatic hydrocarbons (PAHs) such as naphthalene, methyl-naphthalene, anthracene, fluorene, and phenanthrene (Kreamer, 1990, and USEPA, 1988). In general, PAHs can be grouped as follows (ATSDR, 1989):

- Low molecular weight compounds - naphthalene, anthracene, fluorene, and phenanthrene.
- Medium molecular weight compounds - fluoranthene and pyrene.
- High molecular weight compounds - benzo(a)anthracene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(a)pyrene, and chrysene.

Pure diesel fuel also contains low concentrations of volatile aromatic hydrocarbons (Kreamer, 1990 and USEPA, 1988) such as benzene, toluene, ethylbenzene, and xylenes (BTEX).

Under highly "weathered" conditions, as is often encountered at petroleum hydrocarbon contaminated sites, the composition of residual diesel fuel constituents changes considerably due to fate and transport processes. The fate processes that contribute to the "weathering" include: hydrolysis, photolysis, oxidation, reduction, and biological degradation processes (microbial metabolism). The transport processes that contribute to the "weathering" include adsorption to soils, leaching from soil into water, migration in groundwater, volatilization from soil and water into the atmosphere, etc. The fate and transport processes result in reduced soil and groundwater concentrations of the diesel fuel constituents (e.g., low molecular weight PAHs).

Based on these considerations, a sampling protocol was used which addressed the following objectives:

- Sample the areas of highest petroleum hydrocarbon impacts to obtain data regarding the worst-case soil leaching potential.
- Analyze soil, soil leachate and groundwater for Total Petroleum Hydrocarbons (TPH), BTEX, and PAHs.
- Collect quality assurance/quality control (QA/QC) data.

The data generated are compared to:

- General information on the fate and transport characteristics of PAHs and BTEX in soil. The fate and transport information is used in evaluating the migration potential of the soil PAHs.
- Published data regarding the partitioning of diesel fuel constituents (i.e., low molecular weight noncarcinogenic PAHs) into water using pure (non-weathered) diesel fuel. The published data are used in evaluating the migration potential of the soil PAHs.

## BACKGROUND

The central section of the Nampa railyard encompasses approximately five city blocks within a municipal area. Residential, commercial, and industrial areas border the railyard. The property is relatively flat, gently sloping to the northwest. The railyard itself is slightly raised above the surroundings because of the fill material used to support the tracks. This railyard has been active since the early part of the century.

The diesel fuel soil and groundwater impacts are associated with two former UST sites within separate areas of the railyard. The approximate locations Areas 1 and 2 within the railyard are depicted on Figure 1. The diesel fuel impacts in Area 1 are primarily situated north of the former tank berth (Figure 2). Active rail-spurs traverse the impacted area. The diesel fuel impacted soils in Area 2 are primarily situated north of the former tank berth (Figure 2). Active rail-lines traverse the impacted area. These rail-lines provide a main-line corridor for rail traffic through the region. The location of these main-line tracks therefore constrains the over-excavation of the impacted soils.

As is typical for petroleum hydrocarbon releases, the initial site characterization investigations included laboratory analyses for TPH and BTEX in soil and groundwater. The boring and well locations are depicted on Figure 2. Provided in Table 1 are the detection frequencies and the range of soil analytical results. The soil TPH concentrations ranged from below the method detection limit (MDL) to 7200 mg/Kg. Low concentrations (< 1.0 mg/Kg) of BTEX were detected in soils situated within the most highly impacted areas. BTEX was not detected in groundwater above MDLs. No separate phase petroleum hydrocarbons were observed in the wells. A majority of the diesel fuel impacts are situated at depths 12 to 16 feet below the ground surface (at the groundwater table), with the exception of the soils situated within the immediate proximity of the former UST sites.

The TPH soil concentrations exceed the current UST standards. The purpose of the methodology was to obtain site specific supporting data concerning the limited migration potential of weathered diesel fuel constituents from soil to groundwater for regulatory agency review.

## GEOLOGY AND GROUNDWATER CONDITIONS

Fill materials and rail ballast which includes silts, sands and gravel, coal, and various aggregate were encountered at the surface to approximately 8 to 10 feet below the ground surface during drilling. A dark grey clay with silt nodules was observed at depths of approximately 8 to 12 feet below the ground surface. Alluvial materials consisting of sands progressing to sands and gravels were encountered from approximately 12 to 16 feet (total depth) below the ground surface.

**Table 1. Diesel Fuel Delineation Analytical Results - TPH and BTEX**

Constituent	Soil Concentration Detected (mg/Kg)			
	Area 1		Area 2	
	Detection Frequency	Range	Detection Frequency	Range
TPH	7 / 19	BDL - 1,500.0	5 / 29	BDL - 7,200.0
Benzene	0 / 19	BDL	1 / 29	BDL - 0.100
Toluene	2 / 19	BDL - 0.006	2 / 29	BDL - 1.280
Ethylbenzene	3 / 19	BDL - 0.200	1 / 29	BDL - 3.100
Xylenes	4 / 19	BDL - 0.011	8 / 29	BDL - 8.300

BDL - Below Method Detection Limit.

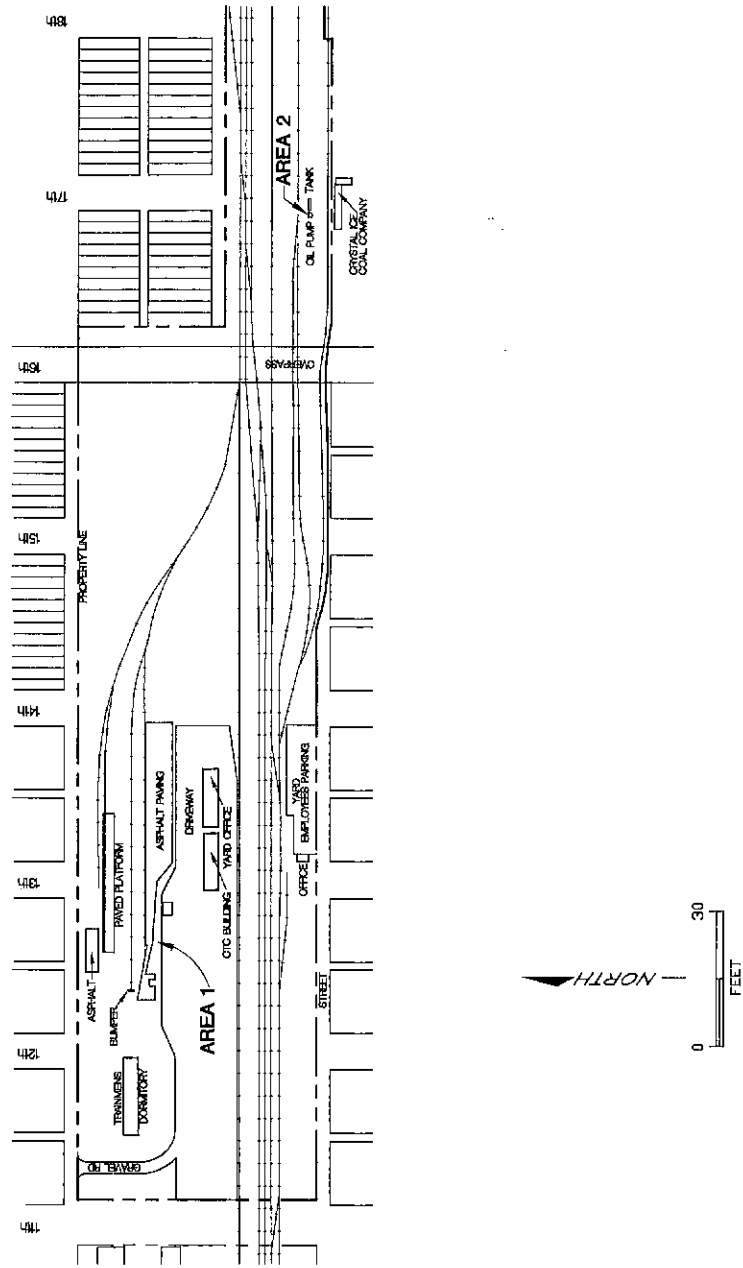


Figure 1. Locations of Areas 1 and 2 within the railway yard.

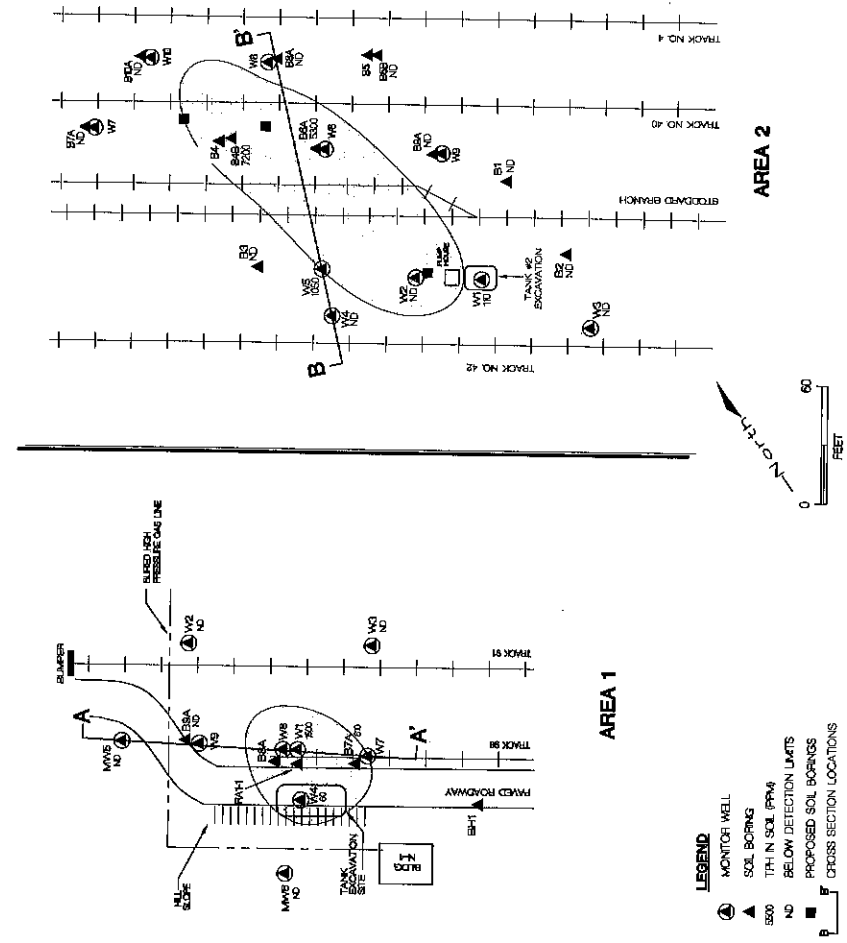


Figure 2. Diesel fuel impacts in area 1 and 2.



Depth to groundwater at the site ranges from approximately 10 to 12 feet below ground surface (March 6, 1991 measurements). Piezometric surface maps for Areas 1 and 2 are provided in Figure 3. Groundwater flow is to the north with a gentle gradient of 0.20 feet per 100 feet.

No separate phase hydrocarbons were observed in wells situated in the central portion (i.e., the area of highest impacts) of the diesel fuel impacts. However, the alluvial coarse grained sands (encountered at depths of approximately 12 to 16 feet below the ground surface) sampled from the maximum impacted area during fate and transport investigation were observed during the drilling operations to be "coated" with residual petroleum hydrocarbons. The residual petroleum hydrocarbon impacts extended several feet under the current groundwater levels. Residual petroleum hydrocarbons were also observed during the drilling operations in the lower foot of the clay layer (encountered at depths of approximately 8 to 12 feet below the ground surface), and are likely due to the former movement of separate phase petroleum hydrocarbons during groundwater fluctuations.

### SYNTHETIC PRECIPITATION LEACHATE PROCEDURE

The soil SPLP (Method 1312) data were used to provide an indicator of the maximum PAH concentrations that might be present in the leachate migrating from the petroleum hydrocarbon impacted soils. The USEPA has developed batch test leaching methods to provide data concerning the leaching potential of soils or waste materials in the environment (USEPA, 1986). Method 1312 provides data for the environment present in an uncapped "mono-fill" subjected to acidic precipitation.

### FATE AND TRANSPORT ANALYTICAL PROTOCOL

The soil analytical protocol included TPH by Method 8015 - Modified for diesel, BTEX by Method 8020, and PAHs by Method 8270. The soil leachate (Method 1312) and groundwater analytical protocol included TPH by Method 8015 - Modified for diesel, BTEX by Method 8020, and PAHs by Method 8310. Method 8310 was used to obtain data with low MDLs. The MDLs were then compared to the Proposed Maximum Contaminant Levels or MCLs (*Federal Register*, 1990) for higher molecular weight - carcinogenic PAHs and the final MCL (*Federal Register*, 1992) for benzo(a)pyrene of 0.0002 mg/l (refer to Tables 4 and 5). The higher molecular weight PAHs were, however, not expected to be present in diesel fuel (Kreamer, 1990 and USEPA, 1988).

