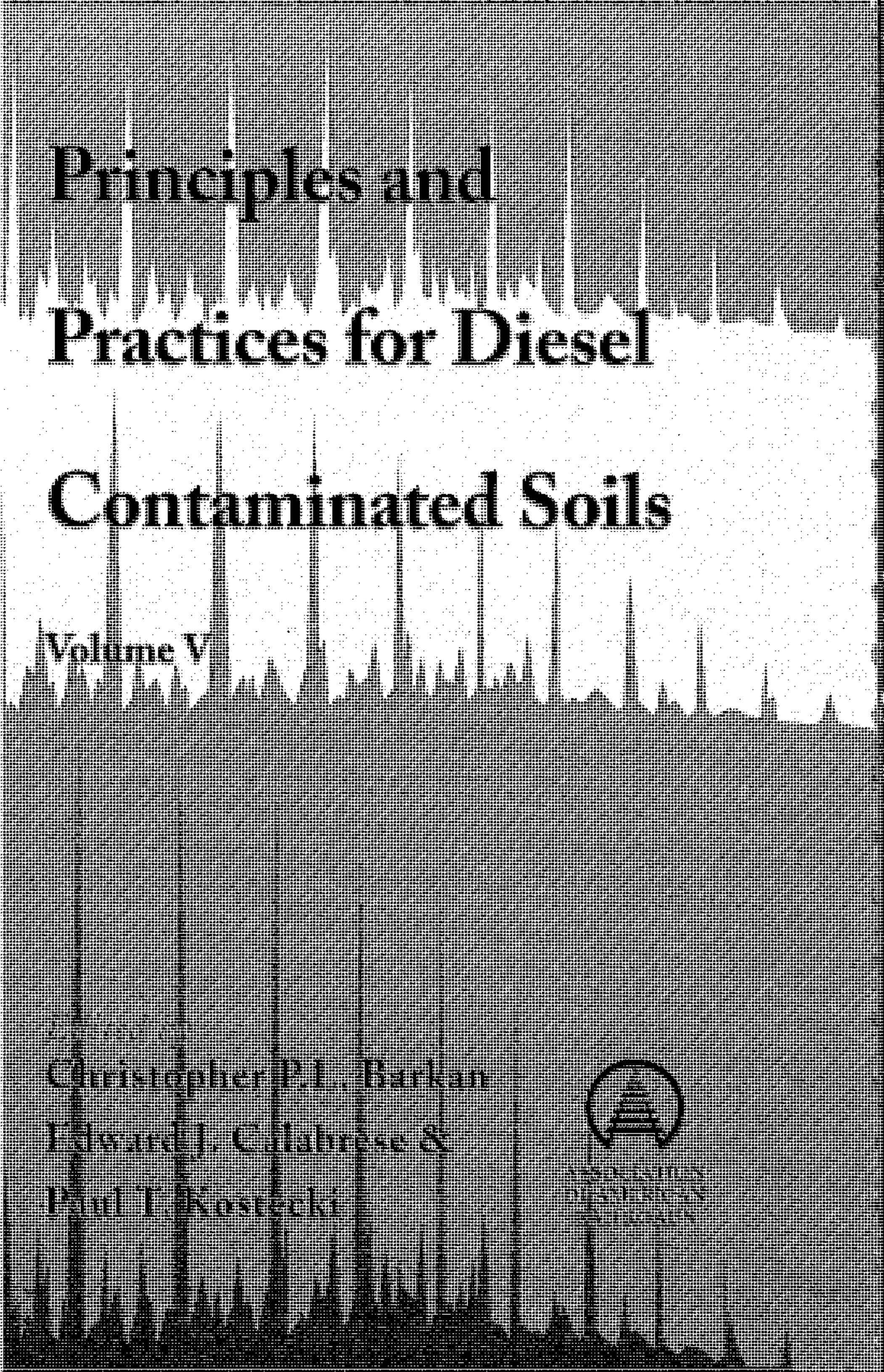

Principles and Practices for Diesel Contaminated Soils

Volume V

Edited by

Christopher P.L. Barkan

Edward J. Calabrese &

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CHRISTOPHER P.L. BARKAN
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Biographies

Christopher P.L. Barkan is Senior Manager of the Environmental and Hazardous Materials Research Program of the Association of American Railroads (AAR). The program sponsors and conducts research for the railroad industry on pollution prevention, remediation technologies and hazardous materials transportation safety. Dr. Barkan also serves as Deputy Project Director of the RPI-AAR Railroad Tank Car Safety Research and Test Project, a cooperative program of the tank car and railroad industries studying tank car safety. Barkan holds graduate degrees in biology from the State University of New York at Albany where he conducted research on the application of stochastic optimization models to ecological processes. He continued this work as a research fellow at the Smithsonian Institution's Environmental Research Center prior to joining the AAR Research and Test Department in 1988. His research at the AAR has included the development and application of quantitative risk assessment models for rail transportation of hazardous materials, with particular emphasis on the environmental impact of chemical skills. Other research for the railroads has included studies of the environmental impact of rail lubrication, stormwater runoff characteristics, toxicity characteristic leaching procedure testing of railroad crossties, and evaluation of the factors affecting successful application of in situ bioremediation. Current projects include options to reduce spillage of diesel fuel, extending the life of cleaning solutions used in railroad shops and, developing new data on the chemical composition of weathered petroleum hydrocarbons typical of railroad sites. He serves on the steering committee of the Total Petroleum Hydrocarbon Criteria Working Group, a cooperative effort of industry, and government that is consolidating data and developing approaches to more effectively apply total petroleum hydrocarbon (TPH) and risk-based cleanup criteria to petroleum contaminated sites. Barkan is an author or editor of a number of papers, reports and books on railroad environmental subjects.

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 co-author 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, 4 and 5; 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, 3 and 4; 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 Soil and Groundwater Cleanup magazine, as well as on the editorial board of the Journal of Human and Ecological Risk Assessment.

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 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: Ecogenetic: 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, 4 and 5; Hydrocarbon Contaminated Soils and Groundwater, Vols. 1, 2, 3 and 4; Multiple Chemical Interactions; Air Toxins 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, Vols. 1, 2, 3 and 4. 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.

Preface

Proceedings of 1995 Symposium on Remediation of Diesel Fuel Contaminated Soil

October 24, 1995, University of Massachusetts, Amherst
Sponsored by the Association of American Railroads

This volume is the fifth in a series of books to be published from an annual symposium on remediation of sites contaminated with diesel fuel and on other related topics. The symposium is sponsored by the Association of American Railroads and is held in conjunction with the Contaminated Soils Conference organized by the University of Massachusetts each year. Both the symposium and this book series are a response to the need for discussion and publication of work on petroleum hydrocarbons other than gasoline. With the publication of this volume, over 50 papers addressing these issues have been published in this series, thereby substantially expanding the knowledge base available to individuals concerned with the cost-effective cleanup of property contaminated with diesel fuel and related issues. The shift away from the strict focus on gasoline issues is part of a larger trend recognizing that all petroleum hydrocarbons do not pose the same level of risk and should not necessarily be treated in the same manner as gasoline. This awareness has led to a nationwide paradigm shift in the approach to establishing cleanup levels for petroleum hydrocarbon contaminated sites. The annual conference and symposium have been an important forum for discussion of this shift, and the railroad industry has been vitally involved in encouraging this effort.

As corporations with operations in many states and provinces in North America, railroads became cognizant of the varying cleanup requirements being demanded of them at diesel fuel spill sites in various locales. Generally, this variability did not reflect differences in risk, instead, it indicated the different, and sometimes arbitrary, approaches to establishing cleanup goals employed by different agencies, and revealed the need for a consistent scientific basis for estimating risk from spilled petroleum hydrocarbons. Railroads, and others encountering these circumstances, are seeking a more rational approach that takes into account both the characteristics of the spilled material and its impact on the environment. The result is a broad-based coalition, involving regulators and the regulated community, who are jointly developing a risk-based approach to setting cleanup requirements. The objective of this effort is more efficient allocation of cleanup resources to protect human and environmental health.

To date, there is limited experience with the new methodology, and several issues remain to be resolved before full advantage of this approach can be taken. The coming years promise to be exciting ones in terms of the development and application of new, more detailed, scientific data on weathered hydrocarbon composition, analysis of the environmental mobility of hydrocarbons in soil, and demonstration of the efficacy of setting cleanup goals using risk-based criteria at a variety of sites. Several of the chapters in this volume deal with topics relevant to risk-based cleanup, including site risk assessment, appropriate site closure levels, and contaminant measurement techniques.

Development and acceptance of methods for establishing appropriate risk-based cleanup levels are important, but achieving these levels by the most cost-effective treatment method is also necessary. Understanding the response of diesel fuel to different remediation approaches under a variety of conditions is essential to planning the most cost-effective approach at a particular site. A number of the papers in this volume describe the site-specific conditions, as well as the rationale and effectiveness of the method employed to contain, remove, or bioremediate the spilled hydrocarbon. As this information accretes, a general picture emerges of the effectiveness and economics of different approaches under different conditions. This provides the environmental professional responsible for cleaning up diesel contaminated sites under the wide variety of conditions encountered in North America with a solid reference base from which to seek firsthand knowledge about what worked, what did not, how long it took, and how much it cost. These are all questions of vital interest to persons responsible for planning, managing, and overseeing the cleanup of sites contaminated with diesel fuel.

Christopher P.L. Barkan
Senior Manager
Environmental and Hazardous Materials Research Program
Research and Test Department
Association of American Railroads

Acknowledgements

This book and the annual diesel symposium from which it comes would be impossible without the enthusiastic support and participation of the railroad environmental community, in particular the members of the AAR Environmental Affairs Working Committee and the Environmental Engineering and Operations Working Committee. The editors and the 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 are due to Roger Andes for his assistance with the preparation of the diesel symposium and the papers presented here, to Linda Rosen for her perennially energetic support of the annual conference, and Tamlyn Oliver for her patience and persistence in bringing together the materials presented in this volume.

Contents

Chapter 1

Integrated Risk Analysis of Residual Diesel Concentrations in Soil Following a Train Derailment

John W. Anthony
Hydrologic Consultants, Inc., Lakewood, CO

Robert J. Sterrett
Hydrologic Consultants, Inc., Lakewood, CO

Glenn C. Millner
Industrial Compliance, Little Rock, AR

Michael J. Grant
Southern Pacific Lines, San Francisco, CA

INTRODUCTION

During the early morning hours of March 19, 1991, a debris flow, that occurred as a result of a heavy rainstorm in the coastal Santa Ynez mountains, washed out the fill embankment spanning the Cañada Agua Vina culvert, three miles southeast of Point Arguello, California (Figures 1 and 2). At 4:15 a.m., an eastbound freight train of the Southern Pacific Transportation Company (SPTCo), consisting of three locomotives and 28 freight cars, reached the damaged structure. Two locomotives successfully passed upright across the embankment. However, the rails then collapsed, resulting in a general pileup of the remaining consist. A total of 24 of the 28 railcars, and two of the three locomotives, were derailed. An estimated five thousand gallons of diesel fuel were spilled from ruptured tanks on the locomotives, together with a large amount of industrial-grade paraffin that leaked from three tank cars. Other spilled freight included canned goods, feed corn, soda ash, shingles, and lumber.

An emergency-response team was able to contain the spilled diesel fuel and paraffin by constructing earthen berms around the spill site. Remediation of the soils that contained diesel fuel constituents became the principal issue of concern, as diesel fuel had infiltrated soils on the site by the time remedial activities commenced. Site remediation, consisting of excavation and off-site disposal of the soils that contained diesel fuel, was conducted from March 22 to April 5, 1991.

Soil samples were collected from the excavations, at the conclusion of remedial activities, to assess whether diesel fuel constituents were still present in soil in the spill area. The analytical results indicated that some fuel hydrocarbons did remain in soils adjacent to the excavations. Accordingly, SPTCo contracted Hydrologic Consultants, Inc. (HCI) to assess the possible vertical and lateral distribution, and quantities of fuel hydrocarbons, remaining in the subsurface, and to evaluate the potential risks to the environment due to the presence of diesel fuel constituents in soil at the derailment site. Dr. Glenn Millner, currently with the toxicology group of Industrial Compliance, Inc., was also contracted, to assess the potential risks to human health, associated with exposure to diesel fuel in soil.

The analysis was carried out by HCI and Industrial Compliance, Inc., using sampling data, including the results of geotechnical and chemical analyses, collected by the remediation contractor during the spill remediation. A series of calculations was conducted by HCI to predict the transport of diesel fuel constituents in the unsaturated zone. The calculations were intended to assess whether diesel fuel constituents originating in the spill area were likely to migrate to the water table beneath the site, in concentrations that would adversely affect ground-water quality. Potential exposure pathways were then characterized, and a residual potential contaminant exposure scenario for hypothetical human receptors ("risk assessment") was developed by Industrial Compliance, Inc., using site-specific data. The risk assessment was intended to estimate the risks to potential human receptors, that might result from No. 2 diesel fuel remaining in soil.

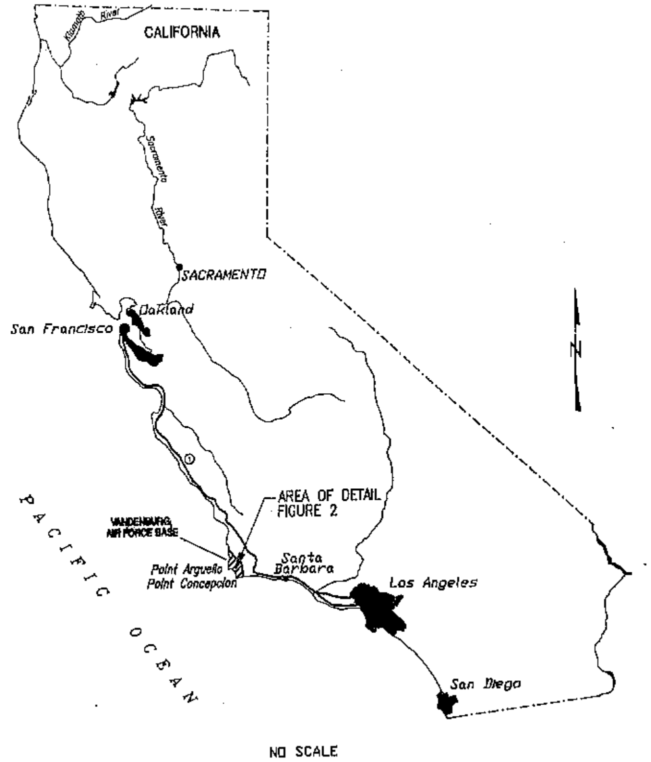
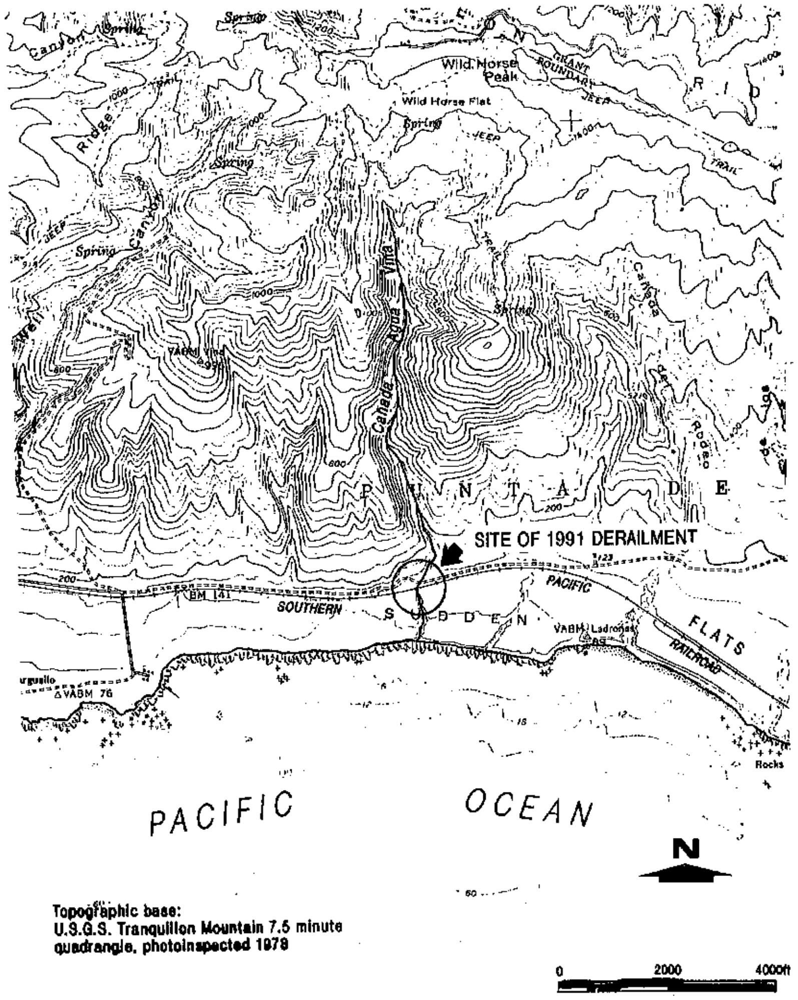


Figure 1 Location of Sndden Derailment Site.

This paper discusses the methods used to conduct the transport and exposure analyses, and summarizes their results.



Topographic base:
U.S.G.S. Tranquillon Mountain 7.5 minute quadrangle, photoinspected 1978

Figure 2 Detailed Topography in Vicinity of Derailment.

BACKGROUND INFORMATION

Location and Description

Site Description

The derailment site is located on the Sudden Flats of South Vandenburg Air Force Base, approximately 14.5 miles southwest of the community of Lompoc in Santa Barbara County, California (Figure 1). The spill area lies on the SPTCo rail right-of-way between mile posts 313.83 and 314.5, within Vandenburg Air Force Base boundaries, approximately 3.4 miles northwest of the Sudden rail siding, and will be referred to as the "Sudden derailment site".

The Sudden derailment site is adjacent to a perennial stream called Cañada Agua Vina, and extends approximately 1,700 feet east-southeast between the Cañada Agua Vina culvert and the East Creek channel (Figure 2). The Pacific Ocean lies 1/4-mile to the south-southwest. The site is bounded on the north and south by Vandenburg Air Force Base and on the northwest by the Point Arguello U.S. Naval Missile Facility. The land immediately surrounding the site is undeveloped and consists of grass-covered, open rangeland.

Physiography and Climate

The Sudden Flats are located near the rocky coastline of the Pacific Ocean and occupy the entire breadth of a gently sloping, alluviated coastal plain (Figure 2). The plain lies on the tread surface (upper flat surface) of an elevated marine terrace that extends from the bordering sea cliff inland to the foothills of the east-west-trending Santa Ynez Mountains, immediately north of Sudden Flats. This plain ranges in elevation from about 25 feet NGVD (National Geodetic Vertical Datum of 1929; equivalent to mean sea level) near the sea cliff, to about 160 feet NGVD at the slope break near the foothills.

The coastal plain and adjacent hill slopes have been dissected by perennial and intermittent drainages that originate in the nearby mountains. The distal edges of alluvial fans, associated with these drainages, bound the plain to the north (U.S. Department of Agriculture, 1958; Dibblee, 1988). The Sudden derailment site itself lies immediately east of a perennial stream (Cañada Agua Vina) that has incised a deep arroyo from north to south into the marine terrace (Figure 2). The SPTCo rail line crosses the stream over an earthen embankment that is pierced by a culvert; at this point, the elevation of the railroad grade is approximately 100 feet NGVD, and the elevation of the streambed is approximately 80 feet NGVD. The land immediately adjacent to the derailment site slopes gently up towards the north, and is vegetated with grasses, chaparral, and sage.

The climatic conditions for the area are similar to those reported for the Central Coast region of California over a 105-year period of record (National Oceanic and Atmospheric Administration, 1991a; ibid., 1991b). While the climate of coastal California is characterized by distinct annual wet and dry seasons, the area experiences mild weather throughout the year.

Archaeological Features

The train derailment occurred within the boundaries of two recognized archaeological sites that occupy the coastal plain, and adjacent slopes and ridgetops, from the sea cliff inland towards the foothills of the Santa Ynez mountains, for a distance of 0.4 miles along Cañada Agua Vina. The creek forms a common north-to-south boundary between the two archaeological sites, while the SPTCo main line traverses both sites from east to west (Figure 3). The two sites were previously occupied by the Chumash Indian community of <u>Nocto</u>, and consist of deep shell middens (refuse heaps) covering a total area of 125 acres. The combined size of the middens, together with their generally excellent state of preservation (Glassow *et al.*, 1976; Spanne and Glassow, 1974), make this an archaeologically-important prehistoric habitation site of the California coastal mainland. The archaeological deposits on the SPTCo right-of-way are either deeply buried beneath the railroad grade and ballast, or are heavily disturbed as a result of past railroad construction.

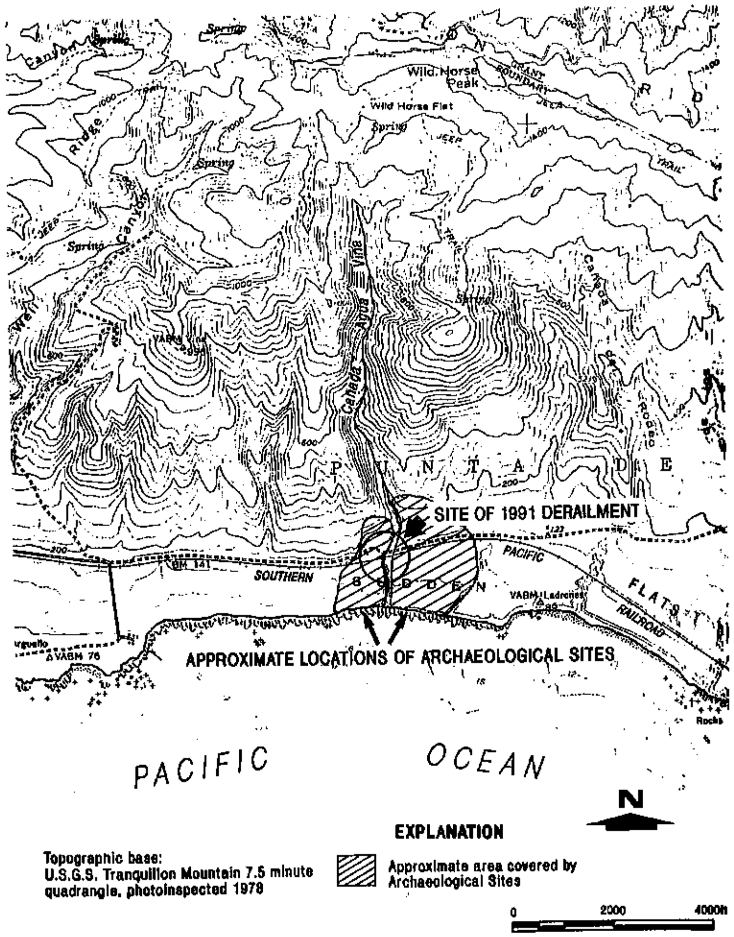


Figure 3 Locations of Archaeological Sites.

Geology

The Sudden Flats are located in the western part of the Transverse Ranges physiographic province, a broadly rectangular region characterized by east-west-trending topographic and geologic features that transect the predominantly northwest-oriented structural grain of California (Norris and Webb, 1990).

The marine terrace that underlies Sudden Flats was cut into bedrock on a dip-slope along the south side of the Santa Ynez Mountains, during a high stand of the Pacific Ocean in late Pleistocene time (Dibblee, 1950; Evenson and Miller, 1963). The local bedrock (Monterey Formation) comprises thin-bedded chert and porcellanous shale. The terrace at the derailment site is covered with a relatively thin veneer of soils that consist primarily of kitchen middens of paleo-Indians, that overlie shaly loam of Arguello-series soils (U.S. Department of Agriculture, 1958). The upper 0 - 19 feet of material is generally a heterogeneous to poorly-stratified deposit, consisting of shell and bone fragments, and some rock and clay material, together with lenses of ash and shell (U.S. Department of Agriculture, 1958; Spanne and Glassow, 1974). These anthropogenic deposits also include artifacts such as fire hearths, rock platforms, man-made living terraces, chipped tools, and burials (Glassow *et al.*, 1976; Spanne and Glassow, 1974). The middens overlie a dark gray to brown silty, sandy loam with a little clay, containing platy to angular fragments of Monterey shale, that was deposited in alluvial fans along the south-facing front of the Santa Ynez Mountains. These soils, where exposed in the walls of the Cañada Agua Vina arroyo, and in excavations, constructed during remedial activities, display a crude stratification defined by thin layers and discontinuous lenses of coarse-grained clasts (pebbles to boulders).

Field observations of outcrop exposures, together with information collected during trench excavation, allowed us to assess the subsurface relationships among the various consolidated and unconsolidated geologic units. Outcrops of Monterey shale are visible several hundred feet up the hillslope north of the derailment site, and are present in the sea cliff to the south. Consolidated Monterey shale bedrock was found seven feet below land surface in the most easterly part of the site; the channel of Cañada Agua Vina appears to be incised into Monterey shale in the vicinity of the railroad embankment crossing. The base of the channel is about 20 feet below the terrace tread surface, suggesting that the combined thickness of the unconsolidated deposits that overlie Monterey shale at the Sudden derailment site is 7 - 20 feet.

Hydrogeology

The ground-water system in the area comprises two distinct hydrogeologic units: the consolidated rocks of Jurassic to Pliocene age, and the unconsolidated formations of late Pliocene to Recent age (Evenson and Miller, 1963; Muir, 1964; ibid., 1968, Upson and Thomasson, 1951). The consolidated rocks, where water-bearing, yield water primarily from fractures (Upson and Thomasson, 1951), and the quantity of water that these rocks produce is likely to be small (Evenson and Miller, 1963; Muir, 1964; Battelle Columbus Division, 1989). The younger unconsolidated deposits form the principal water-bearing unit in the region (Evenson and Miller, 1963; Upson and Thomasson, 1951).

The depth to ground water beneath the derailment site was not known; however, the bed of Cañada Agua Vina at the western edge of the site is approximately 20 feet below the elevation of the rails at the derailment site. The perennial base flow of Cañada Agua Vina is probably fed by ground-water discharge, suggesting that the local water table also occurs at a depth of about 20 feet below land surface.

In the area to the north of the Santa Ynez mountains, ground water is used primarily for irrigation (Berenbrock, 1988). However, the Sudden derailment site is located within the boundaries of Vandenburg Air Force Base, so there is no nearby resident population. Furthermore, the small saturated thickness of the unconsolidated deposits (one to two feet) on the lower coastal plain, together with the low specific yield of the consolidated rocks in the area (Evenson and Miller, 1963; Muir, 1968; Batelle Columbus Division, 1989), suggest that the potential for ground-water development near the derailment site is small; additionally, the quality of shallow ground water is known to decline with proximity to the coast (Berenbrock, 1988). The shallow ground water, therefore, does not represent a potential drinking-water source.

Site Remediation

The area of the derailment lies almost entirely within the 80-foot wide SPTCo right-of-way, bordered on either side by Vandenburg Air Force Base property. During the pileup, one of the locomotives slid along the tracks, and came to rest approximately 1,600 feet east of the stream crossing, resulting in two separate diesel spills within the derailment site. Paraffin, soda ash, and diesel fuel were present in the western area, adjacent to Cañada Agua Vina, while only diesel fuel was spilled in the eastern area.

On the morning of March 19, 1991, immediately following the derailment, emergency-response personnel from the Air Force, and from SPTCo's remediation contractor, mobilized to the site to remove the derailed equipment and begin cleanup activities. Work then began on containment and removal of spilled diesel fuel and paraffin. The paraffin and diesel fuel were contained within hand-excavated berms by 8:00 a.m. on March 19.

During initial remedial activities at the derailment site, soil that presented obvious visual or olfactory evidence of diesel fuel was excavated from two locations in the western derailment area. Remedial excavation activities continued through the week of April 1, 1991; work was conducted under the supervision of representatives of the Air Force and the Chumash tribal elders council. Careful excavation practices were followed to minimize disturbance of the archaeological sites. Additional soil that contained diesel fuel constituents was also removed from a third pit in the western spill area, while diesel fuel and soil from the eastern spill site were removed from a fourth pit, situated approximately 1,200 feet east along the tracks.

Soil that contained diesel fuel was excavated to depths between four and ten feet below land surface, using a backhoe. Excavated soil was stockpiled on plastic sheeting, and later disposed at an off-site facility. Near the conclusion of remedial activities, several shallow trenches were excavated and sampled, to assess the lateral distribution of diesel fuel in soils around the spill areas. Ground water was not encountered in any of the excavations.

Soils in each excavation were screened at frequent intervals using a photo-ionization detector. Excavations were widened and deepened until visual evidence and/or instrument readings suggested that no diesel fuel remained in soil in the walls and base of the excavation, or until excavation activities had to be terminated because of proximity to the railbed or other structures. Representative soil samples were then collected from the sides and bottom of each excavation, and submitted for chemical analysis to assess whether fuel constituents remained in soil adjacent to the excavations. After samples had been collected, each excavation was backfilled with clean soil; backfilling began as soon as field-screening methods indicated that the fuel-affected soils had been removed, or the excavation had been enlarged to the greatest extent practical.

EVALUATION OF REMEDIAL EFFECTIVENESS

Results of Remedial Activities

Volume of Diesel Fuel Removed

During remediation of soils that contained diesel fuel, approximately 1,440 tons of soil material (equivalent to about 1,000 cubic yards) were excavated and disposed. The waste profile suggested that the excavated material contained approximately one percent diesel fuel by weight. Assuming that the waste profile concentration was representative of the concentration of diesel fuel in excavated soil, the results of volume calculations indicated that about 4,500 gallons of diesel fuel — approximately 90 percent of the diesel fuel that was reported to have been spilled — was removed, along with excavated soil.

Results of Closure Sampling

A number of soil samples were collected from the sides and bottoms of the four excavations during remedial activities. These samples were analyzed for total fuel hydrocarbons, quantitated against a diesel standard, so that residual concentrations of diesel fuel in soil could be assessed (Table 1). Several soil samples were also analyzed for the volatile fuel constituents benzene, toluene, ethylbenzene, and total xylene isomers (BTEX), using EPA Method 8020 (Table 2).

Sixteen soil samples were collected from locations near the excavations and analyzed for fuel hydrocarbons, to assess whether diesel fuel was present in soils outside of the known spill areas. Thirteen soil samples were collected from locations near the excavations and along the railbed in the spill area, and analyzed for representative geotechnical properties (grain-size distribution, total porosity, moisture content, Atterberg limits, and saturated hydraulic conductivity).

Laboratory analyses of soil samples collected during remedial excavation activities confirmed the presence of fuel constituents in the bottom and sides of excavations at several locations (Tables 1 and 2). The data also indicated that some fuel constituents remained in soils, in restricted locations around the spill areas, where soil had not been excavated because of engineering concerns regarding the proximity of the railbed or other structures. The maximum concentrations of BTEX that were detected in soil samples (Table 2) were below levels of potential regulatory concern (California

Table 1 Concentrations of Fuel Hydrocarbons Detected in Soil Samples Collected During Remediation Sudden Derailment Site

Sample Number	Sample Location	Depth Below Land Surface (ft)	Concentration of Fuel Hydrocarbons (as diesel) (mg/kg)
10510-1	Excavation #1	(?)	1,320
10510-2	Excavation #1	(?)	62
10510-3	Excavation #1	(?)	160
10510-4	Excavation #1	(?)	11
2-1	Excavation #2	(?)	4,800
2-2	Excavation #2	(?)	72
2-3	Excavation #2	(?)	ND
2-4	Excavation #2	(?)	9,500
2-5	Excavation #2	(?)	47
2-6	Excavation #2	(?)	26,000
2-7	Excavation #2	(?)	ND
2-8	Excavation #2	(?)	1,800
2-9	Excavation #2	(?)	140
2-10	Excavation #2	(?)	550
2-15	Pothole	6	53
2-16	Pothole	6	180
2-17	Pothole	6	20
2-18	Pothole	6	190
2-19	Pothole	4	ND
2-10	Pothole	5	ND
2-21	Pothole	5	ND
2-22	Pothole	4	ND
2-23	Pothole	5	ND
2-24	Pothole	6	ND
2-25	Pothole	5	ND
2-26	Excavation #3	5	34,000

Table 1 (continued)

Sample Number	Sample Location	Depth Below Land Surface (ft)	Concentration of Fuel Hydrocarbons (as diesel) (mg/kg)
2-27	Excavation #3	6.5	ND
2-28	Excavation #3	5	ND
2-29	Excavation #3	6	ND
2-30	Excavation #3	5	9,000
2-31	Excavation #3	5	130
2-32	Excavation #3; Duplicate of 2-31	5	89
2-33	Excavation #3	6	20,000
2-34	Excavation #3	5	ND
2-35	Excavation #3	4.5	2,300
2-36	Excavation #3	6	910
2-37	(Background)	(?)	(Not analyzed)
2-38	Excavation #4	3.5	ND
2-39	Excavation #4	6	ND
2-40	Excavation #4; Duplicate of 2-39	6	ND
2-41	Excavation #4	9.5	4,900
2-42	Excavation #4	6.5	7,400
2-43	Excavation #4	7	11,000
2-44	Excavation #4	9.6	130
2-45	Excavation #4	5.5	34
2-46	Excavation #4	5.5	6,300
2-47	Excavation #4	7	10,000
2-48	Excavation #4	4.5	1,095
2-49	Excavation #4	5.5	ND
2-50	Excavation #4	3.5	869
2-51	Excavation #4	4.5	11
2-52	Excavation #4	7	ND
2-53	Excavation #4	8	ND

Table 1 (continued)

Sample Number	Sample Location	Depth Below Land Surface (ft)	Concentration of Fuel Hydrocarbons (as diesel) (mg/kg)
2-54	Excavation #4	5.5	ND
2-56	Excavation #4	5	71
2-57	Excavation #4	6	18,000
2-58	Excavation #4	5	ND
2-59	Excavation #4	5	ND
2-60	Excavation #4	6	ND
2-61	(Background)	0	22
Arithmetic Mean of 58 Samples[7]			**2,903**
Geometric Mean of 58 Samples[7]			**93**
RML Estimator of The Mean of 58 Samples[8]			**2,333**
Upper 95% Confidence Limit of The Mean of 58 Samples[8]			**3,168**

[1] Soil samples were collected during the period March 21, 1991 through April 4, 1991.

[2] Depth of sample is the depth in feet below a datum marked by the centerline of the rails.

[3] Samples were analyzed for fuel hydrocarbons using the California DHS LUFT method, quantitated against a diesel standard.

[4] "ND" indicates that the concentration of fuel hydrocarbons was below the detection limit. The detection limit for fuel hydrocarbons in all samples was 10 mg/kg.

[5] (?) indicates that the data are unavailable or unknown.

[6] One milligram per kilogram (mg/kg) equals 1 part per million.

[7] Tabulated arithmetic and geometric means are for all samples, and assume that the concentration in samples in which fuel hydrocarbons were not detected was one-half the detection limit.

[8] The restricted maximum likelihood (RML) estimator, and upper 95 percent confidence estimator of the mean, were calculated using methods appropriate to censored data (Atwood *et al.*, 1991; Gilliom and Helsel, 1986a; Haas and Scheff, 1990).

Table 2 Concentrations of Volatile Fuel Constituents Detected in Soil Samples Collected During Remediation Sudden Derailment Site

Sample Number	Sample Location	Depth (ft)	Compounds			
			Benzene (mg/kg)	Toluene (mg/kg)	Ethylbenzene (mg/kg)	Total Xylenes (mg/kg)
2-26	Excavation #3	5	0.022	—	—	—
2-27	Excavation #3	6.5	ND	0.064	0.006	ND
2-28	Excavation #3	5	ND	0.083	ND	ND
2-29	Excavation #3	6	ND	0.080	ND	ND
2-30	Excavation #3	5	0.069	—	—	—
2-31	Excavation #3	5	ND	0.087	0.093	0.514
2-32	Excavation #3; Duplicate of 2-31	5	ND	0.012	ND	0.084
2-33	Excavation #3	6	0.050	—	—	—
2-34	Excavation #3	5	ND	0.084	0.007	ND
2-35	Excavation #3	4.5	ND	0.129	ND	0.171
2-36	Excavation #3	6	ND	0.017	—	—
2-61	Background	0	ND	ND	ND	ND
Maximum Reported Concentration			**0.069**	**0.129**	**0.093**	**0.514**

[1] Soil samples were collected during the period March 21, 1991 through April 4, 1991.

[2] Depth of sample is the depth in feet below a datum marked by the centerline of the Southern Pacific rails.

[3] Samples were analyzed for the volatile fuel constituents benzene, toluene, ethylbenzene, and total xylene isomers, using EPA Method 8020.

[4] "ND" indicates that the concentration was below the detection limit. Detection limits for volatile fuel constituents in all samples were as follow:

benzene - 0.005 mg/kg	ethylbenzene - 0.005 mg/kg
toluene - 0.005 mg/kg	total xylenes - 0.015 mg/kg

[5] A dash (—) indicates that the sample was not analyzed for this constituent.

[6] No other samples were analyzed for volatile fuel constituents.

[7] One milligram per kilogram (mg/kg) equals 1 part per million.

Department of Health Services, 1988). However, the concentrations of total fuel hydrocarbons (as diesel) that were detected in several soil samples were greater than recommended maximum concentrations. (It should be noted that regulatory maximum concentrations for fuel hydrocarbons in soil, as tabulated in the California Leaking Underground Fuel Tank Manual, were derived using the acceptable concentrations of BTEX in soil, calculated by assuming that BTEX would leach to ground water, and then weighting the allowable soil concentration according to the weight-percent composition of BTEX in gasoline.) The arbitrarily-derived maximum concentration criterion was not applicable in the present circumstances, because of the unique characteristics of the spill site; and SPTCo decided that the site-specific risks to human health and the environment should be evaluated. An assessment of the potential for transport of diesel fuel constituents to the ground-water table was identified as an appropriate criterion for protection of the environment, and a human-health-based potential exposure analysis ("risk assessment") was identified as an appropriate criterion for protection of human health.

HCI conducted a series of calculations to assess whether diesel fuel constituents remaining in soil were likely to migrate through the unsaturated zone to the water table beneath the derailment site. Industrial Compliance, Inc. completed a risk assessment, to estimate the risk to potential human receptors resulting from diesel fuel remaining in soils, using exposure scenarios appropriate for the site.

Evaluation of the Potential for Transport of Diesel Fuel Constituents to the Water Table

One-Dimensional Unsaturated-Zone Solute Transport

Sufficient hydrologic and chemical data were available to allow the use of an analytical model to simulate the transport of fuel constituents, through the unsaturated zone, to the water table beneath the Sudden derailment site. The transport model selected was a one-dimensional analytical solution to the unsaturated solute-transport equation (Jury *et al.*, 1983).

Transport in a one-dimensional model is considered to occur only in one direction — that is, solute flux is always downward, while vapor flux is upward (the only dimension is depth). This constraint neglects the possible effects of hydrodynamic dispersion, and tends to over-estimate the total chemical concentration at a given point; hence, the predictive results are "conservative." In the one-dimensional model used, the transport of only a single chemical species at a time can be examined, and the interactions between the various fuel constituents are disregarded. Although solute concentrations in water, resulting from contact with an immiscible mixture containing components that interact in the solvent phase (e.g., diesel fuel) are known to deviate from ideal behavior, the observed deviation from Raoult's law in fuel-water partition coefficients is small (Cline *et al.*, 1991). Therefore, relatively little error results from the calculation of unsaturated-zone transport, for a single solute species in a mixture.

Implementation of Jury Model

The "Jury model" (Jury *et al.*, 1983) used to simulate the transport of diesel fuel constituents in the unsaturated zone is based on a number of simplifying assumptions:

- Chemical transport occurs vertically through a uniform soil column, consisting of a homogeneous porous medium, which is infinite in vertical extent.
- The chemical adsorption isotherm is linear and reversible.
- The equilibrium liquid-vapor partition is linear (Henry's Law applies).
- At time t = 0, the chemical is initially incorporated into some soil layer (the "incorporation layer") at a uniform concentration C_0.
- The volatilization loss of chemical and the evaporative loss of water to the atmosphere are limited by gaseous diffusion through a stagnant-air boundary layer, above which the chemical has zero concentration and the atmospheric relative humidity is at some fixed value.

The conceptual structure of the model that was used to assess the transport of diesel fuel constituents in the unsaturated zone at the derailment site is shown in Figure 4.

Estimates of soil properties (Table 3) were obtained from the results of geotechnical laboratory analyses of several soil samples collected at the Sudden derailment site. The value used for the soil organic carbon content is a published value for a typical sandy loam (Jury *et al.*, 1984). Considering that the soils at the derailment site consist primarily of midden material (refuse heaps) and are known to contain some proportion of charcoal (Glassow *et al.*, 1976), the organic carbon content of the site soils could be much greater than the value that was used (2 percent).