### FATE AND TRANSPORT ANALYTICAL RESULTS

The soil and soil leachate analytical results for Areas 1 and 2 are summarized in Tables 2 and 3, respectively. TPH and BTEX were not detected in the soil leachate above MDLs. PAHs were not detected above MDLs in the soil leachate, with the exception of low concentrations (i.e., less than 0.001 mg/l) of the following low to medium molecular weight noncarcinogenic PAHs:

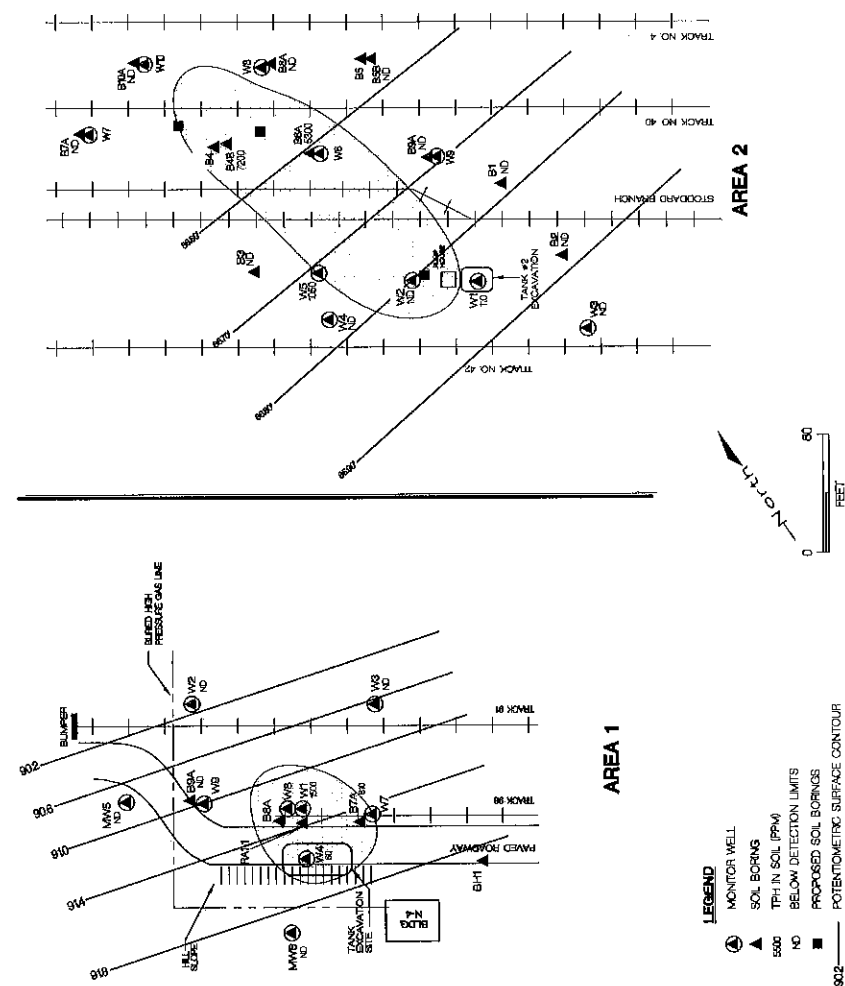


Figure 3. Piezometric surface maps of areas 1 and 2.

Table 2. Area 1 Soil and Soil Leachate Analytical Results - TPH and PAHs

CONSTITUENT	AREA 1 - CONCENTRATION DETECTED					
	Soil mg/Kg	Soil Leachate mg/l	Soil mg/Kg	Soil Leachate mg/l	Soil mg/Kg	Soil Leachate mg/l
	Area 1 / B1 / 8 feet	Area 1 / B1 / 10 feet	Area 1 / B1 / 10 feet	Area 1 / B1 / 14 feet	Area 1 / B1 / 14 feet	Soil Leachate mg/l
TPH - Diesel	< 5.0	< 1.0	5800.0	< 1.0	< 5.0	< 1.0
BTEX	< 0.0025	< 0.0005	< 0.0025	< 0.0005	< 0.0025	< 0.0005
Naphthalene	< 0.330	< 0.003	< 0.330	< 0.003	< 0.330	< 0.003
1-Methylnaphthalene	< 0.330	0.0038	< 0.330	0.0130	< 0.330	0.0033
2-Methylnaphthalene	< 0.330	< 0.003	< 0.330	0.0084	< 0.330	< 0.003
Acenaphthylene	< 0.330	< 0.003	< 0.330	< 0.003	< 0.330	< 0.003
Acenaphthene	< 0.330	< 0.005	0.48	< 0.005	< 0.330	< 0.005
Fluorene	< 0.330	< 0.0004	1.10	0.0029	< 0.330	< 0.0004
Phenanthrene	< 0.330	< 0.0003	2.90	0.0011	< 0.330	< 0.0003
Anthracene	< 0.330	< 0.0001	< 0.330	< 0.0001	< 0.330	< 0.0001
Fluoranthene	< 0.330	< 0.0003	< 0.330	0.0013	< 0.330	< 0.0003
Pyrene	< 0.330	< 0.0004	< 0.330	< 0.0004	< 0.330	< 0.0004
Benzo(a)anthracene	< 0.330	< 0.0001	< 0.330	< 0.0001	< 0.330	< 0.0001
Chrysene	< 0.330	< 0.0002	< 0.330	< 0.0002	< 0.330	< 0.0002
Benzo(b)fluoranthene	< 0.330	< 0.0001	< 0.330	< 0.0001	< 0.330	< 0.0001
Benzo(k)fluoranthene	< 0.330	< 0.0001	< 0.330	< 0.0001	< 0.330	< 0.0001
Benzo(e)pyrene	< 0.330	< 0.0001	< 0.330	< 0.0001	< 0.330	< 0.0001
Dibenzo(ah)anthracene	< 0.330	< 0.0003	< 0.330	< 0.0003	< 0.330	< 0.0003
Benzo(ghi)perylene	< 0.330	< 0.0004	< 0.330	< 0.0004	< 0.330	< 0.0004
Indeno(123cd)pyrene	< 0.330	< 0.0003	< 0.330	< 0.0003	< 0.330	< 0.0003

Table 3. Area 2 Soil and Soil Leachate Analytical Results - TPH and PAH

CONSTITUENT	AREA 2 - CONCENTRATION DETECTED					
	Soil mg/Kg	Soil Leachate mg/l	Soil mg/Kg	Soil Leachate mg/l	Soil mg/Kg	Soil Leachate mg/l
	Area 2 / B3 / 8 feet	Area 2 / B3 / 14 feet	Area 2 / B3 / 14 feet	Area 2 / B3 / 16 feet	Area 2 / B3 / 16 feet	Soil Leachate mg/l
TPH - Diesel	< 5.0	< 1.0	1300.0	< 1.0	< 5.0	< 1.0
BTEX	< 0.0025	< 0.0005	< 0.0025	< 0.0005	< 0.0025	< 0.0005
Naphthalene	< 0.033	< 0.003	1.50	< 0.003	< 0.330	< 0.003
1-Methylnaphthalene	< 0.033	< 0.003	< 0.033	0.0011	< 0.033	< 0.003
2-Methylnaphthalene	< 0.033	< 0.003	3.80	0.0011	< 0.033	< 0.003
Acenaphthylene	< 0.330	< 0.003	< 0.033	< 0.003	< 0.033	< 0.003
Acenaphthene	< 0.330	< 0.005	< 0.033	< 0.005	< 0.033	< 0.005
Fluorene	< 0.330	< 0.0004	0.12	< 0.0004	< 0.033	< 0.0004
Phenanthrene	< 0.330	< 0.0003	0.17	< 0.0003	< 0.033	< 0.0003
Anthracene	< 0.330	< 0.0001	< 0.033	< 0.0001	< 0.033	< 0.0001
Fluoranthene	< 0.330	< 0.0003	< 0.033	< 0.0003	< 0.033	< 0.0003
Pyrene	< 0.330	< 0.0004	< 0.033	< 0.0004	< 0.033	< 0.0004
Benzo(a)anthracene	< 0.330	< 0.0001	< 0.033	< 0.0001	< 0.033	< 0.0001
Chrysene	< 0.330	< 0.0002	< 0.033	< 0.0002	< 0.033	< 0.0002
Benzo(b)fluoranthene	< 0.330	< 0.0001	< 0.033	< 0.0001	< 0.033	< 0.0001
Benzo(k)fluoranthene	< 0.330	< 0.0001	< 0.033	< 0.0001	< 0.033	< 0.0001
Benzo(a)pyrene	< 0.330	< 0.0001	< 0.033	< 0.0001	< 0.033	< 0.0001
Dibenzo(ah)anthracene	< 0.330	< 0.0003	< 0.033	< 0.0003	< 0.033	< 0.0003
Benzo(ghi)perylene	< 0.330	< 0.0004	< 0.033	< 0.0004	< 0.033	< 0.0004
Indeno(123cd)pyrene	< 0.330	< 0.0003	< 0.033	< 0.0003	< 0.033	< 0.0003

- 1-Methylnaphthalene
- 2-Methylnaphthalene
- Fluorene
- Phenanthrene
- Fluoranthene

High molecular weight PAHs were not detected above MDLs in soil leachate.

The groundwater analytical results for Areas 1 and 2 are summarized in Tables 4 and 5, respectively. TPH and BTEX were not detected above MDLs in groundwater. PAHs were not detected above MDLs in groundwater, with the exception of low concentrations (i.e., less than 0.0005 mg/l) of the following low to medium molecular weight noncarcinogenic PAHs:

- Naphthalene
- 1-Methylnaphthalene
- 2-Methylnaphthalene
- Fluorene
- Phenanthrene

The soil SPLP results are indicative of the maximum soil leachate concentrations. Under actual site conditions, the soil leachate concentrations of these constituents would likely be significantly less. The data suggest that it is very unlikely that future concentrations of low to medium molecular weight PAHs in groundwater will exceed the low PAH concentrations currently detected in groundwater.

#### HEALTH RISK ASSESSMENT - HYPOTHETICAL DOMESTIC WELL

A health risk assessment for groundwater impacts was conducted using a methodology consistent with USEPA (USEPA, 1989a; USEPA, 1989b; USEPA, 1991) guidance. The following steps were incorporated into the risk assessment:

- Data collection
- Data evaluation
- Exposure assessment
- Toxicity assessment
- Risk characterization

Due to their volume, the risk assessment calculations are only briefly summarized below. No domestic wells exist downgradient of the site and it is unlikely that a domestic well will be installed on or immediately downgradient of the site in the future. However, for the purpose of the risk assessment, it was conservatively assumed that a hypothetical domestic well will be installed immediately downgradient of the site.

As a conservative measure, the highest Method 8310 groundwater analytical results for each PAH constituent detected were used to estimate the exposure point - groundwater concentrations. The following groundwater exposure pathways, associated with the use of a hypothetical domestic well, are quantitatively evaluated in this risk assessment:

**Table 4. Area 1 Groundwater Analytical Results - TPH, BTEX and PAHs**

CONSTITUENT	CONCENTRATION DETECTED (mg/l)			
	Area 1 / MW-7	Area 1 / MW-8	MCL	Proposed MCL <sup>b</sup>
TPH - Diesel	< 1.0	< 1.0	NL	—
Benzene	< 0.0005	< 0.0005	0.005	—
Toluene	< 0.0005	< 0.0005	1.0	—
Ethylbenzene	< 0.0005	< 0.0005	0.7	—
Xylenes	< 0.0005	< 0.0005	10.0	—
Naphthalene	< 0.0003	< 0.0003	NL	—
1-Methylnaphthalene	0.00056	0.00053	NL	—
2-Methylnaphthalene	< 0.0003	< 0.0003	NL	—
Acenaphthylene	< 0.0003	< 0.0003	NL	—
Acenaphthene	< 0.0005	< 0.0005	NL	—
Fluorene	< 0.00004	< 0.00004	NL	—
Phenanthrene	< 0.00003	0.00012	NL	—
Anthracene	< 0.00001	< 0.00001	NL	—
Fluoranthene	< 0.00003	< 0.00003	NL	—
Pyrene	< 0.00004	< 0.00004	NL	—
Benzo(a)anthracene	< 0.00001	< 0.00001	NL	0.0001
Chrysene	< 0.00002	< 0.00002	NL	0.0002
Benzo(b)fluoranthene	< 0.00001	< 0.00001	NL	0.0002
Benzo(k)fluoranthene	< 0.00001	< 0.00001	NL	0.0002
Benzo(a)pyrene	< 0.00001	< 0.00001	0.0002 <sup>a</sup>	0.0002
Dibenzo(ah)anthracene	< 0.00003	< 0.00003	NL	0.0003
Benzo(ghi)perylene	< 0.00004	< 0.00004	NL	—
Indeno(123cd)pyrene	< 0.00003	< 0.00003	NL	0.0004

<sup>a</sup> Federal Register, Vol. 57, No. 138, July 17, 1992.

<sup>b</sup> Federal Register, Vol. 55, No. 143, July 25, 1990.

NL - Not Listed.

**Table 5. Area 2 Groundwater Analytical Results - TPH, BTEX and PAHs**

CONSTITUENT	CONCENTRATION DETECTED (mg/l)				
	Area 2 / MW-2	Area 2 / MW-6	Area 2 / MW-10	MCL	Proposed MCL <sup>b</sup>
TPH - Diesel	< 1.0	< 1.0	< 1.0	NL	—
Benzene	< 0.0005	< 0.0005	< 0.0005	0.005	—
Toluene	< 0.0005	< 0.0005	< 0.0005	1.0	—
Ethylbenzene	< 0.0005	< 0.0005	0.0110	0.7	—
Xylenes	< 0.0005	< 0.0005	< 0.0005	10.0	—
Naphthalene	0.00071	0.00037	0.00042	NL	—
1-Methylnaphthalene	< 0.0003	0.00091	< 0.0003	NL	—
2-Methylnaphthalene	0.00110	0.00063	< 0.0003	NL	—
Acenaphthylene	< 0.0003	< 0.0003	< 0.0003	NL	—
Acenaphthene	< 0.0005	< 0.0005	< 0.0005	NL	—
Fluorene	< 0.00004	0.00053	< 0.00004	NL	—
Phenanthrene	< 0.00003	< 0.00003	< 0.00003	NL	—
Anthracene	< 0.00001	< 0.00001	< 0.00001	NL	—
Fluoranthene	< 0.00003	< 0.00003	< 0.00003	NL	—
Pyrene	< 0.00004	< 0.00004	< 0.00004	NL	—
Benzo(a)anthracene	< 0.00001	< 0.00001	< 0.00001	NL	0.0001
Chrysene	< 0.00002	< 0.00002	< 0.00002	NL	0.0002
Benzo(b)fluoranthene	< 0.00001	< 0.00001	< 0.00001	NL	0.0002
Benzo(k)fluoranthene	< 0.00001	< 0.00001	< 0.00001	NL	0.0002
Benzo(a)pyrene	< 0.00001	< 0.00001	< 0.00001	0.0002 <sup>a</sup>	0.0002
Dibenzo(ah)anthracene	< 0.00003	< 0.00003	< 0.00003	NL	0.0003
Benzo(ghi)perylene	< 0.00004	< 0.00004	< 0.00004	NL	—
Indeno(123cd)pyrene	< 0.00003	< 0.00003	< 0.00003	NL	0.0004

<sup>a</sup> Federal Register, Vol. 57, No. 138, July 17, 1992.

<sup>b</sup> Federal Register, Vol. 55, No. 143, July 25, 1990.  
NL - Not Listed.

- Ingestion Exposure From Drinking Water - Hypothetical ingestion exposures may result from the drinking groundwater.
- Inhalation Exposure During Showering - Hypothetical inhalation exposures may result due to the volatilization of PAHs during showering. The volatilities of TPH / PAHs are, however, relatively low.
- Dermal Exposure During Showering - Hypothetical dermal exposures may result due to direct contact with groundwater during showering.

USEPA Reference Doses (RfDs) for chronic noncarcinogenic effects were used in the risk evaluation. An USEPA chronic RfD is an estimate (with uncertainty potentially spanning an order of magnitude or greater) of a daily exposure level for the human population, including sensitive subgroups, that is likely to be without an appreciable risk of deleterious effects during a lifetime (USEPA, 1989a).

The potential overall chronic noncarcinogenic risk to an individual from each exposure route was calculated using the Hazard Index approach (USEPA, 1989a). The Hazard Index is the ratio of daily intake of each contaminant from each exposure pathway over the RfDs. The Hazard Index was calculated to be less than 1.0, which indicates that the hypothetical intake would be below the RfDs. The Hazard Index therefore does not exceed levels used by the USEPA to indicate a potential concern.

#### FATE AND TRANSPORT CHARACTERISTICS

Presented in Table 6 are typical  $K_{oc}$  values (Montgomery, 1991) for several volatile aromatic hydrocarbons and several low to high molecular weight PAHs. BTEX have  $K_{oc}$  values of approximately 100, which indicates an intermediate potential (Dragun, 1988) to migrate from soils. The low molecular weight PAHs have  $K_{oc}$  values in the range of 1000 to 10,000, which indicates a low potential to migrate in soils (ATSDR, 1989). The medium molecular weight PAHs have  $K_{oc}$  values in the range of 10,000, and the high molecular weight PAHs have  $K_{oc}$  values in the range of 100,000 to 1,000,000, which indicates that these compounds are relatively immobile in soils (ATSDR, 1989).

Summarized in the Table 6 are typical water solubilities (Montgomery, 1991) for several volatile aromatic hydrocarbons and several low to high molecular weight PAHs. The water solubilities of the PAHs are low when compared to benzene. The water solubilities of the PAHs also decrease substantially as their molecular weight increases. The low water solubilities of the residual PAHs in the soils also indicates that these constituents will tend to partition into (adsorb to) soils.

Another transport process potentially affecting the transport of PAHs in soils is volatilization. Summarized in Table 6 are Henry's constants and vapor pressures values (Montgomery, 1991) for several volatile aromatic hydrocarbons and several low to high molecular weight PAHs. The potential for volatilization of the low molecular weight PAHs from soil is very low compared to BTEX; however, it may be substantial compared to the other PAH fate and transport characteristics. Volatilization is not

Table 6. Physical and Chemical Parameters

CONSTITUENT	Log K <sub>oc</sub> <sup>c</sup>	Solubility <sup>a</sup> mg/l	Vapor Pressure <sup>d</sup> mm Hg @ 25°C	Henry's Constant <sup>e</sup> atm-m <sup>3</sup> /mole @ 25°C	Soil Half Life <sup>b</sup> (t <sub>1/2</sub> ) Days	Groundwater Half Life <sup>b</sup> (t <sub>1/2</sub> ) Days
Benzene	1.69 - 2.00 (K <sub>oc</sub> 49 - 100)	1780	95	5.5 x 10 <sup>-3</sup>	5 - 16	10 - 24
Toluene	2.06 - 2.18	515	Not Listed	6.7 x 10 <sup>-5</sup>	4 - 22	7 - 28
Ethylbenzene	1.68 - 1.83	140	10	6.6 x 10 <sup>-3</sup>	3 - 10	6 - 228
Xylene	2.11 - 3.20	152	10	5.4 x 10 <sup>-3</sup>	7 - 28	14 - 365
Naphthalene	2.74 - 3.52	30	0.23	4.6 x 10 <sup>-4</sup>	17 - 48	2 - 258
1-Methylnaphthalene	NL	NL	NL	NL	NL	NL
2-Methylnaphthalene	3.87 - 3.93	24.6	NL	NL	NL	NL
Acenaphthylene	3.68	3.93	0.0290	2.8 x 10 <sup>-4</sup>	43 - 60	85 - 120
Acenaphthene	1.25	3.47	0.00155	1.5 x 10 <sup>-4</sup>	12 - 102	25 - 204
Fluorene	3.70	1.69	0.00016 @ 33°C	2.1 x 10 <sup>-4</sup>	32 - 60	64 - 120
Phenanthrene	3.72 - 4.59	1.18	6.8 x 10 <sup>-4</sup>	3.9 x 10 <sup>-5</sup>	16 - 200	32 - 375
Anthracene	4.27 - 4.41	1.29	1.95 x 10 <sup>-4</sup>	6.5 x 10 <sup>-5</sup>	50 - 386	100 days - 2.52 years
Fluoranthene	4.62	0.27	5.0 x 10 <sup>-6</sup>	1.7 x 10 <sup>-2</sup>	140 - 440	280 days - 2.41 years
Pyrene	4.66 - 5.13	0.135	6.9 x 10 <sup>-7</sup>	1.1 x 10 <sup>-5</sup>	210 days - 5 years	210 days - 5.2 years
Benzo(a)pyrene <sup>e</sup>	5.60 - 6.29	0.003	5.5 x 10 <sup>-9</sup>	< 2.4 x 10 <sup>-6</sup>	57 - 530	114 days - 2.9 years

<sup>a</sup> Montgomery, 1991.<sup>b</sup> Howard, 1991.<sup>c</sup> Used for comparison to low molecular weight PAH mobility.<sup>d</sup> Used to evaluate benzene volatilization (Refer to the text).

NL = Not Listed.

considered significant for the higher molecular weight PAHs (ATSDR, 1989). The volatilization potential is influenced by both the physical / chemical properties of the PAHs and environmental factors (e.g., soil depth, moisture content, temperature).

Microbial metabolism is the major fate process for the degradation of PAHs in soil (ATSDR, 1989). This pathway is influenced by both the physical/chemical properties of the PAHs, environmental factors (e.g., soil depth, moisture content, temperature), and the characteristics of the soil microbial population. Hydrolysis, photolysis, and oxidation are not considered significant fate processes for the degradation of PAHs in soil (ATSDR, 1989).

Summarized in Table 6 are soil half-life data (Howard, 1991) for several volatile aromatic hydrocarbons and several low to high molecular weight PAHs. The soil half-lives of the PAHs are greater than benzene. The half-lives of the PAHs increase significantly as their molecular weight increases. The half-lives of the higher molecular weight PAHs (e.g., benzo(a)pyrene) indicates that these compounds are relatively persistent in soils.

Note that the soil and groundwater water half-lives of the PAHs and BTEX vary significantly depending on the source of the half-life information. The above referenced literature half-life data are often estimates based on photolysis, biodegradation, etc., half-lives and are generally not obtained from direct experimental measurements.

A review of the above information indicates that the PAHs are considered relatively immobile in soils, particularly as their molecular weight increases. Based on these fate and transport characteristics, the potential for the future migration of PAHs from the soils to groundwater would be limited, given that the diesel impacted soils are highly "weathered" (e.g., the soil PAH concentrations are significantly lower than soils recently impacted by pure diesel fuel).

## DIESEL FUEL / WATER PARTITIONING STUDY

Data (Lee et al., 1992) for the partitioning of PAHs between pure (nonweathered) diesel fuel and water under equilibrium conditions provides an indicator of the maximum PAH concentrations that might be present in the leachate migrating from diesel fuel contaminated soil to groundwater.

The partitioning data were used in this fate and transport assessment to qualitatively evaluate the migration potential of the weathered diesel fuel constituents present at the groundwater / soil interface. It is assumed, for the purpose of this evaluation, that the impacted soils are in contact with the groundwater.

Presented in Table 7 are the partitioning data and the well analytical results. A review of Table 7 indicates the following:

- A majority of the low molecular weight PAHs present in diesel fuel were not detected in the wells.
- The aqueous PAH equilibrium concentrations are approximately two orders of magnitude greater than the groundwater analytical results for naphthalene, methylnaphthalene, fluorene and phenanthrene.

The partitioning data provide an indicator of the maximum PAH concentrations that might be present in the leachate from diesel fuel contaminated soil. Equilibrium conditions are not likely to be present under actual site conditions; therefore, it is very unlikely that the concentrations of PAHs in leachate or groundwater would reach equilibrium concentrations. Under non-equilibrium conditions, the concentrations of PAHs in soil leachate would likely be significantly less.

## SUMMARY

The approach used on this project was based on an evaluation of the migration potential of diesel fuel constituents in soil using site-specific soil leachate analysis data and a health risk assessment of the diesel fuel impacted groundwater. TPH and BTEX were below MDLs in the soil leachate. Low molecular weight noncarcinogenic PAHs were detected in the soil leachate at concentrations similar to the concentrations detected in groundwater. The results of the soil leachate analyses suggest there is low potential for the future migration of low molecular weight PAHs from soils to groundwater. The results of the soil leachate results also suggest "weathering" (fate and transport) processes have likely reduced the concentrations of the more mobile, less persistent constituents. The concentrations of low molecular weight PAHs in published diesel fuel/water partitioning data were two orders of magnitude greater than the soil leachate and groundwater data. The partitioning data provide an indicator of the maximum PAH concentrations that might be present in the leachate migrating from diesel fuel contaminated soil. The maximum concentration of each diesel fuel constituent detected in groundwater (i.e., the low molecular weight - noncarcinogenic PAHs) was used in the risk calculations. The risk assessment results indicate that the concentrations of low molecular weight PAHs detected in groundwater are well below levels used by the USEPA to indicate a potential concern.

**Table 7. Diesel Fuel / Water Partitioning Data**

CONSTITUENT	Diesel Fuel <sup>a</sup>	Water <sup>a</sup>	Maximum Detected In Groundwater
Naphthalene	350 - 1500	0.08 - 0.3	0.00071
1-Methylnaphthalene	2000 - 4000	0.13 - 0.17	0.00091
2-Methylnaphthalene	3500 - 9000	0.18 - 0.34	0.00110
Acenaphthylene	100 - 600	0.004 - 0.014	< 0.0003
Fluorene	350 - 900	0.012 - 0.026	0.00053
Phenanthrene	100 - 1500	0.015 - 0.025	0.00012
Anthracene	100 - 300	0.0004 - 0.002	< 0.00001
Fluoranthene	1.5 - 125	ND <sup>b</sup> - 0.0005	< 0.00003

<sup>a</sup> Lee et al., 1992.

<sup>b</sup> Not Detected Above the Method Detection Limit.

This approach provided sufficient site specific data to support a regulatory agency decision allowing site closure without further active remediation of the site soils. If the methodology had not been applied to the site, a remedial method based on a TPH UST program soil cleanup level would have likely been required. Considering the logistical constraints and financial requirements of the project, remedial options such as off-site disposal or on-site thermal treatment would have been used, resulting in cleanup costs exceeding \$500,000.

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## CHAPTER 11

### **A Case Study: Union Pacific Railroad Emergency Response and Remedial Activities at the Alameda Creek Derailment Site**

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#### INTRODUCTION

At 5:33 p.m. PST, January 30, 1994, a Superbowl Sunday evening, a Union Pacific Railroad (UPRR) intermodal freight train derailed in Fremont, California resulting in the release of hazardous chemicals into the Alameda Creek.

#### Incident Situation

The incident occurred at milepost 29.26 on the Canyon Subdivision of the UPRR. The derailment occurred as a result of railcar truck center bowls that were not properly lubricated. As a result, the railcar trucks failed to properly steer through the curve, causing the wheel to derail. The cars continued to roll on the wooden ties without causing a train separation. Immediately after the initial derailment, the derailed cars struck a through plate girder, causing two intermodal containers to fall off the stack train onto a concrete spillway in the Alameda Creek.

One container caught fire and burned out of control for several hours. Products in this container included paint remover, carpet cleaner, brake fluid, battery cleaner, fuel additives, cleaning fluids, lime remover, glass cleaner, and other products. The train consist reported the following hazardous substances:

Phosphoric acid - 467 pounds

Nitric acid - 41 pounds

Hexane - 2,560 pounds

1,1,1-Trichloroethane - 70 pounds

Dichloromethane - 70 pounds

Sulfuric acid - 1,170 pounds

Hydrochloric acid - 589 pounds

The fire released a plume of smoke which causing interruption of Bay Area Rapid Transit service which operates over a bridge located a few hundred feet downstream of the UPRR bridge. The second container contained inert clay and posed no environmental risk.

The concrete spillway was located directly under the UPRR bridge and immediately downstream of inflatable, rubber dam #1 (RD-1) which is controlled by Alameda County Water District (ACWD). A second inflatable dam (RD-2) is located approximately 3,000 feet downstream of RD-1. This portion of the creek is used as a percolation basin for a groundwater aquifer which provides a portion of the local water supply. The dams control the flow and volume of water in the creek to support both aquifer recharge requirements and downstream ecosystem needs. A diagram of the creek and dam locations is shown on Figure 1.

At the time of the derailment, water flow over RD-1 was approximately 15 cubic feet per second (cfs). Many of the more than 60 products released onto the spillway were subsequently flushed downstream into the section of the creek between the inflatable dams.

#### Chronology of Events (all times given in PST)

The incident was reported to the Harriman Dispatch center at 5:55 p.m. by the train crew. At 6:30 p.m., the local UPRR Special Agent Hazardous Materials (SAHM) was notified and immediately departed for the incident site from Stockton, California. Concurrently, the Director Chemical Transportation Safety (DCTS) was notified and began monitoring the incident at the Harriman Dispatch Center (HDC) in Omaha, NE. OH Materials Company (OHM), an emergency response contractor, was notified at 7:20 p.m. and mobilized their team located at Walnut Creek, CA. At 7:30 p.m. the SAHM arrived at the scene. ACWD prevented all water from flowing over RD-1 and through the spill site at approximately 7:30 p.m. OHM arrived at the incident site at 8:40 p.m.

Preliminary information at the HDC regarding potential loss of product was vague and incomplete. It was known that the incident occurred in a creek, but there was little if any other knowledge by headquarters personnel regarding environmental conditions at the site. Environmental Management representatives began contacting local agencies from the HDC to set up lines of communication with the site and determine which local agency was acting as the incident commander.