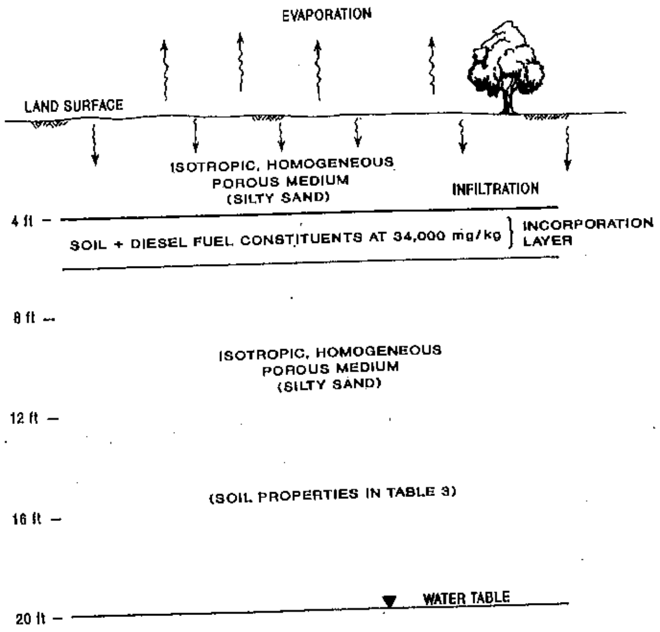


Figure 4 Conceptual One-Dimensional Soil Column Used in Unsaturated-Zone

Table 3 Physical Parameters Used to Calculate Infiltration of Fuel Constituents to the Water Table Sudden Derailment Site

Parameter	Value
Soil bulk density	1.8 g/cm3[1]
Total soil porosity	0.44[1]
Soil volumetric moisture content	0.20[1]
Organic carbon content of soil	0.02[2]
Average temperature	15°C[3]
Average relative humidity	0.60[3]
Average evaporation rate	.6 mm/day[4]
Average infiltration recharge	.5 mm/day[4]
Incorporation layer[5]	4 to 6 ft below land surface[6]
Location of water table	20 ft below land surface[7]

[1] Results of laboratory analyses.

[2] Organic carbon content for a typical sandy loam (Jury *et al.*, 1983).

[3] National Oceanic and Atmospheric Administration (1991b).

[4] Output results from HELP model using default climatological data for Santa Maria, California (Schroeder *et al.*, 1984a; ibid., 1984b; ibid., 1990).

[5] The "incorporation layer" is the soil horizon that contains fuel constituents at a specified concentration.

[6] Results of field sampling.

[7] Estimated from field observations.

Climatological information for Santa Maria, California (National Oceanic and Atmospheric Administration, 1991b), approximately 25 miles north of the derailment site and in a similar climatic regime, was used to estimate the average temperature and relative humidity. The rates of evaporation and percolation of infiltrating water at the site (Table 3) were estimated with the Hydrologic Evaluation of Landfill Performance (HELP) model, using climatological information for Santa Maria, California (Schroeder *et al.*, 1984a; ibid., 1984b; ibid., 1990).

The results of soil sampling and analysis indicated that the maximum residual concentrations of diesel fuel constituents in soil occurred at depths of 4 to 6 feet below land surface (Table 1). A single layer of uniform concentration at a depth of 4 to 6 feet was, therefore, identified as the incorporation layer (Table 3). The water table, identified as the point at which potential environmental impacts would occur, was estimated on the basis of field observations to be about 20 feet below land surface.

In order to assess possible adverse environmental effects, it was necessary to examine the transport of those diesel fuel constituents that are regulated on the basis of toxicity, mutagenicity, teratogenicity, or carcinogenicity. The chemical composition of a typical diesel fuel (Phillips Petroleum Lot C745; Griest *et al.*, 1985) was therefore selected to represent the diesel spilled at the Sudden derailment site. A typical diesel fuel contains the volatile constituents benzene, toluene, ethylbenzene, and styrene in relatively low concentrations (Table 4); xylene isomers and the polycyclic aromatic hydrocarbons (PAHs) naphthalene, fluorene, and phenanthrene are present at somewhat higher concentrations. Benzo(a)pyrene is present in low concentrations, and may not occur at all in some diesel fuels (Griest *et al.*, 1985). The concentrations of regulated constituents in a typical diesel fuel are listed in Table 4.

The chemical properties of a fuel constituent that influence its transport characteristics in the unsaturated zone include (Jury *et al.*, 1983):

- solubility of the chemical in water;
- chemical air-gas diffusion coefficient;
- chemical water-liquid diffusion coefficient;
- chemical organic-carbon partition coefficient;
- Henry's Law constant for the chemical; and
- rate constant for first-order chemical decay.

The values for these chemical properties were taken from tabulated references or were calculated, referenced to the mean annual temperature for Santa Maria. Values of chemical properties that were used in the calculation of unsaturated-zone transport of the various diesel fuel constituents are listed in Table 4.

The solution of the one-dimensional transport model is a description of the total concentration of a single chemical species, as a fraction of the initial concentration, at a given depth below land surface after some period of time. Prior to carrying out the transport calculations, it was necessary to estimate the concentrations of diesel fuel constituents that were initially present in the incorporation layer. Some of the regulated constituents that occur in diesel fuel (BTEX constituents) were detected in soils at the site; the actual maximum concentrations detected were used for those constituents (Table 5). The other regulated constituents of diesel fuel (styrene and PAHs) were not detected at the site, but were suspected to be present in soils because of their near-ubiquitous occurrence in diesel fuels (Table 4). The initial concentrations of these constituents were then estimated by assuming that diesel fuel was present in the incorporation layer at a uniform concentration of 34,000 mg/kg (the maximum residual concentration of diesel fuel that was detected), and that the constituents styrene, naphthalene, fluorene, phenanthrene, and benzo(a)pyrene were present in the diesel fuel at concentrations corresponding to those in a typical diesel fuel (Table 4). The concentrations of diesel fuel constituents in soil, estimated for use in transport calculations, are presented in Table 5.

Table 4 Chemical Properties of Regulated Constituents in a Typical Diesel Fuel

		Chemical Properties							
Constant Constituent	Concentration in Diesel (ppm)[1]	Molecular Weight (g/mol)	Henry's Law Constant(atm-m3/ mol @ 25°C)	Vapor Pressure (mm Hg @ 15° C)	Solubility (g/cm3 @ 15°C)	Diffusion Coeff. (air - gas) (cm2/day @ 15°C)	Diffusion Coeff. (water - liquid) (cm2/day @ 15°C)	$\log K_{oc}$	First- Order Decay (/day)
Benzene	26	78.11(2)	5.480E-03(2)	6.00E+01(2)	1.78E-03(2)	7.98E+03(3)	6.72E-01(3)	1.96(2)	0.001(4)
Toluene	270	92.14(2)	6.740E-03(2)	1.75E+01(2)	5.06E-04(2)	7.08E+03(3)	5.94E-01(3)	2.10(2)	0.001(4)
Ethylbenzene	170	106.17(2)	8.680E-03(2)	6.05E+00(2)	1.40E-04(2)	6.53E+03(3)	5.37E-01(3)	2.20(2)	0.001(4)
Total Xylenes (para xylene)	1,720	106.17(2)	6.300E-03(2)	6.86E+00(2)	2.00E-04(2)	6.44E+03(3)	5.37E-01(3)	2.31(2)	0.002(4)
Styrene	< 40	104.15(2)	2.610E-03(2)	4.25E+00(2)	2.80E-04(2)	6.51E+03(3)	5.54E-01(3)	2.87(2)	0.001(5)
Naphthalene	1,300	128.18(2)	4.800E-04(2)	3.75E-02(2)	2.56E-05(2)	5.99E+03(3)	5.21E-01(3)	3.10(2)	0.200(6)
Fluorene	1,300	166.22(2)	2.100E-04(2)	5.00E-03(2)	8.00E-07(2)	5.08E+03(3)	4.52E-01(3)	3.70(2)	0.200(6)
Phenanthrene	2,400	178.24(2)	2.560E-05(2)	2.10E-04(2)	1.60E-06(2)	4.90E+03(3)	4.37E-01(3)	4.36(2)	0.040(6)
Benzo(a)pyrene	0.05	252.32(2)	2.400E-06(2)	5.00E-05(2)	3.00E-09(2)	4.14E+03(3)	3.69E-01(3)	5.90(2)	0.002(6)

[1] Composition of typical diesel fuel (Phillips Petroleum Lot C745; Griest *et al.*, 1985).
[2] Montgomery and Welkom (1990).
[3] Values estimated using Lyman *et al.* (1990).
[4] Howard *et al.* (1991).
[5] Value estimated from half-life data in Howard (1990).
[6] Park *et al.* (1990).

Table 5 Initial Concentrations of Chemicals Used to Calculate the Infiltration of Fuel Constituents to the Water Table, Sudden Derailment Site

Constituent	Assumed Initial Concentration in Soil[1] (mg/kg)
Benzene	0.069
Toluene	0.129
Ethylbenzene	0.093
Total Xylene Isomers	0.514
Styrene	1.4
Naphthalene	44
Fluorene	44
Phenanthrene	82
Benzo(a)pyrene	0.002

[1] Initial concentrations for the volatile constituents benzene, toluene, ethylbenzene, and total xylene isomers are the maximum concentrations detected in soil samples collected at the site. Initial concentrations for other constituents were estimated by assuming that a typical diesel fuel is present in soil at a concentration of 34,000 mg/kg (the maximum concentration of diesel fuel detected in soil), and using the concentration of each constituent in a typical diesel fuel (Table 4).

[2] One milligram per kilogram (mg/kg) equals 1 part per million.

Results of Predictive Simulations of Unsaturated-Zone Transport

The results of predictive simulations (Table 6) indicated that with the exception of toluene, the maximum concentrations of regulated diesel fuel constituents, reaching the water table, will probably not exceed current detection limits. Toluene may eventually reach the water table, but the maximum concentrations of toluene, calculated to occur at the water table, would not exceed regulatory standards (Table 6).

Drinking-water standards were assumed to be the applicable regulatory standards in the calculations that have been described. However, no ground-water wells could be identified in the vicinity of the Sudden derailment site. Furthermore, the site lies within the boundaries of Vandenburg Air Force Base (access is severely restricted), and within a State archaeological reserve, so that ground water is unlikely to be used in the foreseeable future. The demonstration that the concentrations of diesel fuel constituents originating in the spill area are not likely to exceed drinking-water standards at the water table therefore represents a conservative approach.

Table 6 Maximum Concentrations of Constituents Calculated to Infiltrate to the Water Table, Sudden Derailment Site

Constituent	Assumed Initial Concentration in Soil (mg/kg)	Calculated Maximum Concentration at the Water Table (mg/L)	Regulatory Standard in Ground Water (mg/L)
Benzene	0.069	ND[2]	0.001[4]
Toluene	0.129	0.0005	1[5]
Ethylbenzene	0.093	ND	0.680[4]
Total Xylenes	0.514	ND	1.75[4]
Styrene	1.4	ND	0.001[5]
Naphthalene	44	ND	0.02[6]
Fluorene	44	ND	0.02[6]
Phenanthrene	82	ND	0.02[6]
Benzo(a)pyrene	0.002	ND	0.0002[5]

[1] The concentrations of constituents infiltrating to the water table were calculated using the Jury model.

[2] "ND" indicates that the calculated maximum constituent concentration at the water table was below the detection limit. The detection limit for each constituent was assumed to be the current method detection limit for the constituent in water (U.S. EPA Method 8020 for volatile organic compounds; U.S. EPA Method 8310 for polycyclic aromatic hydrocarbons). Detection limits in water were assumed to be as follows:

Method 8020	Method 8310
Benzene - 0.0005 mg/L	Naphthalene - 0.002 mg/L
Ethylbenzene - 0.0005 mg/L	Fluorene - 0.0002 mg/L
Toluene - 0.0005 mg/L	Phenanthrene - 0.0006 mg/L
Xylenes - 0.0005 mg/L	Benzo(a)pyrene - 0.00002 mg/L
Styrene - 0.0005 mg/L	

[3] One milligram per kilogram (mg/kg) equals 1 part per million. One milligram per liter (mg/L) equals 1 part per million.

[4] Regulatory standard is State of California Maximum Contaminant Level for constituent in drinking water.

[5] Regulatory standard is U.S. EPA Maximum Contaminant Level for constituent in drinking water.

[6] Regulatory standard is State of California Applied Action Level for constituent in drinking water.

Analysis of the Potential for Human-Health-Based Exposure Risk

An analysis of the risks related to potential human exposure to diesel fuel in soil was developed by Industrial Compliance, in order to assess the types and extent of hazards to human health, if any, that could result from exposure to diesel fuel in soil, at the residual concentrations detected at the site.

The preferred model of the U.S. EPA Carcinogen Assessment Group for risk extrapolation (the non-threshold linearized multistage model) was applied to cancer bioassay data to arrive at a risk estimate for human exposure. A potential exposure pathway was then developed, and the amount of daily soil exposure a worker would experience through skin contact, ingestion, and inhalation was calculated. After estimating the amount of daily soil exposure a worker would experience, a quantitative additional lifetime cancer risk for a hypothetical human receptor was calculated.

Exposure Pathway Analysis

As described in the Superfund Public Health Evaluation Manual (U.S. Environmental Protection Agency, 1986), an exposure pathway consists of four necessary elements:

1. a source and mechanism of chemical release to the environment;
2. an environmental transport medium for the released chemical;
3. a point of potential human contact with the contaminated medium (referred to as the exposure point); and
4. a human exposure route at the exposure point.

An exposure pathway is complete when all four elements are present, and incomplete when elements are missing. Exposure estimates can only be calculated for complete exposure pathways: therefore, it was necessary to identify potential pathways for human exposure to diesel fuel constituents that might occur at the Sudden derailment site, before a human-health- based risk assessment could be carried out.

The Sudden derailment site is located in a State historic preserve, within the boundaries of a major U.S. Air Force base. Access to the site is restricted, and little human activity currently occurs, or is anticipated to occur in the future. Any reasonable exposure scenario must, therefore, acknowledge the probable short duration of exposure. The following assumptions were made in developing the exposure pathway:

- The potential at-risk population consists of a worker conducting maintenance or repairs on a subsurface utility line, buried at a depth of approximately 3 feet, along the railroad right-of-way.
- Soil will be excavated during maintenance or repair activities, and workers will be exposed to subsurface soil via the dermal, ingestion, and inhalation routes.
- Workers will conduct maintenance or repair activities five days per year, through a 25-year period.

In light of the remoteness and relative inaccessibility of the derailment site, the exposure frequency assumed for this scenario is extremely conservative.

Calculation of Potential Exposure to Diesel Fuel in Soil

In the exposure assessment, the magnitude, frequency, and duration of exposure were quantified for the assumed exposure pathway. Exposure concentrations were estimated first; then, pathway-specific exposures were determined, using soil intakes calculated for each exposure route and the estimated concentrations of diesel fuel in soil.

The data included in Table 1 consist of measurements of fuel hydrocarbon concentrations, a number of which could only be ascertained to be less than a (pre-determined) detection limit ("ND" in Table 1). These data are censored, because some of the concentrations are unquantifiable — we know only that the concentrations in measurements labelled "ND" are bounded by some value (the detection limit). Methods appropriate to censored data sets were used to estimate the summary statistics for diesel fuel concentrations remaining in soil at the derailment site. The RML estimator for censored data sets (Haas and Scheff, 1990) was used to estimate the mean concentration of diesel fuel in soil. Confidence limits about the mean were constructed using the method of Gilliom and Helsel (1986a), assuming a detection limit of 10 mg/kg, 58 total samples considered, 23 results from the 58 samples below the detection limit (40 percent censoring), and using a = 0.05 (upper 95 percent confidence interval). Because the methods are robust and theoretically well-grounded (Haas and Scheff, 1990; Gilliom and Helsel, 1986a; ibid., 1986b; Helsel, 1990; Atwood *et al.*, 1991), the RML mean (2,333 mg/kg; Table 1) and upper 95 percent confidence limit (3,168 mg/kg) were judged to be representative of fuel concentrations remaining in soil, and were used in subsequent calculations of risk.

After summary statistics for the concentrations of diesel fuel remaining in soil had been estimated, the potential risks to human health resulting from those concentrations of diesel fuel in soil were evaluated, using the estimated amount of daily soil exposure a worker would experience via the dermal, ingestion, and inhalation routes. Exposure conditions resulting from contact with soils containing diesel fuel (in concentrations calculated using the RML estimator of the mean residual concentration of diesel fuel in soil and the upper 95 percent confidence interval of the RML estimator), were used to estimate the potential exposure to diesel fuel in soil at the site for the exposure pathway outlined above. The daily maximum worker intake of diesel fuel in soil, from all three exposure routes, was calculated to be 0.00022 milligrams of diesel fuel per kilogram of body weight per day using the RML estimator, and was calculated to be 0.0003 milligrams of diesel fuel per kilogram of body weight per day using the upper 95 percent confidence interval of the RML estimator.

Calculation of Potential Risks to Human Health

After the amount of daily exposure to diesel fuel in soil that a worker would experience under the assumed exposure pathway conditions had been calculated, the potential risks to human health posed by residual diesel fuel in soils at the site were estimated. Risk estimates, assessing the potential additional lifetime cancer risks under the assumed exposure pathway, were obtained by multiplying the chronic daily intake by the slope factor derived for diesel fuel.

The calculated additional lifetime cancer risks resulting from exposure to diesel fuel in soil at the site, via all three routes, under the assumed exposure scenario, were $2x10^{-7}$ using the RML estimator, and $3x10^{-7}$ using the upper 95 percent confidence interval of the RML estimator. While an "acceptable" level of risk has never been rigidly defined by any Federal regulatory agency, the U.S. EPA has generally considered the range between $1\text{x}10^{-4}$ and $1\text{x}10^{-7}$, for additional lifetime cancer risk, to be acceptable in establishing regulations for potential carcinogens in drinking water and air (U.S. Environmental Protection Agency, 1989). According to Proposition 65 of the California Health and Safety Code (Cal. H&SC §25249.5 *et seq.*) a risk level of $1\text{x}10^{-5}$ represents "no significant risk".

It is unlikely that a worker would be continually exposed to the RML mean estimated residual concentration of diesel fuel in soils, under the assumed exposure pathway conditions. The calculated risk levels, therefore, represent a conservative estimate of the potential threats to human health posed by the concentrations of diesel fuel detected in soils at the derailment site, indicating that the residual diesel fuel presented no significant risk to human health (as defined by California Proposition 65), under the most plausible exposure conditions. A summary of the analysis of potential human-health-based exposure risk is presented in Table 7.

CONCLUSIONS

Approximately five thousand gallons of diesel fuel were spilled from ruptured tanks on two railroad locomotives during a 1991 train derailment on the Sudden Flats, near Point Arguello, California. Remediation of the soil that contained diesel fuel constituents was the principal issue of concern, as diesel fuel had infiltrated into soils on the site by the time remedial activities commenced. Site remediation consisted of excavation and off-site disposal of soils that contained diesel fuel; approximately 1,440 tons of material was eventually removed from four excavations. Representative soil samples were collected from the sides and bottom of each excavation, and the excavations were backfilled.

The results of subsequent chemical analyses indicated that some fuel hydrocarbons remained in soils adjacent to the excavations. Accordingly, a series of calculations was completed, to predict the transport of diesel fuel constituents in the unsaturated zone, and to assess whether diesel fuel constituents originating in the spill area could adversely affect the quality of ground water beneath the site.

The calculations were conducted using a one-dimensional transport model, based on a conceptual understanding of the soil column beneath the site. Predictive simulations were conducted using soil properties appropriate to the site, and chemical properties and initial concentrations corresponding to each of the regulated constituents in diesel fuel. The results of the calculations indicated that with the exception of toluene, the maximum concentrations of regulated diesel fuel constituents that would be transported to the water table would probably not exceed current detection limits. Toluene may eventually reach the water table, but will probably not exceed the current regulatory standard for toluene in ground water.

A risk assessment was also conducted, to estimate the hazards to human health, if any, resulting from exposure to diesel fuel in soil, at the residual concentrations detected at the site. The calculated risks were $2\text{x}10^{-7}$ using the RML estimator of the mean concentration of diesel fuel in soil, and $3\text{x}10^{-7}$ using the upper 95 percent confidence interval of the RML estimator.

Table 7 Summary of Analysis of Potential Human-Health-Based Exposure Risk Sudden Derailment Site

Assumptions	
Source of chemical	Diesel fuel in soil at derailment site
Exposure pathway	Dermal, ingestion, and inhalation routes of maintenance worker (buried utility line)
Duration of exposure	5 days per year, 25 years
Residual concentration of diesel fuel in soils	Restricted maximum likelihood (RML) estimator: 2,333 mg/kg Upper 95% confidence interval of RML estimator: 3,168 mg/kg
Results	
Additional lifetime cancer risk calculated assuming concentration of diesel fuel in soils of 2,333 mg/kg (RML estimator of mean residual concentrations)	$2 \text{ x } 10^{-7}$
Additional lifetime cancer risk calculated assuming concentration of diesel fuel in soils of 3,168 mg/kg (upper 95% confidence interval of RML estimator of mean residual concentrations)	$3 \text{ x } 10^{-7}$

Most of the fuel-affected soils were successfully removed from the Sudden derailment site. The likelihood that diesel fuel constituents remaining in soil in the fuel spill area would subsequently migrate to the water table was demonstrated to be extremely small. The calculated potential threat to human health due to the residual concentrations of diesel fuel in soils at the site represented a risk that was 30 to 50 times less than the level of "no significant risk", as defined by the State of California. In consideration of these factors, HCI and SPTCo recommended that the Sudden derailment site be declared closed, with no associated future remediation or monitoring requirements. The Santa Barbara County Department of Health Services accepted the recommendation, and issued closure documentation in 1994.

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QUESTIONS AND ANSWERS

Q. Was there any subsequent testing of the groundwater or surface water?

None. A no-further-action recommendation was accepted, and no-further-action meant no additional site investigation, as well.

Q. For the human health risk assessment, what were the surrogate compounds that you used?

In fact, there are two different approaches that you can use. In one, all PAHs normalize to benzopyrene to calculate the carcinogenic risk and all PAHs normalize to pyrene to calculate the toxic risk. We didn't use that approach. There are actually six studies which used neat diesel fuel, and we used the results of those studies for diesel fuel.

Q. You actually found studies that were specific to diesel fuel?

Yes, I can cite those for you.

Q. My second question has to do with degradation rates. I've been involved in similar work and there's always a lot of disagreement over what degradation rates to use in the unsaturated zone for hydrocarbons. Where did you come up with your information on which degradation rates to use?

We used several published references listing degradation rates. We also used the results of other site investigations that I and some of my colleagues have been involved in. For example, a typical degradation rate for benzene is about 1 x 10^{-3}/day.

Q. Did you find that was the most sensitive parameter?

I've done sensitivity analyses and in fact, the first order decay rate is the single most-sensitive parameter.

Q. I had a question about your communications with the regulatory agencies, since these often govern whether these kinds of solutions to problems are accepted. In the case of the Santa Barbara local health agency, were they under the oversight of the Department of Toxic Substance Control in California?

They are.

Q. Was there any input from a state agency?

There was no input from D.T.S.C. There was a small degree of oversight from the regional board. Not very much. Ultimately for most fuel releases, the responsibility rests with the county health department.

Q. Did they have any questions on the method, in terms of its appropriateness, or did they recommend any other modifications or need or want an explanation?

After we issued the closure documentation and report, they requested additional verification information which we provided in letters. It was a matter of clarification, rather than recommending a different approach.

Q. So the model was entirely acceptable?

It was entirely acceptable. Bill Jury's unsaturated transport model is pretty well recognized.

Q. You've done the human risk assessment: you've chosen a maintenance worker with a limited exposure risk. Did you consider that there may be an archeological dig at some point in time, and did you assess the risk to humans at that point in time?

We did not. The results of the site investigation indicated that very little or none of the archaeological site had been directly affected by diesel fuel. Most of the diesel fuel had been confined to the railroad right of way, which will not be an archaeological dig site at any point in the future because railroad activities have significantly disrupted any of the archaeological artifacts that are still remaining.

Q. What about ecological risk assessment? Did you consider that at all?

Considering the fact that the diesel fuel constituents are four to six feet below land surface, they are probably inaccessible to mammals and birds. They are certainly inaccessible to fish and probably to most insects. We considered the transfer of fuel to the water table to be the primary ecological risk, because if fuel constituents arrive at the water table, there's the potential that they'll be transported to surface water. At the time they arrive at surface water, then you have to consider ecological risk to other environmental receptors. That is forestalled by the finding that fuel constituents don't even make it to the water table.

Chapter 2

Risk Assessment of Fuel-Contaminated Soils Based on TPH Concentrations

John S. Stansbury
Woodward-Clyde, Inc., Omaha, NE

Cathy A. Forgét
U.S. Army Corps of Engineers, Omaha, NE

PURPOSE

The purpose of this chapter is to present a method developed to evaluate fuel-contaminated sites using risk assessment, based on total petroleum hydrocarbon (TPH) analysis. The method expands on the surrogate approach proposed by J.S Heath, S.S Koblis and C. Day.[1]

Fuel-contaminated sites are a common environmental problem at many facilities. Cleanup of fuel-contaminated sites using conservative TPH cleanup criteria (e.g., state guidance) can result in costly remediation at sites that pose no significant risk to human health or the environment. On the other hand, it is expensive to sample and analyze the fuel-contaminated media (e.g., soil, groundwater) for the full suite of fuel constituents to determine if they are present at concentrations that could pose a significant risk. High fuel concentrations can also cause detection (reporting) limits to be elevated (i.e., by matrix interferences of high levels of nontarget compounds), making identification of individual fuel constituents (especially polycyclic aromatic hydrocarbons [PAHs]) at risk-based concentrations extremely difficult if not impossible. This chapter describes how to determine whether remediation is necessary at fuel-contaminated sites to characterize potential human health risks, using TPH concentrations. It is a conservative and cost-effective method for evaluating fuel-contaminated sites because all potentially present fuel constituents can be evaluated, thus avoiding problems commonly associated with chemical analysis specifically fuel constituents registering as nondetect at elevated reporting limits.

METHODOLOGY

Identification of Chemicals of Concern

Chemicals of concern (COCs) are chemicals that have been released at a site that may contribute significantly to site risk.[2] At fuel sites, COCs include fuel-constituents that have EPA toxicity criteria (Reference Doses [RfDs] for noncarcinogens and cancer slope factors for carcinogens). If the site is known to be contaminated with only fuel, COCs will only be fuel constituents, otherwise COCs may include other chemicals which must be accounted for by additional analyses.

Exposure Assessment

Estimation of Exposure Point Concentrations of Presumed Chemicals of Concern in Fuel

To quantify risks from exposure to fuel-contaminated sites, the concentrations of individual fuel constituents of concern are estimated based on the type of fuel present (e.g., gasoline, JP-4, or diesel), measured as TPH, and the percent composition of the constituents of the fuel.

Two accepted analytical methods are available for total petroleum hydrocarbon analysis: EPA method 418.1 and method 8015. The advantages and drawbacks of each of these methods are matters of current investigation. One advantage of method 8015 is that it allows a distinction to be made between gasoline range organics (GRO) and total chromatgraphable organics (TCO). This could be useful for fuel identification. In addition, results of method 418.1 can include natural hydrocarbons from decaying vegetative matter, for example, which can artificially elevate the fuel-related TPH results.

Published data are used to determine the estimated percent composition by weight of known chemicals in the fuel. All fuel constituents that have toxicity factors are evaluated as COCs in the quantitative risk assessment. When data from more than one source were available to estimate the composition of chemicals with toxicity factors or when the literature indicates a range of concentrations, the maximum percent composition documented in the literature is used as the estimated concentration of each individual chemical.

The only exception to using the maximum reported concentration is for 1,2-dibromoethane (ethylene dibromide). Ethylene dibromide (EDB) is not truly a fuel constituent; however, it was formerly used as an additive in some leaded gasolines, reported by Heath et al.[1] at concentrations ranging from 0.00007- 0.0177 %. The use of EDB was discontinued in 1984[3] and, EDB was not added to all gasoline, it may not even be present in environmental samples. If it had been in the original fuels, a significant fraction would have volatilized since use was discontinued. Therefore, the lower reported additive concentration (0.00007 percent) is used to represent the potential fraction of this constituent in the gasoline.

To estimate exposure point concentrations of individual fuel constituents, the percent compositions of the fuel constituents are multiplied by the reasonable maximum exposure (RME) concentration of TPH. This approach is very conservative because the percent composition is based on fresh fuel, which generally contains a greater proportion of toxic volatile constituents than weathered fuel (the volatile and soluble fraction of the fuel will tend to dissipate over time). In addition, the approach assumes that every known toxic chemical is present in the fuel at the maximum weight percentage reported in the literature. Since the volatile fraction of the fuels tends to dissipate, the fraction of the nonvolatile constituents will actually increase over time. Therefore, this method may overestimate the concentration of volatiles and underestimate the concentration of non-volatiles. Nevertheless, the conservative assumptions used are likely to overestimate concentrations of most fuel constituents in the environment.

A summary of the chemicals of concern in each of the fuels is presented in Table 1.

Exposure Point Concentrations in Soil

Exposure point concentrations of fuel constituents of concern are estimated by multiplying the 95% upper confidence limit (95% UCL) of the mean of the measured TPH concentrations times the constituent percent in the fuel.

Exposure Point Concentrations in Air

Airborne emissions from soils resulting from volatilization of volatile organic compounds (VOCs) and emissions of semivolatile organic compounds (SVOCs), associated with wind erosion of respirable particulate matter (i.e., dust less than 10 microns in diameter [PM_{10}]) can be evaluated using conservative air emissions and dispersion models.[6]

Exposure Point Concentrations in Groundwater

Concentrations of fuel constituents dissolved in groundwater can be estimated from measured TPH concentrations in groundwater. Chemical concentrations in groundwater due to leaching from soils can be estimated using appropriate fate and transport modeling (e.g., vadose zone modeling).

Estimating Chemical Intakes

Using the exposure point concentrations of chemicals of concern in soil, air, and groundwater, intakes (exposure doses) of COCs, expressed in terms of mg chemical/kg body weight/day are calculated. Intakes are estimated in accordance with EPA guidance,[2,7-9] using reasonable estimates of factors such as body weight, inhalation and ingestion rates, and frequency and duration of exposure.

The general equation for calculating intake in terms of mg/kg/day is:

$$Intake = \frac{chemical\ conc. \cdot contact\ rate \cdot exposure\ frequency \cdot exposure\ duration}{body\ weight \cdot averaging\ time} \qquad (1)$$

Pathway-specific intake factors (the intakes divided by the exposure point concentrations) are presented in Table 2.

Toxicity Assessment

EPA-established toxicity factors are used to assess potential health risks from estimated chemical intakes. Toxicity factors are expressed either as a reference dose (RfD) for noncarcinogens or as a slope factor (SF) for carcinogens. An RfD is the daily dose of a noncarcinogen that is considered safe for humans over a lifetime of exposure. The EPA slope factors are upper 95th percentile confidence limits of the probability of response per unit intake of chemical over a lifetime. The SF is used to estimate the

Table 1 Maximum Weight Percent of Fuel Constituents with EPA Toxicity Factors

Chemical	Reference	Carcinogen?	Weight Percent[a]
Gasoline			
Benzene	4	Y	1.4
Ethylbenzene	4	N	1.3
Toluene	4	N	5.8
Xylenes	4	N	6.5
Benzo(a)pyrene	1	Y	0.00028
Benzo(a)anthracene	4	Y	0.00022
Benzo(b)fluoranthene	4	Y	0.00046
1,1-Biphenyl	4	N	0.00053
Chrysene	4	Y	0.0002
Cumene (eip-Isopropyl benzene)	1	N	0.23
1,2-Dichloroethane	1	Y	0.023
2,4-Dimethylphenol	4	N	0.00047
Fluoranthene	4	N	0.00024
Fluorene	4	N	0.00029
3- or 4-Methylphenol (m- or p-Cresol)	2	N	0.0035
Naphthalene	1	N	0.49
Ethylene dibromide (1,2-Dibromoethane)	1	Y	0.00007[b]
n-Hexane	1	N	3.5
JP-4			
Benzene	3	Y	0.5
Ethylbenzene	3	N	0.37
Toluene	3	N	1.33
Xylenes	3	N	2.32
Cumene	3	N	0.3
n-Hexane	3	N	2.21
Naphthalene	3	N	0.5

Table 1 (continued)

Chemical	Reference	Carcinogen?	Weight Percent[a]
Diesel Fuel No. 2			
Benzene	5	Y	0.00008
Ethylbenzene	5	N	0.00031
Toluene	5	N	0.00036
Xylenes	5	N	0.0013
Benzo(a)anthracene	5	Y	0.0001
Benzo(a)pyrene	5	Y	0.000084
1,1-Biphenyl	5	N	0.1
Chrysene	4	Y	0.017
2,4-Dimethylphenol	4	N	0.00084
Fluoranthene	5	N	0.004
Fluorene	5	N	0.15
2-Methylphenol (o-Cresol)	4	N	0.00055
3- and 4-Methylphenol (m- and p-Cresol)	4	N	0.00035
Naphthalene	5	N	0.57
Pyrene	4	N	0.02

[a] If a range was documented or chemical was found in more than one source, the maximum value was used.

[b] Ethylene dibromide (EDB) was used as an additive for some gasolines at reported concentrations of 0.00007 - 0.018 percent. Its use was discontinued in 1984.[3] Since EDB was not used in all gasolines and is highly volatile (its soil concentration would have decreased in ten years), the low end of the reported additive concentrations is used.

upperbound probability of an individual developing cancer as a result of exposure to a potential carcinogen. The primary sources for toxicity factors are EPA's IRIS data base (EPA 1994) and Health Effects Assessment Summary Tables.[10,11] The RfDs and slope factors for all chemicals of concern at the fuel sites are listed in Table 3.

Risk Characterization

Risk characterization is the final step of the risk assessment process. In this step, the toxicity factors (RfDs and cancer slope factors) for the chemicals of concern are

Table 2 Intake Factors

Exposure Route/Intake Route	Intake Factor
Incidental Soil Ingestion (kg/kg-day)	
Noncarcinogenic	4.89×10^{-7}
Carcinogenic	1.75×10^{-7}
Inhalation of Volatile or Particulate Emissions from Soil (m³/kg-d)	
Noncarcinogenic	1.96×10^{-1}
Carcinogenic	6.99×10^{-2}
Dermal Contact with Soil (kg/kg-day)	
Noncarcinogenic	1.93×10^{-5}
Carcinogenic	1.05×10^{-5}

applied in conjunction with estimated chemical intakes to predict noncarcinogenic and carcinogenic health risks to exposed individuals.

The potential for noncarcinogenic effects is characterized by comparing estimated chemical intakes with chemical-specific RfDs. The resulting ratio is called a *hazard quotient*. It is derived in the following manner:

$$\text{Noncancer Hazard Quotient} = \frac{\text{Chemical Intake (mg/kg - day)}}{\text{RfD (mg/kg - day)}} \qquad (2)$$

Use of the RfD assumes that there is a level of intake (the RfD) below which it is unlikely that even sensitive individuals will experience adverse health effects over a lifetime of exposure. If the average daily intake exceeds the RfD (that is, if the hazard quotient exceeds 1.0), there may be cause for concern for potential non-cancer effects.

To assess exposures to multiple chemicals, the hazard quotients for each chemical are totaled and called a hazard index (HI). If the total HI is less than or equal to 1.0, cumulative exposure to the chemicals of concern at the site is judged unlikely to result in an adverse effect. If the sum is greater than 1.0, a more detailed and critical evaluation of exposure concentrations, exposure conditions, and toxicity (including specific target organs affected and mechanisms of toxic action of the chemicals of concern) is required to ascertain whether the cumulative exposure would, in fact, be likely to harm exposed individuals.

Potential carcinogenic effects are characterized in terms of the incremental probability of an individual developing cancer over a lifetime as a result of exposure to a potential carcinogen. Excess lifetime cancer risk is calculated by multiplying the average daily chemical intake by the cancer slope factor (SF) as follows:

$$\text{Risk} = \text{Chemical Intake (mg/kg/day)} \times \text{SF (mg/kg/day)}^{-1} \qquad (3)$$

Table 3 Reference Doses and Slope Factors for Chemicals of Concern

Chemical	Exposure Route	Toxicity Subchronic RfD (mg/kg-day)	Toxicity Chronic RfD (mg/kg-day)	Carcinogenicity Slope Factor (mg/kg-day)⁻¹	Carcinogen Class
Benzene	Inhalation	—	—	2.9E-02	A
	Oral	—	—	2.9E-02	A
Benzo(a)anthracene[1]	Inhalation	—	—	6.1E-01	B2
	Oral	—	—	7.3E-01	B2
Benzo(a)pyrene[1]	Inhalation	—	—	6.1E+00	B2
	Oral	—	—	7.3E+00	B2
1,1-Biphenyl	Inhalation	—	—	—	D
	Oral	5E-02	5E-02	—	
Benzo(b)fluoranthene[1]	Inhalation	—	—	6.1E-01	B2
	Oral	—	—	7.3E-01	B2
Chrysene[1]	Inhalation	—	—	6.1E-02	B2
	Oral	—	—	7.3E-02	B2
Cresol(p)[2]	Inhalation	—	—	—	D
	Oral	5E-02	5E-03	—	
Cumene	Inhalation	2.6E-02	2.6E-03	—	D
	Oral	4E-01	4E-02	—	
2,4-Dimethylphenol	Inhalation	—	—	—	D
	Oral	2.00E-01	2.00E-02	—	
1,2-Dichloroethane	Inhalation	—	—	9.1E-02	B2
	Oral	—	—	9.1E-02	B2

Table 3 (continued)

Chemical	Exposure Route	Toxicity: Subchronic RfD (mg/kg-day)	Toxicity: Chronic RfD (mg/kg-day)	Carcinogenicity Slope Factor (mg/kg-day)$^{-1}$	Carcinogen Class
Ethylbenzene	Inhalation	2.9E-01	2.9E-01	—	D
	Oral	1E+00	1E-01	—	
Fluoranthene	Inhalation	—	—	—	D
	Oral	4E-01	4E-02	—	
Fluorene	Inhalation	—	—	—	D
	Oral	4E-01	4E-02	—	
n-Hexane	Inhalation	5.7E-02	5.7E-02	—	D
	Oral	6E-01	6E-02	—	
Naphthalene	Inhalation	—	—	—	D
	Oral	4E-02	4E-02	—	
Toluene	Inhalation	5.7E-01	1.1E-01	—	D
	Oral	2E+00	2E-01	—	
Xylenes (total)	Inhalation	—	—	—	D
	Oral	4E+00	2E+00	—	

[1] Slope factor derived using toxicity equivalency approach.[12]

[2] Values listed are the most conservative available for cresol. Subchronic and chronic oral RfDs for cresol (m,o) are 5E-01 and 5E-02, respectively.

— No EPA-derived toxicity value

Sources: EPA Health Effects Assessment Summary Tables (HEAST).
IRIS, Integrated Risk Information System (IRIS). One-line database.

The risks of exposure to multiple carcinogens are assumed to be additive. The total cancer risk is estimated by totaling the risks estimated for each chemical of concern and for each pathway.

CASE STUDIES

Case Descriptions

Two case studies are presented to compare results of the constituent method with results obtained using standard site investigation methods.

Study site A is a railroad fueling facility. The data presented from Site A are from subsurface soil where a leak from a diesel fuel underground storage tank (UST) system occurred (years prior to the investigation). Volatilization and non-fuel related contamination are not expected to be significant factors at this site; however, perhaps infiltration could have transported some of the soluble constituents such as VOC vertically.

Site B is a railroad fueling facility that had a release of diesel fuel to surface soils. The data from this site are used to illustrate the potential reduction of concentrations of VOCs due to volatilization and to illustrate potential complications due to nonfuel-related contamination in the soil.

Comparison of Measured and Estimated Constituent Concentrations

Site A

Study Site A is the location of a subsurface release of diesel fuel. Table 4 presents the measured concentrations and estimated diesel fuel constituent concentrations of chemicals of concern at Study Site A. All chemicals that have EPA-established toxicity factors and that were either detected at the site or that are known diesel fuel constituents are listed in Table 4. Table 4 shows that 1,1-biphenyl was not analyzed for in the site investigation. This represents a potential for underestimating site risks under typical investigations because 1,1-biphenyl is not in the typical list (i.e., Appendix IX) of target compounds that are analyzed for in most site investigations, site risks under typical investigations can , thus, be underestimated. However, the constituent method accounts for the potential presence of this compound.