A senior emergency response team was assembled and departed Omaha at 9:45 p.m. via corporate jet. The function of this team was to provide additional environmental and emergency response expertise, and take over incident management from initial UPRR responders. This team also included representatives from public relations, car maintenance, and transportation.

At 9:15 p.m., U.S. Environmental Protection Agency (U.S. EPA) representatives arrived on the scene and met with the Fremont Fire Department (FFD) Incident Commander to assess the situation. According to ACWD, production wells that supply drinking water from this aquifer were shut down at 10:00 p.m.

At 10:30 p.m., the U.S. EPA held a meeting with local, state, federal agencies, on-site railroad personnel, and others to discuss initial response. The federal EPA indicated they were monitoring the incident to ensure that an appropriate response was

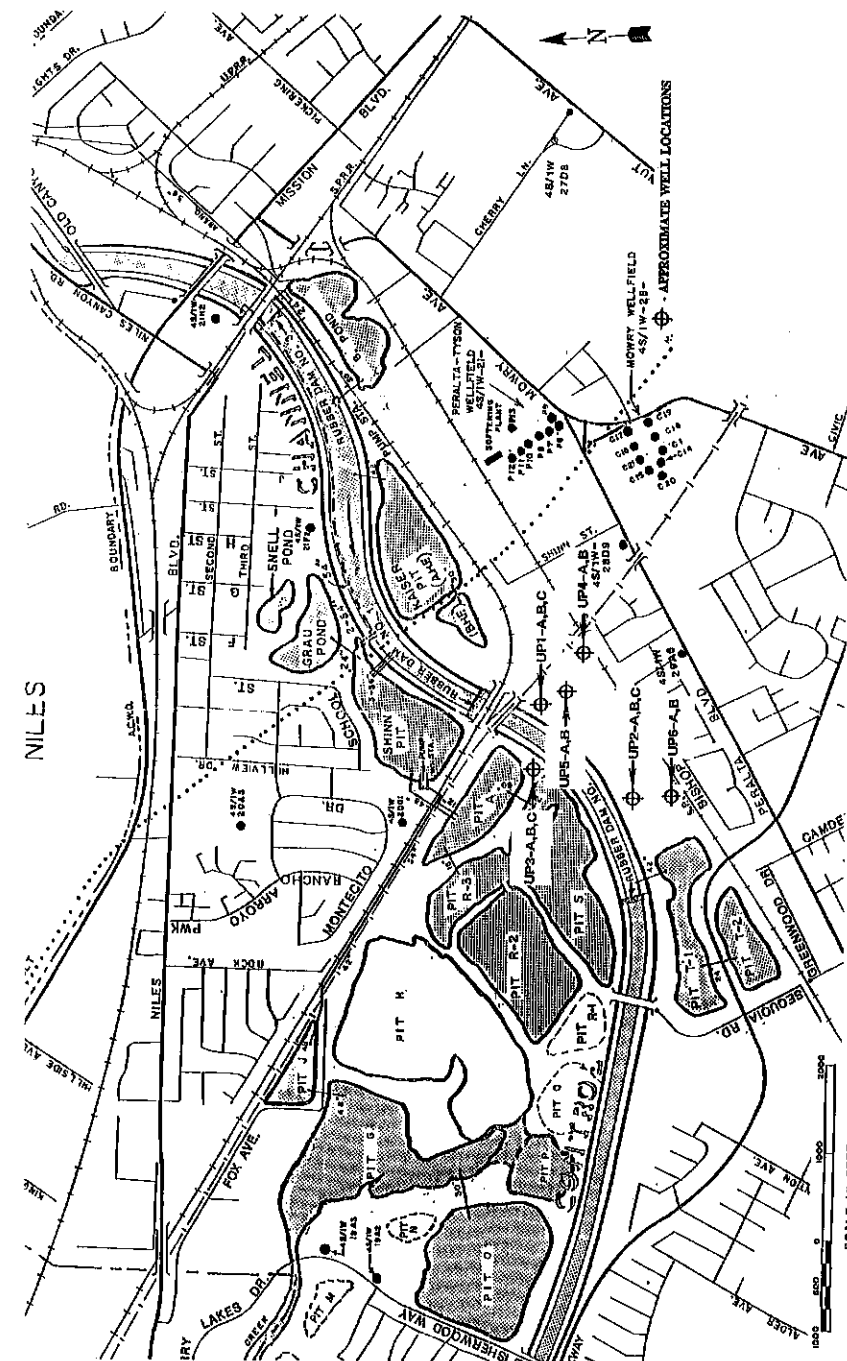


Figure 1. Site map.



forthcoming. It was decided at this time to let the fire burn itself out rather than risk further contamination of the creek by applying water or other fire suppressant materials. Representatives from the Regional Water Quality Control Board (RWQCB), California Department of Fish and Game (CDFG), and Fish and Wildlife Service (FWS) were evaluating options regarding sampling and analysis of the water in the creek. Alameda County Health Department conducted air sampling in the neighborhood closest to the accident.

A plan was worked out between the agencies, UPRR, and its contractor OHM, to select a location downstream from the spill to conduct air monitoring, and if safe, to collect surface water samples from the creek to assess the extent of contamination.

At 1:50 a.m., Monday, the senior emergency response team arrived on-site and a second joint agency meeting was held. At this meeting, ACWD explained that the creek was a percolation zone for the aquifer which was used as a drinking water supply source. At this time, the agencies requested UPRR to provide a work plan for initial site cleanup.

The container fire burned out at 2:45 a.m. An initial work plan was presented and approved by the agencies at a 6:00 a.m. meeting. OHM began work in the hot zone at 6:30 a.m. This work consisted of sorting, repacking, and inventorying the various products distributed around the site, and removing as much of the released material as possible. OHM and ACWD began collecting samples of surface water suspected of having been impacted. A second emergency response contractor, Radian Corporation, was mobilized out of Austin, TX at 6:45 a.m.

Later that Monday morning, UPRR representatives contacted the California governors office and both U.S. senators. Information on the status of the incident and UPRR's response was provided along with assurance that action was being taken to protect the public and the environment.

At 2:00, Monday afternoon, an agency meeting was held to discuss alternatives for managing the estimated 3 million gallons of contaminated water contained between RD-1 and RD-2. Three alternatives were identified and included: pumping the water from the river into tank cars or baker tanks; pumping water from the river to the nearest sanitary sewer inlet; flushing the contaminated water downstream with upstream water.

The percolation rate into the aquifer was estimated at 0.3 feet per day by ACWD. The agencies agreed to give priority to protecting the aquifer, and agreed to flush the contaminated water downstream as soon as the initial cleanup of the hot zone was completed. Although this plan would minimize the impact on the aquifer, the impact on the downstream ecosystem was of great concern. A game reserve and the San Francisco Bay (located 6 miles downstream) could potentially be impacted by the contaminated water unless a method for draining the creek could be immediately implemented.

Union Sanitary District (USD) was analyzing water samples to determine if the contaminated water could be treated by their publicly owned treatment works (POTW). USD also began researching closed sewers in the area that could be used as intakes for contaminated water.

UPRR and the fire chief began exploring possible methods to pump water from the contaminated creek to the sewer system. Portable Water Supply Systems (PWSS) was contacted and had pumps capable of pumping water 160 feet vertically and several thousand feet horizontally. Additionally, these pumps were designed such that the pump itself could be lowered into the creek, avoiding cavitation problems. PWSS was mobilized in the event that USD determined it could take the contaminated water. Radian Corporation arrived on scene for this meeting.

The next agency meeting was held at 8:00 p.m. Monday evening. At this meeting, USD announced they could treat the contaminated water. Initial pumping by OHM began 30 minutes later. Samples of the pumped water were collected by Radian approximately every 2 hours at a downstream manhole. At approximately 11:00 p.m., PWSS finished mobilization and took over the pumping.

Pumping continued until 1:30 p.m. Tuesday, when the spill site initial cleanup was completed, and emergency equipment removed. ACWD lowered the inflatable dams at 2:00 p.m. and flushed the area with approximately 200 million gallons of water for the next 56 hours.

The next agency meeting was held at 5:00 p.m., Tuesday. USD estimated that approximately 2.9 million gallons were pumped to the sewer, or approximately 96% percent of the estimated amount of contaminated water.

Immediately following the completion of the pumping of impacted water from Alameda Creek, Roy F. Weston, Inc. (WESTON®) collected pre-flush sediment samples from two locations downstream of the spill site. The purpose of these samples was to assess the downstream extent of impact to sediments.

#### Pre-Flush Sediment Characterization

The pre-flush sediment sampling consisted of sediment collection just downstream of the spill and downstream of RD-2 to assess the initial impact on the area. Three samples were collected along the creek bed at each location. These samples were analyzed for volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) using EPA Methods 8240 and 8270, respectively.

The samples closest to the spill area contained acetone (500-1,100 micrograms per kilogram ( $\mu\text{g}/\text{Kg}$ )), ethylbenzene (14-62  $\mu\text{g}/\text{Kg}$ ), methylene chloride (150-520  $\mu\text{g}/\text{Kg}$ ), perchloroethylene (PCE) (38-160  $\mu\text{g}/\text{Kg}$ ), 1,1,1-trichloroethane (TCA) (30-62  $\mu\text{g}/\text{Kg}$ ), and xylenes (93-370  $\mu\text{g}/\text{Kg}$ ). The sample collected downstream of RD-2 contained only methylene chloride (5-8  $\mu\text{g}/\text{Kg}$ ).

#### Post-Flush Sediment Characterization

This phase of the sediment characterization program consisted of 10 sampling "stations," located upstream and downstream of the spill area, with a total of 63 sample points, at various depths. The majority of these samples were collected on 5 February 1994, following the sediment flushing program.

Three stations (Stations 0, 1, and 2) were located upstream of the spill site to establish background conditions. The most intense sampling activities occurred at Station 3, the area immediately downstream of the concrete spillway. Stations 4, 5, 6, 7, 8, and 9 all sequentially lie further downstream of the spill site. These stations were established to assess the extent of downstream contamination. All post-flush samples

were analyzed by EPA Methods 8240 and 8270 for VOCs and SVOCs, respectively. The samples were collected in the Alameda Creek channel from 0.5 to 3 feet below ground surface.

Phthalates (450-750  $\mu\text{g}/\text{Kg}$ ) were detected in the samples collected from the background stations. Analytical results did not indicate the presence of VOCs at these locations. Samples collected at Station 3 indicated the presence of eight VOCs and twenty-two SVOCs. The most frequently detected compounds were methylene chloride (6-290  $\mu\text{g}/\text{Kg}$ ), TCA (7-230  $\mu\text{g}/\text{Kg}$ ), and xylenes (32-2800  $\mu\text{g}/\text{Kg}$ ). Of the 34 samples collected at Station 3, methylene chloride was present in 12 samples, TCA was present in 14 samples, and xylenes were present in 12 samples. Figure 2 shows the sample locations.

Downstream sediment samples indicated trace concentrations of acetone (15  $\mu\text{g}/\text{Kg}$ ), methylene chloride (20-24  $\mu\text{g}/\text{Kg}$ ), PCE (8  $\mu\text{g}/\text{Kg}$ ), and xylenes (6-22  $\mu\text{g}/\text{Kg}$ ). Samples from Stations 8 and 9, the furthest downstream stations, did not indicate the presence of any VOCs or SVOCs.

At the request of the RWQCB, additional samples were collected upstream of the spill area to establish background concentrations of metals and total petroleum hydrocarbons. In analyzing the data, the affected length of the channel was estimated to be 2,700 feet, which covers the area between the RD-1 and RD-2. The most highly affected area, Station 3, extended approximately 180 feet downstream of the spill site. An interim remedial measure (IRM) was implemented to remove the contaminated sediments and wash the affected riprap.

## SURFACE WATER CHARACTERIZATION

Two surface water sampling events occurred to document the effectiveness of flushing the channel and the effect on downstream areas. The first sampling event occurred on 1-2 February 1994, immediately following the release of the flush water, and was conducted to evaluate downstream conditions. The second sampling event occurred on 15-16 February 1994 to assess the remaining surface water between RD-1 and RD-2.

### Surface Water Sampling Event 1

The first sampling event consisted of five sampling episodes starting 1 hour after the release of the flush water and continued in approximately 4 hour intervals at four locations between RD-1 and RD-2. Four VOCs were detected, methylene chloride (0.7-25 micrograms per liter ( $\mu\text{g}/\text{l}$ )), TCA (3.8-10  $\mu\text{g}/\text{l}$ ), PCE (2.4-8.4  $\mu\text{g}/\text{l}$ ), and xylenes (3.6-12  $\mu\text{g}/\text{l}$ ), in the downstream surface water samples. The concentrations of these chemicals decreased the further downstream the samples were collected, and the longer the period from the release of the flush water. Further, concentrations decreased to non-detect after the fifth interval sampling event.

### Surface Water Sampling Event 2

On 15-16 February 1994, an additional five surface water samples were collected from the pooled water between RD-1 and RD-2 to evaluate the effectiveness of the flushing. VOCs and SVOCs were not detected in any of the 15-16 February 1994 surface water samples.

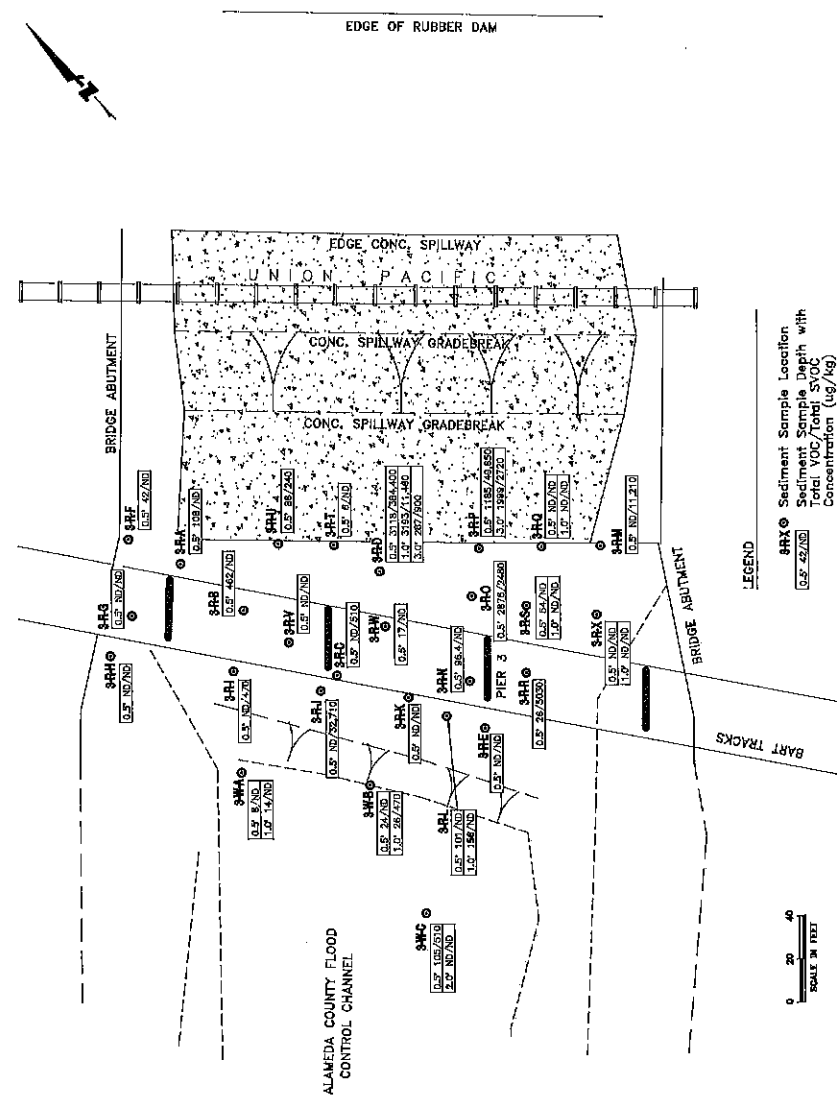


Figure 2. Post flush analytical results, station 3.

## GROUNDWATER CHARACTERIZATION

Groundwater characterization activities commenced on 2 February 1994 (three days after the derailment), following a planning session between UPRR, the regulatory agencies, and WESTON®. During this session, the regulatory agencies requested installation of three clusters of three monitor wells, one cluster upgradient of the spill site (UP-3) and two clusters downgradient of the spill site (UP-1 and UP-2). Each of the three well clusters has screened intervals in the shallow (A wells), intermediate (B wells), and deep (C wells) regions of the upper aquifer to characterize any vertical migration of the released chemicals.

On 14 February 1994, the RWQCB and ACWD requested three additional clusters installed at presumed downgradient locations to assess the lateral movement of chemicals and identify any possible migration to the area drinking water production wells. These clusters were screened in the shallow and intermediate zones and are designated UP-4, UP-5, and UP-6. The locations of the monitor wells are shown on Figure 1. All monitor wells were completed by 26 February 1994.

### Groundwater Sampling

Individual wells were sampled immediately following completion at each of the clusters. UP-1A was the first well to be completed, and was first sampled on 5 February 1994 (six days after the derailment). From 5 February to 26 February 1994, the first three clusters were sampled 4 to 6 times. As the remaining clusters were completed, RWQCB and ACWD required groundwater sampling to occur every 3 days at all 15 wells. As the characterization program progressed, the sampling frequency was reduced to weekly, and finally quarterly.

In addition to the 15 monitor wells installed, four additional domestic wells in the area were sampled during the initial stages of the characterization. These included a domestic and irrigation water supply well located approximately 1,000 feet south of the spill site, and three monitor wells located on an adjacent property south-southeast of the site.

### Groundwater Analytical Results

Initial analytical data for well clusters UP-1 and UP-2, immediately downgradient of the spill site, indicated that the shallow groundwater had been impacted by methylene chloride, TCA, acetone, and xylenes. During the first month of the groundwater characterization program, methylene chloride detections ranged from 5 to 85 µg/l; TCA detections ranged from 5 to 25 µg/l; acetone ranged from 37 to 290 µg/l, and xylenes ranged from 5 to 6 µg/l in the shallow UP-1A and UP-2A wells. The intermediate and deep wells in these clusters had sporadic, validated detections of methylene chloride (5-7 µg/l) and bis(2-ethylhexyl)phthalate (bis) (17-53 µg/l). Upgradient cluster UP-3 also contained scattered detections of bis (47-100 µg/l) and a single early detection of methylene chloride (6 µg/l) in the shallow well (UP-3A).

During the first two months following the incident, the clusters located further downgradient (UP-4, UP-5, and UP-6) indicated limited detections of methylene chloride (2-11 µg/l), TCA (2 µg/l), 2-butanone (15-130 µg/l) and bis (13-14 µg/l). However, UP-5A, a shallow well just downgradient of UP-1A, had validated detections of methylene chloride (3-11 µg/l) and later, validated detections of TCA (1-3 µg/l).

As the groundwater monitoring program progressed, the concentrations of contaminants asymptotically dropped within one to two months. Figures 3 and 4 show the decrease in the initial contaminants of concern (methylene chloride, TCA, and xylenes) in the downstream shallow wells. In studying the data tables, migration of methylene chloride and TCA from UP-1A to UP-5A does appear to occur during the first two months following the derailment. However, UP-4A, a shallow well located even further downgradient, does not indicate the presence of any of the contaminants of concern.

By the end of the third month, the concentrations of all chemicals of concern in the downgradient wells were reduced to below the California and federal Maximum Contaminant Levels (MCLs) for drinking water. However, bis continued to be detected in several of the wells. Although bis is not considered a chemical of concern, and certainly not associated with the derailment, it has been the driving force for required continued monitoring and study of the groundwater.

The source of the bis has not been determined, nor has the true extent of its presence in groundwater. Bis is not a chemical associated with the spill, and was detected in only 1 of over 100 sediment samples collected. Bis has also been detected in upgradient as well as downgradient wells. In addition, many of the equipment, trip, and laboratory blanks indicated the presence of bis. One theory regarding the source of the bis is that the polyvinyl chloride (PVC) monitor wells are actually leaching bis. Bis is a common plasticizer in PVC as well as other polymer products. Another theory is that bis is being introduced into the samples from plastic sampling and/or decontaminating equipment (i.e., bailer, gloves, etc.).

## SITE REMEDIATION

### Sediment Excavation IRM

The objective of the Sediment Excavation IRM was the removal of impacted sediments, as identified during the Sediment Characterization Program, from the Alameda Creek channel at Station 3.

### Plan of Action for Sediment Excavation

The Sediment Excavation IRM was established based on the need to immediately initiate excavation activities at areas of Station 3 where elevated concentrations of organic compounds were detected in sediments. Therefore, only areas of Station 3 with known impacts to sediments, as identified by elevated levels of VOCs and SVOCs detected in post-flush sediment samples, were targeted for excavation.

The sediment excavation activities consisted of three phases: Riprap removal and cleaning; sediment excavation and off-hauling, and fill and riprap replacement. Riprap removal and cleaning began on 11 February 1994 (12 days after the derailment). Soil excavation was initiated on 16 February 1994.

Weather-related issues dictated the start and stoppage of excavation activities at Station 3. Throughout excavation activities, wet weather conditions created the potential for the deflation of RD-1 due to accumulated runoff from the Alameda Creek watershed. This situation imposed time constraints on the duration and extent

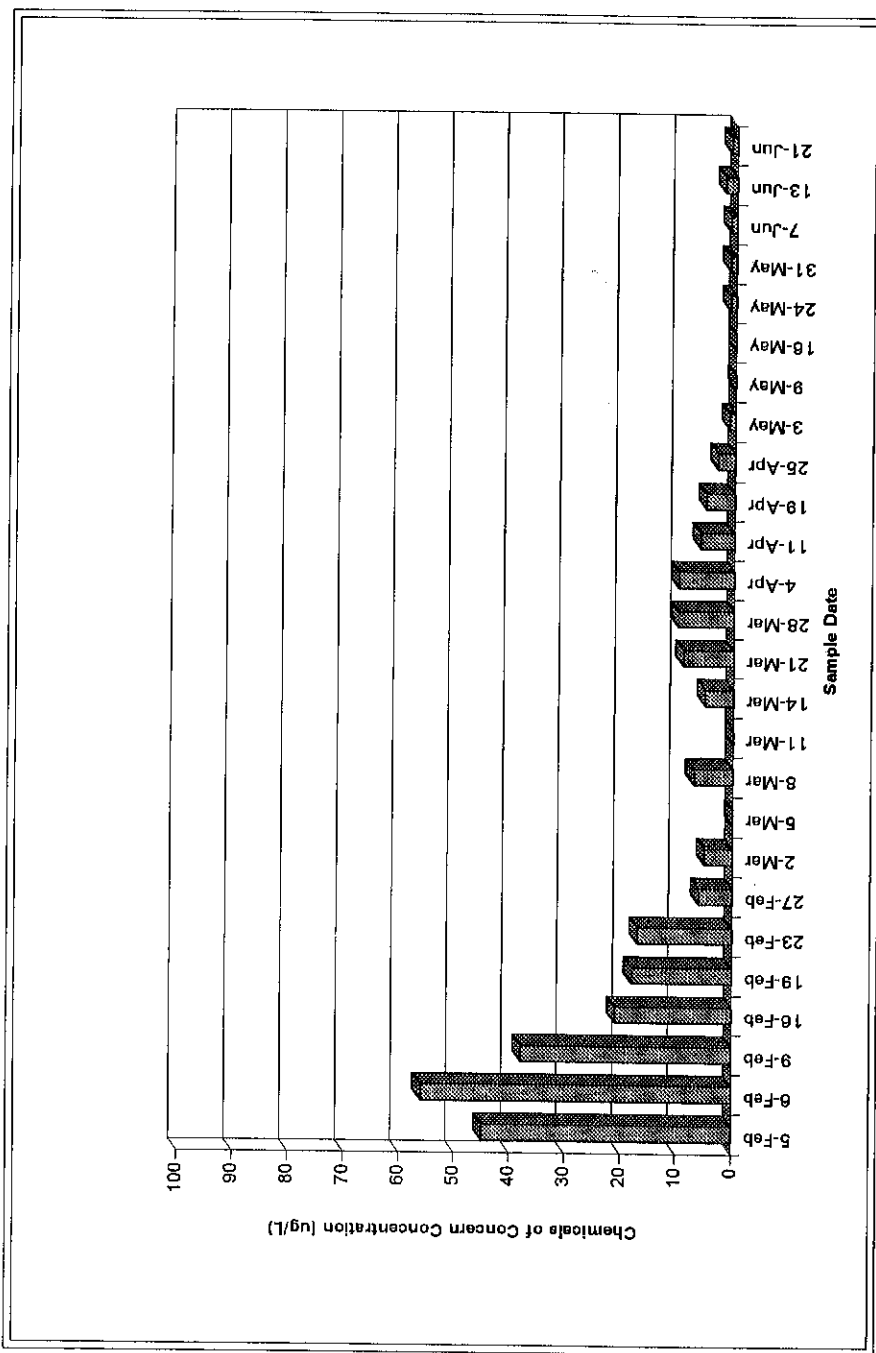


Figure 3. Chemicals of concern vs. time monitoring well UP-1A.

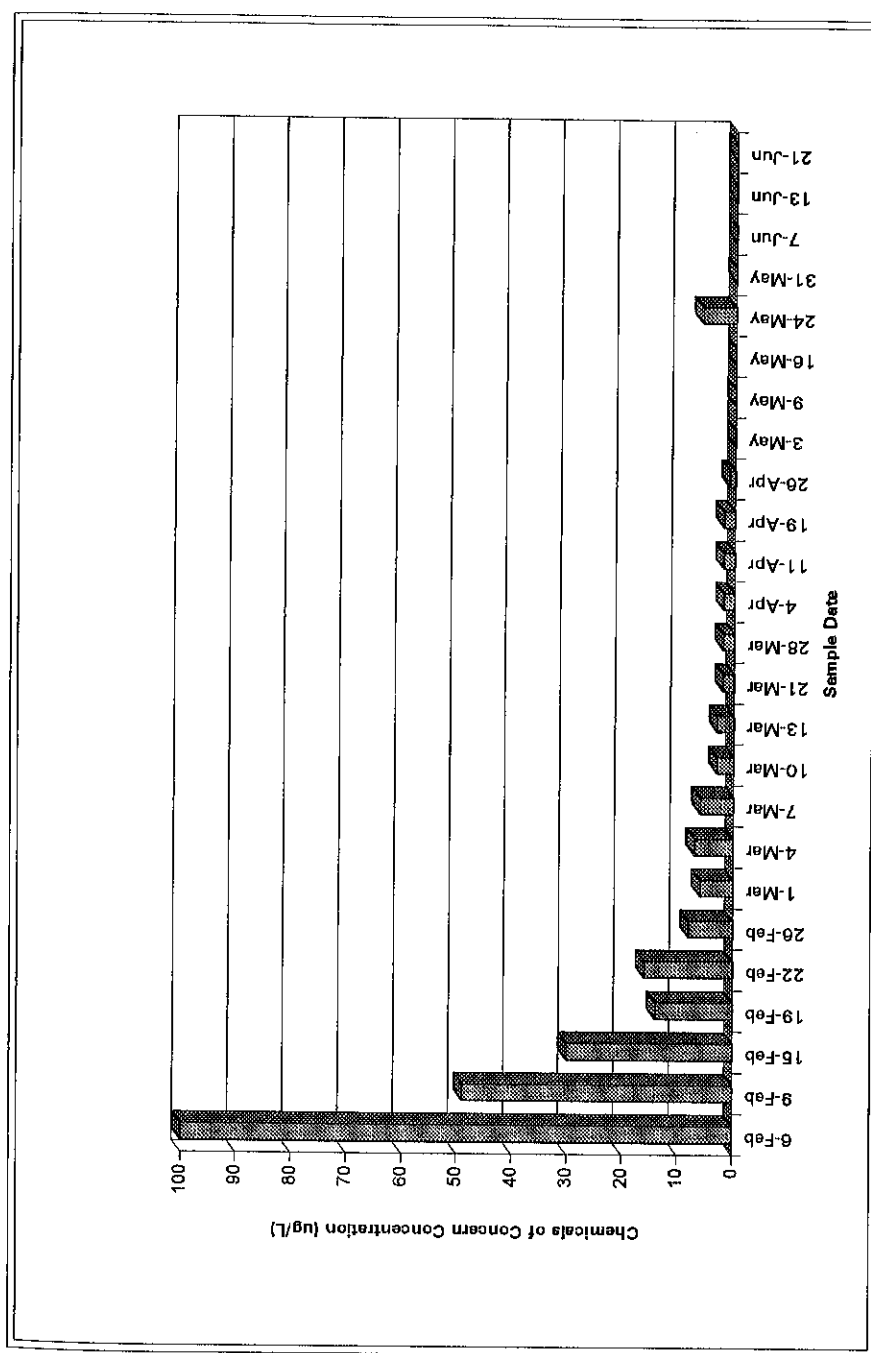


Figure 4. Chemicals of concern vs. time monitoring well UP-2A.

of excavation activities. On 16 February 1994, excavation was suspended due to a rainstorm and the subsequent deflation of RD-1. Excavation operations resumed on 23 February 1994, and were completed on 4 March 1994, 32 days following the derailment.