Table 4 shows that the constituent method predicted significantly higher concentrations of naphthalene than were detected at the site. This could be the result of overestimation in the literature of naphthalene concentrations in diesel fuel. However, overestimation of naphthalene concentrations will not likely affect the results of the risk assessment significantly because naphthalene has a relatively low toxicity and generally does not drive overall site risks (see Table 7).

Table 4 shows that the constituent method predicted significantly lower concentrations of certain PAHs (acenaphthene and fluorene) in some samples. This could be the result of low estimates of constituent fractions in the literature, or it could be the result of non-fuel contamination at the site. Either possibility illustrates the need for refinement of literature concentrations, and the fact that the constituent method may underestimate concentrations (and risks) if non-fuel related contamination is present.

Table 4 Comparison of Measured and Constituent Estimate Concentrations Study Site A

	SB1-10		SB2-11		SB3-5		SB4-7	
	Measured Conc. (µg/kg)	Constituent Meth. Conc. (µg/kg)	Measured Conc. (µg/kg)	Constituent Meth. Conc. (µg/kg)	Measured Conc. (µg/kg)	Constituent Meth. Conc. (µg/kg)	Measured Conc. (µg/kg)	Constituent Meth. Conc. (µg/kg)
Benzene	1 U	0.004 U	1 U	0.032	5 U	0.37	50 U	18.7
Ethylbenzene	1 U	0.016 U	1 U	0.12	5 U	1.4	170	72.5
Toluene	1 U	0.018 U	1 U	0.14	5 U	1.7	50 U	84.2
Xylenes	1 U	0.065 U	1 U	0.52	5 U	6.1	570	304.2
isopropylbenzene	2.5 U	NC	2.5 U	NC	125 U	NC	250 U	NC
n-Butylbenzene	2.5 U	0	2.5 U	0	341	0	250 U	0
n-Propylbenzene	2.5 U	0	2.5 U	0	125 U	0	250 U	0
sec-Butylhnezene	2.5 U	0	2.5 U	0	398	0	250 U	0
Benzo(a)anthracene	169 U	0.005 U	199 U	0.04	192.5 U	0.47	5250 U	23.4
Benzo(a)pyrene	169 U	0.0042 U	199 U	0.034	192.5 U	0.39	5250 U	19.7
"1,1-Biphenyl"	NA	5 U	NA	40	NA	466	NA	23400
Chrysene	169 U	0.85 U	199 U	6.8	192.5 U	79	5250 U	3978
"2,4-Dimethylphenol"	169 U	0.042 U	199 U	0.34	192.5 U	3.9	5250 U	197
Fluoranthene	169 U	0.2 U	199 U	1.6	192.5 U	18.6	5250 U	936
2-Methylphenol	169 U	0.028 U	199 U	0.22	192.5 U	2.6	5250 U	129
3-and 4-Methylphenol	169 U	0.018 U	199 U	0.14	192.5 U	1.6	5250 U	81.9
Naphthalene	2.5 U	28.5 U	2.5 U	228	125 U	2656	250 U	133380

Table 4 (continued)

	SB1-10		SB2-11		SB3-5		SB4-7	
	Measured Conc. (µg/kg)	Constituent Meth. Conc. (µg/kg)	Measured Conc. (µg/kg)	Constituent Meth. Conc. (µg/kg)	Measured Conc. (µg/kg)	Constituent Meth. Conc. (µg/kg)	Measured Conc. (µg/kg)	Constituent Meth. Conc. (µg/kg)
2-Methylnaphthalene	169 U	74.5	199 U	596	2160	6943.4	38200	348660
Acenaphthene	169 U	NC	199 U	NC	192.5 U	NC	5250 U	NC
Fluorene	169 U	NC	199 U	NC	569	NC	6810	NC
Phenanthrene	169 U	0	199 U	0	1090	0	19100	0
Pyrene	169 U	1 U	199 U	8	192.5 U	93	11600	4680
TPH (mg/kg)	5 U		40		466		23400	

U = qualifier designates nondetect sample; values are one-half of reporting limit
NA = Not Analyzed
NC = Not a fuel constituent
* Constituent Method Concentration = TPH concentraiton * fuel constituent fraction

Table 4 (continued)

	SB5-10		SB6-6		SB7-15		SB8-10	
	Measured Conc. (μg/kg)	Constituent Meth. Conc. (μg/kg)	Measured Conc. (μg/kg)	Constituent Meth. Conc. (μg/kg)	Measured Conc. (μg/kg)	Constituent Meth. Conc. (μg/kg)	Measured Conc. (μg/kg)	Constituent Meth. Conc. (μg/kg)
Benzene	50 U	3.3	250 U	6.0	50 U	0.14	1 U	0.0044 U
Ethylbenzenc	170	12.6	250 U	23.3	50 U	0.54	1 U	0.017 U
Toluene	50 U	14.7	250 U	27.0	50 U	0.63	1 U	0.020 U
Xylenes	420	53.0	250 U	98	50 U	2.3	1 U	0.072 U
isopropylbenzene	250 U	NC	1950	NC	2.5 U	NC	2.5 U	NC
n-Butylbenzene	670	0	3340	0	5.3	0	2.5 U	0
n-Propylbenzene	250 U	0	5200	0	2.5 U	0	2.5 U	0
sec-Butylbnezene	610	0	4810	0	8.6	0	2.5 U	0
Benzo(a)anthracene	5300 U	4.1	5300 U	7.5	191.5 U	0.17	178 U	0.0055 U
Benzo(a)pyrene	5300 U	3.4	5300 U	6.31	191.5 U	0.15	178 U	0.0046 U
"1,1-Biphenyl"	NA	4080	NA	7510	NA	174	NA	5.5 U
Chrysene	5300 U	694	5300 U	1277	191.5 U	29.6	178 U	0.94 U
"2,4-Dimethylphenol"	5300 U	34	5300 U	63.1	191.5 U	1.5	178 U	0.046 U
Fluoranthene	5300 U	163	5300 U	300	191.5 U	7.0	178 U	0.22 U
2-Methylphenol	5300 U	22.4	5300 U	41.3	191.5 U	0.96	178 U	0.030 U
3-and 4-Methylphenol	5300 U	14.3	5300 U	26.3	191.5 U	0.61	178 U	0.019 U
Naphthalene	250 U	23256	1300	42807	2.5 U	992	2.5 U	31.4 U

Table 4 (continued)

	SB5-10		SB6-6		SB7-15		SB8-10	
	Measured Conc. (μg/kg)	Constituent Meth. Conc. (μg/kg)	Measured Conc. (μg/kg)	Constituent Meth. Conc. (μg/kg)	Measured Conc. (μg/kg)	Constituent Meth. Conc. (μg/kg)	Measured Conc. (μg/kg)	Constituent Meth. Conc. (μg/kg)
2-Methylnaphthalene	50000	60792	40100	111899	191.5 U	2592.6	178 U	81.95
Acenaphthene	4050	NC	5690	NC	191.5 U	NC	178 U	NC
Fluorene	6500	NC	10100	NC	191.5 U	NC	178 U	NC
Phenanthrene	11400	0	17700	0	196	0	178 U	0
Pyrene	2175 U	816	5300 U	1502	191.5 U	34.8	178 U	1.1
TPH (mg/kg)	4080		7510		174		5.5 U	

U qualifier designates nondetect sample; values are one-half of reporting limit

NA= Not Analyzed

NC = Not a fuel constituent

* Constituent Method Concentration = TPH concentraiton * fuel constituent fraction

A primary benefit of the constituent method, illustrated in Table 4, is that in the more contaminated parts of the site (i.e., SB4-7, SB-5-10, and SB6-6), the SVOCs were reported as nondetect at elevated reporting limits. At these locations, most SVOC concentrations (and associated risks) cannot be determined directly. However, in these cases, and especially at sites that are uniformly contaminated with high fuel concentrations, the constituent method can be used to estimate fuel constituent concentrations and associated risks.

Site B

Study Site B is a surface release of diesel fuel. Table 5 presents the measured concentrations and estimated (by the constituent method) diesel fuel constituent concentrations of chemicals of concern at Study Site B. All chemicals that have EPA-established toxicity factors and that were either detected at the site or are known diesel fuel constituents are listed in Table 5. As was the case with Study Site A, 1,1-biphenyl was not analyzed for in the site investigation, increasing the possibility that site risks may be underestimated because 1,1-biphenyl is not in the typical list (i.e., Appendix IX) of target compounds analyzed for during site investigations. However, the constituent method accounts for the potential presence of this compound.

Table 5 shows that the constituent method predicted significantly higher concentrations of naphthalene than were detected at the site. This could be the result of overestimation in the literature of naphthalene concentrations in diesel fuel. However, overestimation of naphthalene concentrations will not likely significantly affect the results of the risk assessment because naphthalene has a relatively low toxicity and generally does not drive overall site risks (see Table 8).

Table 5 shows that the constituent method predicted significantly lower concentrations of certain PAHs in some samples. This could be the result of inaccurate estimates in the literature, or it could be evidence that contaminants other than diesel fuel are present in soil at this site. Refinement of literature concentrations can address the first case. Diligent care to only use the constituent method at sites where the contamination is a known fuel is needed to address the second case. Alternatively, if the contamination is suspected to be a mixture (e.g., diesel fuel and lube oil), a combination of constituents from each contaminant could be used.

Table 5 also shows that in the more contaminated parts of the site (i.e., SS01, SS-4, SS-6, SS-8, and SS-9), the SVOCs were reported as nondetect at elevated reporting limits. At these locations, the SVOC concentrations (and associated risks) cannot be determined directly; however, these concentrations and associated risks can be estimated using the constituent method.

Exposure Assessment

To facilitate comparisons at the study sites, worker exposures were assumed for each of the sites. EPA standard default exposure factors (SDEFs), were used to develop upperbound estimates of potential exposures and risks at the sites. Intake factors for soil ingestion, dermal contact with soil, and inhalation are presented in Table 2.

Exposure point concentrations based on reasonable maximum exposure (RME) conditions, were calculated for both measured chemical concentrations and for concentrations predicted by the fuel constituent method. For the measured

Table 5 Comparison of Measured and Constituent Estimated Concentrations Study Site B

	SS-1		SS-2		SS-3		SS-4		SS-5	
	Measured Conc. (μg/kg)	Constituent Conc. (μg/kg)	Measured Conc. (μg/kg)	Constituent Conc. (μg/kg)	Measured Conc. (μg/kg)	Constituent Conc. (μg/kg)	Measured Conc. (μg/kg)	Constituent Conc. (μg/kg)	Measured Conc. (μg/kg)	Constituent Conc. (μg/kg)
Benzene	ND	2.4	ND	0.070	ND	0.022	ND	20.1	ND	0.14
Ethylbenzene	ND	9.3	ND	0.27	ND	0.084	ND	77.8	ND	0.54
Toluene	ND	10.8	ND	0.31	ND	0.097	ND	90.4	ND	0.63
Xylenes	ND	39	ND	1.1	ND	0.35	ND	326	ND	2.3
Benzo(a)anthracene	2055 U	3	240 U	0.09	221 U	0.027	1755 U	25.1	192 U	0.17
Benzo(a)pyrene	2055 U	2.5	553	0.07	221 U	0.023	1755 U	21.1	192 U	0.15
Benzo(ghi)perylene	2055 U	NC	348	NC	221 U	NC	1755 U	NC	192 U	NC
Benzo(k)fluoranthene	2055 U	NC	1130	NC	221 U	NC	1755 U	NC	283	NC
“1,1-Biphenyl”	NA	3000	NA	87	NA	27	NA	25100	NA	174
Chrysene	2055 U	510	702	14.8	221 U	4.6	1755 U	4267	192 U	29.6
“2,4-Dimethylphenol”	ND	25.2	ND	0.73	ND	0.23	ND	211	ND	1.5
Fluoranthene	2055 U	120	1280	3.5	221 U	1.1	1755 U	1004	197	7.0
“Indeno(123,cd)pyrene”	2055 U	NC	383	NC	221 U	NC	1755 U	NC	192 U	NC
2-Methylphenol	ND	16.5	ND	0.48	ND	0.15	ND	138	ND	0.96
3-and 4-Methylphenol	ND	10.5	ND	0.30	ND	0.095	ND	87.9	ND	0.61
Naphthalene	ND	17100	ND	496	ND	154	ND	143070	ND	992

Table 5 (continued)

	SS-1		SS-2		SS-3		SS-4		SS-5	
	Measured Conc. (μg/kg)	Constituent Conc. (μg/kg)	Measured Conc. (μg/kg)	Constituent Conc. (μg/kg)	Measured Conc. (μg/kg)	Constituent Conc. (μg/kg)	Measured Conc. (μg/kg)	Constituent Conc. (μg/kg)	Measured Conc. (μg/kg)	Constituent Conc. (μg/kg)
2-Methylnaphthalene	2055 U	NC	240 U	NC	221 U	NC	1755 U	NC	198	NC
Acenaphthylene	2055 U	NC	240 U	NC	221 U	NC	1755 U	NC	192 U	NC
Anthracene	2055 U	NC	247	NC	221 U	NC	1755 U	NC	192 U	NC
Pyrene	2055 U	600	1300	17.4	221 U	5.4	1755 U	5020	233	34.8
TPH (mg/kg)	3000	87	27	25100	174	2320	569	30000	6030	299

U = qualifier designates nondetect sample; values are one-half of reporting limit
NA = Not Analyzed
NC = Not a fuel constituent
ND = Not Detected in any site samples
* Constituent Method Concentration = TPH concentraiton * fuel constituent fraction

Table 5 (continued)

	SS-6		SS-7		SS-8		SS-9		SS-10	
	Measured Conc. (μg/kg)	Constituent Conc. (μg/kg)	Measured Conc. (μg/kg)	Constituent Conc. (μg/kg)	Measured Conc. (μg/kg)	Constituent Conc. (μg/kg)	Measured Conc. (μg/kg)	Constituent Conc. (μg/kg)	Measured Conc. (μg/kg)	Constituent Conc. (μg/kg)
Benzene	ND	1.9	ND	0.46	ND	24	ND	4.8	ND	0.24
Ethylbenzene	ND	7.2	ND	1.8	ND	93	ND	18.7	ND	0.93
Toluene	ND	8.4	ND	2.0	ND	108	ND	21.7	ND	1.1
Xylenes	ND	30.2	ND	7.4	ND	390	ND	78.4	ND	3.9
Benzo(a)anthracene	1715 U	2.3	171 U	0.57	5250 U	30	1660 U	6.0	299	0.30
Benzo(a)pyrene	1715 U	1.9	171 U	0.48	5250 U	25.2	1660 U	5.1	173 U	0.25
Benzo(ghi)perylene	1715 U	NC	171 U	NC	5250 U	NC	1660 U	NC	380	NC
Benzo(k)fluoranthene	1715 U	NC	171 U	NC	5250 U	NC	1660 U	NC	1090	NC
"1,1-Biphenyl"	NA	2320	NA	569	NA	30000	NA	6030	NA	299
Chrysene	1715 U	394	171 U	97	5250 U	5100	1660 U	1025	527	50.8
"2,4-Dimethylphenol"	ND	19.5	ND	4.8	ND	252	ND	50.7	ND	2.5
Fluoranthene	1715 U	92.8	171 U	22.8	5250 U	1200	1660 U	241	618	12.0
"Indeno(123,cd)pyrene"	1715 U	NC	171 U	NC	5250 U	NC	1660 U	NC	361	NC
2-Methylphenol	ND	12.8	ND	3.1	ND	165	ND	33.2	ND	1.64
3-and 4-Methylphenol	ND	8.1	ND	1.99	ND	105	ND	21.1	ND	1.05
Naphthalene	ND	13224	ND	3243	ND	171000	ND	34371	ND	1704

Table 5 (continued)

	SS-6		SS-7		SS-8		SS-9		SS-10	
	Measured Conc. (µg/kg)	Constituent Conc. (µg/kg)	Measured Conc. (µg/kg)	Constituent Conc. (µg/kg)	Measured Conc. (µg/kg)	Constituent Conc. (µg/kg)	Measured Conc. (µg/kg)	Constituent Conc. (µg/kg)	Measured Conc. (µg/kg)	Constituent Conc. (µg/kg)
2-Methylnaphthalene	1715 U	NC	171 U	NC	5250 U	NC	1660 U	NC	173 U	NC
Acenaphthylene	1715 U	NC	171 U	NC	5250 U	NC	1660 U	NC	220	NC
Anthracene	1715 U	NC	171 U	NC	5250 U	NC	1660 U	NC	173 U	NC
Pyrene	1715 U	464	171 U	113.8	5250 U	6000	1660 U	1206	855	59.8
TPH (mg/kg)	3000	87	27	25100	174	2320	569	30000	6030	299

U = qualifier designates nondetect sample; values are one-half of reporting limit
NA = Not Analyzed
NC = Not a fuel constituent
ND = Not Detected in any site samples
* Constituent Method Concentration = TPH concentraiton * fuel constituent fraction

concentrations, the 95% upper confidence limit (UCL) on mean soil concentrations for each COC were calculated using sample analytical results for each site. For the fuel constituent method, UCL concentrations were calculated from 95% UCL concentrations of TPH in soil and the fuel constituent percentages shown in Table 1. Exposure point concentrations of COCs in soil for both methods are presented in Tables 6 and 7.

Screening-level air emissions and dispersion models recommended by EPA were used to estimate air concentrations of volatile organic compounds (VOCs) and emissions of semivolatile compounds associated with wind erosion of particulate matter (dust) less than 10 microns in diameter (PM_{10}).[6] RME air concentrations were estimated using the RME soils concentrations for both methods. Air concentrations calculated using these methods are also presented in Tables 6 and 7.

Potential transport of COCs to groundwater or other exposure pathways was not considered. However, as discussed earlier, these pathways could be addressed either by sampling and analysis of appropriate media or by modeling (as was done for the air pathway).

Toxicity Assessment

EPA-established reference doses and slope factors were used in the risk assessment. Toxicity factors are presented in Table 3.

Risk Characterization

Noncarcinogenic hazard indexes and carcinogenic health risks to occupational receptors were estimated for soil ingestion, dermal contact, and inhalation of volatile and particulate emissions from soil for all COCs, using the approaches described above. Potential risks due to dermal contact were estimated assuming 1.0% absorption for VOCs and 10% absorption for SVOCs.[9] In accordance with EPA guidance,[2] dermal risks were not assessed for carcinogenic PAHs. The calculated hazard indexes and cancer risks using measured concentrations and concentrations predicted by the constituent method are presented in Tables 6 and 7.

Site A

Risk estimates for Site A are presented in Table 6. The noncarcinogenic hazard index estimated for the constituent concentrations is higher than that for the measured concentrations. This difference is primarily due to the higher estimate of the concentration of naphthalene by the constituent method.

Table 6 clearly illustrates how elevated reporting limits can result in underestimation of both site concentrations (see Table 4) and risks, and how the constituent method overcomes the problem: because of elevated reporting limits, no cancer risk would be predicted for this site based on standard sampling, analyses, and risk assessment methods. On the other hand, the constituent method accounted for all of the fuel constituents and their associated risks. Nevertheless, the estimated risk was not unacceptable at this site, even though significant diesel fuel contamination was present. This illustrates the relatively low toxicity of diesel fuel, and why using current TPH soil cleanup criteria can be too conservative.

Table 6 Comparison of Risk Estimates Using Measured Concentrations and Concentrations Predicted by the Fuel Constituent Method Site A

	Total Soil Concentration Measured[1] (mg/kg)	Total Soil Concentration Constituent[2] (mg/kg)	Air Concentration Measured[3] (mg/m3)	Air Concentration Constituent[4] (mg/m3)	Non-cancer HQ Measured[5]	Non-cancer HQ Constituent[6]	Cancer Risk Measured[7]	Cancer Risk Constituent[8]
Benzene		0.023	nt	4.05E-06				8.40E-09
Ethylbenzene	0.17	0.090	8.17E-07	4.31E-07	1.88E-06	9.92E-07		
Toluene		0.10		9.63E-06		1.76E-05		
Xylenes	0.57	0.38	5.93E-05	3.91E-05	2.23E-07	1.47E-07		
Isopropylbenzene	2		4.32E-10					
"1,1-Biphenyl"		28.9		6.24E-09		1.98E-03		
"2,4-Dimethylphenol"		0.24		5.24E-11		4.15E-05		
2-Methylphenol		0.16		3.43E-11		1.09E-05		
3-Methylphenol		0.10		2.18E-11		6.92E-06		
4-Methylphenol		0.10		2.18E-11		6.92E-06		
Acenaphthene	5.69		1.23E-09		3.24E-04			
Benzo(a)anthracene		0.029		6.24E-12				3.69E-09
Benzo(a)pyrene		0.024		5.24E-12				3.10E-08
Chrysene		4.9		1.06E-09				6.28E-08
Fluorene	10.1	43.4	2.18E-09	9.36E-09	8.63E-04	3.71E-03		

Table 6 (continued)

	Total Soil Concentration Measured[1] (mg/kg)	Total Soil Concentration Constituent[2] (mg/kg)	Air Concentration Measured[3] (mg/m3)	Air Concentration Constituent[4] (mg/m3)	Non-cancer HQ Measured[5]	Non-cancer HQ Constituent[6]	Cancer Risk Measured[7]	Cancer Risk Constituent[8]
Fluoranthene		1.16		2.50E-10		9.88E-05		
Naphthalene	1.2	165	2.59E-10	3.56E-08	1.03E-04	1.41E-02		
Pyrene	11.6	5.8	2.51E-09	1.25E-09	1.32E-03	6.59E-04		
TPH	28,900							
		Totals		0.003	0.02	0E+00	1E-07	

[1] 95% Upper confidence limits of actual measured site concentrations
[2] Estimated concentration based on constituent method (95% UCL of TPH conc * fraction in diesel fuel)
[3] Air concentration based on emissions modeling using measured site concentrations
[4] Air concentrations based on estimated concentrations using constituent method
[5] Non-cancer hazard quotients based on measured site concentrations (occupational exposures)
[6] Non-cancer hazard quotients based on constituent method concentrations (occupational exposures)
[7] Cancer risks based on measured site concentrations (occupational exposures)
[8] Cancer risks based on constituent method concentrations (occupational exposures)

Table 7 Comparison of Risk Estimates Using Measured Concentrations and Concentrations Predicted by the Fuel Constituent Method Site B

	Total Soil Concentration Measured[1] (mg/kg)	Total Soil Concentration Constituent[2] (mg/kg)	Air Concentration Measured[3] (mg/m3)	Air Concentration Constituent[4] (mg/m3)	Non-cancer HQ Measured[5]	Non-cancer HQ Constituent[6]	Cancer Risk Measured[7]	Cancer Risk Constituent[8]
Benzene		0.011		1.86E-06				3.86E-09
Ethylbenzene		0.041		1.98E-07			4.56E-07	
Toluene		0.048		4.43E-06			8.08E-06	
Xylenes		0.17		1.80E-05			6.76E-08	
Acenaphthylene	0.55		1.19E-10		6.27E-05			
Anthracene	0.231		4.99E-11		2.63E-06			
Benzo(a)anthracene	0.269	0.013	5.81E-11	2.87E-12			3.44E-08	1.70E-09
Benzo(a)pyrene	0.553	0.011	1.19E-10	2.41E-12			7.07E-07	1.43E-08
"1,1-Biphenyl"		13.3		2.87E-09		9.09E-04		
Benzo(ghi)perylene	0.348		7.52E-11		3.97E-05			
Benzo(k)Fluoranthene	1.13		2.44E-10				1.44E-07	
Chrysene	0.702	2.26	1.52E-10	4.88E-10			8.97E-09	2.89E-08
2,4-Dimethylphenol"		0.11		2.41E-11		1.91E-05		
Fluoranthene	1.28	0.53	2.76E-10	1.15E-10	1.09E-04	4.54E-05		
Fluorene		19.94		4.31E-09		1.70E-03		
2-Methylphenol		0.073		1.58E-11		5.00E-05		
3-Methylphenol		0.047		1.00E-11		3.18E-05		

Table 7 (continued)

	Total Soil Concentration Measured[1] (mg/kg)	Total Soil Concentration Constituent[2] (mg/kg)	Air Concentration Measured[3] (mg/m3)	Air Concentration Constituent[4] (mg/m3)	Non-cancer HQ Measured[5]	Non-cancer HQ Constituent[6]	Cancer Risk Measured[7]	Cancer Risk Constituent[8]
4-Methylphenol		132.977		2.87E-08		9.09E-02		
Naphthalene		75.8		1.64E-08		6.48E-03		
Indeno(123-cd)pyrene	0.355		7.67E-11				4.54E-08	
Pyrene	1.3	2.66	2.81E-10	5.74E-10	1.48E-04	3.03E-04		
TPH	13,293							
			Totals		0.0004	0.10	9E-07	5E-08

[1] 95% Upper confidence limits of actual measured site concentrations
[2] Estimated concentration based on constituent method (95% UCL of TPH conc * fraction in diesel fuel)
[3] Air concentration based on emissions modeling using measured site concentrations
[4] Air concentrations based on estimated concentrations using constituent method
[5] Non-cancer hazard quotients based on measured site concentrations (occupational exposures)
[6] Non-cancer hazard quotients based on constituent method concentrations (occupational exposures)
[7] Cancer risks based on measured site concentrations (occupational exposures)
[8] Cancer risks based on constituent method concentrations (occupational exposures)

Site B

Risk estimates for measured concentrations and predicted constituent concentrations at Site B are presented in Table 7. The differences in the risk estimates are primarily due to higher estimates of concentrations of BTEX, 1,1-biphenyl, and naphthalene, and lower estimates of concentrations of some PAHs (especially benzo(a)anthracene, benzo(a)pyrene, benzo(k)fluoranthene, and Indeno(123-cd)pyrene) by the constituent method. These differences are likely due to volatilization of VOCs and the presence of non-fuel related contaminants that were not accounted for in the constituent method. As can be seen from Table 7, the constituent method underestimated risks at this site, demonstrates that this method should only be used at sites where the contamination is known to be fuel and where non-fuel related contamination is not present at significant concentrations, or in situations where these constituents can be accounted for.

Table 8 presents the results of the constituent method at four areas of an NPL site on an Air Force Base. The TPH was measured by method 8018 at these sites and was reported as GRO and TCO. This analytical method, in addition to site history, provided information regarding the types of fuel (i.e., gasoline, diesel fuel, or JP-4) that may have been released at each site. The constituent method was used at these sites because repeated attempts to characterize the sites had resulted in SVOCs being reported as nondetect at elevated reporting limits. It was modified for use at these sites by using analytical results for BTEX (benzene, toluene, ethylbenzene, and xylenes) in conjunction with constituent method estimates of the remaining fuel constituents. The results of the evaluations were accepted by federal and state agencies resulting, in No Further Action decisions at the sites. Table 8 shows that although significant levels of fuel are present in the soil, health risks are considered acceptable.

RISK-BASED CLEANUP CONCENTRATIONS

Table 9 presents risk-based cleanup concentrations using the constituent method for diesel fuel- contaminated industrial soil. The cleanup concentrations are based on soil ingestion, dermal contact with soil, and inhalation of air-borne emissions from soil, calculated using the same occupational exposure assumptions (Standard Default Exposure Factors) used in the case studies. The cleanup concentrations do not factor in potential transport to groundwater and risks associated with the groundwater pathway. Therefore, actual cleanup concentrations would need to be modified to account for this and any other pertinent pathway. The cleanup concentration calculated in Table 9 demonstrates that typical TPH regulatory levels for soil (e.g., 100 mg/kg) are lower than necessary to protect human health.

Table 10 presents risk-based cleanup concentrations for gasoline in industrial soil. The cleanup concentrations in Table 10 are based on the same assumptions used to calculate the diesel fuel cleanup concentrations shown in Table 9. Table 10 shows that risk and the associated cleanup concentration for gasoline are driven by inhalation of benzene. While this may be the case for fresh fuel, much of the benzene in weathered gasoline contaminated soil especially at the surface is likely to have volatilized; therefore, using the maximum benzene concentrations reported in the literature for the

Table 8 Results of Constituent Method Used at an NPL Site on an Air Force Base

Subsite	Fuel Type	Fuel Concentration as TPH (mg/kg)	Estimated Non-cancer Hazard	Estimated Cancer Risk
Flightline Spill	JP-4	2,200 (as GRO)	0.3	1 x 10^{-6}
BX	Gasoline	6,400 (as GRO)	0.7	4 x 10^{-5}
MX	Gasoline	11,300 (GRO + TCO)[1]	1.0	6 x 10^{-6}
Fuel Hydrant	JP-4	4,200 (as GRO)	0.3	No carcinogens detected in soil

[1] Gasoline and diesel may have been released at this site; to be conservative, gasoline was assumed to be the fuel present.

Risks are based on industrial exposures.

Results are based on analysis of BTEX and constituent method estimates of other fuel constituents.

GRO = Gasoline Range Organics

TCO = Total Chromatagraphable Organics

Table 9 Risk-Based Cleanup Concentrations for Diesel Fuel Contaminated Soils Based on Soil Exposure Pathways

Constituent	Percent in Diesel (mg/kg)	Diesel (asTPH) Conc. in Soil (mg/kg)	Constituent Conc. in Soil[a]	HQing[b]	Risking[c]	HQder[d]	Riskder[e]	HQinh[f]	Riskinh[g]
Benzene	8.00E-05	250,000	2.00E-01		1.02E-09		6.09E-10		7.10E-08
Ethylbenzene	3.10E-04	250,000	7.75E-01	3.79E-06		2.27E-06		2.52E-06	
Toluene	3.60E-04	250,000	9.00E-01	2.20E-06		1.32E-06		1.48E-04	
Xylene	1.30E-03	250,000	3.25E+00	7.95E-07		4.76E-07			
Benzo(a)anthracene	1.00E-04	250,000	2.50E-01		3.19E-08				2.30E-12
Benzo(a)pyrene	8.40E-05	250,000	2.10E-01		2.68E-07				1.93E-11
1,1-Biphenyl	1.00E-01	250,000	2.50E+02	2.45E-03		1.47E-02			
Chrysene	1.70E-02	250,000	4.25E+01		5.43E-07		3.91E-11		
2,4-Dimethylphenol	8.40E-04	250,000	2.10E+00	5.13E-05		3.08E-04			
Fluoranthene	4.00E-03	250,000	1.00E+01	1.22E-04		7.33E-04			
Fluorene	1.50E-01	250,000	3.75E+02	4.58E-03		2.75E-02			
o-Cresol	5.50E-04	250,000	1.38E+00	1.34E-05		8.06E-05			
m-Cresol	3.50E-04	250,000	8.75E-01	8.56E-06		5.13E-05			
p-Cresol	3.50E-04	250,000	8.75E-01	8.56E-06		5.13E-05			
Naphthalene	5.70E-01	250,000	1.43E+03	1.74E-02		1.04E-01			
Pyrene	2.00E-02	250,000	5.00E+01	8.15E-04		4.88E-03			
				0.03	8.44E-07	0.2	6.09E-10	0.0002	7.11E-08
						Total Noncancer Hazard			0.2
						Total Cancer Risk			9E-07

[a] Soil concentration = constituent fraction * TPH concentration

[b] HQing = Hazard Quotient via soil ingestion = Soil concentration * Noncarcinogenic Ingestion Intake Factor /RfDoral

[c] Risking = Risk via ingestion of soil = Soil concentration * Carcinogenic Ingestion Intake Factor * Oral Slope Factor

[d] HQder = Hazard Quotient via dermal contact with soil = Adjusted soil concentration * Noncarcinogenic Dermal Intake Factor /RfDoral

[e] Riskder = Risk via dermal contact with soil = Adjusted soil concentration * Carcinogenic Dermal Intake Factor * Oral Slope Factor

[f] HQinh = Hazard Quotient via inhalation = Air concentration * Noncarcinogenic Inhalation Intake Factor /RfDinhalation

[g] Riskinh = Risk via inhalation = Air concentration * Carcinogenic Inhalation Intake Factor * Inhalation Slope Factor

Table 10 Risk-Based Cleanup Concentrations for Gasoline Fnel Contaminated Soils Based on Soil Exposure Pathways

Constituent	Percent in Gasoline (mg/kg)	Gasoline (asTPH) Conc. in Soil (mg/kg)	Constituent Conc. in Soil[a]	HQing[b]	Risking[c]	HQder[d]	Riskder[e]	HQinh[f]	Riskinh[g]
Benzene	1.40E+00	250	3.50E+00		1.78E-08		1.07E-08		1.24E-06
Ethylbenzene	1.30E+00	250	3.25E+00	1.59E-05		9.52E-06		1.06E-05	
Toluene	5.80E+00	250	1.45E+01	3.55E-05		2.12E-05		2.39E-03	
Xylene	6.50E+00	250	1.63E+01	3.97E-06		2.38E-06			
n-Hexane	3.50E+00	250	8.75E+00	7.13E-05		4.27E-05		3.25E-02	
"1,2-Dichloroethane"	2.30E-02	250	5.75E-02		9.16E-10		5.49E-10		1.14E-07
Benzo(a)anthracene	2.20E-04	250	5.50E-04		7.03E-11				5.07E-15
Benzo(a)pyrene	2.80E-05	250	7.00E-05		8.94E-11				6.45E-15
Benzo(b)fluoranthene	4.60E-04	250	1.15E-03		1.47E-10				1.06E-14
"1,1-Biphenyl"	5.30E-04	250	1.33E-03	1.30E-08		7.76E-08			
Chrysene	2.00E-04	250	5.00E-04		6.39E-12				4.60E-16
Cumene	2.30E-01	250	5.75E-01	7.03E-06		4.21E-05		9.36E-09	
"2,4-Dimethylphenol"	4.70E-04	250	1.18E-03	2.87E-08		1.72E-07			
Fluoranthene	2.40E-04	250	6.00E-04	7.34E-09		4.40E-08			
Fluorene	2.90E-04	250	7.25E-04	8.86E-09		5.31E-08			
m-Cresol	3.50E-03	250	8.75E-03	8.56E-08		5.13E-07			
p-Cresol	3.50E-03	250	8.75E-03	8.56E-08		5.13E-07			
Naphthalene	4.90E-01	250	1.23E+00	1.50E-05		8.97E-05			
				0.0001	1.90E-08	0.0002	1.12E-08	0.03	1.36E-06
						Total Noncancer Hazard			0.04
						Total Carcinogenic Risc			1E-06

[a] Soil concentration = constituent fraction * TPH concentration

[b] HQing = Hazard Quotient via soil ingestion = Soil concentration * Noncarcinogenic Ingestion Intake Factor /RfDoral

[c] Risking = Risk via ingestion of soil = Soil concentration * Carcinogenic Ingestion Intake Factor * Oral Slope Factorz

[d] HQder = Hazard Quotient via dermal contact with soil = Adjusted soil concentration * Noncarcinogenic Dermal Intake Factor /RfDoral

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[f] HQinh = Hazard Quotient via inhalation = Air concentration * Noncarcinogenic Inhalation Intake Factor /RfDinhalation

[g] Riskinh = Risk via inhalation = Air concentration * Carcinogenic Inhalation Intake Factor * Inhalation Slope Factor

constituent method is certainly a conservative approach that is likely to overestimate actual risks at the site.

SUMMARY AND CONCLUSIONS

A method was developed to perform risk assessments at fuel-contaminated sites based on TPH measurements. The method allows calculation of risks from soils even when analytical interferences caused by heavy contamination prevent analysis of individual contaminants. The method was used successfully to calculate risks at an NPL site on a federal facility. The risk assessment method showed that even though soils had significant levels of fuel, they did not pose an unacceptable risk. Therefore, no remedial action was necessary to protect human health or the environment. The assessment was accepted by state and federal agencies, resulting in a No Further Action decision at the site. This same method has also been used at several railroad sites (results are undergoing regulatory review).

Further research that might improve this procedure include refining estimates of the percentages of fuel constituents in fuels, developing analytical methods that can accurately characterize fuel concentrations in soil and water, improving ways to predict constituent concentrations in weathered fuels, and refining methods and models that can be used to predict transport to groundwater or the air.

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QUESTIONS AND ANSWERS

Q. Are your case studies published?

They will be. The case studies are actually parts of investigations that have been done on RCRA/CERCLA sites. They are published in the sense that they are in the public record, and the case studies will be published in the proceedings.

Q. What states or EPA regions have been receptive to this technique?

We got this through Region 10 in Idaho. We developed this for a Department of Defense site in Idaho. It was accepted there for a no-action, no-further-action decision. We've also used it in Texas and it's in the process there. We believe that they are going to be favorable to it. They've said they would likely be, but it is not completely finished.

Chapter 3

Screening for PAHs at a Railroad Site with a Passive Soil Gas Survey

Wayne M. Wells, II
W. L. Gore & Associates, Inc., Elkton, MD

Stephen G. McMahon
Integrated Environmental Solutions, Jacksonville, FL

INTRODUCTION

Polyaromatic hydrocarbons (PAHs) and higher molecular weight hydrocarbons (C11 to C20) are common compounds of concern when assessing the environmental impact of past operations at current and former railroad sites. Common sources of these constituents are journal boxes, diesel fuel storage facilities, and maintenance yards. Available options for testing for these compounds are limited and involve collecting discrete soil and/or ground water samples followed by analysis using one (or possibly more) standard methods. Discrete soil and ground water samples have the disadvantage of being point samples only, offering little or no information about the matrix six feet or even six inches away. In addition, the standard methods are usually compound-specific, and tend to be fairly expensive when analyzing for multiple classes of compounds.

There has been only limited success with the use of traditional soil gas investigation methods (i.e., active soil gas testing) as alternatives for delineating soil and/or groundwater impact from PAHs and long-chain alkanes, mainly due to the vapor pressures of these compounds (see Table 1).[1] Generally, as the molecular weight increases, solubility in water and the volatility decrease, causing a tendency to adsorb onto soil particles and sediments.[2] Therefore, only minute levels are generally available in the soil gas at any given time. One solution to this problem is time-integrated (passive) sampling.

PASSIVE SOIL GAS TECHNOLOGY

A unique passive soil-gas screening technology has been developed and validated over the past two years by W. L. Gore & Associates, Inc. This technology is used in screening for volatile and semi-volatile organic compounds and can be applied at sites

Table 1 Vapor Pressures of Selected PAHs/SVOCs

Compound Name	Vapor Pressure, (Pa at 25 degrees C)”
Undecane	52.2
Naphthalene	10.4
2-Methylnaphthalene	9
2,6-Dimethylnaphthalene”	1.4
Acenaphthylene	0.9
Acenaphthene	0.3
Fluorene	0.09
Phenanthrene	0.02
Fluoranthene	0.00123
Anthracene	0.001
Pyrene	0.0006
Benz(a)anthracene	2.80E-05
Benzo(a)pyrene	7.00E-07
Chrysene	5.70E-07
Benzo(k)fluoranthene	5.20E-08
Dibenz(a,h)anthracene”	3.70E-10

with low permeability and/or saturated soils. This technology features a patented soil gas collector called the GORE-SORBER module, a thermal desorption/GC/MS analysis of each module, and a final report of the results complete with data tables and color contour maps showing relative distributions of the detected analytes.

The “sensing element” is constructed of a hollow insertion/retrieval cord made completely of GORE-TEX membrane. An expanded polytetrafluoroethylene (ePTFE) GOR-TEX membrane, is a chemically inert, microporous, and hydrophobic material. The node and fibril structure of ePTFE facilitates vapor transfer, while simultaneously preventing liquid water and soil particles from impacting sample integrity. Inside the insertion/retrieval cord are smaller, hollow ePTFE tubes filled with sorbent material and sealed at both ends (sorbers). Tenax TA® is the sorbent most commonly used, although alternative sorbents can be utilized for specialized applications. Because the entire module is made of ePTFE, vapor transfer can occur across the entire surface area. The vapor-permeable, water-repellent GORE-TEX membrane around the sorbent is well-suited for application in dry, wet, and saturated soils. Modules are installed in narrow pilot holes created with simple hand tools, with retrieval typically occurring after a two week exposure time.

Table 2 Bench-Scale Experimental Results, Natural Matrix Certified Reference Material, Jar-Exposure Experiment

Target Compound	Amount Detected, μg	Reference Value, ppm
Naphthalene	4.49	15.7
2-Methylnaphthalene	6.08	27.0
Acenaphthylene	2.14	16.7
Acenaphthene	65.80	640.5
Dibenzofuran	47.66	256.4
Fluorene	31.83	368.3
Carbazole	3.52	39.4
Pentachlorophenol	0.02	1202.6
Phenanthrene	51.30	1153.4
Anthracene	17.99	415.2
Fluoranthene	6.81	1409.8
Pyrene	4.40	1059.6
Benzo(a)anthracene	0.03	251.0
Chrysene	0.03	316.5
Benzo(b)fluoranthene	N.D.	99.8
Benzo(k)fluoranthene	N.D.	64.8
Benzo(a)pyrene	N.D.	84.0
Indeno(1,2,3-c,d)pyrene	N.D.	21.5
Dibenz(a,h)anthracene	N.D.	10.9
Benzo(g,h,i)perylene	N.D.	22.6

BENCH-SCALE EXPERIMENTS

In order to determine which PAHs can realistically be screened using passive soil gas technology, bench scale experiments have been conducted using a natural matrix reference material purchased from Resource Technology Corporation containing certified concentrations of various PAHs and pesticides. One hundred grams of this soil were placed in a jar along with a GORE-SORBER module. The jar was sealed and allowed to sit in a fumehood for approximately five weeks. The modules were then analyzed using standard thermal desorption/gas chromatography/mass spectrometry conditions. Results are summarized in Table 2.