As excavation operations proceeded, the lateral extent of excavation areas was refined, based on results of field organic vapor monitor (OVM) surveys and confirmation samples at excavation sidewalls and bases. The final excavation areas are shown on Figure 5. Excavation depths ranged from a few feet to over 6 feet. A total of 1,300 cubic yards of soil and riprap was excavated and transported to East Carbon Development Corporation's landfill in Utah for disposal.

### GROUNDWATER EXTRACTION IRM

At the request of RWQCB and ACWD, two groundwater extraction systems were installed at well clusters UP-1 and UP-2 to assist in the remediation of detected chemicals from the groundwater. The extracted water was discharged to the USD sanitary sewer for treatment at their facility. A temporary permit was obtained from USD for this discharge.

Groundwater extraction was initiated on 3 March 1994 and concluded on 28 July 1994, at which time all contaminant levels had decreased to non-detect or below MCLs. Initial concentrations of methylene chloride and TCA both ranged from 4 to 7  $\mu\text{g}/\text{l}$ . Extraction rates ranged from 1 to 3.5 gallons per minute from each well. A total of approximately 747,000 gallons of water was extracted and discharged.

### SITE RESTORATION

#### Alameda Creek Restoration

In cooperation with the Alameda County Public Works Agency, U.S. Army Corps of Engineers, East Bay Regional Park District, and ACWD, a restoration plan was established to restore the channel bed, the channel sidewalls, the bike path, and the general area to original conditions.

After the sediment IRM at Station 3, the excavation was filled with new soil and the cleaned riprap was replaced. Additional riprap was brought in to replace the riprap off-hauled and to replace the sidewalls of the channel that were graded to allow access to the channel bed. All gravel roads created for the remediation activities were removed and the paths cleaned. Restoration activities concluded in mid-March, approximately six weeks after the derailment.

#### Final Groundwater Results

The groundwater monitoring program will continue until RWQCB and ACWD approve the closure of this site. The most recent validated groundwater monitoring data from the 15 wells indicate non-detect to 1  $\mu\text{g}/\text{l}$  for all VOCs and SVOCs. ACWD has, or will in the near future, begin pumping from their production wells.

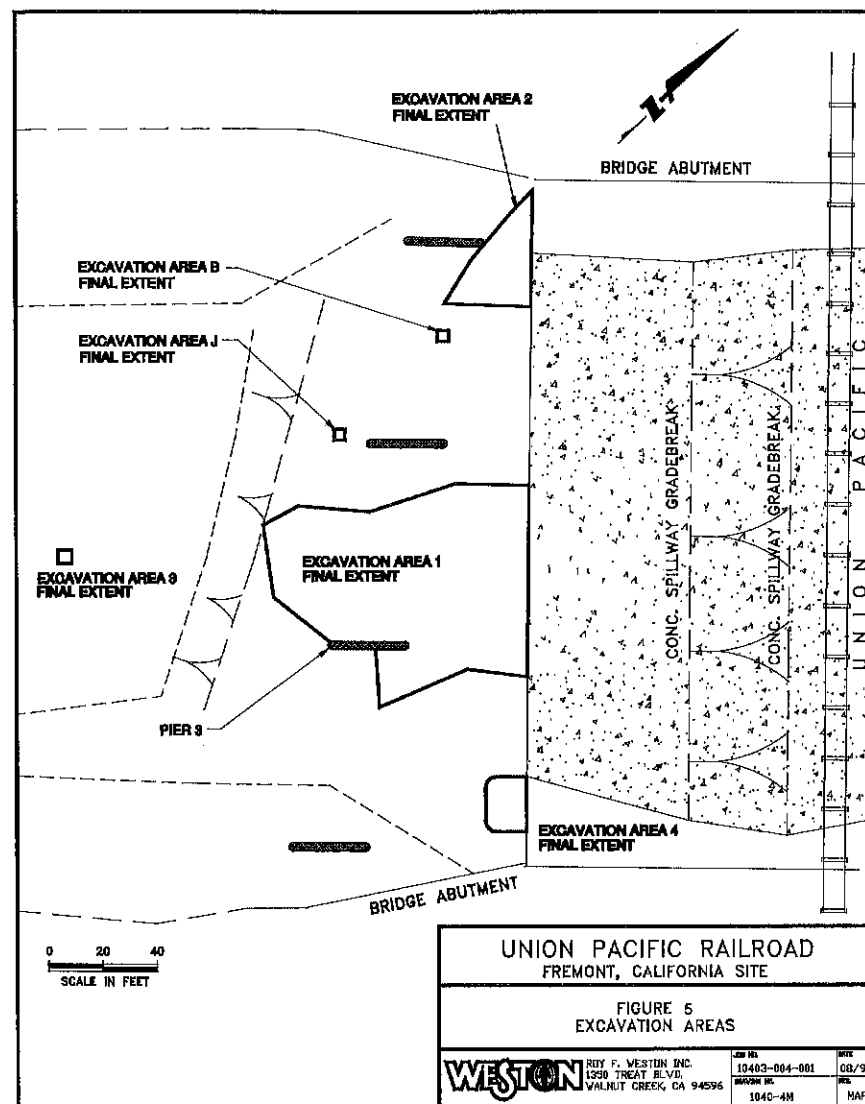


Figure 5. Excavation areas.

## CONCLUSIONS AND ANALYSIS

Less than 8 months after January, 30 1994 UPRR derailment and spill, the site remediation and restoration have been completed. Although the project has been considered a success, there are several issues that, under different circumstances, would likely have been addressed differently.

Several factors account for the success of the initial response efforts to this incident. Senior railroad officials recognized the potential for a high risk incident very early, even though initial reports were incomplete. Early reports indicated that the container which contained hazardous materials was in the creek and on fire. There was no report of a release and in fact, early reports from the site indicated there was no release of product. However, because of the location of the incident and the materials involved, senior management decided that a high level response was warranted. This level of response contributed the confidence of the local incident responders that the railroad was committed to properly managing the incident.

Mid-level railroad officials made numerous contacts from Omaha to various agencies in the area to determine which agency had jurisdiction and to obtain real time information from the incident site. These contacts served as a direct information link between UPRR headquarters and the incident commander until the point when UPRR response forces were physically on-site. This contact was important in directing resources and building trust, well in advance of the arrival of railroad responders. The level of cooperation that was established early in the incident between the incident commander and the railroad led to access and identification of resources that might otherwise have been unavailable.

The railroad committed to putting resources in-place as early as possible, without knowing the extent of the situation. For example, the railroad and fire department initiated actions to locate appropriate pumping services long before it was determined that the contaminated water could be pumped to the sewer. It is important to commit resources to contingencies even though this may appear to be a waste of resources in hindsight.

It is extremely important to reach a general consensus on priorities and action plans when multiple agencies are involved. (Table 1 provides a list of agencies responding to the Alameda Creek derailment.) To accomplish this, responders must recognize existing leadership, support it, and be willing to be directed by it. In this incident, 26 federal, state, and local agencies were involved at the initial response meetings. The public agencies had differing concerns and priorities. For example, ACWD was concerned about protecting the aquifer; the CDFG was concerned about local wildlife; the FFD's primary concern was human health; and the USD was concerned about the operation of their waste treatment plant. An early consensus was reached that once human health concerns were resolved, protecting the aquifer would have priority over downstream wildlife. In order to progress in a coordinated manner, each representative had to relinquish some of their authority. Achieving this consensus and group identity requires a high degree of diplomacy and recognition of each person's statutory needs and basic requirements.

**Table 1.** Agencies Responding to Alameda Creek Derailment. (Number of individuals involved in emergency response meetings).

Alameda County District Attorney's Office . . . . .	(2)
Alameda County Flood District. . . . .	(1)
Alameda County Hazardous Materials. . . . .	(1)
Alameda County Water District. . . . .	(9)
Alameda County Public Works Department . . . . .	(5)
Alameda County Health Agency . . . . .	(1)
Bay Area Air Quality Management District. . . . .	(1)
Bay Area Rapid Transit . . . . .	(3)
California Department of Fish and Game . . . . .	(3)
California EPA - Department of Toxic Substances Control . . . . .	(6)
California Regional Water Quality Control Board . . . . .	(3)
California Public Utilities Commission . . . . .	(2)
California Department of Health Services . . . . .	(1)
California Occupational Safety and Health Administration . . . . .	(1)
East Bay Regional Park Police . . . . .	(1)
East Bay Park District . . . . .	(1)
City of Fremont. . . . .	(1)
City of Fremont Fire Department . . . . .	(1)
National Transportation Safety Board . . . . .	(1)
Newark Fire Department. . . . .	(1)
San Francisco Water Department. . . . .	(1)
Union Sanitary District . . . . .	(5)
U.S. Coast Guard . . . . .	(2)
U.S. Environmental Protection Agency . . . . .	(6)
U.S. Corps of Engineers . . . . .	(1)
U.S. Fish and Wildlife. . . . .	(1)
<b>Union Pacific Railroad Response Teams</b>	
Morgan Environmental . . . . .	(2)
OH Materials . . . . .	(6)
Radian Corporation. . . . .	(1)
Portable Water Supply Systems . . . . .	(1)
Union Pacific Railroad. . . . .	(13)
Roy F. Weston, Inc. (WESTON®) . . . . .	(3)
ZEP . . . . .	(1)

To maintain a good working team and coordinated direction, it is also extremely important to keep outside political indifference to a minimum. The best way to ensure this is to keep key political figures informed. In this instance, the governor and senators from the state were contacted the morning after the incident and informed of actions being taken and assured of UPRR's commitment to protect the public and the environment.

Environmental consultants should be brought in early in the process to allow a coordinated environmental response which dovetails with the emergency response. The soil and water sampling that immediately followed the flush required significant manpower forces which had to be mobilized and coordinated. This provided early information as to the probable extent of contamination. Agencies involved had early information and felt comfortable allowing the railroad's consultant to conduct the site assessment and develop a plan of action. Emergency response contractors should be ready, under contract, and preapproved. In this incident OHM was on-site within 1 hour and 25 minutes of notification.

#### Several opportunities for improvement have been identified:

Railroads need to identify environmental sensitive areas and develop easy to use response plans. These plans need to incorporate resources available from public agencies and other private companies, and have up-to-date contacts with local authorities. In this instance, it was not known that the creek was a major drinking water source. UPRR has since developed new emergency response procedures and planning systems which are vastly simpler than former contingency plans. These procedures call for a general mapping of a territory by company response personnel along with local maintenance of way forces to identify important bodies of water or other environmental concerns. Local authorities are contacted and general roles and responsibilities identified. Contacts with other companies are made to identify resources and establish agreements for their common deployment if needed.

Good on-site communications are required to coordinate emergency and environmental responders as well as agencies and off-site parties. Even though regular meetings were being held, communication was sometimes difficult between the several railroad responders and consultants. Post-incident reviews have led to an improvement in availability of portable communication systems for major incidents.

With major incidents, it is important to keep good documentation of events, parties involved, on-site agreements, as well as needed support for development of work plans, press releases, etc. In this incident, there was little clerical and computer support.

Finally, it is imperative that each agency appoint a single representative to speak for that agency. It is difficult enough to manage the many different agencies involved, but this problem is compounded when there is more than one spokesperson for each agency. In some instances, agencies had up to six participants at a single meeting, and in some cases different representatives attended different meetings.

#### Acronyms

ACWD	Alameda County Water District
bis	bis(2-ethylhexyl)phthalate
CDFG	California Department of Fish and Game
cfs	cubic feet per second
DCTS	Director Chemical Transportation Safety
EPA	U.S. Environmental Protection Agency
FFD	Fremont Fire Department
FWS	U.S. Fish and Wildlife Service
HDC	Harriman Dispatch Center, Omaha, Nebraska
IRM	Interim Remedial Measure
MCLs	Maximum Contaminant Levels
µg/Kg	micrograms per kilogram
µg/l	micrograms per liter
OHM	OH Materials Company
OVM	organic vapor monitor
PCE	tetrachloroethene
POTW	Publicly Owned Treatment Works
PVC	polyvinyl chloride
PWSS	Portable Water Supply Systems
RD-1	Rubber Dam 1
RD-2	Rubber Dam 2
RWQCB	Regional Water Quality Control Board
SAHM	Union Pacific Railroad Special Agent Hazardous Materials
SVOCs	semi-volatile organic compounds
TCA	1,1,1-trichloroethane
UPRR	Union Pacific Railroad
USD	Union Sanitary District
VOCs	volatile organic compounds
WESTON®	Roy F. Weston, Inc.

**Questions and Answers:**

Q. You discharged about 2 million gallons of water into the POTW ( Publicly Owned Treatment Works)?

A. 2.9.

Q. Over what period of time?

A. Over about a 15 hour period.

Q. Was it a city treatment plant?

A. It was a county treatment plant and that was one of the concerns. They had a number of tanks that they could have used to divert about a million gallons for further processing, but they did not have a problem with what we gave them.

Q. So 2.9 million gallons represented some fraction of a fairly large, substantial treatment plant.

A. Yes, it was a large system.

Q. How were they persuaded to take this material?

A. That's probably one of the most interesting parts of that whole story. Basically there was no other choice. There were a number of agencies that were asked. They were brought into a room and were presented with the choices: we either go down stream or we go into the aquifer or we do what is best overall. The consensus was that it was best to go into the treatment plant and there was no adverse effect from that. It took quite a bit of persuading. It took closed door sessions with the agencies and a recognition by everybody that everybody had to give up some of their priorities and their goals to reach the solution that was best for all involved.