The target compounds in Table 2 are in GC elution order, which closely approximates decreasing vapor pressure order. Compounds up to chrysene were detected in the exposed sorbers. Because of sensitivity concerns, however, pyrene is probably a practical cut-off. Similar results have also been obtained in other experiments at two and three week exposure times.

FIELD TRIAL

A major East Coast railroad company had a closed journal box oil recycling plant at one of its rail yards. Apparently, when the plant was in operation, poor housekeeping and containment procedures led to an appreciable loss of oil and petroleum products. Visible soil staining was present at the site. Initial sampling in the area detected the presence of heavy-ended diesel related contaminants containing high levels of lead.

The extent of the subsurface organic contamination had to be determined because the area's relatively small size (1.66 acres) made traditional sampling and analyses cost prohibitive. Less costly alternatives for determining the horizontal extent of soil contamination were therefore evaluated. A GORE SORBER Screening Survey was selected to delineate the areal extent of subsurface contamination. Total lead and oil and grease analyses were also performed on soil samples obtained from across the site, using EPA Methods 3050/6010A and 9071, respectively. The area to be investigated was gridded in a 50 foot centered pattern. Thirty modules were installed to approximately 2.5 feet below the surface and retrieved 25 days later. (Modules are not usually exposed for such an extended period of time, but due to the semi-volatile nature of the contaminants and their low vapor pressures, longer than normal exposure times were thought necessary. Subsequent work has shown that a two-week exposure would have been sufficient).

The GORE-SORBER Screening Survey made it possible to delineate the extent of organic contamination. Gore did a preliminary analysis of a soil sample from the site that was known to be contaminated with journal box oil; dimethylnaphthalene was found to be the best tracer compound for this purpose. (It should be noted that dimethylnaphthalene is not typically on a target compound list, so its presence might not be noted by many environmental testing laboratories).

Figures 1, 2, and 3 show the interpolation and mapping of the total lead, dimethylnaphthalene, and oil and grease results. The dimethylnaphthalene results were obtained using passive soil gas sampling. As lead can be associated with journal oil and is generally immobile, the three "hot spots" on the lead map are likely to be the original source areas. The oil and grease results seem to agree with only two of the three hot spots and don't give much indication as to the extent of contaminant migration. The dimethylnaphthalene map, however, has three hot spots set slightly off from the lead hot spots in the expected direction of surface and ground water flow. The dimethylnaphthalene map also clearly indicates the contaminant plume and its expected direction of migration.

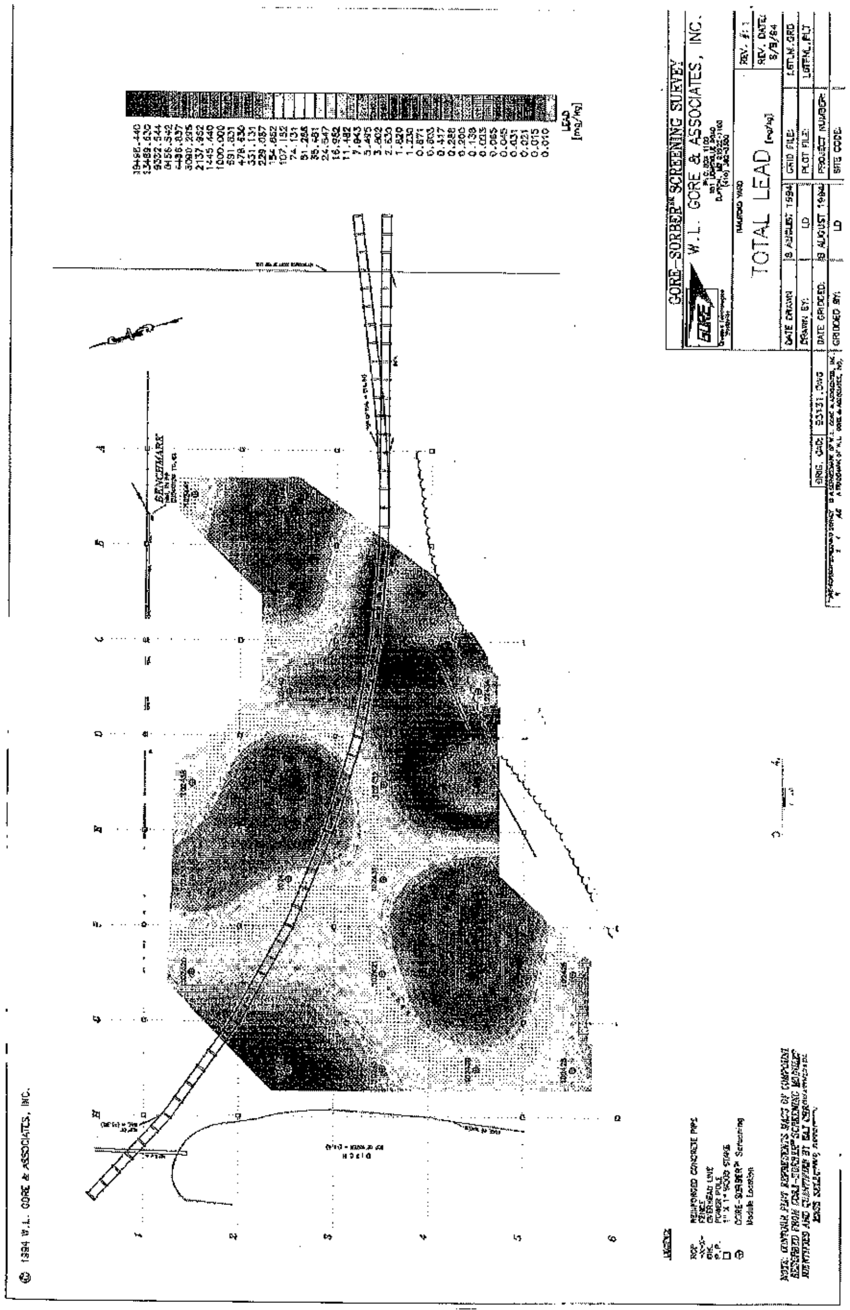

Figure 1 Relative Distribution of Total Lead

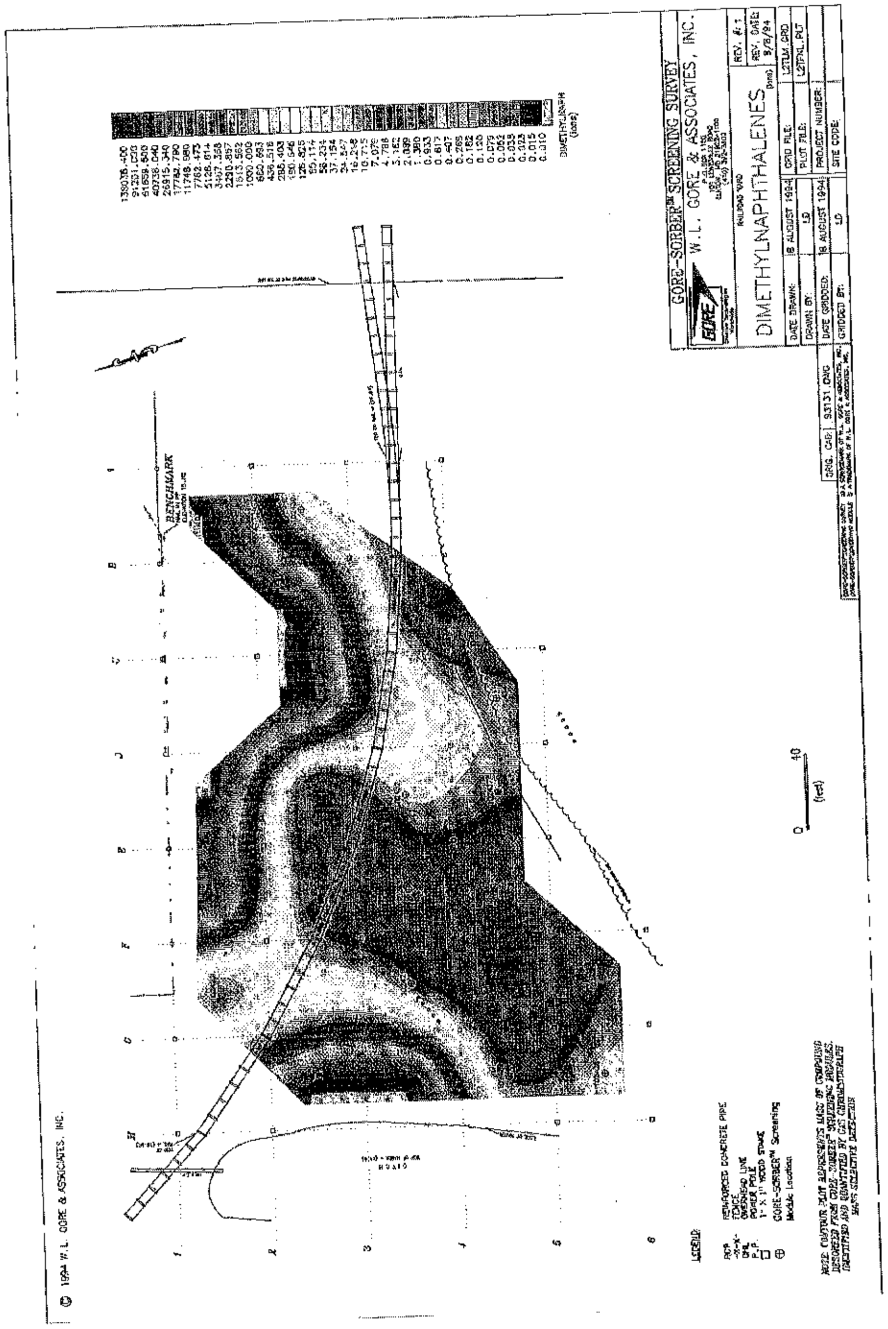

Figure 2 Relative Distribution of Dimethylnaphthalenes

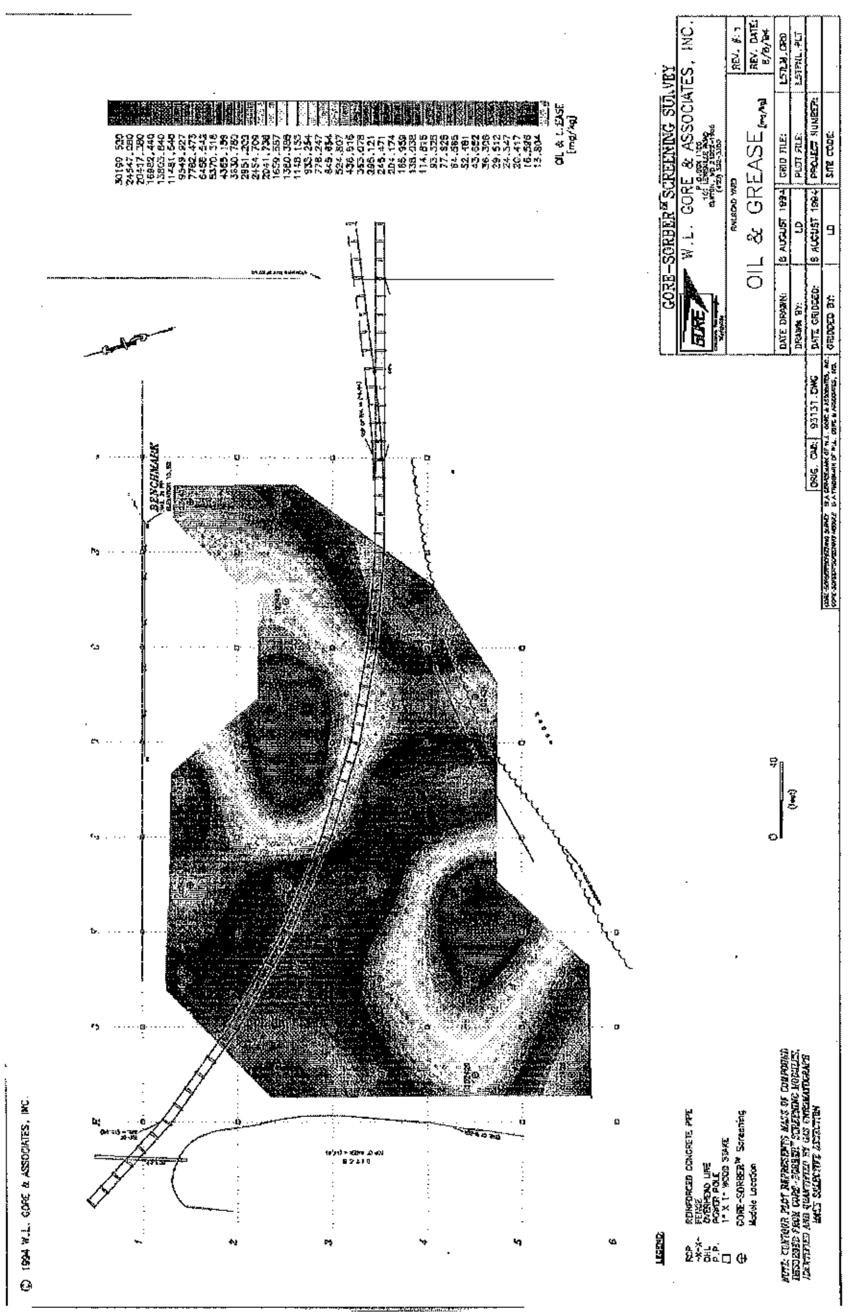

Figure 3 Relative Distribution of Oil and Grease

CONCLUSIONS

The survey outlined the contaminated areas and provided a focus for action. Use of the GORE-SORBER Screening Survey made it possible to accurately determine the extent of subsurface organic contamination without mobilizing costly soil boring equipment and field personnel. In addition, a compound-specific visual representation of the contamination was obtained. GORE-SORBER Screening Survey and GORE-TEX are registered trademarks of W. L. Gore & Associates, Inc. Tenax TA is a registered trademark of Enka Research Institute.

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2. Ibid., pp. 335-336.

QUESTIONS AND ANSWERS

Q. With the groundwater depth being four to five feet and the installation being three feet, how does that work if we were to go down to a 17-foot depth, or something like that?

We've actually worked on sites with groundwater depths of a hundred or two hundred feet with absolutely no problems whatsoever. Due to the fact that you're doing passive sampling over about two weeks or so, that gives it plenty of time for those molecules to reach the surface or, actually, three feet below the surface. Not to mention the fact that it's happening continuously, so there were some things from that depth that were already at three feet when we did the initial installation. This is a continuous process.

Q. The probe depth is still three feet?

Yes. Three feet is chosen to mitigate some of the surface effects. Biodegradation and things like that.

Q. Does the amount of time of exposure matter? Are we waiting to reach equilibrium with the soil vapor?

The answer is no. We're not waiting to reach an equilibrium. I believe the time does matter, but seeing as what we're really doing is mapping relative concentrations from one absorber to the next, time matters in that all the absorbers have to be in for the same amount of time. That's the approach that we've taken there and it works quite effectively.

Q. What's the radius of capture of your units? I've heard some pretty fancy claims lately (100 feet, 200 feet sometimes), and it's hard to think that PAHs would move that far in a soil matrix. Could you expand on that a little bit?

I can't say for certain whether we've been able to pick up PAHs at a hundred feet or greater. I'm not real sure that some of our sites where we've done PAHs have that depth to groundwater. I do know that PAHs interact quite readily with the soil particles, which I believe is the reason that you can't see past pyrene. More important than the vapor pressure is the actual interaction of the compounds with the soil, and they become attached to the soil and are no longer available as soil gas. It is my belief that anything that is in the soil gas in sufficient quantities will be detectable by my gas mass spectrometer.

Q. Do you see this technique being valuable for defining the free product plume, or just the soil matrix?

Obviously, we would be able to detect free product quite readily with this technology. It saturates out the detector. What we're typically using the GORE-SORBER for is to ascertain the plume, that is where pollutants have migrated since they were put in the ground.

Q. At this site, did you do any borings to identify the free product plume to see how it agreed with your results?

My understanding is that they did not do any borings to determine where the product actually is. Their main concern on this site was the lead. What we were trying to do was use an organic marker to try to show them where the journal box oil was, so they could go back and attribute that and do some testing for the lead itself.

They haven't finished remediating this site, by the way.

Q. That graph that you showed, did you make any attempt to correlate any actual grab samples that you took, to how much was diffused on the samplers?

No, we did not. Not at the site.

Q. You just talked about relative concentrations?

Relative distributions, exactly. We did no soil sampling for the PAHs themselves.

Q. Do you think it would be possible to sample for PAH's, given what their vapor pressures are?

It would be possible. Part of the problem is that with the passive soil gas technology, you're not just determining what's in the soil. You're also determining what's in the groundwater. So getting soil samples to correspond with soil gas samples is actually very difficult to do, because you're taking a complete picture of the subsurface gas not just the soil itself.

Q. What about an upper limit to the amount of material that can be sorbed onto the detector? Would you see sort of an upper plateau, after which you wouldn't be able to resolve differences in concentrations?

The upper plateau that we've seen so far is saturation of the detector. And to be honest with you, I've seen upwards of 4,000 or 5,000 micrograms onto the sorber of various compounds.

Q. What would that relate to in soil?

It actively relates to free product.

Q. What about cost down the road for materials?

The screening survey involves installation and surveying, we provide the absorbtion module. The consultant or yourself would do the installation, and we would do the complete GC/MS laboratory analysis, the color contour mapping onto a customer-supplied CAD map, as well as a final report that we provide. In addition to this, throughout the entire process there's consultation going on with our client. This survey, this service, costs approximately $225.00 per point and we do the volatiles and the semi-volatiles simultaneously with this. I've done as volatile as vinyl chloride and again as semi-volatile as pyrene. And we can do these simultaneously.

Q. Does the $225.00 include installation?

We don't do the installation. The customer does the installation, so that would not be included in the cost.

Chapter 4

Use of No-Excavation Impermeable Barrier to Control Subsurface Hydrocarbon Migration

Jeffrey C. Brown
Radian Corporation, Milwaukee, WI

James A. Ewert
Atchison, Topeka and Santa Fe Railway Company, Topeka, KS

INTRODUCTION

Historic diesel fuel releases in railyards are an unfortunate fact of life for most railroads. The storage and use of large quantities of diesel fuel, extensive underground distribution systems, and rapid, high-volume fueling equipment have produced uncontrolled releases in the past. Recovery and remediation of these releases are often hindered by the presence of tracks and other equipment essential to operation.

Construction of rail lines in river valleys where grades are low creates conditions where hydrocarbon releases are often adjacent to major water ways. In these circumstances, direct discharge of petroleum products to surface water can occur. Such releases create high visibility problems that often require expensive emergency corrective action to satisfy regulatory agencies and the public.

Recently, a flexible system of interlocking, high density polyethylene (HDPE) panels that can be driven into place from the surface has become available. This system provides a less expensive alternative to other hydrocarbon retention systems. This HDPE system was used successfully at the Atchison, Topeka and Santa Fe (ATSF) Railyard in Ft. Madison, Iowa. This chapter presents a description of conditions which resulted in its use and describes its installation.

SETTING

The ATSF Railyard at Ft. Madison, Iowa, occupies an area of 200 acres along the north side of the Mississippi River (Figure 1). The yard, was once a major division point with extensive engine and car shops, and employed as many as 2000 workers.

Fueling of both passenger and freight trains was included in yard activities. Currently, the yard is both a marshalling area for regional freight trains and a crew change location. Engine fueling no longer occurs at the yard.

The yard is located on the Mississippi River flood plain about 10 feet above the normal river level. A navigation and flood control dam downstream controls river levels, but considerable river level fluctuation occurs with attempts to control flow in lower reaches of the river. Dry Creek, a local tributary, crosses the ATSF yard from north to south, and joins the river near the east end of the yard (Figure 1). Flow in the creek varies, but water is present in the channel year-round. At the mouth of Dry Creek, a delta area of deposited stream sediments and extends about 450 feet into the river channel. Periodic dredging has maintained the Dry Creek channel through the center of this deposit, separating the sediment into two triangular-shaped peninsular areas.

PROBLEM

In the past, two 30,000 gallon day tanks were located on the eastern half of the Dry Creek delta deposits, approximately 75 feet south of the mainline tracks (Figure 2). The tanks provided diesel fuel to two mainline fueling stations: one immediately to the north, and the other about 1200 feet to the west. The tanks were removed in the late 1950s when the west mainline fueling facility was closed.

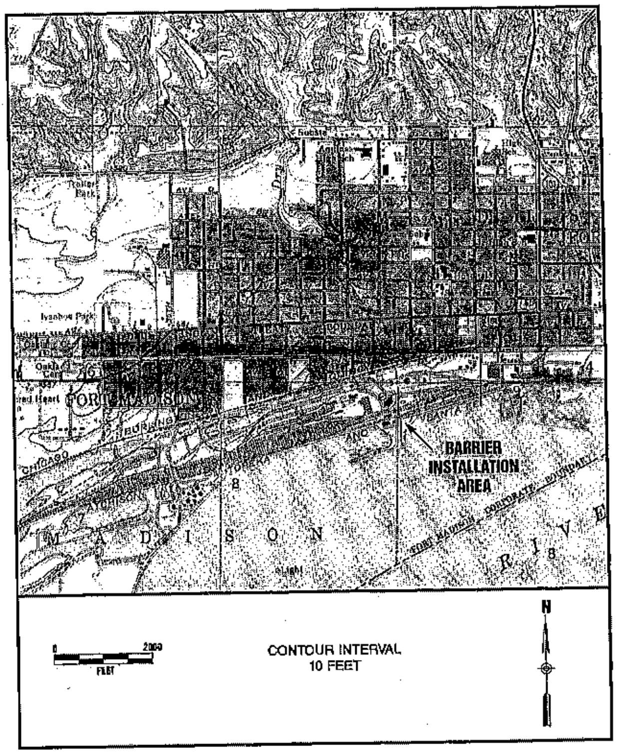

Figure 1 Location of ATSF Railyard, Ft. Madison, Iowa

During related site investigation activity, evidence of subsurface free-phase hydrocarbon was discovered in the former day tank area. In 1992, investigations were initiated to determine its extent. Results of this investigation are shown in Figures 2 and 3. Sediments in this area are sands, silts, and clays typical of flood and stream deposits of varying energies. Subsurface investigation indicates that sand and silty sands extend to depths of at least 20 to 30 feet, becoming finer grained at greater depths. The water table is convex in shape, with discharge occurring both to the river on the east and southeast, and to Dry Creek to the west (Figure 3).

Free-phase hydrocarbon was present as a thin lens generally limited to the immediate area of the day tank, tapering to a thin edge in down gradient directions. While no hydrocarbon discharge to either the river or Dry Creek was evident, black staining along the adjacent banks indicated that hydrocarhon had migrated as far as each of these streams. Subsurface free-phase hydrocarbon is more widely distributed along Dry Creek than along the river to the east.

Installation of a product recovery system was planned for 1993; however, construction was delayed by severe flooding in the area during that summer. During this time the entire yard, except for the mainline tracks, was under water. Effects of this flooding on subsurface hydrocarbon distribution were not immediately apparent, and recovery system installation was delayed until they could be determined. Hydrocarbon

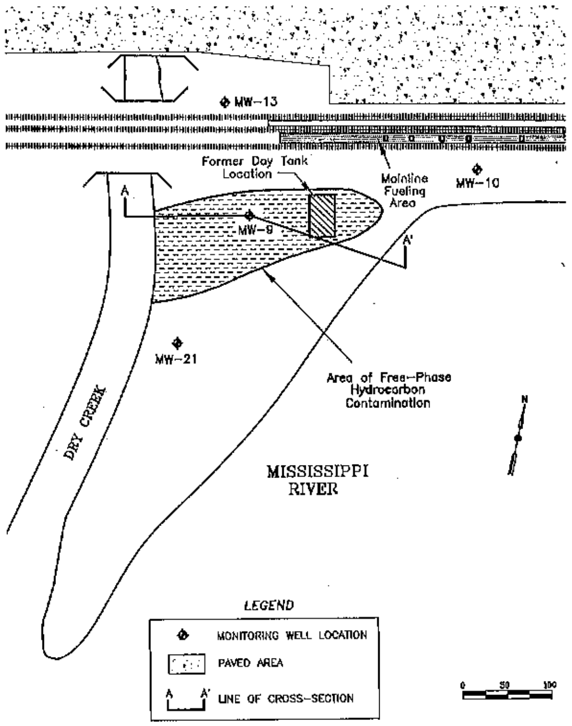

Figure 2 Area of Interest, ATSF Railyard, Ft. Madison, Iowa

product thickness that reached a maximum of three feet in well MW-9 before the flood was less than 0.5 feet when flood waters receded. This change in thickness and the general subsurface distribution of the product suggested that movement of flood waters to the west may have moved the product in that direction (Figure 2).

An additional consequence of the flooding was the silting in of the Dry Creek channel. In early summer of 1994 the city dredged the channel, placing dredge spoil on land immediately adjacent to it. Much of the dredge spoil collected from the channel immediately south of the mainline tracks was petroleum-contaminated, and ATSF incurred considerable expense in the removal and disposal of this contaminated spoil. To make matters worse, once channel dredging was complete, free-phase hydrocarbon discharge into the creek started to occur.

CORRECTIVE ACTION

The discharge of free-phase hydrocarbons into Dry Creek prompted a request for action from the regulatory authorities. Preliminary evaluation indicated that a vertical barrier was needed to retain the free-phase hydrocarbon while recovery efforts were implemented. However, the loose nature of the sediments and the high water table presented problems for any method that required excavation, and such methods were likely to be expensive. Having just disposed of the contaminated dredge spoil, ATSF was not eager to invest resources in disposal of additional contaminated soil. The corrective approach taken was influenced by these factors.

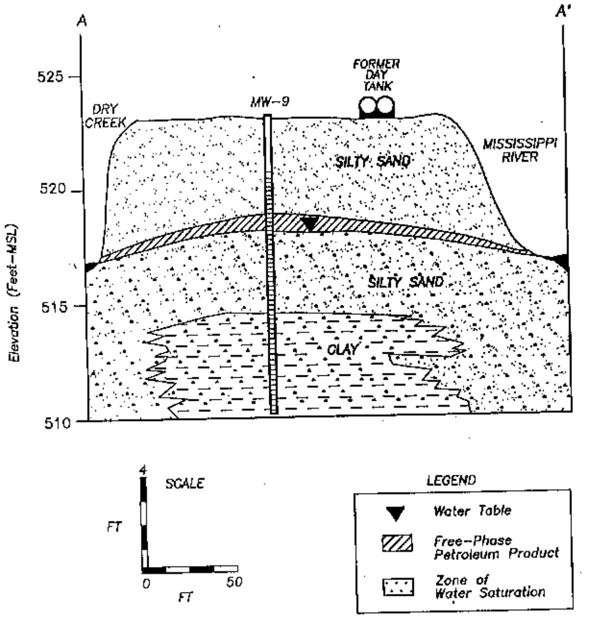

Figure 3 Section Across Area of Interest, ATSF Railyard, Ft. Madison, Iowa

Approach and Design

Given the nature of the source and existing site conditions and constraints, a set of design objectives for the barrier system was developed. These objectives included:

- The barrier must be continuous and impermeable to free phase hydrocarbons, but must not impede groundwater movement;
- The barrier must prevent hydrocarbon discharge to both the Mississippi River and Dry Creek;
- The volume of hydrocarbon contaminated soil excavated must be kept to a minimum;
- The barrier system should be cost effective and generally maintenance-free.

Several Options using these objectives were evaluated; installation of an HDPE curtain around the affected area appeared to be the most viable. Such a curtain is impervious to most liquids, is flexible and continuous, and can be installed to intermediate depths to contain free-phase hydrocarbon, yet still allow flow of groundwater. In the past, installation of such curtains has required extensive excavation and trench stabilization. Recently, however, a system has been developed that uses individual locking panels driven from the surface using standard sheet pile driving techniques. This installation method requires minimum equipment and eliminates the need for excavation and soil disposal.

Site data indicated that a shallow lens of hydrocarbon was present on the water table near monitoring well MW-9, extending to surface water bodies both to the east and west. To contain this product, a linear barrier was designed to surround the down gradient sides of the affected area and prevent further surface discharge. The barrier was designed to be installed as close as possible to the edges of adjacent water bodies without jeopardizing bank stability. A 10-foot depth was selected, which placed the barrier bottom well below the historic water table elevation, but still permitted continued groundwater movement through the coarser-grained near-surface sediments.

System Description

The system selected for this site was the Gundwall vertical barrier system manufactured by Gundle Lining Systems of Houston, Texas. The system consists of 6-foot wide, 80-mil thick HDPE panels installed adjacent to one another. Panels are interlocking and each joint includes a hydrophilic rubber seal (Figure 4) which swells when exposed to water. This interlocking feature creates a continuous impermeable barrier that can be installed with varying degrees of curvature. Laboratory tests performed on the HDPE and interlock seal have shown both to be resistant to chemical degradation or changes in material properties when placed in prolonged contact with hydrocarbon compounds.

Seventy 6 x 10-ft panels fabricated with the interlock system were delivered to the site within three weeks. Panel material and fabrication costs were about $6.00 per square foot. A local contractor was retained for barrier installation.

Installation

Mobilization to the site occurred in November, 1994. Equipment included a two-drum 50-ton crane and a vibratory hammer system used for standard sheet pile installation. The system included the hammer suspended from the crane and a power pack located on the ground nearby. The power pack provided hydraulics necessary to operate the vibrating hammer.

Each HDPE panel was constructed with a female part of the panel interlock system bonded to one edge and the corresponding male part bonded to the other. A reinforced "J" shaped channel was bonded to the bottom edge of each panel. To drive a panel, the bottom edge of a 6 x 15-foot steel insertion plate was placed in the "J" channel. The plate and panel were then positioned adjacent to the previously driven panel, and the companion parts of the interlock connected. The insertion plate was then driven using the vibratory hammer. As the panel moved down, hydrophilic seal material lubricated with a soap solution was fed into the joint, continuously filling the interlock. Once the panel was in place, the insertion plate was pulled back, leaving the HDPE panel in place. During the panel driving procedure, water was sprayed between the panel and insertion plate, thus reducing friction and allowing the plate to be withdrawn without binding on the HDPE panel. This driving process was then repeated for each additional panel.

The entire 390-foot barrier was installed in 1.5 days. In general, installation was smooth. However, during the driving process a few problems maintaining proper alignment and plumb of the insertion plate during driving. If proper alignment and plumb are not maintained the "J" channel can be sheared easily or the interlock can be pulled apart. If this happens, the damaged panels have to be removed and discarded.

Figure 5 shows the layout of the completed barrier installation. The barrier was placed within a few feet of the bank of Dry Creek, along the reach where evidence of hydrocarbon discharge was present. The 6-foot panel width permitted a moderately tight radius of curvature, and a "V" shaped layout was achieved. Near the east end of the barrier, considerable buried concrete foundation material was encountered and threatened to prevent successful installation in that area. However, a tractor-mounted backhoe was used to locate the foundation pieces ahead of panel installation. The sectional flexibility of the panel made it possible to vary the line of installation to avoid these obstructions without compromising the integrity of the linear barrier. Barrier end points were dictated by overhead power and signal lines, which prevented equipment access. Following barrier installation, a product recovery system was installed inside the barrier and hydrocarbon recovery took place. Total cost for the material, installation, and contractor oversight was about $15 per square foot of panel installed.

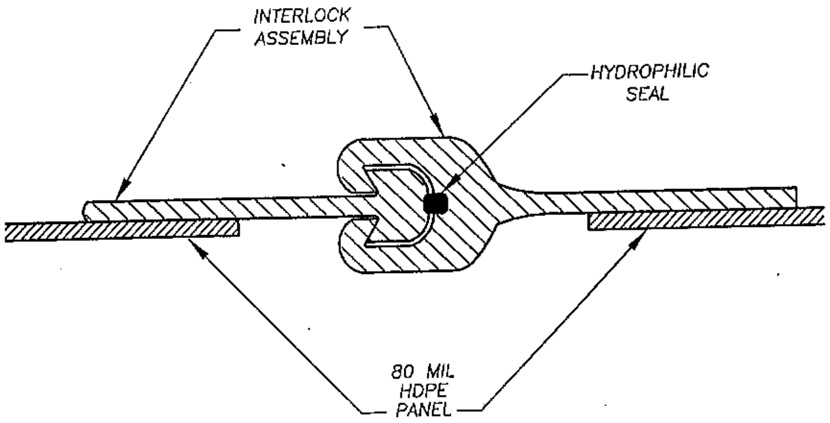

Figure 4 Detail of Panel System Interlock

RESULTS AND CONCLUSIONS

The barrier has been in place for nine months, and no evidence of hydrocarbon discharge to adjacent surface water has been detected. Following barrier installation, a piezometer (PZ-1) was installed inside the barrier (Figure 5). Table 1 presents a comparison of liquid levels in PZ-1 with those in well MW-21 located outside the barrier. Product thickness in PZ-1 fluctuates in response to water level changes, but no product has been detected in MW-21. The lack of evidence of product outside the barrier indicates it has been effective in retaining the floating free-phase hydrocarbon.

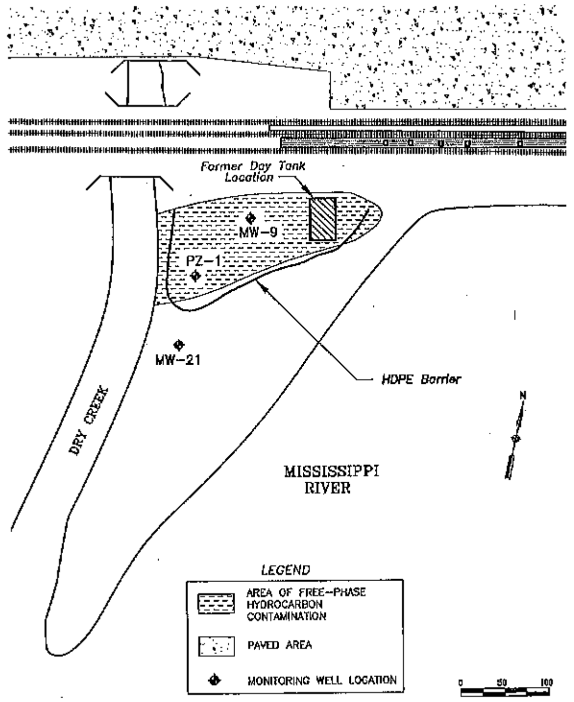

Figure 5 Position of Vertical Barrier, ATSF Railyard, Ft. Madison, Iowa

Table 1 Comparison of Liquid Level Measurements from the Barrier Area ATSF Railyard, Ft. Madison, Iowa.

	MW-21		PZ-1	
Date	Water Elevation (ft)	Measured Product Thickness (ft)	Water Elevation (ft)	Measured Product Thickness (ft)
12/15/94	517.44	-	516.58	-
4/19/95	519.09	-	518.33	0.47
6/19/95	518.01	-	517.62	1.22
6/26/95	517.39	-	517.32	0.99
7/2/95	517.18	-	517.26	0.92
7/9/95	517.21	-	517.40	0.87
7/18/95	517.12	-	517.14	0.81
7/23/95	517.01	-	516.99	0.69
7/25/95	516.95	-	516.99	0.63

Results of this project demonstrate that use of the surface-driven HDPE panel barrier is a cost-effective approach in preventing subsurface hydrocarbon migration. Under proper conditions, installation is rapid and no disturbance or excavation of subsurface materials is necessary. The thin, sheet-like nature of the material permits installation in narrow areas where installation of trenches and wider barriers is not possible. Once in place, the barrier prevents free-phase hydrocarbon discharge to nearby steams and other surface water bodies.

QUESTIONS AND ANSWERS

Q. Are the seams and sheets 100% impermeable?

I don't know how one might verify that through its whole length. Probably the best way that I know of to verify the effectiveness is to do whatever level of monitoring that you need to do on either side of the barrier. Short of excavating and examining the barrier, there really isn't any way that I know of that you can really confirm that it is 100% continuous.

Q. What is the design life and the compatibility of the product?

We did investigate. We were concerned about the effect that fuel oil might have on this material. We gathered quite a bit of information on the relationship and the effect of fuel oil on high density polyethylene. The results were that, in fact, there is some reported softening of the material that occurs, but there was no evidence that it affected the permeability or caused the product to degrade in any way. The lifetime is really sort of an unknown factor. Several of these installations are in place and insofar as we were able to determine, they don't really know what the lifetime is. They've been in place, some of them, for ten to fifteen years now and they haven't seen any problems. I don't know that anybody has determined what the true life span of this material is.

Chapter 5

CASE STUDY: Emergency Response, Site Characterization, Spill Containment and Remediation at a Derailment Site in Southern Illinois

John H. Smith
Illinois Central Railroad, Chicago, IL

Jeffrey E. Rebenschied
ENSR Consulting and Engineering, Westmount, IL

Robert P. Cohorst
PM Environmental, Inc., Lansing, MI

INTRODUCTION

At 2:15 a.m. Central Standard Time on August 12, 1994, two rail-tank cars containing approximately 29,700 gallons of perchlorethylene (PCE), a dense, non-aqueous phase liquid (DNAPL), derailed on the Illinois Central Railroad (ICRR) line 1.5 miles north of Thompsonville, Illinois, in southeastern Franklin County (Figure 1). The derailment occurred in a rural farming community near North Kegley, at a former Steam Locomotive Station Shop. Approximately 22,000 gallons of PCE were released into the environment. The spill occurred near Milepost 68, and adjacent to an existing intermittent stream channel that feeds into a designated wetland and Thompsonville Lake, which is owned by the Illinois Central Railroad (ICRR).

A substantial amount of the free product flowed into the intermittent stream channel, meandering in a northeasterly direction away from the point of impact at the railroad tracks. The railroad tracks run in an approximate north-south direction. The railroad took immediate action to impede and remove the free product and impacted groundwater within the intermittent steam channel. The railroad hired an emergency response contractor to build an earthen dam located approximately 1,700 feet downstream of the derailment to impede the impacted surface water, and excavated fourteen product removal sumps within the stream bed to remove free product, impacted surface water, and groundwater.

ICRR notified the United States Environmental Protection Agency (USEPA), the Illinois Environmental Protection Agency (IEPA), and other state and local agencies of the release. The IEPA allowed ICRR to remediate the site under the Illinois Pre-Notice Sites Cleanup Program by constructing a groundwater remediation system to treat the free product and impacted groundwater and discharge the treated groundwater on site. Also installed was a containment and cover system to impede the horizontal migration of the contaminant within the soil and groundwater. The IEPA assisted ICRR in expediting issuance of the proper air permit, wastewater provisional variance request, and NPDES permit in order to perform the necessary remediation efforts at the site. IEPA also approved a Site Sampling Plan that would allow ICRR to perform analysis of PCE-impacted soil and groundwater using an on-site gas chromatograph (GC).

The free product and impacted groundwater collected during the emergency removal efforts was temporarily stored in 22,000-gallon storage tanks prior to being disposed of off-site. Impacted water with a PCE concentration less than 5.0 mg/l was transferred (by tanker truck) to a nearby wastewater treatment plant for treatment. Free product and impacted water with PCE concentrations greater than 5.0 mg/l were transferred (by tanker truck) to a recycling facility for proper disposal. As of September 1995 approximately 1.1 million gallons of impacted water and 9,000 gallons of free product have been removed from the site.

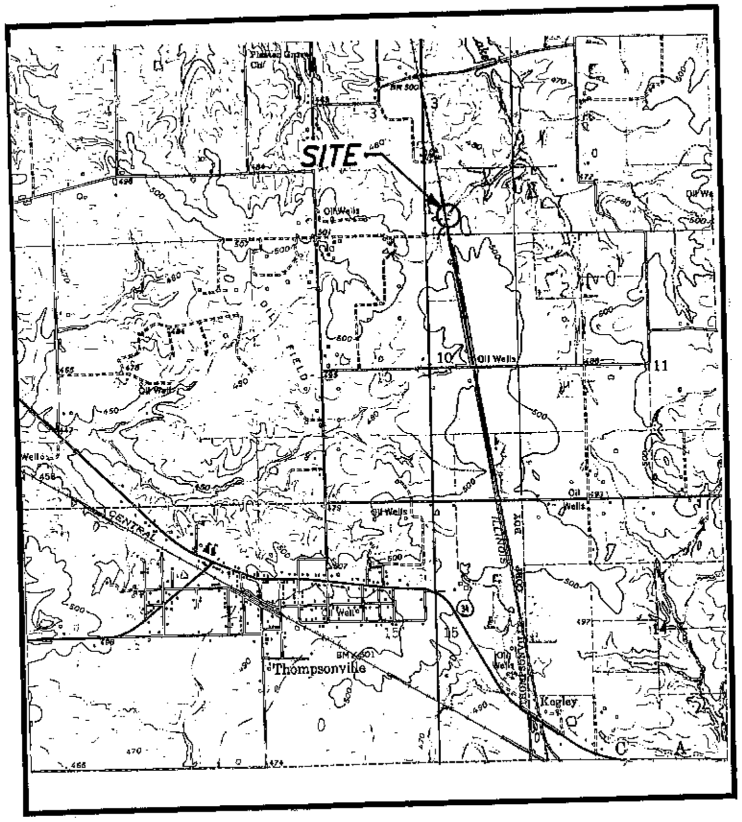

Figure 1 Derailment Site in Franklin County, Illinois

In order to determine the extent of the PCE plume, ICRR performed a soil gas headspace survey within a matter of weeks after the spill occurred. A total of 72 subsurface borings were conducted along the intermittent stream bed. The PCE plume extended approximately 1,500 feet downstream of the derailment site and stretched over 100 feet across. In addition to the headspace survey, a ground-penetrating radar study (GPR) was performed in order to determine the depth to bedrock for remediation purposes (Figure 2).

GEOLOGICAL AND HYDROGEOLOGICAL INVESTIGATION

Geological Investigation

In order to further determine the lithology at the site, ICRR conducted a subsurface geological investigation. Soil borings and bedrock corings were conducted at 20 locations spaced at intervals of approximately 200 feet around the perimeter of the site. The soil borings and bedrock corings were completed to provide information on the bedrock and to determine the optimum locations for installation of groundwater monitoring wells and piezometers around the site. The boring locations are shown in Figure 3, and Figures 4 and 5 present the geologic cross-sections.

Site Geology

The glacial deposits at the site were from 0 to 15 feet thick, and were comprised of brown sandy clay till with some gravel. The till was eroded along the intermittent

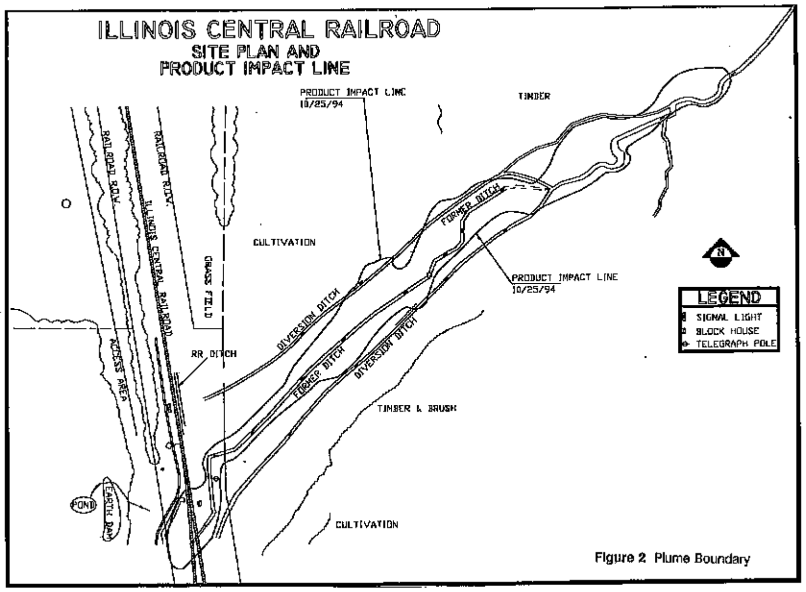

Figure 2 Plume Boundary

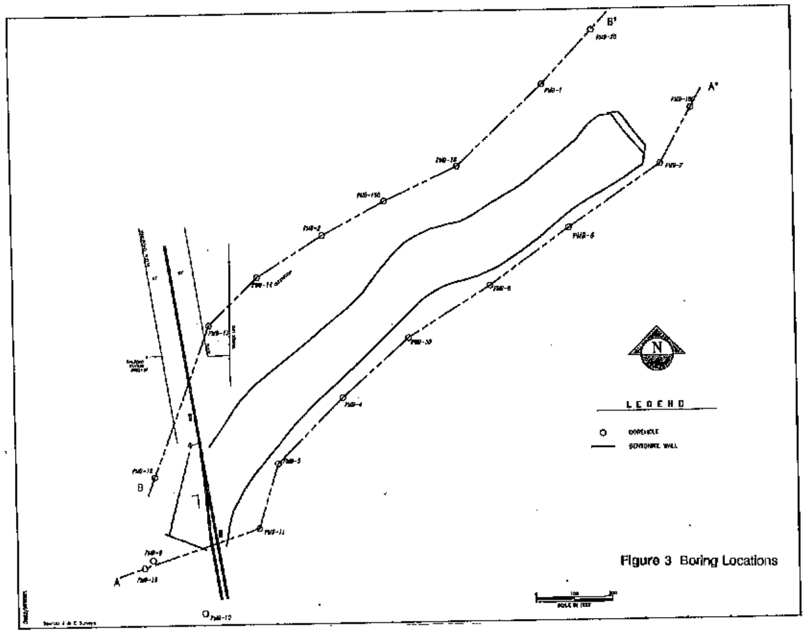

Figure 3 Boring Locations

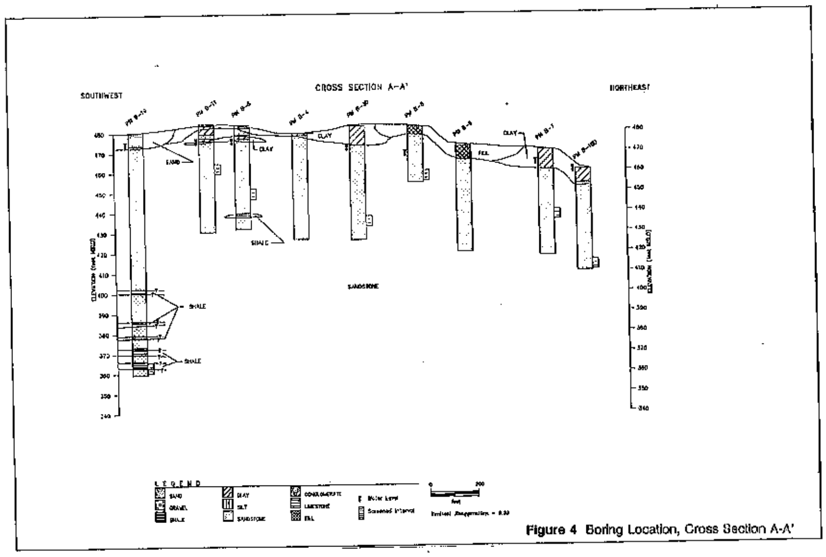

Figure 4 Boring Location, Cross Section A-A'

stream bed and became thicker away from the stream bed. Alluvial deposits comprised of brown fine-grained sand were present at the southwest end of the site. The saturated hydraulic conductivity of the glacial deposits at the site ranged from 1.2×10^{-7} cm/sec to 5.6×10^{-8} cm/sec, and the calculated porosity decreased from 42% to 38% with respect to depth.

The shallow bedrock beneath the till consisted of fine-grained horizontally-layered sandstone. The upper few feet of the sandstone was tan-to-orange-brown with iron staining. The sandstone was weathered in the upper (1-4 feet) zone and became harder and less weathered after five feet. It also showed a color change to gray and an increase in grain size to a medium-grained sandstone with depth. Interbedded layers of sandstone and dark gray shale were also encountered at depths ranging from 78 to 117 feet.

The saturated hydraulic conductivity of the sandstone ranged from 3.1×10^{-4} cm/sec within the upper heavily-weathered sandstone to 4.8×10^{-8} cm/sec within the lower less weathered sandstone, and the calculated porosity decreased from 45% to 26% with respect to depth. Impacted soil and groundwater impacted with PCE and free product was observed mostly within the soil and bedrock interface as well as within the upper four feet of the bedrock.

The sandstone bedrock at the site appears to be the McWain Sandstone Member of the lower Bond Formation, Pennsylvanian in age. The McWain Sandstone is thickest where it fills in ancient stream channels that were cut into the underlying bedrock formations. This sandstone becomes as much as 80 feet thick in southwestern Illinois. The McWain Sandstone is either underlain by the Shoal Creek Limestone Member of the Bond Formation or the upper Modesto Members. The Modesto

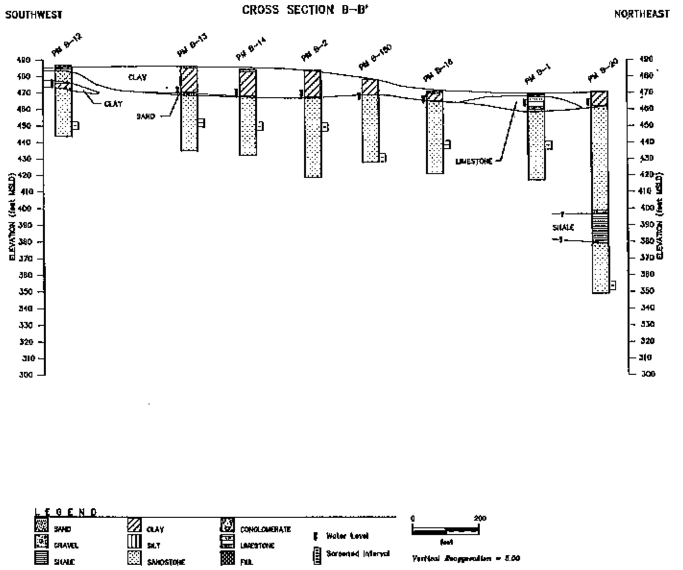

Figure 5 Boring Location, Cross Section B-B'

Formation is similar to the Bond Formation and contains several principal coal seams that are mined in the area.

Hydrogeological Investigation

Fifteen monitoring wells and seven piezometers were installed in the boreholes conducted during the geological investigation to assess the groundwater at the site. Additionally, twenty-eight piezometers were installed inside and outside of the hydrated bentonite containment wall, and seven recovery wells were installed within the heavily impacted area at the east side of the railroad tracks. The locations of the monitoring wells, piezometers, and recovery wells are shown in Figure 6.

The monitoring wells were installed to provide groundwater quality samples for long-term groundwater monitoring. In addition, water level measurements obtained from the monitoring wells and piezometers are being used to evaluate groundwater flow direction within the impacted area. Prior to installing the monitoring wells and piezometers, packer tests were performed in each borehole to determine the depth of the screens and overall length of the screened interval.

Eleven shallow and four deep monitoring wells were installed using a 2-inch inside-diameter (I.D.), flush-threaded, Type 304 stainless steel well screen and riser pipe. Well screens were five feet long with 0.020-inch slots. Screens for the shallow wells were set at intervals ranging from 15 to 37 feet below ground surface (BGS). The well screens for all deep monitoring wells were placed at a depth interval of 45 to 50 feet BGS.

The seven recovery wells were installed using 6-inch diameter, flush-threaded, Type 304 stainless steel well screen and carbon steel riser pipe. Well screens were 10 feet long with 0.050-inch slots. The tops of the well screens were set from a depth of approximately 15 to 20 feet BGS. Installation techniques were the same as those for the monitoring wells.

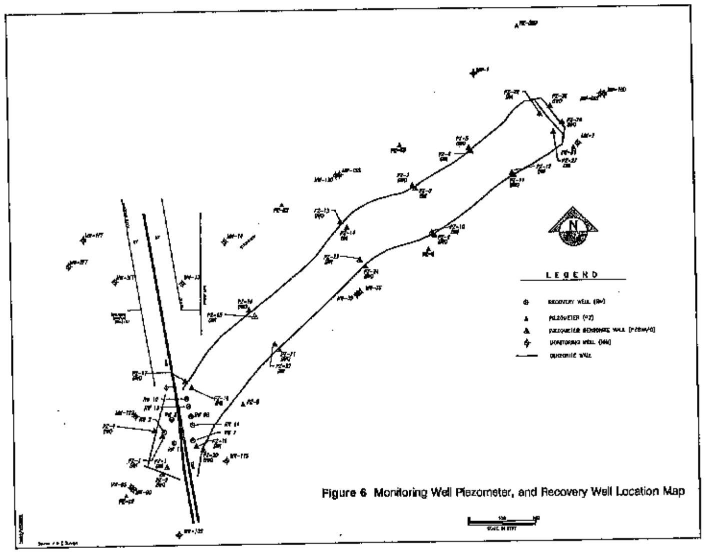

Figure 6 Monitoring Well Piezometer and Recovery Well Location Map

The seven piezometers located around the impacted area were installed using 1-inch I.D., flush-threaded schedule 40 PVC well screen and riser pipe. The screens of the piezometers located around the impacted area were placed at intervals of approximately 30 to 35 feet BGS for piezometers PZ-2, PZ-5, PZ-8, and PZ-16, and at intervals of 115 to 120 feet BGS for piezometers PZ-19, PZ-20, and PZ-21.

The twenty-eight piezometers placed around the hydrated bentonite wall were installed using 2-inch I.D., flush-threaded well screen and riser pipe. The piezometers located on the outside wall were constructed out of schedule 40 PVC, and the piezometers located on the inside of the wall were constructed out of Type 304 stainless steel. All piezometer screens were five feet long with 0.010-inch slots, and set approximately one to two feet above the bottom of the bentonite containment wall.

Groundwater Sampling and Analytical Results

Groundwater samples were collected from the 15 groundwater monitoring wells located around the perimeter of the site. Each monitoring well is equipped with a dedicated 3-foot stainless steel bailer for bailing and sampling purposes. Prior to sampling, approximately one volume of groundwater was purged from each well in order to remove the standing water and to ensure that representative formation water was sampled. The groundwater monitoring wells have been sampled seven times since January 20, 1995. Based on the most current analytical results performed in September of 1995, none of the 15 monitoring wells around the perimeter of the site have shown the existence of PCE within the groundwater.

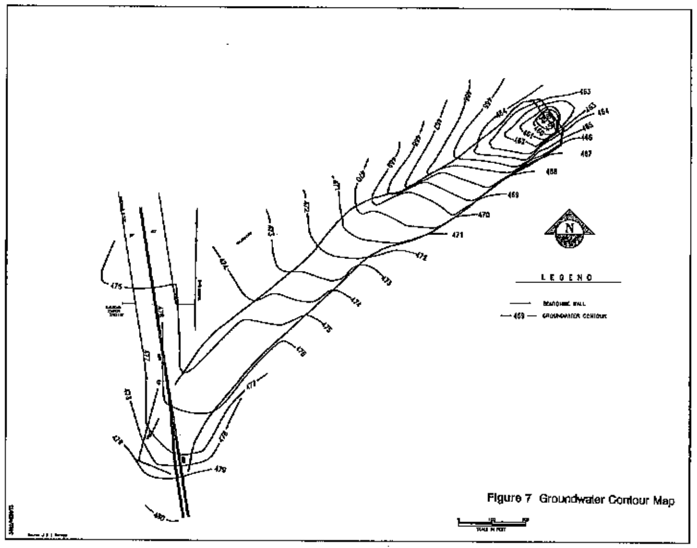

Figure 7 Groundwater Contour Map

Site Groundwater

Groundwater is found within both the shallow and deep layers of the sandstone bedrock and within the unconsolidated deposits in the northeast end of the intermittent stream bed. The depth to the water table at the site decreases in a northeasterly direction away from the railroad tracks, and decreases approaching the stream bed from either the north or south.

A groundwater contour map was drawn from the water table level data obtained on April 18, 1995 (Figure 7). From the contour map, it was determined that the shallow groundwater at the site flows inward toward the intermittent stream bed and in a northeasterly direction along the former stream channel. The data obtained from the shallow and deep cluster monitoring wells (MW-3S and MW-3D, MW-9S and MW-9D, MW-15S and MW-15D, and MW-18S and MW-18D) revealed an upward hydraulic gradient. This upward gradient, which was consistent in all water level measurements, clearly indicated that there is an upward groundwater flow from the lower sandstone bedrock along the intermittent stream. The depression shown in Figure 7 is caused by on going groundwater pumping activities conducted at the site.

Regional Groundwater

The hydrogeology of southern Illinois consists of aquifers found in the sandstone bedrock, and in sand and gravel layers found in the unconsolidated glacial and alluvial deposits which overlay the sandstone bedrock. In Franklin County, little or no groundwater is found within the unconsolidated deposits, except in areas impacted by streams and rivers. This is due to an absence of thick sand and gravel layers. Shallow aquifers found within the sandstone bedrock tend to have poor water yields, due to fine silts and clays which limit the hydraulic conductivity of the sandstone. Wells which obtain water from depths of 100 to 200 feet BGS tend to have better groundwater yields.

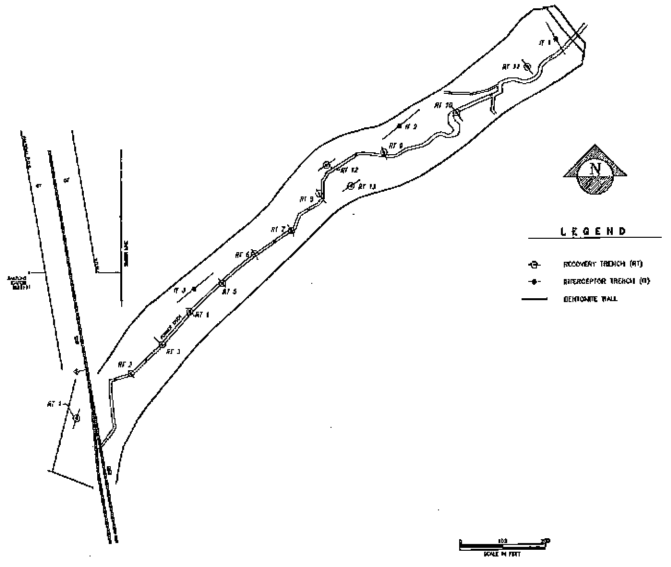

Figure 8 Recovery and Interception Trench Location Map

INSTALLATION OF RECOVERY TRENCHES AND INTERCEPTION TRENCHES

Due to the geological and hydrogeological investigations conducted at the site, shallow product recovery trenches and groundwater interception trenches were installed within the impacted area to enhance recovery of free product and impacted groundwater, and to control groundwater gradient across the hydrated bentonite wall. A total of eleven recovery trenches and three interception trenches were installed within the impacted area. The recovery trenches and interception trenches were installed perpendicular to the intermittent stream channel using a mechanical trencher machine.

Engineering Design and Installation of Recovery Trenches and Interception Trenches

The first recovery trench (RT-1) was installed approximately 50 feet west of the railroad tracks and the second recovery trench (RT-2) was installed approximately 100 feet east of the railroad tracks. The first and second recovery trenches were installed within 100 feet of where the derailment and spills occurred. The following six recovery trenches (RT-3 through RT-8) were installed in sequence, moving eastward along the stream channel and spaced a distance of 100 feet apart from RT-2. The remaining three recovery trenches (RT-9, RT-10, and RT-11) were installed at 200-foot intervals east of RT-8. Two of the eleven recovery trenches (RT-12 and RT-13) were installed

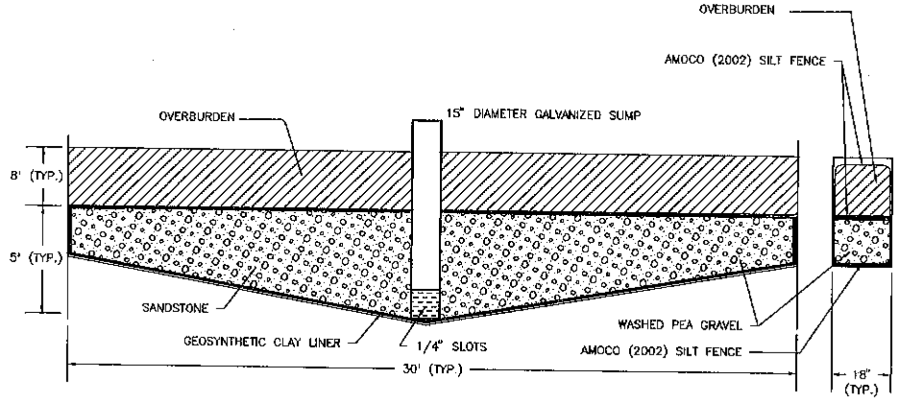

Figure 9 Recovery Trench Cross Section

parallel to the former ditch line, due to visual evidence of outward migration of free product during construction of the hydrated bentonite containment wall (Figure 8).

Three interception trenches were installed at various locations within the impacted area. The first interception trench was installed near the headwall at the far eastern side. The purpose of this interception trench (IT-1) was to collect the groundwater that was mounding up against the headwall, thus eliminating possible off-site migration. The second and third interception trenches (IT-2 and IT-3) were installed along the south side of the north bentonite containment wall to assist in reversing the natural northeasterly groundwater flow.

Prior to the installation of the trenches, the overburden soil was excavated in order to uncover the bedrock surface. The recovery trenches were then installed into the bedrock by cutting a 30-foot-long by 18-inch-wide and 3-foot-deep trench, and the interception trenches were installed in the bedrock by cutting a 100-foot-long by 18-inch-wide and 5-foot-deep trench (Figure 9).

Once the recovery trenches were installed, a geosynthetic clay liner was placed on the bottom of the trench to impede downward migration of the DNAPL. A silt fence was then placed inside the trench to minimize any infiltration of sediment and silt from the sidewalls. Once the silt fence was properly placed, a sump consisting of a 12-foot-long by 15-inch-diameter, corrugated metal pipe (CMP) was installed in the middle of the trench. A series of slots 1/4-inch wide and six inches long were cut horizontally on the lower foot of the CMP to allow impacted water and free product to infiltrate. In addition, a 17-inch square metal plate was welded on the bottom of the CMP to eliminate silt build-up.

Interception trenches IT-2 and IT-3 were installed in a manner similar to the recovery trenches, with the exception of interception trench (IT-1), located at the headwall. Interception trench IT-1 was installed with two horizontal 6-inch-diameter, 0.05-inch screened infiltration pipes extending from both sides of a 24-inch-diameter CMP. The 24-inch CMP is also equipped with a 2-foot sump cavity at the bottom to collect groundwater.

Once the sump was installed, the trench was backfilled with washed pea gravel to the bedrock surface. A silt fence was placed over the trench, to ensure that surrounding silt and fine soil would not infiltrate and foul the trench. The overburden soil was then replaced over the trench and brought to grade.

HYDRAULIC CONTAINMENT AND TEMPORARY COVER SYSTEM

The hydraulic containment and temporary cover system were designed to impede horizontal and vertical migration of free product, impacted groundwater, and surfacewater through the soil and bedrock. The hydraulic containment system consists of a bentonite containment wall that extends 8-9 feet into the sandstone bedrock, surrounding the entire 2.5-acre impacted area.

Prior to the installation of the hydraulic containment and temporary cover system, the impacted area was cleared of trees and vegetation to facilitate construction. A permanent stormwater diversion system was also constructed to route off-site stormwater around the impacted area, and to prevent stormwater from entering the intermittent stream channel.

The hydraulic containment wall was constructed by removing the overburden soils and loose rock and sawing a trench in the exposed bedrock. The trench was then filled with bentonite and water to construct the barrier wall. To impede groundwater from flowing into the impacted area through the soils, the hydraulic barrier was extended from the bentonite wall to the ground surface using a geosynthetic clay liner. The geosynthetic clay liner consisted of sodium bentonite incorporated in a geotextile mat. The hydraulic conductivity of both the bentonite cutoff wall and GCL are much lower than that of the adjacent soil and bedrock, thereby creating a subsurface containment wall around the impacted area.

Upon completion of the product recovery and gradient control and stormwater diversion systems, the impacted area was graded and capped with a reinforced linear low-density polyethylene cover. The entire site was then fenced in to provide site security and to prevent deer and other large animals from damaging the cover system.

Bentonite Moisture Content/Hydraulic Conductivity Study

Prior to beginning the bentonite containment wall (BCW) construction, a moisture content hydraulic conductivity pilot study was conducted in order to establish an acceptable moisture content range for placement of the hydrated bentonite. Bulk bentonite material taken from a sack of the material to be used in construction of the test sections was used to prepare the test samples.

The samples were prepared by moisture conditioning the bentonite and compacting the sample in a mold for testing. The hydraulic conductivity of the samples was tested in accordance with ASTM D-5084, Method C, Rising Tailwater Level. The lowest water content providing a moldable sample was 63%; the upper limit was 261.4%. Additional samples were prepared and tested at water contents of 119.8%, 161.5%, and 183.7%. The hydraulic conductivity of the samples tested ranged from 7.4 x 10^{-9} cm/sec.

The maximum design hydraulic conductivity for the bentonite wall was established at 1 x 10^{-8} cm/sec, exceeding most specified requirements for landfill liners and slurry wall construction. The moisture content/hydraulic conductivity study indicated that the hydraulic conductivity of the material used to construct the BCW exceeded the design standard. Furthermore, the study indicated that the bentonite could be placed at a wide range of moisture contents and still achieve acceptable in-situ hydraulic conductivity results.

The first section of the BCW was constructed primarily as a test section in order to provide initial containment at the east end of the site and an assessment of the proposed construction procedures, Q.C. inspection procedures, and in-situ conditions. The first section was constructed at the far east end of the impacted area, using a mechanical trencher machine with a maximum cutting depth of 6 feet. This section of the BCW was described as the "Old East Wall." Three Shelby Tube samples were collected from the completed test section and analyzed using the same procedures described for the moisture content/hydraulic conductivity study. The hydraulic conductivity of the samples ranged from 3.0 x10^{-9} to 4.9 x 10^{-9} cm/sec.

As exploration of the site and construction of the wall progressed around the impacted area, ICRR decided to extend the BCW deeper into the sandstone at the east end of the impacted area using the same mechanical trencher machine that was used in constructing the north, south, and west sections of the BCW. The larger trencher had a maximum cutting depth of approximately 8-9 feet, allowing the contractor to extend the BCW deeper into the sandstone. A schematic cross-section of the BCW is included in Figure 10.

BCW Construction and Monitoring Procedures

The BCW was constructed by excavating the overburden soil and loose rock to create a benched cross-sectional area of construction. The benched area had to be approximately 20 feet wide to accommodate the mechanical trencher ; its dept varied anywhere from 2-15 feet. The trencher, used to cut a trench approximately 8-9 feet deep and 18 to 21 inches wide, was also fitted with a "crummer shoe" to scavenge the loose material out of the bottom of the trench (Figure 11).

Once a sufficient length of trench was cut and prepared, the trench was filled with crushed and dried sodium bentonite, which was provided in large sacks weighing approximately 2,500-4,000 pounds each. The bentonite placement procedure involved filling the trench with clean water from a tanker and then placing the bentonite into the water to facilitate proper hydration. The sacks were fitted with a bottom discharge to allow placement of a regulated flow of bentonite into the trench and then suspended from the bucket of a hydraulic excavator. The water and bentonite were placed in lifts until the trench was filled (Figure 12).

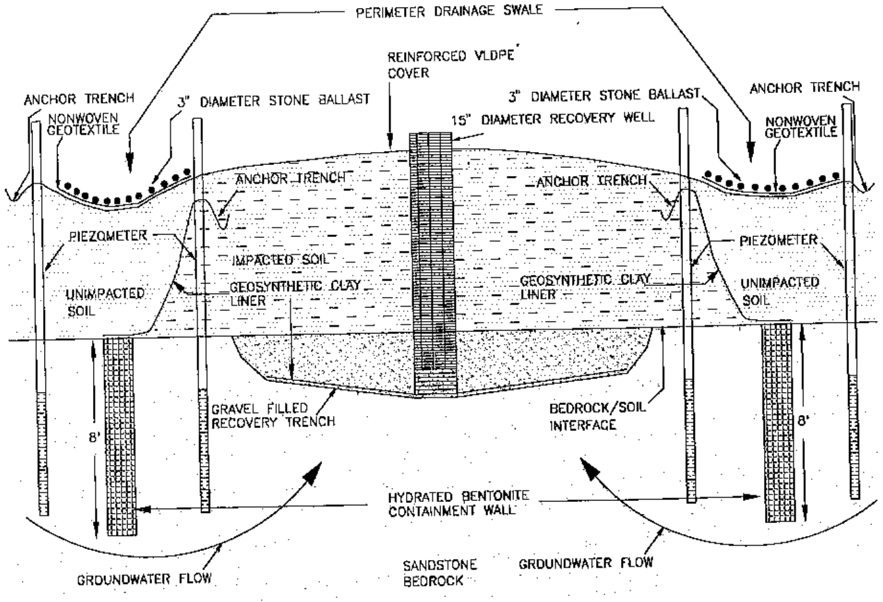

Figure 10 Bentonite Containment Wall Cross Section

Figure 11 Mechanical Trenching Machine Cutting 8-9 Foot Trench into Bedrock

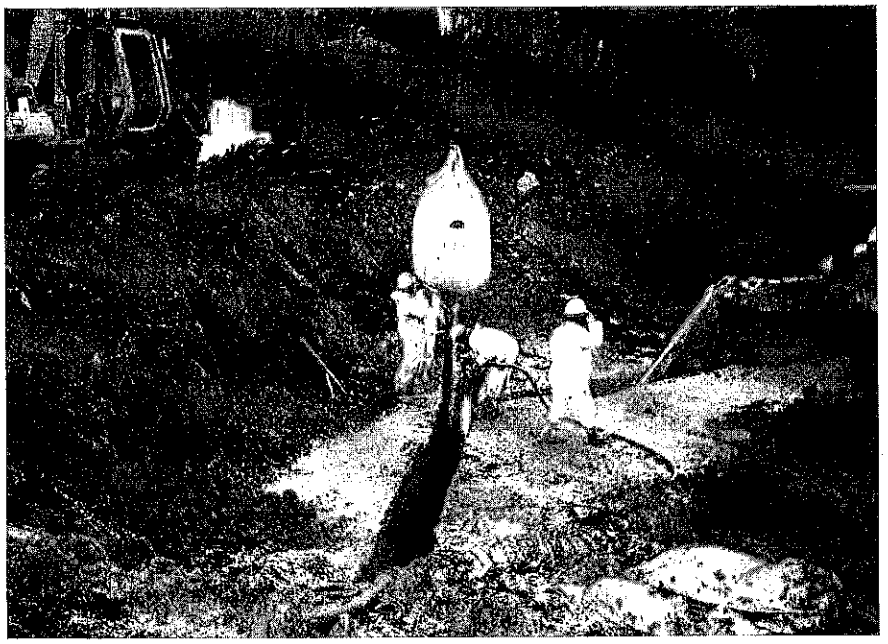

Figure 12 Installation of Bentonite Containment Wall (BCW)

The benching and trenching operations were monitored to assure conformance with the design requirements and procedures established during construction of the test section. The excavation was checked for cleanliness and the presence of loose material at the bottom of the trench; A backhoe fitted with a 12-inch bucket was used to clean the trench of excessive amounts of loose material prior to the bentonite placement. The cuttings at the sides of the trench left by the trencher were shoveled away to prevent sloughing during bentonite placement.

The rate of placement and application of dry bentonite was monitored and controlled to maintain the moisture content within the range established by the pilot study.

Laboratory Testing

Thin wall Shelby Tube samples were obtained from the completed BCW at intervals of approximately 200 feet to document the in-situ hydraulic conductivity of the BCW. The samples were obtained by hand augering a 4-inch borehole to the desired sample depth interval and pushing a Shelby Tube into the bentonite with a hydraulic excavator or backhoe. Samples were obtained at various depths to represent conditions throughout the vertical section of the BCW. The tubes were extracted, cleaned, and waxed to preserve the moisture content of the sample. Shelby Tube samples were tested in accordance with ASTM D-5084, Method C, Rising Tailwater Level. The hydraulic conductivity of the samples ranged from 5.9 x 10^{-9} cm/sec to 8.5 x 10^{-9} cm/sec.

Geosynthetic Clay Liner

A geosynthetic clay liner (GCL) was used to extend the hydraulic barrier from the top of the BCW to the elevation of the perimeter ditch inverts of the temporary cover system. A GCL was chosen as the hydraulic barrier because it could be installed with minimal preparation of the existing benched area adjacent to the BCW.

The GCL consists of a top and bottom layer of woven geotextile and a core of granular sodium bentonite, supplied in rolls approximately 13.5 feet wide and 100 feet long. Each roll is numbered to correspond with the manufacturer's quality control certification for the material. The GCL exhibits typical hydraulic conductivity values on the order of 5 x 10^{-9} cm/sec when tested in accordance with ASTM D-5084.

GCL Construction and Monitoring Procedures

The sides of the existing BCW excavation were prepared to provide a relatively uniform surface for the placement of the GCL. In areas where the depth of the overburden soils exceeded two or three feet, an anchor trench was constructed to prevent slippage or movement of the panels during backfill operations.

The GCL was installed by suspending rolls of GCL from the bucket of a hydraulic excavator using a spreader bar and unrolling them to cover the subgrade and the BCW. The GCL panels were then overlapped the full width of the BCW at the toe of each panel. The panels were overlapped a minimum of 6 inches at each seam to provide a hydraulic seal. Overlaps were oriented vertically at the slopes per manufacturer recommendation (Figure 13), and extended past the bottom of the anchor trench.

A hydraulic excavator and small wide truck-bulldozer were used to backfill the GCL with the silty clay native soils removed during excavation of the BCW. The anchor trench was backfilled prior to the placement of backfill at the slopes to prevent movement of the panels. A sufficient depth of soil was placed over the GCL prior to spreading and compaction with the wide track bulldozer; in order to prevent disturbance of the GCL. Backfill was placed in lifts and compacted with the bulldozer until final elevations were reached; the final surface was then graded to provide a drainage swale around the perimeter of the impacted area.

The condition of the subgrade and anchor trench was visually monitored and major irregularities, large stones, and sharp objects were removed and/or repaired prior to the placement of the GCL. Placement of the GCL was also monitored for conformance to manufacturer recommendations. The panel overlap was checked to ensure that a the 6-inch minimum lap was maintained at all locations; horizontal seams were not permitted on slopes. Each GCL panel cut from the roll was assigned a panel identification number, which was then indexed to the roll numbers provided by the manufacturer.

The location and elevation of the GCL was surveyed to develop a record drawing of the installation. The placement of backfill was monitored to prevent disturbance of the GCL during backfill and compaction operations.

Temporary Cover System

After completion of the BCW and GCL installation, the product recovery and hydraulic gradient control system was installed and the impacted area was filled and

Figure 13 Layout of Geosyntehtic Clay Liner (GCL)

graded to provide surface drainage. A perimeter ditch was constructed to channel surface drainage around the impacted area to the existing stream channel at the east end of the site (Figure 14). Upon completion of the grading, the surface of the impacted area was covered with a 3-ply Linear Low Density Polyethylene (LLPDE) and nylon yarn laminate, a cover material used to prevent the infiltration of surface water or contact of surface water with the impacted soil.

Materials

The temporary cover material consisted of a 3-ply laminate: two layers of black LLPDE, and a high strength non-woven nylon cord grid. The non-woven cord grid provides a uniform loading resistance of over 740 pounds per yard in all directions. The material has a useable temperature range from -40°F to 170°F, and can be fabricated in panels up to approximately one acre in size.

TCS Installation and Monitoring Procedures

The surface of the impacted area was graded to provide a relatively uniform surface, with a crown in the center to provide drainage to the perimeter ditches. An anchor trench was excavated around the perimeter of the covered area to secure the TCS into the soil and prevent slippage or movement of the cover.

Sixteen panels were needed to cover the impacted area, ranging in size from 7,650 square feet to 40,600 square feet. (A panel layout drawing is provided in Figure 15.)

Figure 14 Perimeter Ditch Around Impacted Area

The panels were overlapped a minimum of three feet at the seams, which were sealed with a double-sided seaming tape to provide a continuous weather-tight seal.

The perimeter anchor trench was backfilled after placement of the temporary cover. The interior areas of the cover system were ballasted using sand bags constructed of the cover material, rather than less expensive agricultural sand bags, because the less expensive bags degrade in sunlight and will not last as long as the cover material. Sand bags were placed in the 15-foot grid pattern recommended by the manufacturer.

Upon completion of the TCS installation, geotextile and 3-inch stone were placed at the ditch inverts around the perimeter of the impacted area. The geotextile was rolled out manually to prevent damage to the TCS. The 3-inch stone was placed on the filter fabric using a hydraulic excavator and spread manually to cover the fabric. The final installation of the TCS is shown in Figure 16.

Subgrade preparation and installation was monitored in order to remove any major irregularities, large stones, and sharp objects, and ensure proper drainage.

Proper placement and seaming of panels was critical to assure proper cleaning and adhesion. Material used to backfill the anchor trench was monitored for the presence of stones and sharp objects: objectionable materials were removed during backfill placement. Sandbag placement was checked to assure a uniform 15-foot grid spacing. Placement of the geotextile and stone was also monitored, both to prevent damage to the cover material and to assure uniform coverage of the geotextile with the stone

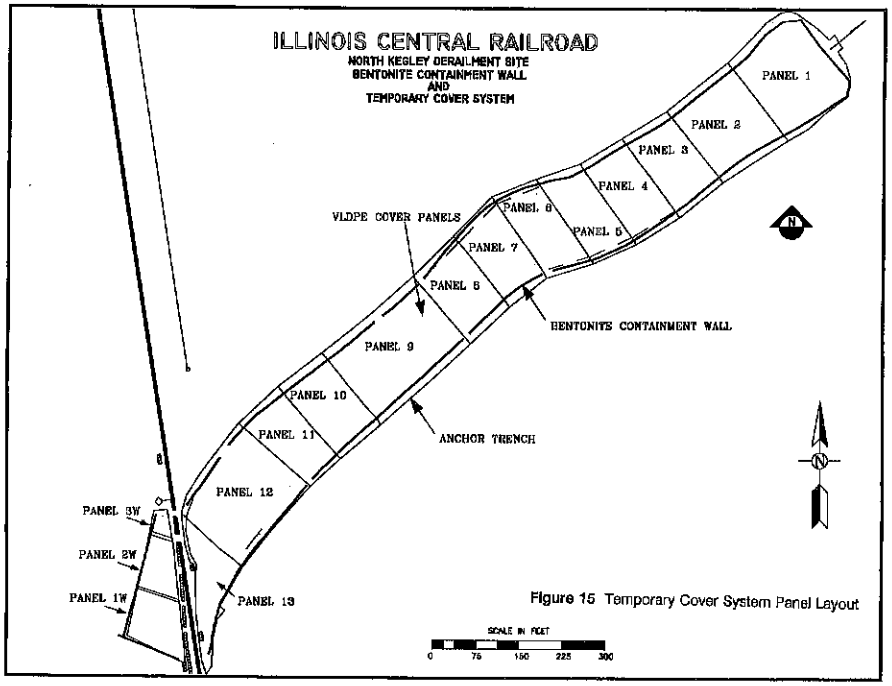

Figure 15 Temporary Cover System Panel Layout

ballast. Upon completion of the TCS installation, the cover system was surveyed to produce a record drawing of the installation.

GROUNDWATER REMEDIATION SYSTEM

In order to separate free product and treat impacted groundwater collected from the recovery trenches and interception trenches, a groundwater remediation system was installed at the site.

Groundwater Remediation System Design and Installation

Operational Overview

The groundwater remediation system consists of two vertical 10,000-gallon lined carbon steel storage tanks with coned bottoms, one horizontal 3,500-gallon carbon steel-lined free product and sludge storage tank, two prefilter units, one 250-gallon clean water holding tank, an air stripper unit, two 2,000-pound carbon units, stainless steel valves and piping, and a series of centrifugal transfer pumps (Figure 17).

The 10,000-gallon storage tanks temporarily store the groundwater collected from the recovery trenches and interception trenches. The holding tanks have an average residence time of eight hours to allow for settling of silts, sludges, and free product. Any silt, sludges, or free product is decanted from the bottom of the storage tanks and transferred to the 3,500-gallon free product and sludge storage tank. The impacted water within the two 10,000-gallon tanks is then transferred by centrifugal pump through a sand filter and pumped into the air stripper. The PCE is stripped from the water and discharged into the atmosphere. The remaining PCE within the impacted water is further removed by two 2,000-pound carbon vessels prior to being discharged on site.