Q. Which agency or person acted as incident commander?

A. The local fire department, the Fremont Fire Department. The initial commander was one of the fire chiefs and the commander that took over the next morning was somebody who was specially trained in hazardous materials.

Q. An obvious question came to mind. When you dewatered that canal, were there any fish there? I was involved in a similar thing one time and after we pumped it down we found a lot of trout.

A. Yes there were some fish in the creek. There was a minor fish kill, probably on the order of 40 fish, primarily in that section of the creek between the two dams. It's not a fishing stream primarily but there are fish in there.

**PANEL DISCUSSION ON RISK BASED CLEANUP**

*Held on October, 18, 1994, following the symposium on diesel contaminated soil.*

My name is Chris Barkan and I manage the Environmental and Hazardous Materials Research Program for the Association of American Railroads. I'd like to invite the audience and all the speakers to participate in the last event of the diesel symposium this year. We have organized this panel to discuss issues affecting risk based cleanup at railroad contamination sites. I want to emphasize that this is meant to be an informal participatory discussion. We have developed a set of questions to stimulate discussion. Each individual will be asked to briefly respond to one question and then we want to encourage members of the audience to ask questions or express your perspective on these issues. You may direct your question or response to any member of the panel.

Let me introduce the panel. Paul Kuhlmeier is Director of Remedial Technologies for the Environmental Affairs Group at the Southern Pacific Railroad; Rick Eades is Director of Environmental Site Remediation for the Union Pacific Railroad; Joe Kreitinger is an Environmental Scientist with RETEC and is involved with the Gas Research Institute's work on environmentally acceptable endpoints; Frank Peduto is Chief, Technology Evaluation Section, Division of Spills Management for the NY State Department of Environmental Conservation and he will be presenting the regulator's perspective on some of these issues; Deborah Edwards is Staff Toxicologist, Site Remediation Planning and Environmental Sciences Division for Exxon Biomedical and finally Tom Potter is Director of the Gas Chromatography Lab at the University of Massachusetts at Amherst.

Barkan. Let me start by expressing why, from my standpoint and from both the railroad industry and the broader public interest perspective, there's a lot of interest in risk based corrective actions. Consider a simple example. Suppose you have a million dollars to spend on site remediation. You could use that million dollars to clean up one site and reduce the risk by 99% or you might be able to reduce the risk by 90% at 10 equivalent sites for that same million dollars. From a public policy standpoint you have done a lot more to reduce the public health risk in the latter case than the former. That's one of the reasons why industry is interested, and I think the public should be interested, in employment of risk-based clean up criteria. On the other hand we have to understand the regulator's perspective on this. It may not be as easy to evaluate the appropriate risk-based clean up level and it may require defending a decision to leave some of the contaminant in the ground. There is a need for us to understand the science that we're going to be drawing on to identify those cleanup levels. With that brief introduction as to why this discussion of risk-based cleanup is important, I'd like to start by posing the first question to Rick Eades,



Q. Why is a risk based approach to diesel fuel cleanup important to the railroads?

A. Eades... I think my answer is probably a widely held view among a lot of people here. First of all the railroad industry, is interested in and willing to do the right thing for the environment. We are in compliance and intend to comply with all the rules and regulations of the states in which we operate. But we also want to make sure that we spend our environmental dollars where they will do the most good. The reason risk based approaches are important to us is that we have limited resources and limited funds and want to make sure that they're used in the right way. The environmental community today knows that there's a difference in the different types of petroleum compounds that might have been released in the environment. For example if you are looking at 2000 milligrams per kilogram of gasoline in soil, there's a distinct difference between that and 2000 milligrams per kilogram of diesel fuel in soil. If you start looking at weathered situations, which we find on many of our sites since we have been around for a hundred years or so, there are also big differences there. We used a lot of fuels that were much heavier than diesel and have different effects than diesel. For instance, there are differences in solubility, mobility and toxicity. I think that's a widely accepted viewpoint today. There are also significant differences in site-specific effects and influences on various situations such as land use and land control, types of soil, depth to groundwater and groundwater uses. There are many different things that need to be considered when looking at sites. They can't all be just lumped into one package. So it's important that those differences be considered when setting action levels and treatment endpoints, and being sure that industry itself and the country can wisely use its environmental dollars.

Q. I have looked at a few railroad sites in Canada and they're probably no different than some of the slides you have seen during the presentations today. A fairly clear observation is that you can go to some areas where they have large fuel transfer facilities and find almost no problems. Go another 60 miles and find overly abundant problems. I'm wondering with the risk based type of analysis if you could actually work that into an employee loss control scenario in which you're bringing your employees along in terms of preventing these problems and identifying the risks. Have you looked at that in any way, in eliminating future problems?

A. Eades. Yes, we spend a lot of time and a lot of money upgrading our facilities and educating our employees. Most of the releases that we're working on today are not current releases. In most cases what we're dealing with are problems that happened 20, 30 or 50 years ago. Certainly in the case of Bunker C this goes back to the pre-1950s. These are old problems for the most part. The more current problems are not from practices but probably more often from leaks in systems that we can't detect yet. Union Pacific is spending a lot of money upgrading its facilities to make sure that does not happen. We're bringing underground pipes above ground for instance. We're putting on nozzles at our fueling facilities that have automatic shut-off valves that don't continue to pump fuel once a locomotive tank is full. Yes, we're trying very hard to make sure there are no continuing problems.

Audience comment. What you're really doing is physically removing the risk by, bringing your pipes up above ground. I think that makes a lot of sense because 10 to 15 years ago there was a much different operating practice. You recognize not only an environmental risk assessment but a risk assessment from a true loss control standpoint, making sure that your employees know what is going on. I think you would have better arguments with the regulators in that regard too and accomplish the same things that you're setting out to do.

Q. I wanted to get a viewpoint from a regulatory standpoint as to why the states or why the regulators are not considering risk based approaches more often and considering some of the things the Canadian government has done, for instance, in looking at different uses for residential, commercial and industrial property.

A. Frank Peduto. To date we haven't, but we're beginning to. It seems to be the trend nationally now, that risk based issues be addressed.

What are the benefits, drawbacks and obstacles from a regulator's point of view? I tried to write those out and I could come up with only one benefit, and that's site closure. We can close the site and that's a definite benefit for us. Everything else, technically, is a drawback: it's time consuming; we have limited resources in personnel, it's not scientifically supported to any great degree. We're in the midst of it but no one can come to us and really hang their hat on anything. There is no consistent modeling. It's also not all that popular. Now this is not a major criteria with us but it is a criteria. In essence, you are leaving contamination at the site. For all the arguments that you can have for why it may or may not pose any risk to anybody, they don't hold a lot of water with the public who look at us as regulators and as their spokesperson to protect their environment. Of course these things cost a lot of money to clean up. Is cost a benefit to us? I can make an argument that says not really, not to the regulator. To the community to the industry absolutely, but what is the benefit to us? The industry is coming to us with a request to leave contamination in the environment and the arguments are not all that solid yet. We are not educated in applying these principles.

Another part of that question is, what are the obstacles? There are regulatory restrictions in many states which prevent this kind of approach of doing business unless you implement regulatory change. Practically speaking as an environmental regulator, we have to balance the protection of the environment with industry's involvement in the program and in the state itself. We know just from a technological standpoint that you can't clean everything up all the time to the levels we would like to see. We have to try to establish a balance. What we need from industry is some education for us because it's going to be impossible for us to evaluate every single model or every approach that you walk in the door with. We deal with dozens, hundreds. How are we physically, practically, going to do that? I know in New York State we're working on, for the spills program, a closure policy and we're probably going to recommend the elements of what is now known as RBCA (Risk Based Corrective Action), tiered levels of risk assessment. Tier 2 numbers need to be developed. I don't know where they're coming from right now. Who's going to establish them? How are we going to get them? Tier three, industry is going to come in with their arguments establishing levels.

How are we going to evaluate each and every one? We don't have a map for doing it, let alone an answer. That's the essence of it probably, why we haven't embraced this approach in the past.

A. Paul Kuhlmeier. My colleague from the State of New York has echoed a lot of the things that we find problematic when we're trying to negotiate cleanup levels, not only with petroleum, but at our other sites throughout the western United States. If one happens to look back on the annual survey that I believe AEHS (Association for the Environmental Health of Soils) does, you will find that some 40+ states in the United States still utilize the ubiquitous TPH value in both soils and groundwater to establish cleanup levels. If we look back on where those numbers, such as one hundred parts per million in soil and 50 parts per billion in groundwater, come from, we quickly realize that they come from modeling, very simplistic modeling done many years ago utilizing basically benzene in a fresh gasoline matrix to determine what will constitute leaching benzene above the MCL to groundwater or contact with pure benzene within soils. As we have noted earlier today in a lot of our discussions, that clearly does not characterize the weathered materials that often are found in our railroad yards.

Looking beyond that, I see at least three other fundamental obstacles that we have in front of us. One is the precedent that's being set by the Federal Government that applies what I like to call the "listing mentality". Give me a numerical number that I can just look to. As points and examples we can look at RCRA's Land Disposal Regulations, (CFR 261) at the listed waste and the characteristic waste, which promulgate numbers either by process or by concentration for cleanup. We can even more recently look at the new Universal Treatment Standards which were published in the Federal Register, September 19 of this year, that again provide us a list for wastewaters and non-wastewaters. Finally we can even look to the CERCLA program where recently EPA has published what they call "presumptive remedies". If you have a certain type of chemical in the ground, there is a certain list of remedies that you just go out and do. So there's that type of mentality that we just have to get past.

The second obstacle that we need to get past is one that my colleague at New York State mentioned, and that is education. As he noted there is a lack of education, on the part of both our state regulatory agencies and the public. We have to understand the fate and transport processes of petroleum in the ground, as well as what the real risk is associated with paraffins and waxes where that research has not been done to date.

Finally, I think there's a general resistance, and I noted that a little earlier here, among members of our regulatory community to apply risk guidance which is available but not necessarily mandated in various states. I point to the State of California where they routinely apply their guidance documents for a hundred parts per million of TPH cleanup in soil even though an entire treatise has been written on the topic of application of risk reduction. That's not to say that Southern Pacific and other railroads haven't made some strides. We clearly have. We're working with the State of California to apply mobility arguments by utilizing soil column analysis to determine how clean is clean in vadose soils as well as groundwater. We're making some good strides in that area. We're also working with the State of Oregon and other states, Nevada for instance, on constituent determinations for cleanups, some based on PAHs as opposed to the ubiquitous TPH.

But ultimately, as Chris mentioned in the beginning, we have to turn to ourselves and ask what is it that we want to achieve and where is our dollar best spent. We have limited resources everywhere we go. A study done in the mid 1980s by an economist, I believe from the University of California at Berkeley, evaluated the value, the cost-benefit ratio, of government regulations, some 85 of them as I recall. What he found was that the best law that we have out there in terms of the cost to comply with the law per life saved is the seat belt law which is worth \$100 per life saved. At the very bottom of the list, is each and every one of EPA's regulations. The very bottom being the land disposal regulations with an estimated value to society of 80 million dollars per life saved. Somewhere along the line society has to ask where it wants to apply its scarce resources, cleaning up petroleum along railroad tracks that's been there for perhaps a hundred and fifty years, or insuring the safety of our lives and our children's with better automotive safety?

Audience Comment. I'd just like to briefly state some of the issues that the State of Washington is facing in looking at risk based cleanup standards. We are not allowing them at the present time. One of the reasons for that is the fact that there is very little toxicological data available on petroleum. It's a very complex mixture, there are two to three hundred components in it. The only good data are on BTEX and contaminants like naphthalene, and we're frankly worried about using just those as indicator compounds. What is the result of all the contamination that you leave behind? Our toxicologist has looked at EPA's RFDs for petroleum and it is his opinion that they were not scientifically derived and they are not scientifically supportable. We have gone to the Western Petroleum Marketers Association and the American Petroleum Institute and asked them to please provide us with some good data that we can evaluate so that we can come up with some good risk based cleanup standards. Those are some of the issues that regulators are struggling with because there really is not a lot of data on the majority of petroleum constituents.

Deb Edwards. Based on my interactions with many regulators since I have worked with Exxon I agree with the woman from Washington that for most petroleum mixtures there are not a lot of data that a regulator would consider adequate for developing RFDs or slope factors or things that are normally used to develop cleanup standards. At most sites what you're finding is a mixture of petroleum products, not just diesel, or not just gasoline, but maybe a mixture of the two. Ideally, what you would like to have, to do a risk assessment on that site, is some tox data on the weathered material. That just does not exist because there are many variables that go into weathering a product, including the soil and the climate at the site. Those data have never been developed. As far as data on fresh, single products there are some data on that. Those data were used by the EPA to develop their provisional RFDs and slope factors for gasoline and diesel. However a lot of that is not by the exposure route you would like to see. In other words, it was dermal or it was an inhalation of a mixture that was artificial. The tox data on weathered products is not there. For a large part, the tox data on fresh products is not there. What we have come down to, and what most states that don't use something like TPH are using, is that they're looking at single products like BTEX or PAHs and they're developing their standards on that basis. They're looking at

essentially surrogates. I think one way we could go beyond that is to use a number of surrogates not only for the BTEX and the PAHs, but also for the material that is still left there. However, what we will have to do is validate those surrogates on sites and in some way we will have to develop some tox data to address your issues. The other problem that we have always had is that you can't prove a negative so we develop a lot of tox data and it costs a lot of money. We always get into a contest with the regulators because we never can seem to develop enough tox data. What I think we really need is regulators and the people who really are interested in their products to sit down and say if you develop these data and they show no toxicity then we will accept that.

Kuhlmeier. If you have subsurface soils, you don't have direct exposure, but when you're looking at direct exposure then you're worried about the mixture. As the talk I gave noted, at most of the sites that the railroads are involved, the soils are subsurface soils, so you're really interested in the constituents that are mobile. What's mobile are BTEX and some of your PAHs. Typically your TPH value is zero in your soil samples. So you could technically set a TPH standard in those cases based on the surrogates. I think what you're bringing up is completely directed towards direct exposure.