Figure 16 Final Installation of Temporary Cover System

NPDES Permit and Provisional Variance Requirements

Prior to installing the groundwater remediation system, the railroad secured a National Pollution Discharge Elimination System (NPDES) permit in order to discharge the treated groundwater on site.

Because of the emergency nature of the clean-up and the project approval by the Illinois Pre-Notice Sites Cleanup Program, the IEPA Water Pollution Control Board assisted the railroad by issuing an NPDES permit in approximately 45 days. In the interim, the IEPA Water Pollution Control Board allowed the railroad to treat and discharge treated water on site under a provisional variance, until the NPDES permit was issued.

In accordance with permit requirements, the railroad treatment operator at the site passed the class K exam and is licensed to operate the groundwater remediation system.

A Spill Prevention Control Countermeasures (SPCC) Plan is currently being prepared for the groundwater remediation system. The SPCC plan will include all information required by 40 CFR Part 112.

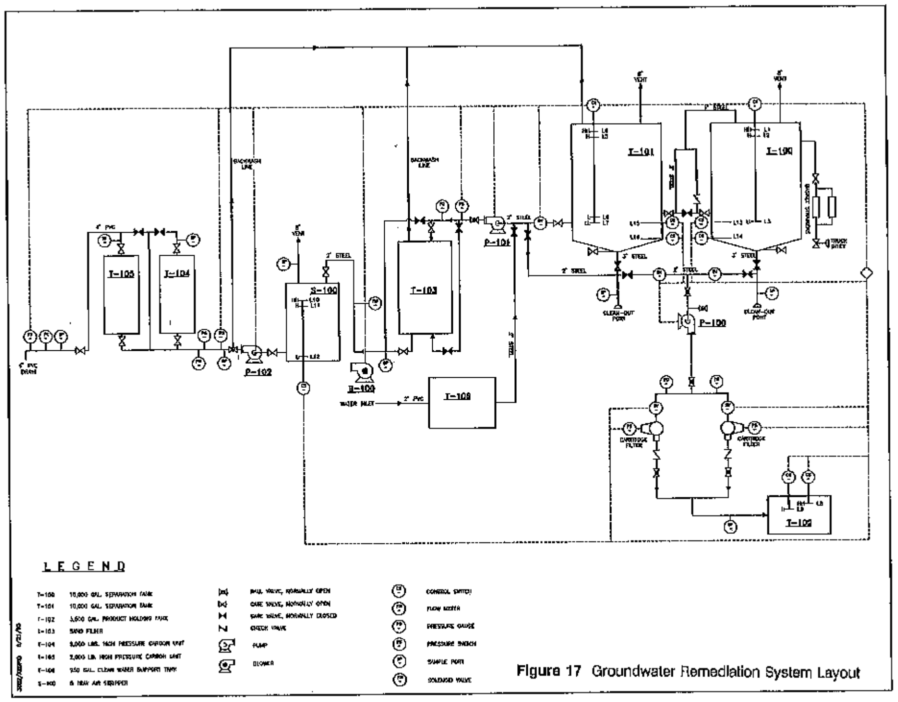

Figure 17 Groundwater Remediation System Layout

Air Permits

The air permit issued by the IEPA, Division of Air Pollution Control Board within two weeks after application allowed ICRR to discharge VOM (volatile organic materials) emissions at a rate of 2.18 lb/hr in connection with operation of the air stripper unit.

Groundwater Remediation System Treatment Efficiency

The efficiency of the groundwater remediation system is measured by the PCE influent and effluent concentrations as well as the performance of the air stripper and carbon absorption units. The air stripper unit consists of a Modular Remediation Systems RTS-25-A five-tray air stripper, capable of pumping water at a maximum rate of 25 gallons per minute (GPM) at a maximum air flow rate of 800 cubic feet per minute (CFM). Based on the average PCE influent concentration of 150 mg/L, the removal efficiency for the air stripper has been around 96.3%. The VOM discharge concentrations are within the limits set forth by the permit.

Carbon Adsorption Limits

The remaining PCE within the effluent is treated within two (primary and secondary) 2,000-pound high pressure carbon vessels. The treated effluent concentrations on the average have been around 8 ug/L with a removal efficiency of 96.5%. The effluent concentrations are within permitted limits.

In order to comply with the SPCC plan, a concrete containment wall was constructed around the groundwater remediation system. The 3-foot high concrete containment wall constructed out of 8x8x16 concrete masonry units (CMUs). The total holding capacity of the containment is approximately 11,500 gallons.

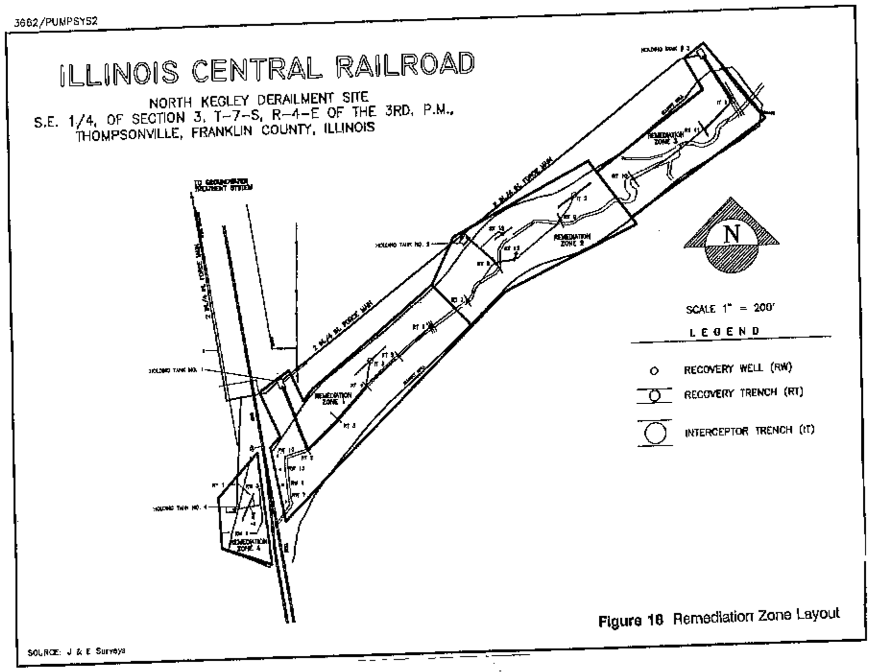

Figure 18 Remediation Zone Layout

AUTOMATIC GROUNDWATER PUMPING SYSTEM

ICRR is currently designing and installing an automatic groundwater pumping system within the impacted area, which will consist of a series of submersible pumps located within selected recovery and interception trenches. The submersible pumps will be grouped into four separate remediation zones (Figure 18).

The groundwater from each zone will be pumped into a 3,500-gallon vertical holding tank. Once the holding tank is full, the free product and impacted water will be transferred through a double-walled distribution line to the groundwater remediation system for treatment.

Groundwater Pumping System Design

Each selected recovery and interception trench will contain a non-explosion proof electrical submersible pump capable of pumping groundwater from 5 to 15 GPM, and a high/low float switch to control the pump. The sump pump will transfer the impacted water and free product through a distribution line to a 3,500-gallon holding tank located within its remediation zone.

3,500-Gallon Holding Tank

Each 3,500-gallon vertical holding tank will consist of a carbon steel tank measuring 8'6" in diameter and 10 feet high, fitted with a coned bottom to allow for settlement of free-product and sediments. The holding tank is supported on four I-beam support legs to raise the bottom 1.5 feet off of the ground surface. Each holding tank will be equipped with an internal agitator and heater, insulated with polyurethane foam to prevent freezing during the winter months.

Distribution Pumps

Each 3,500-gallon holding tank will be equipped with one distribution pump. The distribution pumps are single-phase, electrical non-explosion-proof centrifugal pumps capable of pumping at a flow rate of 15 to 25 GPM with a maximum pressure of 50 psi. The purpose of these distribution pumps is to transfer the impacted water from the 3,500-gallon tank to the groundwater remediation system through an underground doubled-walled distribution force main.

Since each groundwater pump station is over 1,500 feet away from the groundwater remediation system, ICRR has engineered the distribution pumps to feed into one central holding tank (holding tank 1), prior to being pumped to the groundwater remediation system. A description of the flow schematic for holding tanks 1, 2, 3, and 4 is as follows: Impacted water collected from holding tank 3 will be transferred to holding tank 2, which will then transfer the impacted water to holding tank 1. Impacted water collected from holding tank 4 will be transferred to holding tank 1. Holding tank 1 will then transfer the impacted water to the groundwater remediation system.

Holding Tank Pad and Containment Area

A 23-foot-long by 14-foot-wide concrete pad was constructed at each of the four holding tank locations. The 3,500-gallon holding tank will be surrounded by a four foot containment wall constructed out of reinforced CMUs. The volume of the containment capacity will comply to the SPCC plan being prepared for the site.

Pump House

A prefabricated 8-foot-wide by 8-foot-long by 9-foot-high metal building will house all pumps, electrical supply panels, piping manifold system, and distribution piping required to transfer the impacted water from the trenches to the on-site groundwater remediation system. The pump houses will be insulated and seasonally heated.

Radio Receiver and Transmitter System

In order to automatically operate and control the groundwater pumping system, a radio receiver and transmitter (transceiver) system will be installed at the groundwater remediation system and at each of the four holding tank areas.

Main Transceiver System

The main transceiver system will consist of a D620 programmable, special-purpose controller (PSPC), capable of controlling all system components located at each holding tank location. The PSPC will control and record all tank levels, transfer pump flows and totalizers, running meters, pressure indicators, and system alarms. Location of the PSPC system at the groundwater remediation system will allow the plant operator to track the performance and failures of the entire system via computer screen and printer.

Holding Tank Transceiver System

Each holding tank will also be equipped with a D620 radio transceiver system. The transceiver will be enclosed in a NEMA (National Electric Manufacturers Association) free-standing two-door enclosure for operation on a 230-Volt single-phase, three wire service with battery backup. Each holding tank transceiver system will be able to control the pumps, monitor the tank level, and sound alarms when required, as well as be able to communicate with the other holding tanks and groundwater remediation system.

CONCLUSIONS

Since the August 12, 1994 derailment, ICRR has managed to collect and properly dispose of approximately 9,000 gallons of PCE liquid collected from the site. ICRR estimates that approximately 2,100 gallons of PCE liquid evaporated into the atmosphere, leaving approximately 11,000 gallons of the 22,000-gallons of PCE that impacted the environment on the ground.

After the installation of the bentonite containment wall (BCW), ICRR has been evaluating the effectiveness of the hydrated containment and groundwater gradient by collecting static water level measurements from the piezometers located around the BCW in conjunction with the manual removal of free product and impacted water from the interception and recovery trenches. Based on the results of the static water level measurements conducted from June through September of 1995 showing groundwater flow toward the impacted area, hydraulic containment is being achieved.

ICRR anticipates that the groundwater remediation system and groundwater pump-and-treat system will be on line and fully automated by the end of November,1995.. Once the system is fully automated, operation and maintenance activities are expected to be reduced from five days to two days a week.

ICRR is currently preparing a full risk assessment to determine the overall impact of the release to the environment and plans to present these findings to the IEPA Pre-Notice Sites Cleanup Program in late December of1995. Operation of the groundwater remediation system is expected to continue , with the covered PCE-impacted soils left in place.

ACKNOWLEDGEMENTS

Illinois Central Railroad would like to thank ENSR Consulting and Engineering (ENSR) of Westmont, Illinois, PM Environmental, Inc. (PME) of Lansing, Michigan, Central States Environmental Services (CSES), Inc. of Centralia, Illinois and J & E Surveys, Inc. (JES) of Salem. Illinois for their able assistance both technically and professionally under the severest of weather conditions and rigid deadlines in making this emergency clean up a success.

QUESTIONS AND ANSWERS

Q. This looked like a fairly elaborate project. Do you have any idea of the total cost or breakdown into subcontractor costs?

Yes. To date we've spent a little over six million dollars. Just to put this site in perspective, back in 1982, we spilled about 10,000 gallons of perc into the environment in Louisiana. The cost of that cleanup ran about $28,000,000. All things considered we spilled 22,000 gallons in North Kegly. We've taken about ten months to address the issues, and we've spent a little over $6,000,000. If we were to pro-rate that money, and compare present value for what it cost to do the cleanup at Livingston, LA. I would say we did a heck of a job.

Q. Did you consider using a soil/bentonite mixture instead of pure bentonite?

Well, we considered using a soil/bentonite mixture, but there are several reasons why we chose to go with pure bentonite. The first one being we get a much lower permeability. Soil/bentonite mixtures are on the order of 1 $1x10^{-7}$. We're seeing permeabilities in the order of $5x10^{-9}$. Secondly, one of the drawbacks to soil/bentonite mixtures is the actual task of mixing the material on-site, making sure that it's properly proportioned, and making sure that it's properly installed. All those factors cause you a lot of trouble in maintaining your hydraulic conductivity values throughout the section. Also, when you do your test results, if you get pockets of soil, if you don't get adequate mixing, you can run into construction problems. We found that the cost of the pure bentonite when balanced against the cost of mixing bentonite in soil was really not that much more expensive. In fact, by some estimates it could even be equal or less costly.

Q. I believe you mentioned early in the presentation that there was a rail car of plasticizer, as well. Was that addressed in the cleanup program?

Yes, we cleaned that up. That was non-hazardous. We took that right to a landfill.

Q. Did you consider soil vapor extraction?

Due to the groundwater table being so high, soil vapor extraction wasn't an alternative. We did look at it, but it was ruled out.

Chapter 6

Enhancing the Extraction of Petroleum from Alluvial Sediments with Surfactants

Paul D. Kuhlmeier
Southern Pacific Lines, Boise, ID

Michael J. Grant
Southern Pacific Lines, San Francisco, CA

INTRODUCTION

The mobilization of residual oil by contact with a flowing surfactant-rich solution (microemulsion) is a complex process that is not well understood. Most of the complexities arise because the trapped phase and the surfactant solution are not in chemical equilibrium and there is a mass transfer from one phase to another. If the two phases are in equilibrium, then the mechanism of mobilization appears to be satisfactorily established. An oil globule is displaced when the interfacial tension is reduced to an extent that the pressure gradient created by the motion of the continuous phase is sufficient to overcome the capillary forces holding the globule in place. Several early experimental studies performed with a focus on oil production enhancement have applied the concept of critical capillary number (N_{CP}) required to displace the oil[1-3] globule. N_{CP} may be calculated from microvisual cell tests as:

$$N_{CP} = \mu u/\phi\sigma \tag{1}$$

where μ = viscosity

u = flooding velocity (m/s)

ϕ = porosity (unitless)

σ = interfacial tension (dyne/cm).

Early enhanced oil recovery (EOR) studies performed by Hill *et al.*[4] concentrated on displacing crude oil with a flooding medium and decreasing the "surface tension" between the phases. The technique might work for a soil highly contaminated with a hydrophobic hazardous waste similar to that found at Dunsmuir. As an example of tertiary EOR, Hill *et al.*[4] described the development of an aqueous surfactant system for recovering Far Springs crude oil in Benton, Illinois. Petroleum sulfonate was selected as the surfactant because of the wide range of commercial types available and their low cost. The addition of sodium chloride to the 3.1% active surfactant further lowered the interfacial tension between the crude oil and the aqueous solution. A sequestering agent, sodium tripolyphosphate, was included to further improve compatibility with Benton reservoir water. Once the surfactant-oil emulsion slug was injected, a higher viscosity water wash containing a soluble polymer (such as Dow Pusher 520) was introduced to achieve a stable plug flow displacement. A final water drive completed the recovery. The technique was considered successful at the time, recovering approximately 65% of resident hydrocarbons. However, the remaining oil mass was in excess of 5000 mg/kg.

A unique approach for in situ removal of oily wastes from soils is to employ micellar solution flooding, another tertiary oil recovery technique. Micellar solution flooding is a process in which a solution containing a surfactant-stabilized dispersion of water and hydrocarbons is injected into the oil reservoir. The microemulsion is miscible with both the crude oil and water. After injecting the micellar solution, a high viscosity mobility buffer was injected to protect the emulsion from degradation by the drive water. The composition of typical micellar material, (e.g., Richburg Micellar Solution) is as follows:

Water	68.03%
Diesel oil	17.97
Witco Sulfonate TRS 16	5.46
Witco Sulfonate TRS 406	5.51
Amyl alcohol	2.37
Butyl alcohol	0.66

Chou *et al.*[5] studied the effect of soluble salts and caustic soda on the solubility and adsorption of hexachlorocyclopentadiene on soils. While increasing the concentrations of brine, sodium chloride, and sodium hydroxide caused an increase in adsorption, sodium hypochlorite caused a slight decrease. The salts causing the greatest depression in solubility also caused the greatest increase in adsorption. No explanation was given for the reduced adsorption caused by the sodium hypochlorite, but more intensive study may be warranted.

Law Engineering Testing Company[6] completed an inventory of treatment techniques applicable to gasoline-contaminated ground water for the American Petroleum Institute, and proposed a number of treatment options for further study. Texas Research Institute[7] completed several laboratory column and two-dimensional modeling studies on the use of surfactants to enhance gasoline recovery from sand. The results showed that a combination of commercial nonionic (Hyonic® PE-90) and anionic (Richonate®-YLA) surfactants was effective in displacing gasoline from the column sand packs. Up to 40% of the residual gasoline after initial flooding was removed from the sand using this surfactant combination.

Subsequently, Texas Research Institute[8] completed a study on surfactant-enhanced gasoline recovery in a large-scale model aquifer. Three surfactant application procedures were tested: a single application which percolated down through the sand bed, multiple applications by percolation, and daily application into the water table. The percentages of gasoline removed associated with each procedure were 6, 76, and 83, respectively.

SURFACTANT SELECTION

Alteration of drawdown pumping or placement of a drainage sink can cause some flow and recovery of resident NAPL in ground water. As previously discussed, simple pumping cannot reduce NAPL partitioned in the capillary fringe much below residual saturation. The forces which retain the NAPL and govern the volume in which it is retained have been shown to be directly related to the interfacial tensions between water and oil and water and air. From these considerations, an initial series of tests was performed in the laboratory to determine the plausibility of surfactant use in ground water at the SPTCo Dunsmuir Yard in Dunsmuir, California.

The basis for evaluating the effectiveness of surfactants in recovering three representative petroleum compounds, pyrene, n-decane, and n-eicosane were:

- The surfactant, in aqueous solution, must markedly reduce the interfacial tension between that solution and oil in reasonably low concentrations.
- Surfactant solutions must be tolerant to polyvalent concentrations that may be encountered.
- The surfactants must be sufficiently soluble or dispersable in water to he entrained in ground water flow to the recovery well, and delivered to the actual zone of oil contamination in concentrations high enough to be effective in mobilizing bound containment.
- Surfactant should not adsorb onto the substrate to the point of ineffectiveness.
- The toxicity of the surfactant must be low enough that residual quantities will not form a health or environmental hazard, should they enter the Sacramento River.

A variety of structural types of nonionic, anionic, amphoteric, and cationic surfactants are available and have been applied to oil recovery. Interfacial tension measurements on gasoline and diesel fuel are available from the respective manufacturers. Values for several commercially available surfactants are provided in Table 1. Two surfactants, the anionic Richonate-YLA and the nonionic Hyonic PE-90, were used in concentrations of 0.1%, 1.0%, 2.0%, and 5.0%.

MATERIALS AND METHODS

Flushing columns were manufactured out of 12-inch sections of cast acrylic tubing with a four-inch inner diameter in accordance with ASTM standard D 4874-89. End plates were constructed of 8" x 8" pieces of 3/4-inch-thick polyvinyl chloride. A circular groove was machined in each end plate to accommodate a gasket and four-inch column. A 3/8-inch stainless steel compression fitting was placed in the center of the outside surface of each face plate. A 1/4-inch-thick, porous polyethylene flow distribution disk (70 microns nominal pore size) was placed inside the column at each end. The end plates were attached to the cylinder by eight 1/4-inch threaded rods. Pressure reservoirs contained the liquid feed and provided a pressure gradient for flow through the packed columns. These pressure reservoirs were identical to the columns described above, with the exception of the distribution disks.

Prior to the start of each flushing test, the moisture levels of the contaminated soils were adjusted to target values by drying the soils in a dispatch oven or adding uncontaminated ground water. The target moisture levels for the sand was 12%.

Before packing with contaminated soil, the column assemblies were cleaned with an Alconox solution, rinsed with a 20% nitric acid solution, and triple rinsed with deionized water. A vibrator was attached to the cylinders while the sand was being added, to ensure maximum packing. When necessary, measured quantities of water were added or removed from the cylinders to keep the water level above the sand. When the cylinders were filled with saturated sand, the vibration was discontinued.

The discharge of the sand pack was situated over a graduated cylinder and the level of the reservoir was adjusted so a desired difference in hydraulic head could be attained. Permeability of the sand pack was determined by measuring the rate of water flow through the test cylinders under constant head conditions. There was no appreciable difference in flow-through between the test cylinders.

One pore volume of a given chemical was introduced into each of the reservoirs. This quantity was sufficient to displace all but residual water, so that only the hydrocarbon was flowing from the sand pack. The hydrocarbon addition was immediately followed by more water to the reservoirs, to ensure that air was not introduced to the sand pack.

The void volumes (VV) of the packed columns were calculated using the relationship provided in the ASTM 4874-89 method descriptionas follows:

$$VV = Vc-[M/((1+w) \times S \times D)] \qquad (2)$$

where:
VV = void volume in the column in cubic centimeters (cm^3)
Vc = the volume of the of the empty column in cm^3
M = as-packed weight of the waste in grams
w = moisture content of the waste as g water per gram (g H_2O/g) solids
S = specific gravity of the waste
D = density of the water in g/cm^3

The effluent was monitored for composition, volume, and flow rate. In most cases, displacement with water was discontinued when hydrocarbon was no longer present in the effluent in a distinctly hydrocarbon phase. In general, 3 to 8.5 pore volumes of water was sufficient to displace the hydrocarbon as a separate phase. Several runs were performed to develop a reproducible sequence of observations.

Table 1 Interfacial Tensions of Selected Surfactanats

Surfactant, 0.1% (unless otherwise noted)	Interfacial Tension with Gasoline at 25°C, dynes cm^{-1}
Deionized Water	11.5
Nonionics	
Hyonic PE-90, Diamond Shamrock	0.12
Hyonic PE-100, Diamond Shamrock	0.72
Hyonic PE-120, Diamond Shamrock	1.2
Poly-Tergent B-500, Olin	1.3
Alrosol O, Ciba-Geigy	1.9
Anionics	
Duponol G, DuPont	1.0
Aerosol OT, Cyanamide	1.2
Alfonic 1412-S, Conoco	2.4
Richonate YLA, Richardson	0.61
C-550 Slurry, Conoco	1.2
Aerosol MA, Cyanamide	7.1
Sarkosyl NL, Ciba-Geigy	1.8
Fluorosurfactants	
Zonyl FSN, 0.05%, DuPont	3.9
Zonyl FSA, 0.05%, DuPont	11.0
Lodyne S-102, p.1%, Ciba-Geigy	2.3
Lodyne S-102, 0.05%, Ciba-Geigy	3.2
Lodyne S112, 0.05%, Ciba-Geigy	6.9

Flushings with surfactant were conducted in much the same manner as those with water. Observations were made of the breakthrough volume, as well as composition of the effluent and changes in flow rate when effects of surfactant were noticed. The volume of surfactant solution introduced to the sand pack was approximately two pore volumes. Surfactant flushing was followed by additional water to more accurately simulate a real environment.

The dissolved hydrocarbon in the effluent was measured by gas chromatography using a flame ionization detector. Multiple standards for each chemical were prepared over a wide range of dilutions in water.

DISCUSSION OF RESULTS

Plots of volume eluted versus time were constructed for n-decane; the average of two runs is shown in Figure 1. The Richonate-YLA did displace NAPL, but it quickly bound up the sand (evidenced by a dramatically decreasing flow rate through the cylinders). The plugging phenomena has been observed in both field and laboratory studies, and it is commonly attributed to the formation of a viscous emulsion. Similar plugging problems were not encountered with the anionic surfactant, Hyonic-90. A threshold on surfactant concentration was noticed at approximately 2% in both n-decane and n-eicosane columns. Higher concentrations did not demonstrate any additional performance capabilities. Results of n-decane treatment with a 2% solution of Hyonic-90 is given in Figure 2. The first peak depicts the hydrocarbon, n-decane, eluted by natural drainage and by water displacement after the residual hydrocarbon in the pack was 0.25 pore volumes. The second peak reflects the addition of surfactant which caused 25% of the residual decane to be released. It was observed that both n-decane and n-eicosane can be present at a level of 5% in the surfactant solution and not appear as a distinct separate phase. This, too, is not uncommon and is believed to be due to the formation of a microemulsion consists of micelles of petroleum too small to scatter light in a visible spectrum. Reintroduction of surfactant was performed after every five pore volumes up to 30 pore volumes. Distinctly declining utility was evidenced as decane concentrations approached 500 mg/l. Relative permeabilities were generated by division of two phase flow rates by the flow rate of water in clean sand.

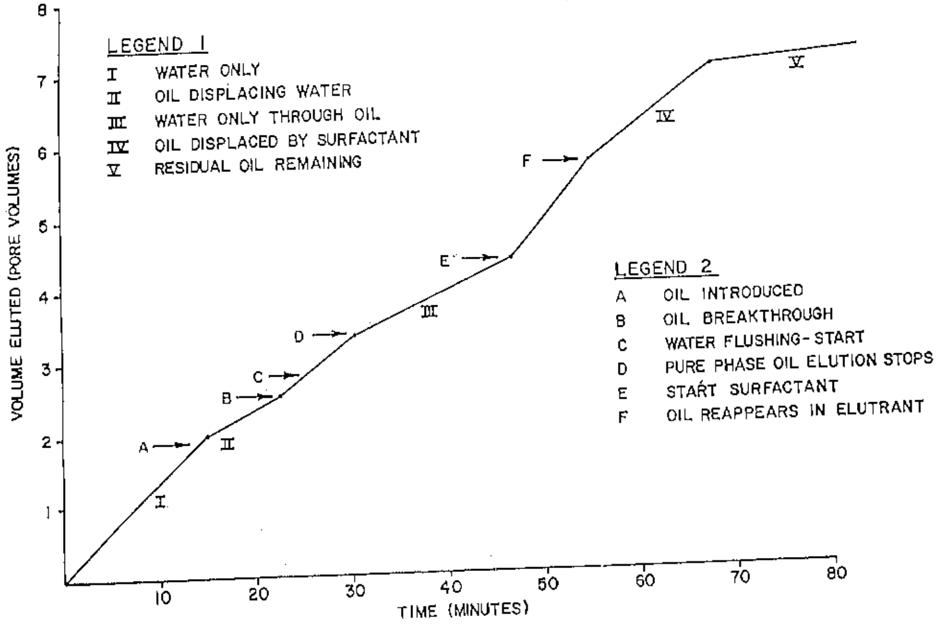

Figure 1 Displacement of n-Decane from Sand: Richonate YLA

The effects on mass removal of the various surfactant additions to n-decane and n-eicosane applied sands are summarized in Tables 2 and 3, respectively. The reduction of flow rate after water flooding can be interpreted as being caused by individual droplets of hydrocarbon trapped in voids, making some flow paths inaccessible to water. The general upward shift in permeability seen when anionic surfactant is introduced is interpreted as evidence for redistribution of hydrocarbon droplets from larger restrictions to smaller ones under the influence of reduced interfacial tensions.

Formation blockage by viscous emulsion is an effect taken into consideration in tertiary oil recovery work. This seems to be the case with the Richonate-YLA observed to reduce flow rates. It is known to be a good emulsion stabilizer, and lab tests show the emulsion it forms with pyrene and n-decane to be stable and viscous. Although not attempted, combining the two surfactants may serve to elicit synergistic effects, which could produce improved results over Hyonic PE-90 alone.

Two other observations are supportive of the mechanism of hydrocarbon being retained and subsequently displaced as a non-wetting medium as the principle process occurring in the displacement studies. The first of these is the abrupt transitions that take place when hydrocarbon is being eluted and when it is not. The other is the shift seen in flow rate when surfactant flows through hydrocarbon-contaminated sand. There is either sufficient hydraulic potential to displace hydrocarbon, or the conditions remain static, giving further support to the notion of a critical capillary number. Any shift in interfacial tension is capable of causing a redisposition of hydrocarbon in the interparticle voids.

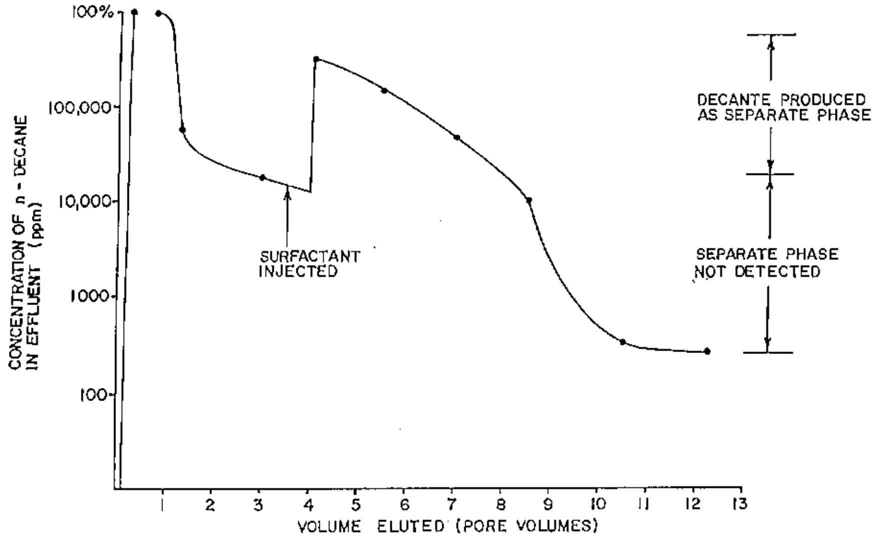

Figure 2 Displacement of n-Decane from Sand: 2% Hyonic PE-90

Table 2 Surfactant Displacement Studies: n-decane

Surfactant	Soil	Pressure Gradient (atm/cmx10^{-3})	Permeability (to H_2O cm/s)	Residual Hydrocarbon n-decane	Relative Permeability After Hydrocarbon Sat. H_2O	Relative Permeability After Hydrocarbon Sat. Surfactant	Percent n-decane Recovered
PE-90 0.1%	20-50 sand	1.5	0.084	0.29	0.38	0.49	34
PE-90 1.0%	20-50 sand	1.3	0.080	0.27	0.48	0.55	37
PE-90 2.0%	20-50 sand	1.2	0.075	0.27	0.42	0.58	45
PE-90 5.0%	20-50 sand	1.2	0.071	0.28	0.45	0.54	43
YLA 0.1%	20-50 sand	1.0	0.078	0.26	0.43	0.13	28
YLA 1.0%	20-50 sand	1.2	0.074	0.29	0.33	0.09	21

Table 3 Surfactant Displacement Studies: n-eicosane

Surfactant	Soil	Pressure Gradient (atm/cmx10^{-3})	Permeability (to H_2O cm/s)	Residual Hydrocarbon n-decane	Relative Permeability After Hydrocarbon Sat. H_2O	Relative Permeability After Hydrocarbon Sat. Surfactant	Percent n-decane Recovered
PE-90 0.1%	20-50 sand	1.4	0.080	0.31	0.36	0.44	16
PE-90 1.0%	20-50 sand	1.4	0.077	0.33	0.44	0.50	24
PE-90 2.0%	20-50 sand	1.3	0.081	0.30	0.37	0.55	30
PE-90 5.0%	20-50 sand	1.3	0.073	0.29	0.39	0.51	29
YLA 0.1%	20-50 sand	1.1	0.082	0.31	0.37	0.21	19
YLA 1.0%	20-50 sand	1.2	0.076	0.30	0.35	0.14	7

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Chapter 7

Remediation of a Former Diesel Refueling Area

James T. Tallon
ENSR, Pittsburg, PA

Frank J. Myerski
ENSR, Pittsburg, PA

Sabina Strautman
Consolidated Rail Corporation, Philadelphia, PA

BACKGROUND

Description of Facility

The Consolidated Rail Corporation (Conrail) Meadville Yard is located in the southern portion of Meadville, Pennsylvania. The northern portion of the yard, known as the Diesel Shop, is the location of the subject groundwater product recovery system. Figure 1 identifies the layout of the diesel yard, including roads and other related site features. The Diesel Shop area was used as a staging point for Conrail's regional maintenance operations. In the past, the facility was used for equipment maintenance and refueling operations. The area was used for locomotive fueling operations as far back as the 1940s until fueling operations ceased in 1970.

As shown in Figure 1, French Creek forms the western boundary of the Diesel Shop area, while Linden Street forms the eastern boundary. A manufacturing facility exists across Linden Street to the north, and the remainder of the portion of the rail yard parallels French Creek to the south. The Diesel Shop area contains a diesel shop, approximately a half dozen active rail lines, a coal tower, and an earthen dike from a former tank farm. Also present are two oil-water separators.

Abatement History

Past locomotive refueling and fuel storage operations resulted in the periodic release of diesel oil into soil and groundwater. The Pennsylvania Department of Environmental Protection (PADEP) initiated an investigation of oil released into French Creek, adjacent to the Meadville Yard, in the early 1970s while the yard was being operated by the Erie-Lackawanna Railroad. The Erie-Lackawanna Railroad took corrective action during this period, installating an oil/water separator to treat storm water runoff discharged into French Creek. Conrail began its investigation and remedial activities in 1979 following the reappearance of an oil sheen in French Creek. At the conclusion of hydrogeological investigations, Conrail installed an oil recovery system in late 1982 and began operating the system in early 1983. The system operated until 1989 when it was shut down. During this period, approximately 9,000 gallons of product were recovered.

The re-emergence of an oil sheen along French Creek in 1991 prompted Conrail to re-evaluate the yard. Additional investigations were performed in December of 1991 and into 1992 to further characterize the area. Based on the results developed from the investigations, the groundwater recovery system was modified in late 1992 and early 1993, and in April of 1993, it was back in operation.

Present remedial activities involve the operation of the groundwater product recovery system. Figure 1 identifies the locations of the recovery wells associated with the system, along with related treatment tankage and piping. Recovery and monitoring wells installed in the early 1980s as part of the original recovery system were used during remediation. A series of both product and groundwater pumps have been installed in recovery wells (i.e., RW-1 to RW-5) along the bank of French Creek to provide a hydraulic barrier and collect free floating oil. The product recovery pumps are piped directly into a 500 gallon temporary storage tank. Recovered groundwater is then piped to a series of oil/water separators, and the treated effluent is discharged into French Creek. Conrail has been operating the groundwater product recovery system at its Meadville Yard under the terms and conditions of a temporary authorization letter issued by the PADEP. An NPDES permit application has been submitted for the system and is currently being reviewed.

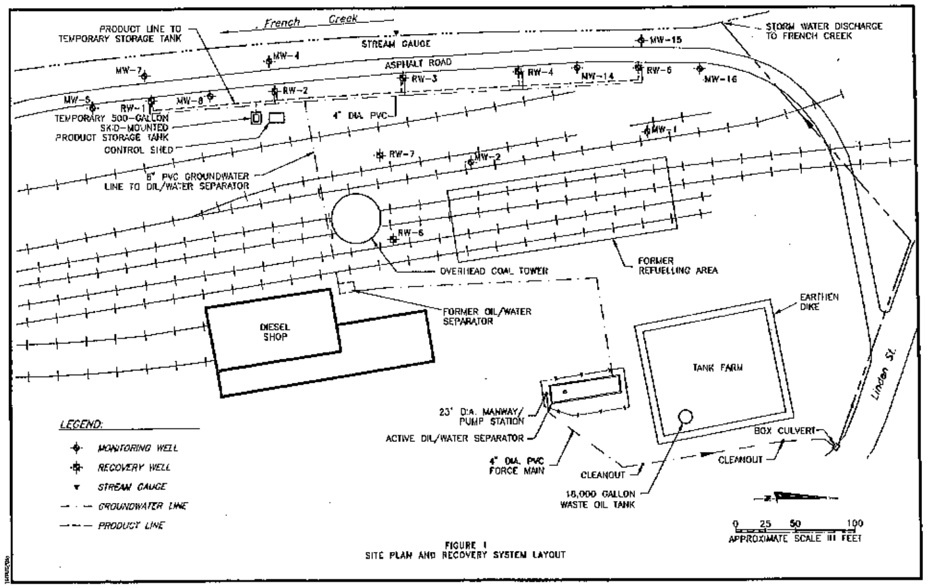

Figure 1. Site Plan and Recovery System Layout

Unique Site Features

Several site-specific issues had to be considered while remediating the free product layer. The property being remediated includes a section of an active railyard. French Creek also borders the property to the east. As noted in Figure 1, the recovery wells are within 40 feet of French Creek, and are separated by a narrow asphalt road. Seasonal fluctuation in the level of the creek have resulted in corresponding variations of up to 10 feet in the levels of the recovery wells. making it difficult to maintain a cone of depression needed to remove floating diesel.

Another important factor influencing site remediation is the presence of several rare species of fish, only found in French Creek. For this reason, stringent discharge limits were established by the PADEP to ensure protection of these fish. This also made it important to quickly contain visible seeps which initially produced a noticeable sheen. Moreover, the PADEP Regional office is within a mile of the site, making it easily accessible for visits.

As noted previously, the same monitoring wells utilized for the site restoration activities conducted during the 1980s are being used for ongoing work. No additional wells have been installed at the site. The existing recovery wells, projected to be capable of recovering and containing the floating product layer, have been successful.

The monitoring wells installed previously have not been as beneficial. They have generally not aided in identifying the potential location(s) of source area(s) that continue to contribute to the floating product seeping in the direction of the creek. A total of 20 former monitoring wells have been staggered across the suspected source area upgradient of the recovery wells. Three monitoring wells are also in place downgradient of the recovery wells. Several of these monitoring wells go dry during low levels in the creek, which contributes to the difficult assessing recovery of floating product.

Another complicating factor associated with product recovery activities is that previous soil removal actions were not well documented, for example, the facility records indicate that soil in the refuelling area was removed during a past response action; however, the location, depth and volume of soil removed is not well documented. Because suspected source areas like this were not well-defined, the refuelling area cannot be ruled out as a potential source area.

In addition to managing groundwater, the separator system also manages the storm water collected from in and around the diesel shop building (Figure 2). During storm events, the increased volume can create a sudden surge on the separator, requiring routine monitoring and removal of floating oil and settled solids.

The roof drains from the diesel shop also discharge to the separator. In the past, diesel repairs introduced organic materials to the separator that contained problem constituents such as benzene. These organics can linger in the piping as well as in the separators. The presence of these kinds of constituents lowers the overall quality of the groundwater discharged, making system monitoring critical. The influence of organic constituents from past facility operations is discussed later in this chapter.

Discharge Requirements

The discharge limits for the recovered groundwater are listed at the top of Table 1. It should be noted that these are temporary limits; a formal NPDES permit application for the recovery system has been submitted to the PADEP. Past discussions with the PADEP indicate that the facility limits were based on similar limits used for groundwater recovery at gasoline stations and petroleum underground storage tank sites. It appears that these limits were the only available guidance for recovering petroleum products at the time the permit was issued.

The limits proposed by the PADEP are not generally considered to be applicable for the remediation work being conducted at the Meadville railyard. Specifically, the use of benzene and total BTEX limits for the discharge are not considered to be appropriate for the following reasons:

- Weathered diesel fuel would not be likely to contain benzene, toluene, ethylbenzene and xylenes (BTEX), although gasoline would contain BTEX.
- Regulatory authorities assumed that a new treatment system would be installed as part of any remedial action. However, this was not the case at Meadville, since an existing system was used. Groundwater remediation technology such as air stripping (which formed the basis for these low limits) was not proposed for use at the site, since BTEX was not expected to be an issue.