Edwards. One of the big issues, I think, for the railroads, is the fact that they really haven't had anyone look at their exposure scenarios. They are really looking at exposure scenarios for industries like refineries where people can come onto the refinery and trespass. Also, most of those railroads will never become residential properties. There's very little data on how often a child might run out to a railroad site or a track.

Eades. Right now the State of Texas, for instance, is a good example. Their new risk reduction regulations take into account deed restrictions and that sort of thing for the railyards. Although you can never say there won't be a residential area there, the State is considering land use scenarios.

Edwards. I understand the regulators' perspective also. If you sit down and really explain to them what your products are, discuss the data with them regarding the fate and transport and mobility of the material, you realize that a lot of them don't understand a lot about your material and they really don't trust you, but it's a matter of education as well as resources on their part to review what you have done.

Kuhlmeier. Both the State of Idaho and the State of Colorado were able to easily understand direct data from the site versus paper arguments which are often used in risk assessments. That's somewhat harder and takes a lot more education.

Barkan. I'm interested in one aspect of Mr. Peduto's earlier response. It seemed to me there were two elements to his comments. One was a policy aspect and the other was technical. The policy aspect was that if a material has been spilled, it needs to be cleaned up. You need to have a good explanation for why you're going to leave some product in the ground. If it costs a lot of money to remove it, strictly speaking that's not the regulator's problem. The technical aspect was limitations in the data and uncertainty about the validity of the models that are being used. I think I heard a response to the technical portion of that from Paul Kuhlmeier. I'm not sure I have heard anybody respond to the policy aspect of Mr. Peduto's comment. Does anybody care to comment on that either on the panel or from the audience?

Peduto. In New York, we have regulatory cleanup standards. However, we also have another avenue, because we know groundwater standards often cannot be achieved. We have done risk assessment on an informal basis for a long time and have closed sites this way. We are beginning to look at risk assessment on a more formal basis now. One of the things I'd like to ask industry is, don't wait for your site to show up. Why can't we look at this now in a more generic sense and study the issue? Hopefully we will come to some agreement or at least a direction and a roadmap. I think the time to get together is now. It could be that old railroad yards will have certain conditions or levels because we can identify human exposure. You can establish a set of criteria for typical situations like this that occur nine times out of ten and deal with the odd issue when it comes along. I think there has to be some cooperation. I think we have got to look to someone like EPA to set direction in determining acceptable risk assessment procedures.

Q. I think those are some very good comments and the question or comment to the AAR is, do we have some plans or do we need to put together some plans to hold some sort of national symposium between the railroads, their consultants and the agencies to try to set standards and to educate the agencies on the risk based procedures that we now use?

A. Barkan. The AAR is working cooperatively with both the Gas Research Institute and the US Air Force sponsored TPH Criteria Working Group. Among the objectives of both groups is just this sort of thing. Joe Kreitinger, Deh Edwards and Tom Potter, on our panel today, are all involved with these efforts, perhaps we can ask them to elaborate.

A. Joe Kreitinger. I would just provide a little information on the Gas Research Institute's (GRI) program. What GRI has done is looked at bioremediation and recognized that there is a tremendous data base. In fact we saw some of the data presented here today that shows that hydrocarbons are reduced through biological treatment techniques, but there is a residual hydrocarbon fraction that remains following biological treatment. There are some questions about the bioavailability of the remaining hydrocarbons and the ability of microorganisms in soil environments to metabolize those contaminants. It begs the question as to the real availability of those hydrocarbons to target organisms, and the mobility of those hydrocarbons that remain as residual fractions. That ties right into the aged or weathered hydrocarbon issue in soils, and the toxicity of what may be relatively high constituent levels of PAHs or other compounds that remain resistant to biodegradation and appear not to be particularly mobile. GRI is reviewing the data that currently exist in the grey literature, the published literature, and from the U.S. EPA and other technical agencies, to try to get a handle on this because it is going to be part of the risk assessment modeling equation that has not yet been looked at in a significant way. It's an important issue that GRI is pursuing and they are planning a meeting next spring, to discuss environmentally acceptable endpoints and the relationship between hydrocarbon residue in soils and their impact on toxicity to target organisms. (Editor's Note. This meeting was held in Washington, DC in May, 1995.)

A. Tom Potter. I'd like to say a few words about the Total Petroleum Hydrocarbon Criteria Working Group. I think that the word that I want to emphasize is "team" because there are lots of people involved, including state and federal agency personnel, consultants, and representatives of industry, a large group of people at this stage. It's an informal association in the sense that anyone that wants to belong can belong. We started back in February of this year and have had several meetings. Tomorrow is the fruition of our efforts up to this point in the sense that we will have technical presentations outlining our progress in evaluating the issues surrounding the use of total petroleum hydrocarbon measurements to evaluate risk and/or to identify remediation endpoints at release sites. Within the Total Petroleum Hydrocarbon Criteria Working Group there are five technical advisory groups. One of the tech advisory groups is entitled Analytical and Environmental Fate, the group that I chair. We have three basic objectives.

Objective one - as a group we identified a compelling need to systematically compile information describing the chemical composition of common petroleum products of commerce. I never cease to be amazed at how little quality information is available describing petroleum product chemistry. I think the best evidence for that is the fact that we continue to use total petroleum hydrocarbon measurements, an exceptionally crude analytical approach, in testing programs implemented at release sites, hopefully in an effort to gain some insight into risk. A more subtle point was referred to earlier in some of the presentations. We often talk of PAHs in a generic sense. PAHs are for the most part, by definition, those compounds that have been targeted in the EPA analytical methods as part of regulatory programs such as RCRA. Those particular target compounds are not necessarily the most appropriate target compounds with regard to analyzing petroleum products or petroleum product residues derived from crude oil. We have some major data gaps that we need to develop information on and hopefully move ahead in guiding the design of more appropriate analytical methods and developing a more detailed target compound list. That's one of the other objectives of our TPH Criteria Working Group. The third objective of the Criteria Working Group is simply to get the word out about just what total petroleum hydrocarbon measurements mean. Certainly we're not going to scrap them, but we need to use the information appropriately. That's really the sum total of our activities. It's a large plateful and I hope that we're going to make some progress on it in the years to come and certainly I, for one, would welcome anyone's participation.

A. Peduto. I had mentioned earlier about how we have to get together to do things. This TPH group caught my interest. If this group takes it to fruition, it will hopefully be the most recent, current and scientifically acceptable approach to using and applying TPH. If we can take that same collaborative approach with other items, whether it's risk assessment or other methods, it will be accepted by the population as a whole, both regulatory and industrial as well as the scientific community, because everyone will have played a part. Maybe this will be a model for how things should start to occur in the future.

Barkan. I'd like to ask some of the railroad people that are either on the panel or in the audience a question. Both the regulators and the academicians have referred to data limitations; what are some of the specific data limitations that you're encountering, in terms of trying to employ risk based corrective actions on railroad remediation sites? Are there some particular chemicals for which the toxicological or other kinds of data are limiting?

A. Kuhlmeier. From the perspective of Southern Pacific, most of our weathered fuels are very long chain paraffins and waxes, asphaltines, for which there are no toxicological data presently available nor any studies to our knowledge that are even being undertaken. But perhaps more important with respect to the application of risk assessment is not the fact that we don't have salient data on long chain paraffins and waxes, but rather the complex nature of the risk assessment process itself. I have often likened the risk assessment approach to the application of a very complex three dimensional numerical groundwater model in the sense that it has a tremendous number of parameters and assumptions that you have to put into it. Is it reasonable to assume that everybody in a low income neighborhood will dig fifteen feet deep to install a pool? Is it rational to assume that a child at six years old will jump an eight foot barbed wire fence three times a week for eight years and eat two tenths of a gram of soil? I don't believe so, yet SP has run up against those assumptions being applied in risk assessments. So we have to look at things like what is a rational risk scenario with respect to trespassers, with respect to workers, with respect to potential residents. Do kids actually run to the garden and dig in three feet deep into the earth and then eat the two tenths of a gram per day from that garden each and every day? Well of course they don't, but often times we're compelled to use those types of unreasonable assumptions. Similarly within the chemical arena, there's considerable debate as to what the slope factor should be with respect to these various chemicals which then are transformed into exposure factors. There are a whole myriad of assumptions that go into risk assessment. The debate over what those assumptions should be needs to be ironed out to some form of consensus as to what is rational to apply before we're going to be able to make a lot of headway in the use of risk assessment.

A. Eades. I agree with Paul Kuhlmeier. I just want to add, though, that we are making a little bit of progress. There are some states that are beginning to look at risk. The state of Texas' risk reduction rules both for solid waste and for the underground storage tank program that it runs, are providing relief for us so we will applaud that. We're hearing that it's beginning to spread. Adjoining states are looking at Texas regs and thinking about applying them. We know that some states have been holding public meetings on the new ASTM guidelines on risk, so I'm encouraged. I think there is some movement and we look forward to that continuing.

A. Kuhlmeier. Often times though we found it boils down to the individual regulator that we're working with on an individual case basis. In Nevada we worked with a regulator who was very innovative and saw that there was a way for us to remedy an old bunker fuel problem in an innovative way that was both productive and cost effective. Yet in many other instances, in various states, we have run up against a stone wall with the regulators not wanting to apply basic scientific or engineering knowledge, but rather fall back on default type of guidance or mandates. So, in essence what we're finding is it's a case by case situation with how to clean up various sites within an individual state, or even smaller counties or regions within a state.

Peduto. One of the things we always look for are toxicity data. For all of the money you're spending trying to satisfy every regulator you run into, why doesn't the railroad apply some of that money and get toxicological data. At least you will have something to put on the

table and we will have something to react to. You have to spend some money to make some money, that's the old adage. I think we've traditionally looked to the regulatory agencies to do that. I don't deny that we probably should be the people to do that but we don't have those kind of resources. In New York State, we clean up and set criteria for the cleaning up of oil spills. However, we don't make the standards, our Health Department makes the standards for groundwater. Our Health Department needs more toxicity data. To apply resources where they can get the most mileage is important.

Edwards. I think the participation of industry in the TPH Criteria Working Group organized by the US Air Force initiative and also GRI and PERF (Petroleum Environmental Research Forum) and other organizations like that, indicates their willingness to provide that kind of data. I think that we need regulators to sit down with us and tell us what kind of data would be acceptable for them to take and develop regulations on that basis, because we're not just going to go out and spend money developing tox data that we will never be able to use.

Potter. I think that we're going to have to help them understand what it is they need to know. Having worked in a state regulatory agency for a number of years and have been on that side of the fence, it's an educational process but I don't think we can expect the regulators to give us the wish list. I say us, meaning people who are not within the regulatory framework. I think we need to help them understand.

Barkan. The TPH Criteria Working Group has actively solicited the input of regulators and I think that the more that regulators participate the better off we will be. The objective is a scientific meeting of the minds on the subject.

We're running out of time so I'd like to conclude the discussion by referring you all to the session tomorrow morning. The Cleanup Standards Setting session is going to be held in the Campus Center Auditorium. The TPH Criteria Working Group's work to date will be presented. Furthermore, a number of the people who are involved with the Gas Research Institute effort are going to be speaking on Thursday in several of the sessions. I would encourage anybody who's interested in more depth in the subjects discussed today and in the efforts of these groups, to attend those sessions. I would also like to thank our panelists and our speakers today for a very interesting set of talks and discussion.

## ACRONYMS

ACWD	Alameda County Water District
AFB	Air Force Base
ANOVA	Analysis of variance
AS/SVE	Air sparging and soil vapor extraction
AS	Air sparging
ASTM	American Society for Testing and Material
BETX	Benzene, ethylbenzene, toluene and total xylenes
BTEX	Benzene, toluene, ethylbenzene and xylenes
BTXE	Benzene, toluene, total xylenes, ethylbenzene
CAP	Corrective action plan
CDFG	California Department of Fish and Game
CERCLA	Comprehensive Environmental Response Compensation and Liability Act
cfs	cubic feet per second
CME	Central Mine Equipment
CSF	Carcinogenic slope factor
DCTS	Director Chemical Transportation Safety
DNR	Department of Natural Resources
DO	Dissolved oxygen
DOT	Department of Transportation
EPA	Environmental Protection Agency
FFD	Freemont fire department
FID	Flame ionization detector
FWS	Fish and Wildlife Service
GC/MS	Gas chromatograph/mass spectrometry
GC	Gas chromatograph
HDC	Harriman Dispatch Center
IR	Infrared spectrophotometer
IRM	Interim remedial measure
LNAPL	Light nonaqueous phase liquid
MCLs	Maximum contaminant levels
MDL	Minimum detection limit

MODF	Mineral oil dielectric fluid
MS/MSD	Matrix spike/matrix spike duplicate
MS	Mass spectrometry
MTBE	Methyl tert-butyl ether
NAPLs	Nonaqueous phase liquids
ND	Non detected
OHM	OH Materials Company
OVA	Organic vapor analyzer
OVM	Organic vapor monitor
PAH	Polyaromatic hydrocarbons
PCE	Tetrachloroethene
PCS	Petroleum containing soils
PHC	Petroleum hydrocarbon
PID	Photoionization detections
POTW	Publicly owned treatment works
PVC	Polyvinyl chloride
PWSS	Portable water supply systems
QA	Quality assurance
QC	Quality control
RCRA	Resource Conservation and Recovery Act
RD	Rubber dam
RfD	Reference dose
RfIs	RCRA facility investigations
RWQCB	Regional Water Quality Control Board
SAHM	Special Agent Hazardous Materials
SLAEM	Single layer analytical element model
SPLP	Synthetic precipitation leaching procedure
SVE	Soil vapor extraction
SVOC	Semivolatile organic compounds
TCA	1,1,1-trichloroethane
TCLP	Toxicity characteristic leaching procedure
TIC	Tentatively identified compounds
TNRCC	Texas Natural Resource Conservation Commission
TPH	Total petroleum hydrocarbons
TRPH	Total recoverable petroleum hydrocarbons
UPRR	Union Pacific Railroad

USD	Union Sanitary District
USEPA	United States Environmental Protection Agency
UST	Underground storage tank
VIW	Vapor injection well
VMP	Vapor monitoring points
VOC	Volatile organic compounds
WDNR	Wisconsin Department of Natural Resources
WPDES	Wisconsin Pollutant Discharge Elimination system
XRF	X-ray fluorescence

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