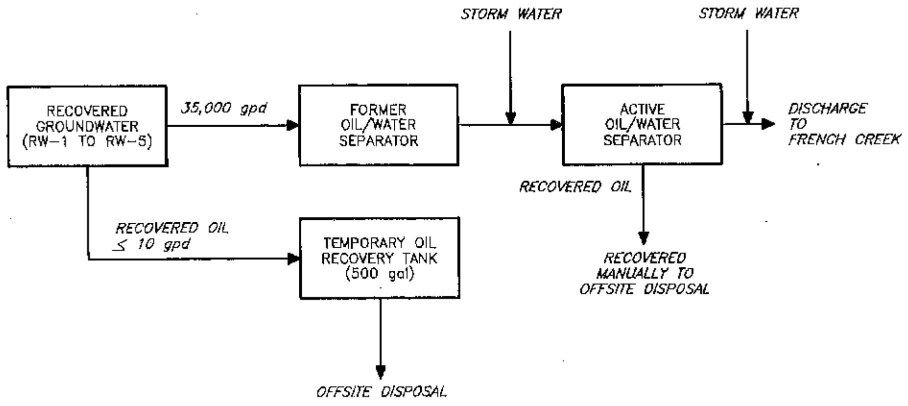

Figure 2 Groundwater Product Recovery System Configuration

Table 1. Monthly Summary of Groundwater Discharge Analytical Results Conrail's Meadville Yard Groundwater Product Recovery System

	Total Average Concentrations (mg/l) (a)			Instantaneous Maximum Concentrations (mg/l) (a)		
	Benzene	Total BTEX (b)	Oil and Grease	Benzene	Total BTEX	Oil and Grease
Permit Limits	0.001	0.100	15.0	0.0025	0.250	30.0
1993						
MAY	<0.001	<0.001	<5.0	<0.001	<0.001	<5.0
JUNE	<0.001	<0.001	<5.0	<0.001	<0.001	<5.0
JULY	<0.001	<0.001	<5.0	<0.001	<0.001	<5.0
AUGUST	0.0018	0.0018 (c)	<5.0	0.0026	0.0026 (c)	<5.0
SEPTEMBER	0.0018	0.0018 (c)	<5.0	0.002	0.002 (c)	<5.0
OCTOBER	0.0019	0.0019 (c)	<5.0	0.0023	0.0023 (c)	<5.0
NOVEMBER	0.0015	0.0015 (c)	<5.0	0.002	0.002 (c)	<5.0
DECEMBER	0.0015	0.0015 (c)	<5.0	0.0019	0.0019 (c)	<5.0
1994						
JANUARY	0.0014	0.0014 (c)	<5.0	0.0016	0.0016 (c)	<5.0
FEBRUARY	0.0013	0.0013 (c)	<5.0	0.0014	0.0014 (c)	<5.0
MARCH	0.0014	0.0014 (c)	<5.0	0.0015	0.0015 (c)	<5.0
APRIL	0.0012	0.0012 (c)	<5.0	0.0013	0.0013 (c)	<5.0
MAY	0.0017	0.0017 (c)	<5.0	0.0018	0.0018 (c)	<5.0
JUNE	0.0014	0.0014 (c)	<5.0	0.0016	0.0016 (c)	<5.0
JULY	0.0013	0.0013 (c)	<5.0	0.0016	0.0016 (c)	<5.0
AUGUST	0.0012	0.0012 (c)	<5.0	0.0012	0.0012 (c)	<5.0

Table 1. Continued

	Total Average Concentrations (mg/l) (a)			Instantaneous Maximum Concentrations (mg/l) (a)		
	Benzene	Total BTEX (b)	Oil and Grease	Benzene	Total BTEX	Oil and Grease
1994 (Cont.)						
SEPTEMBER	0.0011	0.0011 (c)	<5.0	0.0011	0.0011 (c)	<5.0
OCTOBER	<0.001	<0.001	<5.0	<0.001	<0.001	<5.0
NOVEMBER	<0.001	<0.001	<5.0	<0.001	<0.001	<5.0
DECEMBER	<0.001	<0.001	<5.0	<0.001	<0.001	<5.0
1995						
JANUARY	<0.001	<0.001	<5.0	<0.001	<0.001	<5.0
FEBRUARY	<0.001	<0.001	<5.0	<0.001	<0.001	<5.0
MARCH	<0.001	<0.001	<5.0	<0.001	<0.001	<5.0
APRIL	<0.001	0.0012 (d)	<5.0	<0.001	<0.0011	<5.0
MAY	<0.001	<0.001	<5.0	<0.001	<0.001	<5.0
JUNE	<0.001	<0.001	<5.0	<0.001	<0.001	<5.0

(a) Results based on average of two grab samples.
(b) Total BTEX includes total concentration of benzene, toluene, ethylbenzene, and total xylene.
(c) The toluene, ethylbenzene, and total xylene results were below detection limits (i.e., <0.001 mg/l) for both grab samples.
(d) The total xylene result was 0.0012 mg/l for one of the grab samples in April 1995.

- The fact that the separator periodically handles storm water was also not addressed by regulators.

The discharge limits are presently being reviewed by the PADEP prior to final approval of the discharge plan.

GROUNDWATER PRODUCT RECOVERY SYSTEM CONFIGURATION

The overall groundwater product recovery system consists of a series of recovery wells connected to an oil/water separator system which eventually discharges into French Creek (Figure 2). The groundwater pumps are connected to a piping network that empties into a small oil/water separator. It should also be noted that the separator system receives an unquantified amount of storm water and diesel shop roof drainage. The groundwater then flows by gravity through an underground pipe into a larger oil/water separator adjacent to the former tank farm. The effluent from the larger separator is then discharged into a culvert (under the terms of a temporary NPDES discharge permit), which then drains to French Creek.

Recovery Wells

The recovery system consists of five wells identified as RW-1 through RW-5. The recovery wells are 25 inches in diameter and approximately 25 feet deep, screened over a 10 foot interval (from approximately 15 to 25 feet) below the groundwater level. The wells are 100 feet apart, located parallel to French Creek. The groundwater recovery wells are equipped with submersible pumps and operated to provide hydraulic control of the product plume by establishing overlapping cones of depression within the groundwater. The groundwater recovery pumps have 1/2 horsepower motors, and are capable of withdrawing up to 12 gallons per minute (gpm).

Each well also contains a product recovery pump to remove floating oil contained within the cone of depression. The product pumps are designed to withdraw product at a rate of up to 1 gpm. The product pumps are piped directly to a temporary storage tank for eventual recycling.

Initially, wells RW-1, RW-2, and RW-3 were used to recover the diesel oil. During the fourth quarter of 1994, the system was expanded to include RW-4 and RW-5 in removing an oil sheen identified in a northern hydrologically upgradient area bordering French Creek. Since these wells have been brought on-line, the sheen has been significantly reduced.

Oil/Water Separator

The groundwater being pumped from the recovery wells initially discharges into a small separator (approximately 10 feet square by 8 feet deep), and then into a large separator (approximately 12,000 cubic feet) adjacent to the tank farm. The smaller separator only removes settable solids; the larger separator by contrast, removes both settable solids and floating oil. The water is discharged to a manhole, and then pumped with a high volume sump pump (i.e., 100 gpm) into a culvert draining into French Creek.

The bulk of the floating oil is currently being collected directly into recovery wells by the product recovery pumps. Consequently, no significant quantity of oil is being pumped directly to the separators; so no automated skimming is used. Settable solids, however, are being collected in the separators. Any oil sheen present in the separators is removed manually with oil booms and adsorbent pads.

Control System

The operation of the recovery system is regulated by two control panels located in an instrumentation shed adjacent to the recovery wells. Each groundwater and product pump is controlled by a manual/automatic pump switch. Most of the time, it is in the automatic mode. A flow meter is provided to measure the individual flow of the groundwater pumps. The control panel containing indicators to monitor the operational status of the pumps, also have tank-full shut-off circuitry connected to each product pump to prevent the temporary storage tank from overflowing, and built-in circuit breakers to prevent damages from electrical surges.

Recovered Product Storage

Oil recovered from the groundwater product recovery system is stored in a 500-gallon steel storage tank with an integral containment system, located near the system control shed. This tank is used to temporarily store oil that is directly recovered from the RW-1, RW-2, RW-3, RW-4 and RW-5 recovery wells. The 500 gallon tank is emptied of recovered oil and sent to a recycler. The material being recovered is approximately 65% oil and 35% groundwater. Typically, this tank is emptied every two to three months, depending upon the quantity of product recovered.

SYSTEM PERFORMANCE

Recovered Groundwater Volume

Since the groundwater system began operation in April of 1993, approximately 24 million gallons of groundwater have been recovered and sent through the oil/water separator system. The average quarterly withdrawal rate for the past 26 months of operation is listed in Table 2. As illustrated, the average flow rate has been 36 gpm for the overall system since the five recovery wells were put into operation.

Recovered Product Volume

The volume of product recovered on a quarterly basis is identified in Table 3. As noted, the volume of product recovered increased approximately threefold since the number of recovery wells was increased from three to five. The total volume of product recovered during the past 19 months of operation is approximately 1340 gallons. The system has been shut down approximately 10 days per year for repairs and preventative maintenance.

Effluent Concentrations/Discharge Limits

As required by Conrail's temporary discharge permit, grab samples of the treated effluent have been taken twice a month since the system was put into operation in April, 1993. A monthly summary of the effluent data gathered through June, 1995 is summarized in Table 1. (For comparison purposes, the NPDES effluent discharge limits are also presented in this table). As illustrated, the effluent parameters have been consistently below the discharge limits for total BTEX and oil and grease. However, the total average benzene concentration permit limit has been exceeded 14 times, while the instantaneous concentration permit limit for benzene was exceeded only once.

Table 2 Quarterly and Cumulative Summary of Groundwater Recovery Conrail's Meadville Yard Groundwater Product Recovery System

Time Period	Average Groundwater Recovery Rate (gpm)	Gallons of Groundwater Recovered in Time Period	Total Gallons of Groundwater Recovered To Date
1993			
April 30 (a) - September 30	(b)	704,950	704,950
October 1 - December 31	24	2,563,940	3,268,890
1994			
January 1 - March 31	23	2,969,140	6,238,030
April 1 - June 30	22	2,810,750	9,048,780
July 1 - September 30 (c)	39	3,209,550	12,258,330
October 1 - December 31	39.5	4,494,550	16,752,880
1995			
January 1 - March 31	34.7	3,525,210	20,278,090
April 1 - June 30	32.7	3,553,800	23,831,890

(a) System was placed on-line April 30, 1993.
(b) System startup period.
(c) Recovery wells RW-4 and RW-5 were brought on-line on August 19, 1994.

Table 3 Quarterly and Cumulative Summary of Product Recovery Conrail's Meadville Yard Groundwater Product Recovery System

Time Period	Gallons of Product Recovered in Time Period	Total Gallons of Product Recovered To Date
1993		
December 9 - December 31 (a)	25	25
1994		
January 1 - March 31	355	380
April 1 - June 30	35	415
July 1 - September 30 (b)	70	485
October 1 - December 31	275	760
1995		
January 1 - March 31	310	1,070
April 1 - June 30	265	1,335

(a) Product pumps were installed in the three recovery wells on December 9 and December 20, 1993 and January 6, 1994.
(b) Note the product pumps in RW-4 and RW-5 were brought on-line August 19, 1994.

The higher levels have been attributed to the presence of other streams managed through the separators and materials accumulated in the separators during previous operation. As noted previously, the oil/water separator also manages storm water from a portion of the railyard and diesel shop area, along with the groundwater from the recovery system. As a result, during initial operation the separator basins were filled with sediment and emulsified product, suspected to contribute to the elevated benzene level noted in the discharge. To help improve the quality of the effluent and correct the problem, both separator basins were cleaned and baffles were installed in the large separator to reduce the surface area requiring skimming. Oil adsorbent booms were also installed in the baffled area to contain hydrocarbons. Since separators were cleaned in October of 1994, the benzene level has been consistently below the discharge limits.

REMEDIATION ACTIVITIES

Ongoing activities associated with the program include operation and maintenance of the system, groundwater discharge sampling, off-site product recycling, reporting and record keeping, and project management. The following section identifies the requirements for each of these activities in further detail.

Operation and Maintenance

Several operation and maintenance (O&M) requirements are associated with keeping the system up and running and in compliance with regulatory requirements. Annual Operation and Maintenance activities include the following:

- conducting NPDES effluent sampling (twice per month);
- measuring product and water levels in recovery wells twice a week and monitoring wells twice a month;
- removing recovered oil from the storage tank for off-site recycling (every other month);
- maintaining/replacing oil booms and oil pads in separators and at the groundwater discharge point to French Creek as needed;
- monthly servicing of equipment, to include: operational testing of the withdrawal pumps; cleaning of pump screens, pump floats, filters, and pipes as needed; calibrating water level sensor and flow measurement devices; and providing necessary materials and supplies for routine maintenance and repair.

Reporting and Recordkeeping

Documentation and reporting requirements associated with the subject system are summarized below. They include internal and external correspondence, as well as data collection and tracking. Specific reporting items include:

- maintaining a field log book to document day-to-day remediation activities (including all field work and subcontractor activities);
- recording field log sheet information twice per week (i.e., flow totalizer readings, free product volumes, pump readings, rainfall amounts, river gauge readings, etc.);

- preparation and submittal of monthly discharge monitoring reports to PADEP;
- development of internal monthly progress reports;
- preparation and submittal of quarterly status reports to PADEP.

Project Management Support

The principal project management support requirements associated with the operation and maintenance of the groundwater product recovery system include the following:

- ensuring that health, safety, and quality assurance requirements are adhered to during all on-site activities;
- preparing and participating in internal quarterly review meetings;
- preparing and participating in meetings with the PADEP;
- providing overall technical management support including: coordination of on-site technicians; procurement, management and cost tracking of subcontractors, assistance in addressing concerns of regulatory authorities and PADEP, and responding to system malfunctions/upsets.

RECOVERY SYSTEM - PROBLEMS & SOLUTIONS

During the 26 months the system has been online, there have been a variety of recovery system equipment problems. The following section identifies these problems and their solutions.

Recovery Well Equipment

Pumps

The Meadville system consists of a dual pump configuration in each well - a groundwater pump and a product pump. The groundwater pump is positioned below the oil/water interface and is operated to form a cone of depression to capture the floating product. The groundwater pump achieves a maximum flow from the well without pumping it dry. The product pumps are positioned at the oil/water interface to allow for the removal of the floating product. The major challenges associated with operating this type of pumping system include groundwater fluctuations and filter fouling.

Groundwater Fluctuations

Besides the seasonal fluctuation in the water table, the site is subject to a change in groundwater elevation of a few feet or more during a single storm event. As a result, the level of the product pumps must be adjusted to ensure that they are positioned at the oil/water interface.

One type of product pump being utilized has a 3 foot teflon-type filter sleeve which is saturated with diesel prior to positioning at the oil/water interface. If the water level rises above the top of this filter, water can enter the pumping chamber and be pumped into the temporary storage tank.

If water enters the chamber, the filter needs to be removed and cleaned and dried and resaturated with diesel; water must also he removed from the product storage tank.

The second type of product pump being utilized has an approximately 2 inch metal screen to capture the product. This pump is designed so that it will only pump product, thus eliminating tbe possibility of pumping water into the temporary storage tank. However, maintaining the position at the oil/water interface has proven difficult. This type of pump requires less maintenance, however, so it may be more appropriate for pump and treat systems with a more static groundwater table.

Fouling of Filters

Both the groundwater pumps and product pumps and filters tend to accumulate iron solids and bacteria. Each of the pump systems are consequently dismantled and cleaned on a regular basis to keep them operating efficiently.

Lesson learned: The pumps are helpful and perform well if they are serviced on a regular schedule. In the case of this system, maintenance includes a minimum of two checks per week on the position of the pumps in the well, and once-a-month removal and cleaning.

Heat Tracing

The subject system, located in northern Pennsylvania, is subjected to temperatures of (-20 degrees F) and lower during winter operation. Most of the groundwater and product lines are buried three feet below the ground; however, the lines are exposed inside the recovery wells and around the temporary storage tank. Experience has proven that in addition to the groundwater lines, the product lines need to be heat-traced (i.e, electrically). These lines froze regularly during the first year of operation.

Heating is also required for the Signet meters, since LCD displays do not function in extremely cold conditions (i.e, below 0 degrees F). Conversely, because the LCD displays malfunction at high temperatures, arrangements need to be made to keep the meters below temperatures of 100 degrees F.

Electrical Surge Protection

Electrical surges from lightning storms damaged control panels on two occasions. As a result, both panels were returned to the vendor, who installed surge protectors into the panels to increase the surge protection.

Iron Oxidation/Scale Removal

As previously discussed, monthly cleaning of the pumps is required to remove iron deposits, which must also be addressed in the piping network between the recovery wells. The lines are flushed at least once every three months to maintain the desired flow rate. The paddle wheels used to measure the flow rates directly in the groundwater lines are removed and cleaned on a monthly basis to ensure accurate flow measurements.

Separator System Equipment

The product line freezing and flow meter problems associated with operation of recovery well equiptment during temperature extremes also occur in operating the separator. There were also several equipment/maintenance problems.

Sludge Accumulation

As noted, the large oil/water separator also serves as a settling chamber for suspended solids. Experience has shown that the level of solids in the separator should be maintained at low levels to help ensure oil/water and solids separation. In tbis case it requires a total cleanout of the system approximately 18 to 24 months.

Oil/Water Separation

The subject system was initially designed to receive both the groundwater and product recovered from the five recovery wells. This necessitated use of oil skimming devices in the large separator. During the initial startup of the system, a variety of oil skimmers were evaluated in the baffled end of the large separator for removal of the recovered diesel. No skimming device was determined to fit the need, mainly because the diesel material was emulsified once it reached the second separator. The most efficient way determined to recover the oil was to pump it directly to a temporary storage tank adjacent to the wells. This decision has prevented more than 99% of the oil from entering the separators, and eliminated the need for an automated oil recovery system, as well as the maintenance associated with this system. This method of recovery also prevents any upsets that may occur when using an oil/water skimmer which could discharge floating oil.

Maintenance

Since the majority of the oil is recovered at the well heads, little if any oil is encountered in the separators. As a precaution, however, oil booms and absorbent pads are maintained in both the separators. Experience has shown that if an upset occurs, the separators will contain any hydrocarbon release until the material can be manually removed from the separators. In most cases, the booms and pads have minimized the iron solids and oil sheen that occasionally appear on top of the water in the separators. The booms and pads are changed as needed, generally once per month.

OPERATIONAL REQUIREMENTS/COSTS

The overall system operational costs are summarized in Table 4. The cost breakdown is based on an annual expenditure of approximately $100,000. Approximately 50% of the cost is for the day-to-day operation and maintenance of the system. On average, technicians visit the site two to three times per week for a total of 14 hours week. The cost breakdown includes 10% for NPDES required sampling and analysis; 16% is attributed to PADEP and internal reporting, and 19 percent for subcontracted management support. The latter may include agency correspondence, attendance at meetings, permit negotiation/compliance, and the management of the subcontractors at the facility.

Table 4. Operational Costs Conrail's Meadville Yard Groundwater Product Recovery System

Activity	Cost (a)(b)	Average Annual Manpower Requirements (hrs)
Operation/Maintenance	47%	670
Product Disposal	3%	(c)
Equipment Repair/Replacement	5%	(c)
Sampling/Analysis	10%	50
Reporting	16%	200
Subcontracted Management Support	19%	170
TOTALS	100%	1,090 Hours

(a) Cost is based on $100K annual budget.
(b) Cost includes both labor and other direct costs (ODC).
(c) Included with O&M hours.

CONCLUSION

This presentation outlines the inherent maintenance problems of a standard pump and treat system that, on paper, are not obvious to persons not familiar with them. A cautionary note to the reader, the overall cost to operate and maintain a pump and treat system should be closely scrutinized and considered before choosing such a system. When the overall costs of operating and maintaining a pump and treat system over the long term are compared to the higher costs of generally short-term remediation alternatives (e.g., landfilling, incineration, thermal desorbtion, etc.), pump and treat may not be as cost-effective an alternative as it appears.

QUESTIONS AND ANSWERS

Q. Have you done any additional investigation to find out areas or sources that may be more directly addressed?

I'm glad you raised this issue. One of the things that we looked at is we expected the plume or the amount of product we were recovering to taper off. It didn't. So we're looking at other options right now. Presently, we're putting together an investigation workplan to go out and look at the site and possibly other source areas, which will involve trenching. From this, we're hoping that we can look at possibly some other technologies to help speed along this remediation process, including other types of recovery approaches, as well as in-place treatment.

Q. Have you considered segregating the storm water from the recovery water?

Yes, my first thoughts on that were, wouldn't it be nice if we could just break this out and take this portion of the system out? Unfortunately, the plumbing that we're looking at goes through an active railyard. It's buried. There's several sources that we're picking up from in and around the yard that just make it, at this time, look cost prohibitive and impossible at this point, in some cases, for some of the sources.

Q. How much product has been recovered?

We've recovered in the past two years, about 1,600 gallons of diesel. They started off in the 1980s picking up about 9,000 gallons, so we're looking at about 10,500 gallons total since this system has been operated in the 1980s and into the 1990s. But there was that break in between.

Q. The original Conrail designed system was shut down in 1989. Do you know why that was shut down?

It was shut down because the seepage that they were looking at disappeared from French Creek, and the amount of product that they were collecting had also tapered off.

Q. How long will the system remain in service, and when do you plan to decommission it?

Right now, we're hoping to wrap things up within five years. However, we're not sure what the sources are at this point. We hope that this would be a good remedy for the site just by pumping and recovering this free product layer. We're not seeing a sheen on the creek. We thought we had it well maintained, but in late 1994 we saw a sheen coming down from the top part of the yard. So we had to start up another pumping system.

Chapter 8

Integrating Physical, Chemical, and Biological Technologies to Remediate an Active Railroad Site

John Haddad
Eder Associates, Ann Arbor, MI

Timothy J. Geddes
Blue Planet Technologies, Madison Heights, MI

Paul J. Kurzanski
Environmental, CSX Transportation, Inc., Jacksonville, FL

Don J. Nuss, Jr.
CSX Transportation, Inc., Fort Wright, KY

INTRODUCTION

Many technologies are currently available to remediate diesel fuel in soil. They include: excavation and disposal, soil vapor extraction, soil venting, soil flushing, vitrification, and bioremediation. Some of these techniques are prohibitively expensive and/or are not a permanent solution. Due to the unique nature of every site, a combination of two or more of these technologies is often the most effective way to achieve closure. Since the various technologies require a wide range of expertise, cooperation and coordination between the various engineering and scientific disciplines is necessary.

The objective of this project was to remediate a diesel fuel spill along an active railroad track. The project evolved into a rational, cost-effective, and scientifically sound remediation plan that can be applied to diesel fuel in railroad beds. The process can also be modified to remediate a wide range of sites.

SITE HISTORY

A derailment occurred in October of 1990 when a truck collided with a train on a single main line track, part of a high-volume rail corridor used by approximately 20 trains per day. Commercial development adjacent to the right-of-way precluded the construction of a rail detour around the accident.

The derailment ruptured locomotive fuel tanks, releasing approximately 5,200 gallons of diesel fuel. Emergency response activities recovered about 95% of the spilled fuel. After the free product and fuel-soaked soil were removed, approximately 500 gallons of diesel fuel remained in approximately 600 cubic yards of roadbed ballast, subgrade material, and native soil beneath and adjacent to the tracks.

The areal and vertical extent of the fuel oil residual in the ballast and soil was delineated by soil borings. The soil borings also revealed that the groundwater was not threatened, because the site is underlain by 30 feet of low permeability clay. Figure 1 shows the extent of the residual fuel oil.

REMEDIAL ACTIONS

Excavation, disposal, and site restoration was identified as the most effective remedy for roadside soils. After laboratory testing and a feasibility analysis, in situ soil flushing followed by bioremediation was selected as the remedy for soil beneath and directly adjacent to the track.

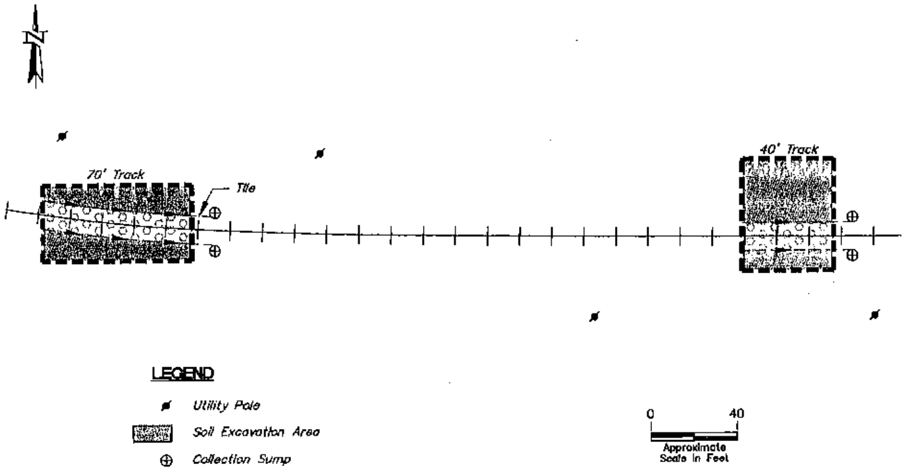

Figure 1 Extent of Impacted Area

EXCAVATION AND DISPOSAL OF ADJACENT SOILS

The underlying clay effectively impeded vertical migration. Soil adjacent to the tracks was excavated to a depth of six to twelve inches into the clay to remove the hydrocarbons that may have leached into the clay. The excavation began at the toe of the ballast and progressed at a slope not greater than 1:1 to prevent infringing the load triangle of the railroad ties. Approximately 290 in-place cubic yards of soil were excavated. An estimated 134 tons (100 cubic yards) of limestone aggregate was used to backfill the trenches and support the ballast under the tracks. During the excavation, perforated drainage pipe was laid adjacent to the tracks for use during soil flushing. A cross section of the excavation area is detailed in Figure 2. The photographs in Figure 3 illustrate the excavation effort and show the extent of diesel fuel in freshly exposed soil.

Excavating impacted soil in areas adjacent to the tracks reduced the total mass of residual petroleum at the site, and the risk of human and wildlife exposure to residual diesel fuel. The extent of petroleum residuals in the soil was found to be limited to areas below the tracks. Backfilling the trenches adjacent to the tracks with limestone aggregate improved the hydraulic connection between the layers impacted beneath the tracks and the collection system in the trenches. This hydraulic connection facilitated water retention, established a moisture level favorable for biodegradation, and improved the collection of flushed residuals in the sumps.

Post-excavation verification was performed by collecting and analyzing twelve floor, wall, and background soil samples for polynuclear aromatic hydrocarbons

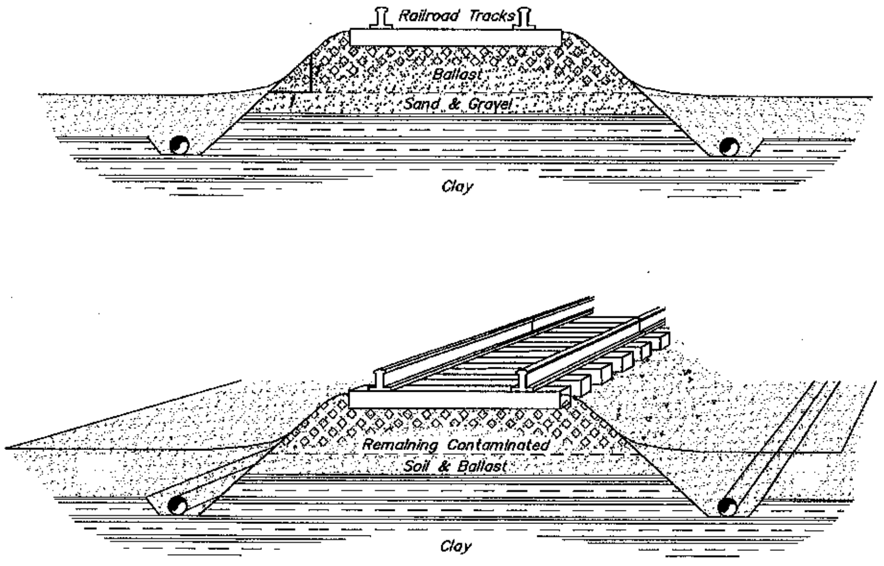

Figure 2 Impacted Soil to be Excavated and Drainage System Cross Section Layout

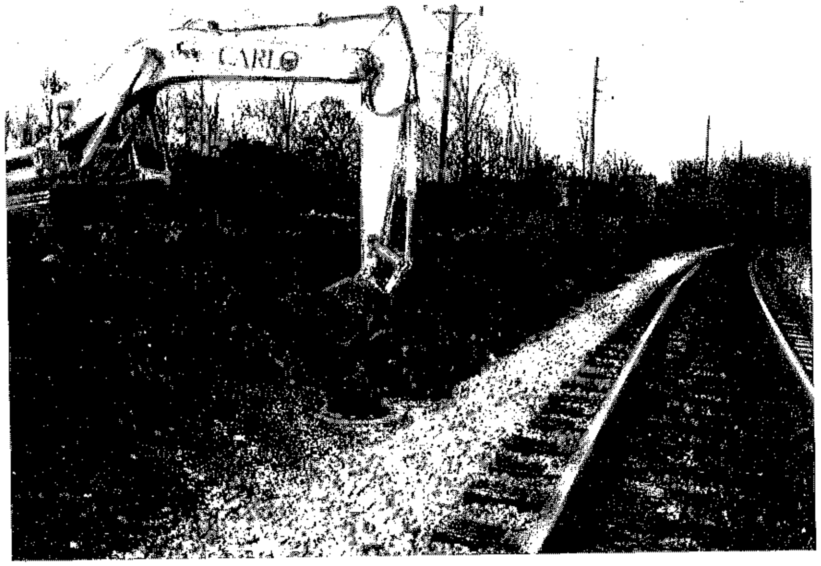

Figure 3a Activities in Preparation for Soil Excavation

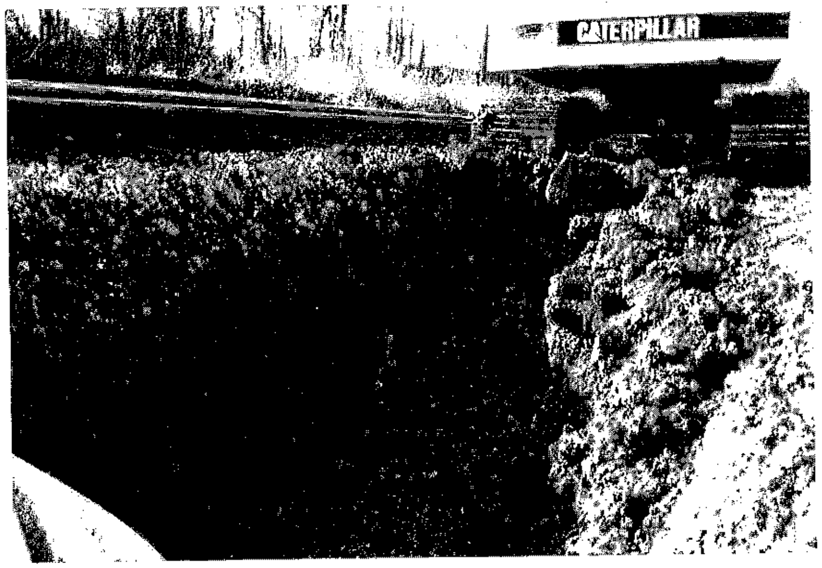

Figure 3b Vertical Profile of Contaminant in the Railroad Bed

(PAHs). The analytical results confirmed the reduction of PAH levels in areas adjacent to the tracks to below the State of Michigan Act 307 Type B Criteria, with residuals limited to the area under the tracks. The Michigan Type B cleanup criteria for soil (based on groundwater protection) are 20 times the health-based drinking water cleanup criteria. The Michigan Department of Natural Resources (MDNR) adopted risk-based soil and groundwater cleanup criteria for residential, commercial and industrial sites in June, 1995.

SOIL FLUSHING

The soil/ballast flushing process involved the application of a surfactant solution at the trackbed surface. The solution was allowed to infiltrate through the ballast and underlying soils, with eventual collection in the perforated drainage pipe (Figure 4). Since the vertical conductivity of the sand and gravel is likely orders of magnitude less than the horizontal conductivity of the ballast, almost all of the flow was through the ballast.

A treatability study of site soils was conducted to determine the most effective blend of surfactants for the flushing solution. Three surfactants (Biosolve, Tween 80, and Emcol Cocobetaine) were chosen, based on their favorable comparison to the following criteria: pre-water solubility, high hydrophobic-lipophilic balance (HLB), biodegradability, and minimization of detergency. Since contact times were short, a pre-water soluble surfactant was necessary to maximize contact between the surfactant solution and the contaminants. The following criteria were also considered:

1. HLB should be high, enhancing the water solubility of hydrophobic substances.
2. Surfactants should be biodegradable, to provide a supplemental food source for microorganisms.
3. Surfactant should maximize solubility to ensure that the residual hydrocarbons dispersed during washing will be quickly solubilized, thus preventing the transport of NAPLs to the soil below the site.

All three of the surfactants used in the study compared favorably with these criteria.

A homogeneous soil sample was collected from the derailment site and used in the treatability study. Soils were placed into containers and various surfactant solutions were added. Once solutions were applied, samples were shaken and the solution was decanted from the soils. The washed soil samples along with decanted solutions were sent to an analytical laboratory for PAH analysis. The results are presented in Table 1. It was concluded that a combination of Tween 80 (0.45%) and Emcol Cocobetaine (0.51%) removed the largest amount of PAHs.

Application of the surfactant solution to the site was achieved by first excavating trenches and then installing drainage tile and collection sumps. Approximately 12,500 gallons of flushing solution were applied to the soils and ballast. The flushing solution was mixed in a polyethylene tank, pumped to the impacted areas, and dispersed through irrigation sprinklers. The flushing solution drained through the ballast and underlying sandy soils, into the drain tile, into 550 gallon collection sumps. The solution was pumped from the sumps to a 20,000 gallon Baker tank for storage before

Figure 4a Remedial Activities

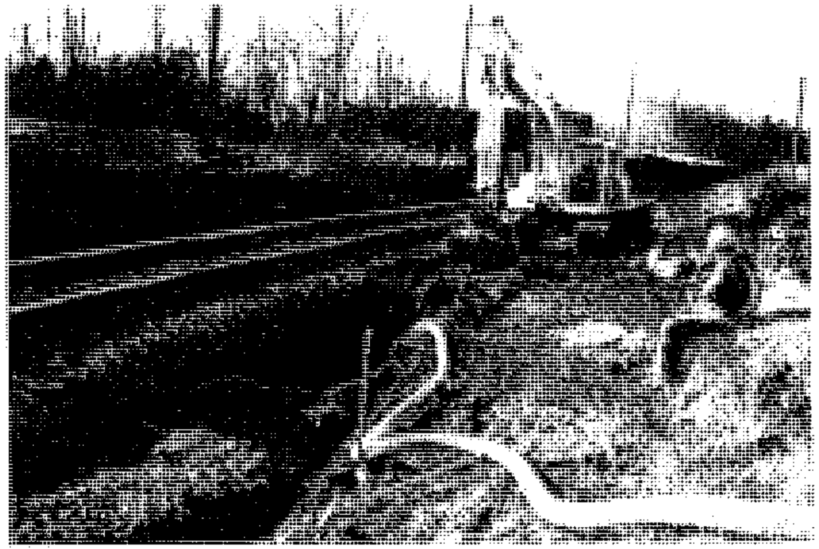

Figure 4b Excavation Activities

Table 1 Treatability Study for Soil Flushing. Concentration values are given in parts per billion (ppb).

Sample ID	Surfactant
B-1s	Water
B-2s	Biosolve (1.6%)
B-3s	Emcol Cocobetaine (1.0%)
B-4s	Biosolve (0.48%) Emcol Cocobetaine (0.48%)
B-5s	Tween 80 (0.94%)
B-6s	Biosolve (0.46%) Tween 80 (0.81%)
B-7s	Emcol Cocobetaine (0.51%) Tween 80 (0.45%)

Treatability Study Results (ug/kg)

Compound	Background Sample	B-1s	B-2s	B-3s	B-4s	B	B-5s	B-6s	B-7s
Anthracene	3482	1604	1095	678	833	855	1563	1492	219
Benzo(a)anthrecene	139104	44782	27140	26622	30340	15478	35409	28336	21853
Benzo(b)flouranthen	97123	26432	13948	15250	16239	8308	20822	19938	12913
Benzo(k)flouranthene	106844	35620	18131	20183	21212	10692	26815	21212	16933
Chrysene	47456	16048	9469	9359	10916	5496	12572	10353	7601
Flouranthene	250092	9459	67569	50938	64121	33560	8297	3501	1838
Flourene	6251	3290	3327	1601	2982	625	2611	2543	167
Naphthalene	5209	3082	802	1363	2052	3202	2950	33258	666
Phenanthrene	17700	6144	6359	4001	5226	859	5152	5103	3343
Pyrene	252940	82494	75069	54336	69533	35972	67522	61213	44745

Removal Percentages

Compound	B-1s	B-2s	B-3s	B-4s	B	B-5s	B-6s	B-7s
Anthracene	53.93	68.55	80.53	76.08	75.45	55.11	57.15	93.71
Benzo(a)anthracene	67.81	80.49	80.86	78.19	88.87	74.54	79.63	84.29
Benzo(b)flouranthene	72.79	85.64	84.30	83.28	91.45	78.56	79.47	86.70
Benzo(k)flouranthene	66.66	83.03	81.11	80.15	89.99	74.90	80.15	84.15
Chrysene	66.18	80.05	80.28	77.00	88.42	73.51	78.18	83.98
Flouranthene	96.22	72.98	79.63	74.39	86.58	96.68	98.60	99.27
Flourene	47.37	46.78	74.39	52.30	90.00	58.32	59.32	97.33
Naphthalene	40.83	84.60	73.83	60.61	38.53	43.37	36.17	87.21
Phenanthrene	65.29	64.07	77.40	70.47	95.15	70.89	71.17	81.11
Pyrene	67.39	70.32	78.52	72.51	85.78	73.31	75.80	82.31

disposal. A total of 5,500 gallons of flushing solution were recovered for disposal. Figure 5 shows the flushing system.

The effectiveness of soil flushing was determined by post-flushing sampling and analysis. The results revealed that soil flushing was successful in removing the majority of the PAHs (Table 2). Some minor residuals remained above the MDNR Type B Criteria. This necessitated a third cleanup technology in the form of bioremediation.

ASSESSMENT OF BIOREMEDIATION POTENTIAL

There is little precedence for successful application of a commercially available bioaugmentation product to remediate PAHs in soil, and there are few documented examples of successful bioaugmentation using non-indigenous microbes[1]. This probably is due to the inability of imported organisms to survive in environments where they are not acclimated. It also follows that the existing microbe population would possess the characteristics needed to survive in that particular environment. The third phase of site remediation focuses on the development of a rational, cost-effective, and scientifically sound process based on the theory of augmenting the site with an active, enriched PAH degrading bacteria consortium isolated from the site to be remediated. The result will increase biodegradation rates, due to the density of PAH specific degrading bacteria.

A preliminary assessment of site conditions and analysis of soil samples was conducted to appraise the potential benefits of bioaugmentation. These analyses included the determination of the levels of PAH, and other residuals such as BTEX

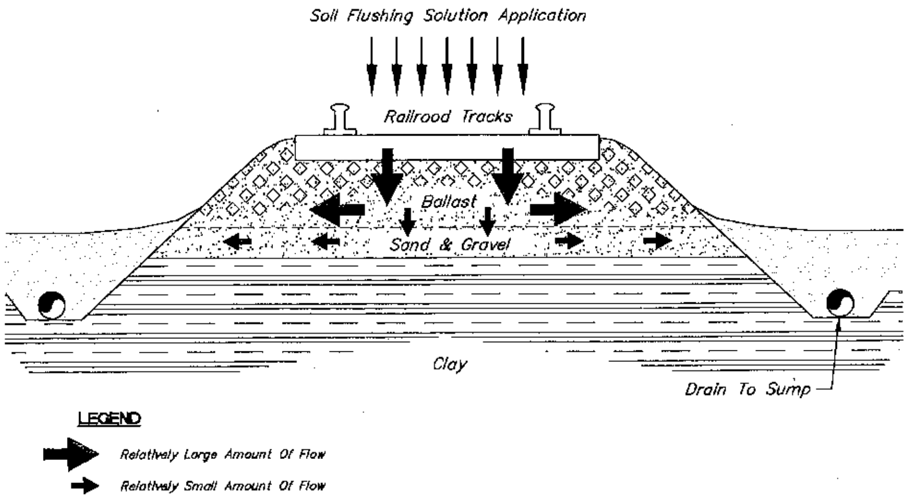

Figure 5 Diagram of Soil Flushing Flow Dynamics

Table 2 Results of Soil Flushing. Concentrations are given in parts per billion (ppb). Asterics (*) denote levels above MDNR Type B criteria. The upper chart represents PAH concentrations prior to flushing, while the lower chart represents post-flushing results.

	Type B	West Area	East	Area
PAH Analysis	Criteria	SL-BR-SB-8 (2-4') (Feb. 93)	SL-BR-GP-8 (0-2') (Dec. 93)	SL-BR-SB-16 (0-2') (Feb. 93)
Anthracene	1.4E+5	810	520	6,200
Benzo(a)anthracene	1,800	3,100 *	2,000 *	3,900 *
Benzo(b)flouranthene	1,800	<330	1,300	880
Benzo(k)flouranthene	18,000	<330	<330	1,300
Chrysene	330	790 *	<330	3,700 *
Flouranthene	17,000	17,000 *	19,000 *	15,000
Flourene	17,000	2,100	3,700	2,000
Indeno(1,2,3-cd)pyrene	1,800	490	<330	<330
Naphthalene	5,000	2,900	3,800	580
Phenanthrene	500	4,400 *	12,000 *	13,000 *
Pyrene	10,000	11,000 *	40,000 *	1,300

Table 2 Continued

Compound ug/kg	Type B Criteria	West CPR-BR-HA3	West CPR-BR-HA4	West CPR-BR-GP3	West CPR-BR-GP4	West CPR-BR-GP5	East CPR-BR-HA1	East CPR-BR-HA2	East CPR-BR-GP1	East CPR-BR-GP2
Acenaphthene	24,000	3571	5700	3449	18488	8856	1493	52	510	1041
Acenaphthylene	500	148	2481 *	15393*	17328*	6490*	71	106	175	1112
Anthracene	140,000	39	60	26	40	51	10	76	-	-
Benzo(a)anthracene	1,800	184	431	-	677	-	166	240	-	-
Benzo(a)pyrene	330	130	481*	156	-	149	144	206	-	-
Benzo(b)flouranthene	1,800	181	878	-	-	-	288	48	-	-
Benzo(ghi)perylene	930,000	45	288	-	-	-	82	101	-	-
Benzo(k)flouranthene	18,000	-	781	803	-	269	242	248	-	-
Dibenzo(a,h)anthracene	330	156	139	-	-	840*	113	171	-	-
Flouranthene	17,000	253	481	537	-	-	205	415	-	-
Flourene	17,000	16	159	875	518	512	37	57	-	31
Indeno(1,2,3-cd)pyrene	1,800	80	415	-	-	-	116	135	-	-
Naphthalene	5,000	183	258	965	-	1010	122	-	32	104
Phenanthrene	500	180	208	1514*	794*	1155*	54	264	19	-
Pyrene	10,000	860	1620	15,007*	9303	14236*	242	481	-	-

and metals. Concentrations of critical nutrients were established to determine any deficiencies. Soil pH and soil moisture content were also determined to establish if the site was amenable to bioaugmentation. The analytical results are shown in Table 3.

INITIAL BACTERIA SCREEN

Soil bacteria were enumerated to establish the presence of significant microbial diversity for future enrichments. It was important to determine the percentage of total bacteria (as determined by direct soil counts) that could be cultured in the lab, since it has been reported that the total number of plate count bacteria is usually 0.1 - 10% of the total obtained from direct counts[2]. The enumeration findings are shown in Table 4.

An initial screening method was developed to quickly assess a soil sample for the potential of indigenous microbial PAH degradation. Bacteria from the site were introduced into a microtiter plate containing a panel of PAH compounds, a buffered nutrient medium, and the redox dye tetrazolium violet (Biolog MT Microplate™). The plates were incubated for a pre-determined period. In microtiter plate wells where PAHs are being metabolized, the tetrazolium dye is reduced during bacterial respiration, resulting in the appearance of a color in the well. This method is a modification of one developed to work with BTEX degrading organisms[3]. Negative control microtiter plate wells lacked PAHs; therefore, they did not contain a carbon source. The negative control allows evaluation of metabolism that is not caused by PAH oxidation.

Following the assessment of the consortium, individual isolates were screened for PAH degrading ability. Over 60 colonies were isolated from six independent soil samples and screened in microtiter plate wells containing a mixture of the 16 priority pollutant PAH compounds (Figure 6). Positive reactions were observed from 18 of the isolates, and these were assessed for their ability to degrade specific PAH compounds in a similar assay technique.

Due to suspected false-positive results from carry-over metabolism and the presence of solvents to solubilize the PAHs, the initial findings were validated by a method in which a mineral salts agar is coated with a solution of an individual PAH compound[4]. The solvent containing the PAH was then evaporated, leaving a fine coating of PAH crystals. After inoculating with isolated strains and incubating the plates for one week, PAH degradation was indicated by either growth and/or clearing PAH crystals surrounding the colonies.

ENRICHMENT OF PAH DEGRADING BACTERIA

Bacteria indigenous to the soil were enriched in the laboratory in selective media containing a limited carbon source and the 16 priority pollutant PAHs. Cultures were enriched for various time periods and then analyzed for their ability to biodegrade PAHs. Enriched bacteria consortia were scored positive if they were capable of proliferation in media containing PAH compounds as the exclusive carbon source (Figure 7). Bacteria growth on phenanthrene coated mineral salts agar medium (MM2) was also used as an indicator of successful enrichment (Figure 8). The

Table 3 Chemical and physical analysis of contaminated soil. The values reported are from a composite made up from six exclusive samples. ppb = parts per billion (ug/kg), ppm = parts per million (mg/kg), ND = not deteected.

Chemical Analysis	Compound	Concentration
Volitile Organics	Naphthalene	467 ppb
Method 8260	all other VOC in scan	ND
Semi-volitile Organics	Acenaphthene	<330 ppb
Method 8270	Acenaphthylene	339
	Anthracene	811
	Benzo(a)anthracene	403
	Benzo(a)pyrenc	<330
	Benzo(b)flouranthene	688
	Benzo(g,h,i)perylene	545
	Benzo(k)flouranthene	505
	Chrysene	450
	Dibenz(a,h)anthracene	<330
	Flouanthene	683
	Flourene	507
	Indeno(1,2,3-cd)pyrene	538
	Naphthalene	367
	Phenanthrene	<330
	Pyrene	870
Metals	Arsenic	9.83 ppm
Method 7000	Chromium	9.43
	Copper	33.85
	Iron	12700
	Lead	46.33
Nutrient Analysis	Ammonia Nitrogen	1.8 ppm
	Total Nitrogen	11
	Orthophosphate	0.21
	Total Organic Carbon	82000
Physical Parameters	Soil pH	7.95
	Soil Moisture Content	13.9%

Table 4 Microbiological analyses of contaminated soil. Enumerations were performed on the soil composite prepared as described iu Table 3.

Micro-biological Analysis	Method	Result
	Spread plates	1.1 $^{+/-}$ 0.2 x 10^{7} CFU/g (n=5)
	Acridine orange direct counts	1.2 $^{+/-}$ 0.2 x 10^{8} CFU/g (n=6)
	Percent culturable soil bacteria	9.2 %

effectiveness of the enrichment was observed as an increase in the percentage of phenanthrene positive colonies when a random population was screened.

PAH DEGRADATION IN STANDARD SOIL

A soil consisting of sand coated with PAH compounds at concentrations similar to those encountered at the site was treated with an enriched PAH degrading consortium in laboratory microcosms. PAH losses in microcosms containing a viable consortium were compared to losses in an abiotic control under the same nutrient conditions (Figure 9). The initial chemical analysis revealed limiting amounts of both nitrogen and phosphorus. These findings are based on the carbon to nitrogen to phosphorous ratio (C:N:P) of 100:10:1 reported in the literature. To achieve this ratio, additional nitrogen and phosphorus are required, but care should be taken in this case to cover the TOC load (82,000 ppm) with nitrogen or phosphorus salts to avoid a hypertonic environment which would be detrimental to general bacterial metabolism[5].

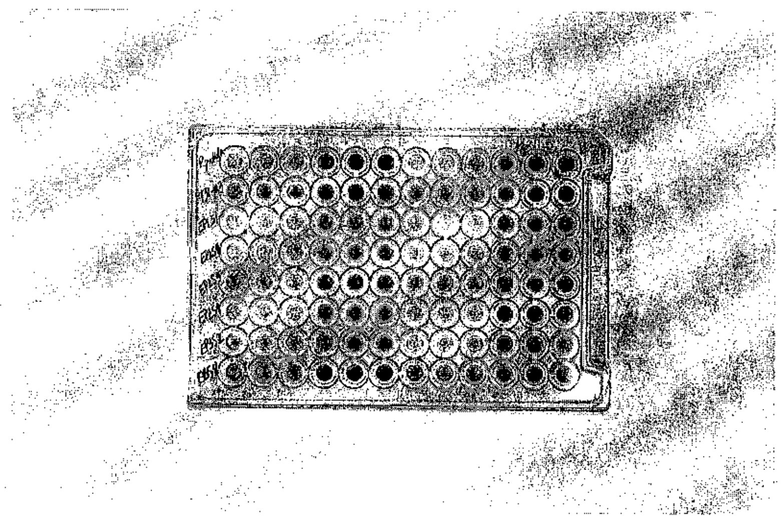

Figure 6 Initial Screen for PAH Degraders. Using Biolog MT Microplates™ with wells containing PAH compounds as the sole carbon source, a bacterial consortium and isolated strains from the site were inoculated into plate wells. Bacterial inocula were prepared as instructed by Biolog. The plates were monitored visually for the development of a colored metabolic by-product. A positive result is indicated by the appearance of color in the well. Columns 1,2,3 and 7,3,9 (left to right) are negative control wells that lack PAH compounds. Wells in the top row are positive controls containing the naphthalene degrading bacteria *Psuedomonas Putida* Biotype B strain (ATCC 17484).

BENCH-SCALE BIODEGRADATION STUDIES

A soil composite from the derailment site was used to test the effectiveness of the enriched bacterial consortium in biodegrading PAHs in a bench-scale study. Soil was treated in microcosms in one of four ways:

1. Amending with nutrients only.
2. Amending with nutrients and augmenting with the enriched consortium.
3. No treatment.
4. Addition of a biocide.

The last of these was to control for abiotic losses. The results of this study are presented in Figure 10.

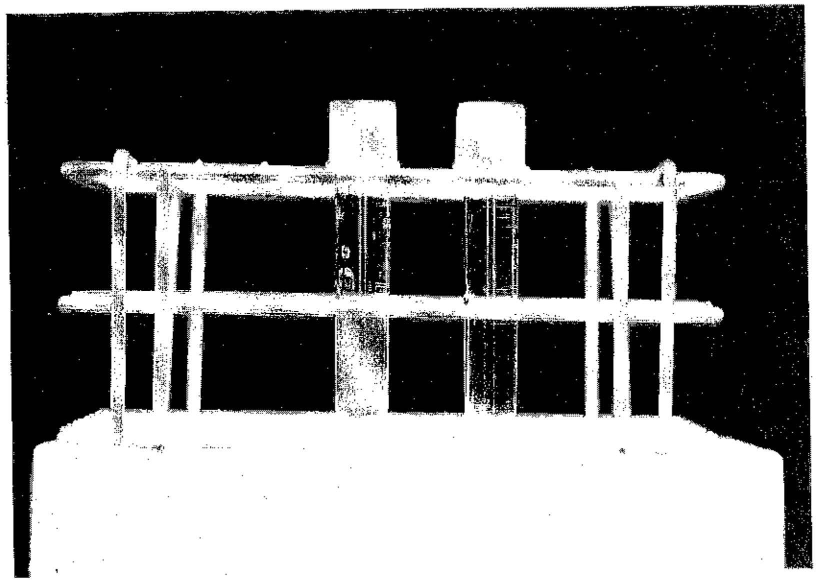

Figure 7 Enrichment of PAH Degrading Bacteria. Using soil from contaminated site, extracts were prepared and used as inocula for enrichment cultures. Enrichment medium was nutrient-limited and contained the sixteen priority pollutant PAHs. After a number of passes through this medium, the cultures were evaluated for growth in a mineral salts medium (Bushnell Haas) containing only PAHs as a carbon source. The culture on the left was inoculated with bacteria enriched for PAH degradation, while the culture on the right was inoculted with a non-enriched control.

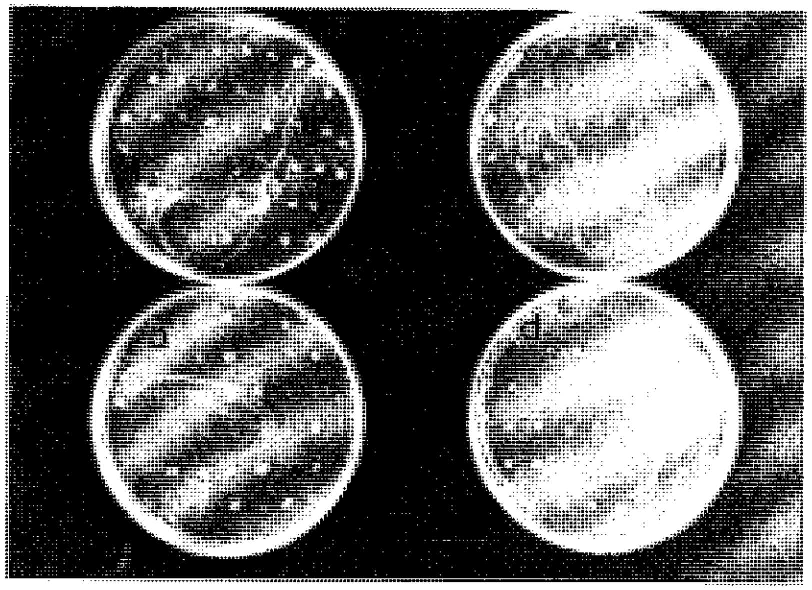

Figure 8a Example of Phenanthrene Degrader Enrichment. The percent of phenanthrene degrading bacteria in each enrichment passage was obtained by spreading serial dilutions of the cultures onto R2A agar. Random colonies were then analyzed on phenanthrene coated minimal medium (MM2) plates. Colonies were scored positive for growth and compared to duplicate platings on rich medium.

a = original soil extract plated on rich medium, b = original soil extract plated on phenanthrene coated MM2 medium, c = 7th enrichment pass plated on rich medium, d = 7th enrichment pass plated on phenanthrene-coated MM2 medium.

Culture Passage	Number of Colonies Assayed	Number of Phenanthrene Positive Colonies	Percent Phenanthrene Positive Colonies
Soil Extract	45	17	37.7%
4th	45	23	51.1%
7th	45	42	93.3%

Figure 8b Verification of Phenanthrene Degrader Enrichment. Colonies from enrichment passes were replica plated onto a mineral salts medium and a rich medium, both coated with phenanthrene. Growth was observed and compared after four days of incubation.

Since the results from the bench-scale bioaugmentation study indicated that the PAH compounds were effectively degraded by the enriched consortium, the next step will be to apply copious amounts of the bacteria to the derailment site.

FIELD STUDY

The PAH concentrations at the site are less than the new MDNR Residential Cleanup Criteria. However, the bacterial consortium will be added to the railbed to confirm the results of the bench-scale tests. This will be accomplished by first using scale-up culture methods developed in the laboratory to rapidly produce an inoculum to achieve between 1×10^6 and 1×10^7 augmented bacteria per gram of soil. This will involve culturing and applying approximately 200 liters of the enriched bacterial consortium. Application will be accomplished by a series of multi-depth injections directly into the soil underneath the tracks. The effectiveness of this procedure will be monitored monthly by sampling and analyzing for PAHs, and comparing them to non-treated and nutrient amended control plots. The results of the field study will be published in the future.

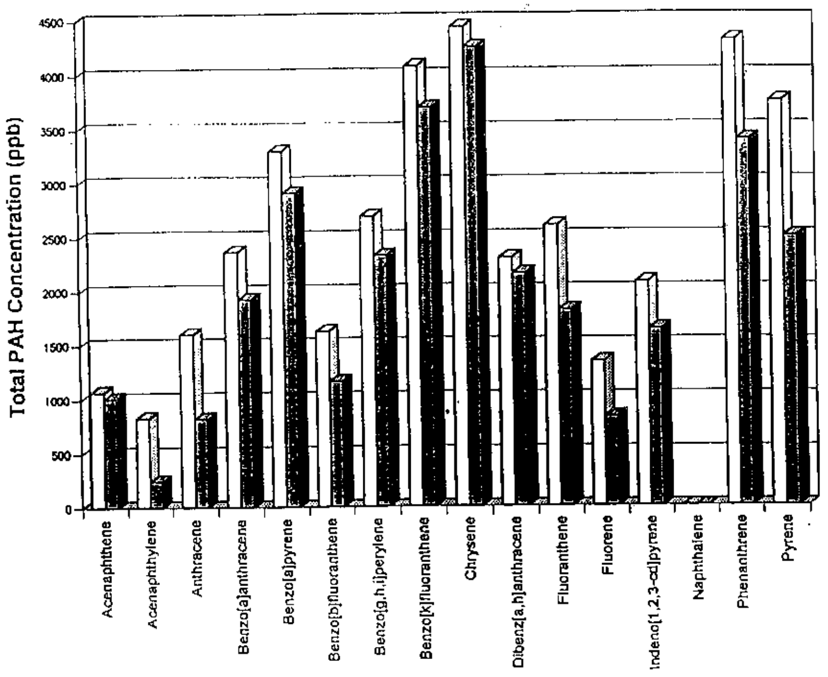

Figure 9 PAH Biodegradation in Standard Soil. Bacteria from an enrichment culture were inoculated into microcosms containing a standard soil contaminated with a mixture of the sixteen priority pollutant PAHs. Standard soil was prepared by coating silica with a methylene chloride solution of PAH standards. The solvent was evaporated, leaving behind the less volatile PAH compounds. Naphthalene, a relatively volatile PAH, was volatilized in the process (as evidenced by its absence at the start of the study). The microcosms were incubated for seven days. Abiotic controls did not contain bacteria, but otherwise were identical to the viable microcosms. The reported values are the averages of triplicate analyses. Unshaded bars represent PAH concentrations in the entire abiotic microcosm, while the shaded bars represent PAH concentrations in the bioaugmented microcosms.

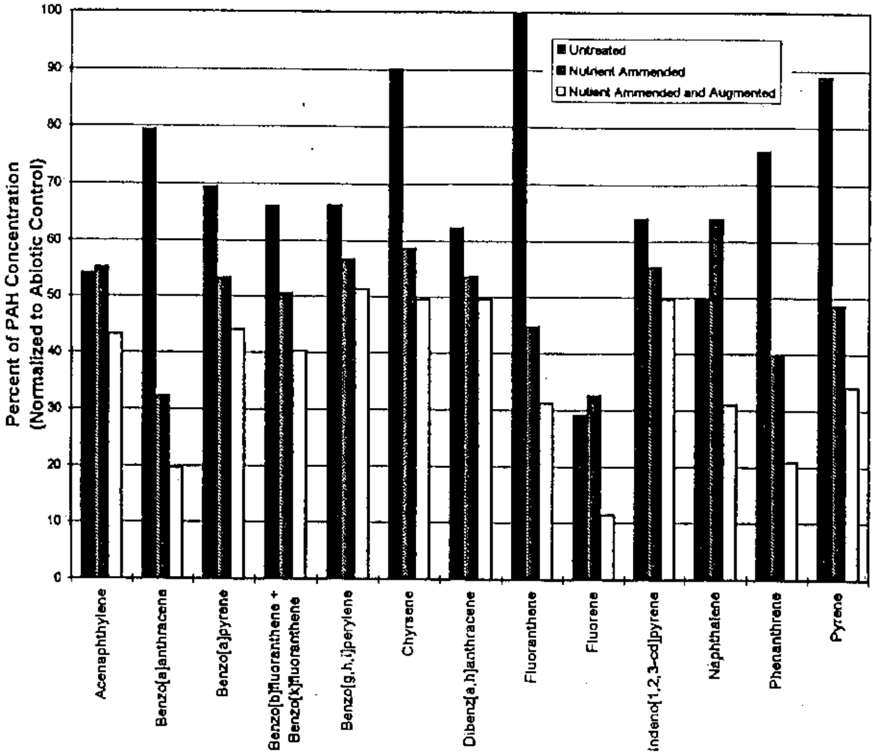

Figure 10 Bench-scale Biodegradation Study. Soils were treated as described in the text. Data is presented as a percentage of the individual PAH compounds remaining in an abiotic control. Augmented = addition of bacteria that have undergone laboratory enrichment for PAH biodegradation.

CONCLUSION

The data demonstrate the successful remediation of residual fuel oil at a railroad accident site. This case study also illustrates the benefit of a coordinated effort involving diverse disciplines to develop a sound and innovative remedial approach. The total cleanup of the site will be completed with the field-scale implementation of bioaugmentation.

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QUESTIONS AND ANSWERS

Q. If the concentration of the TPH after the surfactant washing was done, was 82,000. What was the concentration before the washing was done?

I can't address that question. I can tell you that the PAH compounds originally were between 10-50 ppm. We didn't do an analysis of the TPH at that point.

Q. So the overall TPH reduction during your program wasn't monitored during the bioremediation stage?

Correct.

Q. What were the levels of nitrogen phosphate that you were adding? What's the likelihood of regulators accepting that addition, philosophically?

I can't really answer either one of your questions. In this case, the total organic carbon load was so great in order to cover that under a 10:1 ratio, we would have had to amend with much more nitrogen and phosphorus salts. That would have been inhibitory to bacterial metabolism. It would have been a very salty environment. We did it in little steps. I'm sorry that I can't answer your question about the regulatory issues.

I'd like to make one more comment about the earlier question about the regulatory agencies. This was a, more or less, research project, so we weren't trying to achieve cleanup levels. We were trying to develop a method.

Q. What was the cost at each phase of this remediation? Soil washing and bioremediation?

Geddes: I can address the bioremediation portion. Again, since this was a research effort, we don't have concrete numbers for that.

Haddad: As far as the cost, actually the whole issue was to find a cost-effective alternative for our client. We simply summarized the cost as the cost of excavation and disposal. In this same time for soil flushing, it was also very simple. Actually, we did not divide the total cost by the volume, but I can say that $100,000 was the total cost that covered all the expenses for subcontractors, administrative fees, up to the bioremediation stage.

Q. Were you able to measure surfactant recovery?

Actually, we did but we were not worried about how much we recovered because it is biodegradable.

We knew that it will disappear with time. We also knew the initial concentration of the soil flushing solution. Simply by taking a sample after the flushing you can compare how much you recovered, as compared to what you started with. We did recover most of the surfactant.

CHAPTER 9

Deep Multi-Point Bioslurry Injection: In-Situ VOC Biodegradation in Low Permeable Clays

Full Scale Case History

Derek K. Rhodes
MARCOR Environmental, Hunt Valley, MD

Art Pengelly
Hayward Baker, Inc., Fort Worth, TX

TECHNOLOGY BACKGROUND

Poor subgrades have plagued the construction industry for years, particularly for shallow building foundations, roadways, pipelines, and railroad tracks. Subgrade failures are typically the result of fill applied over unconsolidated areas, trapped water, mud pumping, subgrade squeezing, or deep shear failure. Failures of these types are found across the country, as shown in Figure 1.

Conventional stabilization techniques employed to improve subgrades (such as roller compaction) may be costly, require removal of the existing structures, or may prove ineffective on expansive clays or water sensitive silts. Lime/fly ash injection and chemical injection were two economical systems developed in the late 1960s to provide economical subgrade stabilization. The process fills voids within the soil or chemically alters the clay matrix of the soil.

Lime/fly ash injection uses multiple, direct-push injectors to introduce a lime/fly ash slurry into the subgrade to fill cracks, weakness planes, voids and ballast pockets. For expansive clays, a water solution is injected to swell the clay soils prior to construction.

Chemical injection is utilized to treat montmorillonite clays, the clay mineral most associated with expansive soil behavior. These clays are composed of two silica sheets slightly bonded to one alumina sheet. A net negative charge deficiency exists between the silica sheets and the alumina sheet. These forces create a condition whereby water and other exchangeable ions can enter between the silica sheets and cause the clay to expand. Multiple, rotating injectors are used to introduce a proprietary potassium-based solution into montmorillonite clays. By providing intimate contact of the solution with the clay matrix, chemical injection is capable of changing the clay mineral into an illite clay mineral. (Illite does not exhibit the severe swelling potential of montmorillonite.)

Extensive subgrade stabilization experiences prompted the development of numerous injection machines that can penetrate and treat soils to depths ranging from 10-40 feet below grade, through the use of injectors which push simultaneously into the subsoil. Single-point injection machines are used within existing building structures or around utilities. The equipment is readily available, and has been used effectively over the past 25 years. Figure 2 shows the kind of injection machine typically used in rail or pipeline work.

Injection technology is based on the ability to effectively saturate subsurface soils with a slurry. It offers an inexpensive, yet proven alternative for *in-situ* contaminant degradation or destruction. The technology achieves *intimate contact* of the bioslurry or chemical oxidation reagents with the subsurface soils for biostimulation, bioaugmentation, or chemical oxidation/reaction. Biostimulation introduces appropriate inorganic nutrients (i.e., nitrogen, phosphorus), electron acceptors (oxygen), and moisture to stimulate the growth of indigenous microbial populations. Bioaugmentation adds microorganisms with demonstrated metabolic capabilities to degrade the specific waste concern. More often, bioaugmentation employs soil sampling, and identifies indigenous microbes for culturing and repopulation on-site. The following case history outlines how injection technology has successfully treated contaminants through bioaugmentation within low permeable clays.

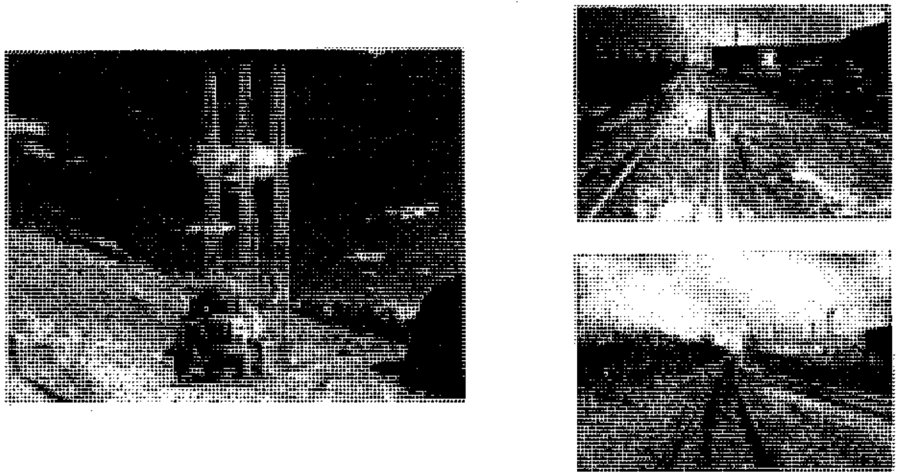

Figure 1 Failures Due to Poor Subgrade Conditions

CASE HISTORY

A Gulf Coast petrochemical plant had historical hexane contamination of soils resulting from leaking process-gravity sewers. Contamination was discovered along 535 linear feet of sewer lines, extending 5 feet from the pipe center line and 12 feet below grade. Hexane concentrations were as high as 7,200 mg/kg, averaging 250 mg/kg across the affected area. Because sewer line flowed through active process areas of the plant, its position made excavation an unacceptable alternative. Excavating the affected soils would have removed the sewer from service and required a temporary plant shut-down.

An *in-situ* technique was called for. Several alternatives were considered, including vapor extraction and bio-venting. These options were rejected because the contaminated zone soils consisted of very dense, low permeable clays. This site was determined to be an ideal prospect, however, for the application of Bioslurry Injection™.

The Process

Bioslurry Injection™ achieves *in-situ* bioremediation of hydrocarbons by pressurized subsurface injection of a slurry consisting of a proprietary mixture of controlled-release oxygen sources, controlled-release nutrient sources, and microbial cultures. This is applied in an overlapping grid pattern to ensure complete coverage of the contaminated zone, as illustrated in Figure 3. Successful *in-situ* bioremediation relies on contacting sufficient nutrients and oxygen with the contaminated media. Most *in-situ* bioremediation systems depend on subsurface movement of water or air to contact nutrients and oxygen with contaminated soils and groundwater. Bioslurry

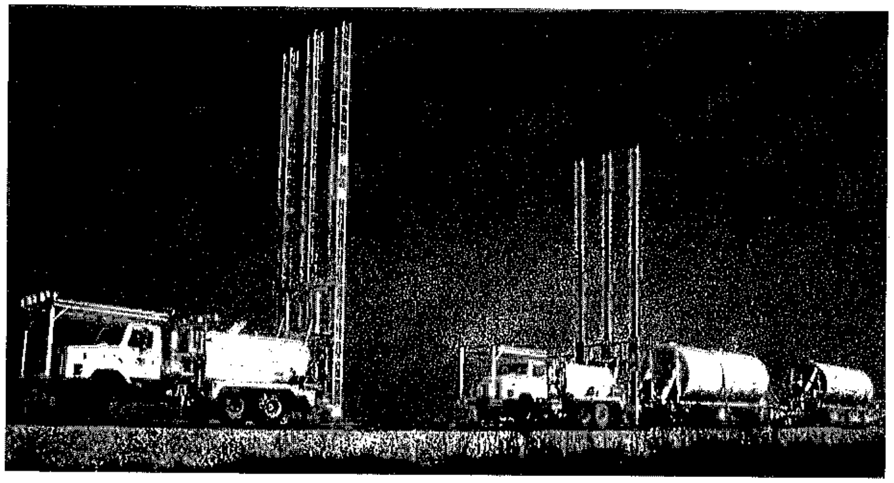

Figure 2 Injection Equipment for Treatment Depths to 40'

Injection™ allows *in-situ* bioremediation to proceed independently of a formation's ability to transmit water or air, by physically permeating the contaminated zone with a mixture of controlled-release sources of oxygen, nutrients, and microbes. The time required for Bioslurry Injection™ remediation is much shorter than that of traditional extraction and reinjection techniques. This is because the remedial time-frame is driven by microbial kinetics, rather than by groundwater velocity. Conditions suitable for enhanced biological activity can be maintained for over 50 days.

The injection material consists of three main proprietary products:

- Chemical Oxygen Source
- Accelerator Nutrients
- Biological Cultures

Hydrogen peroxide (H_2O_2) is well documented as an oxygen supply source for *in-situ* soil and aquifer bioremediation applications. The disadvantage of hydrogen peroxide is its limited life: It typically degrades in a matter of days or hours, depending upon site conditions. Since Bioslurry Injection™ is based on a preferred one-time application, an extended oxygen release material was required. An oxygen source material with a manufacturer-claimed oxygen release rate of three to six weeks was selected. The material yields approximately 53 liters of oxygen at 25° C per pound: the volume of application was determined by the microbial treatability laboratory study.

The selected oxygen source material was provided in dry powder form with a shelf life of one year. The O_2 source material and nutrients were slurried with potable water in batches using separate agitation tanks. Specialized bacteria were cultured on-site and transferred to a third tank for injection.

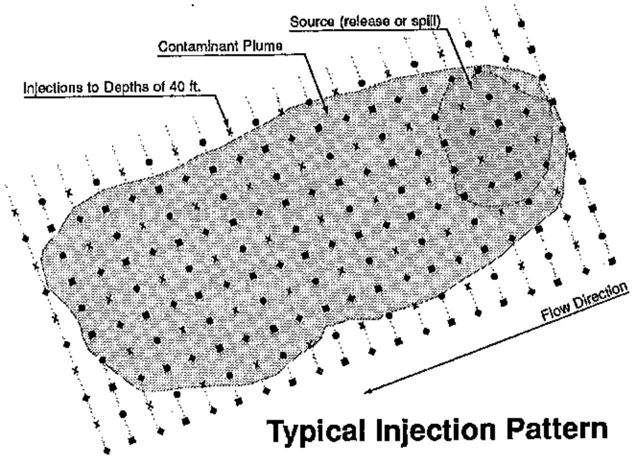

Figure 3 Overlapping Grid Pattern

Bio-slurry agents were pumped from the slurry tanks and combined at the point of injection. To introduce these agents to the subsurface, a hydraulic injection rig was used. The injection rig consisted of a rubber-tired vehicle with a hydraulically powered, vertical injection mast. One to four injection rods are typically mounted on the injection mast, spaced on 2-5 feet centers. Although up to four rods can be used, two rods spaced six feet apart were better suited for the injection layout. This equipment is capable of penetrating to 12 feet below grade, the maximum depth of contamination at the site (Figure 4). The lower portion of each injection rod is tapered to allow easy penetration into the soil.

The 15% to 25% dry weight solid slurry was pumped under pressure during the injection rods' downstrokes. The slurry was continuously injected — horizontally through each of the rod tips. For this project, a 2 1/2 foot spacing was used to ensure complete penetration of the contaminated zone. (The injection pattern used over the majority of the site is presented in Figure 5.) Paved areas were pre-drilled prior to injection and patched after the work was complete. Some areas were covered by existing containment slabs, and coring was not permitted. For these areas, angled injections were used to reach the soil beneath the slab. Excellent transmittance of bio-slurry material was achieved through the dense clay soils, and slurry was observed flowing from natural fissures and previous injection points up to 15 feet from the point of injection.

Figure 4 12' Chemical Injection Machine

As the design materials are injected into soil mass, they flow through the paths of least resistance. These are generally desiccation cracks, fissures, sand lenses, and other geologic conditions that are predominant in most soil formations (These are the same pathways that the contaminants followed into the soil.) Injection pressure is used to ensure that materials are well distributed into the soil mass. As the soil mass seeks to equilibrate the additional injected moisture, soil suction and diffusion mechanisms further distribute the soluble injected materials. This, and a close grid spacing, provide excellent distribution of the injected material, particularly along pathways where contaminants are more concentrated.

Project Results

Definitive soil samples were collected in the area of highest contaminant concentrations. The five borings were drilled six weeks after injections were complete, with additional borings drilled after an additional four weeks. VOC and TPH concentrations from the definitive samples were less than 2.0 mg/kg, with most samples falling below detection limits. Initial concentrations were as high as 7,200 mg/kg; the cleanup criterion was established at 50.0 mg/kg or less.

CONCLUSIONS

Bioslurry Injection,™ which provides intimate *contact and control* of reagents and microbes with subsurface soil contaminants is an effective remedial technology for *in-situ* treatment of hydrocarbon-affected soils. The strength of Bioslurry Injection™ is its ability to work across a wide range soils, regardless of soil structure or permeability. The case history demonstrates the technology's effectiveness within low permeable clays. However, it also offers cost-effective remediation for permeable sands and gravels.

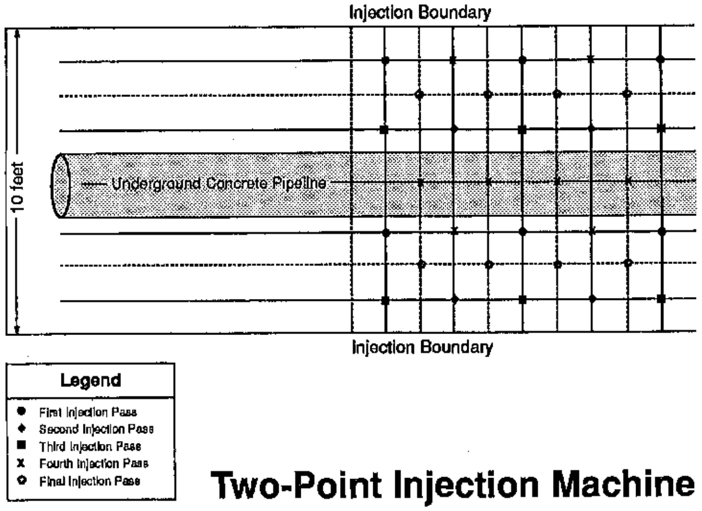

Figure 5 Two-point Injection Pattern Along Pipeline

The advantages of Bioslurry Injection™ over other remedial technologies are as follows:

1. The remedial time frame is shorter than traditional *in-situ* systems.
2. No above-grade equipment is required after injection of materials.
3. No operator attention is required after initial injection.
4. Remediation is independent of the formation's ability to transmit water or air.
5. Biological agents are deposited into the same paths that contaminants followed.
6. Remediation can be accomplished at operating facilities and *even below buildings* without interruption of operations.

Effective remediation of compounds that are more resistant to bioremediation or are of higher contaminant concentrations can be achieved by combining injection technology with current bioventing or sparging systems. Oxygen source material is the most costly aspect of bioslurries. Sparging or venting can supply an inexpensive and continuous oxygen source. Bioslurry Injection,™ therefore, provides complete saturation of the soil mass with nutrients and microbes, but it can also be used to directly increase degradation of residual compounds.

Injection technology has also been used for other remediation applications such as for acid neutralization and subsurface injection of oxidants for reduction of chlorinated solvents. Its cost effective advantages make it a legitimate remediation alternative.

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Chapter 10

In Situ Diesel Fuel Bioremediation at an Active Fueling Facility

A Case History

Derek K. Rhodes
MARCOR Environmental, Hunt Valley, MD

George Burke
Hayward Baker Inc., Odenton, MD

David Clark
Atchison, Topeka, and Santa Fe Railway Company, Topeka, KS

INTRODUCTION

The BioSparge^{SM} system is a closed-loop, *in-situ* remediation technology that uses a designed system of gas injection sparge/purge wells and surrounding vapor extraction wells. A mobile surface treatment system provides injection, capture, and treatment without gas venting and emissions (Figure 1).

The same technology has been applied to a select number of petroleum hydrocarbon sites in the southwestern United States and in Wisconsin. The site presented is a unique and challenging *in-situ* remediation problem which demonstrates the effectiveness of BioSparge^{SM} technology in remediating low to non-volatile, free-product compounds.

SITE BACKGROUND

The site is a truck refueling terminal located within a railway complex in central New Mexico. It consists of a maintenance building, a pump island with an overhead canopy, and a 15,000 gal. above-ground storage tank (AST) located approximately 110 ft. from the pump island. The entire property is paved with 3-inch thick asphalt.

In 1987, the 3-inch fiberglass product line ruptured, releasing approximately 4,000 gal. of #2 diesel fuel into underlying soils. A consulting firm was contracted to characterize subsurface conditions and determine potential impact to the site. The firm installed fifteen 2"-diameter monitoring wells and completed a site characterization study based on information obtained from the wells.

Borings indicated that site stratigraphy consisted of low-plasticity clay for the upper 4-6 feet, underlain by 20 to 25 feet of poorly graded sand. Beneath the sand was a medium plasticity, cohesive clay that acted as an aquiclude. Groundwater was typically 21 to 23 ft. below the surface. Slug tests were performed, and an average transmissivity of 12,800 gpd./ft. was calculated, with maximum horizontal product migration of 90 feet in six years. The released fuel migrated through the soils and pooled at the groundwater surface, with a maximum thickness exceeding two feet. Based on groundwater samples, it was determined that no substantial dissolved-phase contamination existed within the groundwater. The firm installed a free-product recovery system consisting of two recovery pumps placed in the wells showing the thickest product.

The pumps recovered a few hundred gallons of free-product; however, production dramatically decreased after about a year. It was suggested that this decrease was due to free product trapped in the capillary fringe where horizontal migration to the wells was minimal. The consultant prepared a preliminary, free-product contour based on the well data and characterized the plume as being approximately 100 ft. x 130 ft. (Figure 2). Considering the average thickness of capillary fringe contamination by diesel fuel the consultant calculated the volume of total contaminated soil to be 480 yd^3, holding at least 1,020 gal. of #2 diesel at the start of remediation.

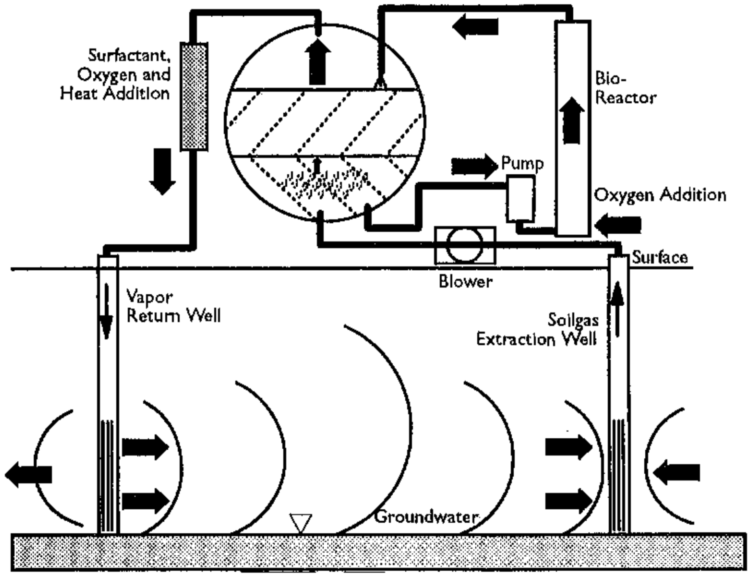

Figure 1 BioSparge/BioPurge^{SM} Schematic

REMEDIATION SYSTEM

Wanting to bring the site to closure, the owner felt additional remediation efforts would be required to remove the product still remaining in the soils. Another consulting firm was selected to install two additional monitoring/recovery wells and prepare a remediation bid package outlining the site conditions. The bid package allowed potential contractors to submit a bid based on the technology of their choice. A number of firms submitted soil vacuum extraction system and excavation/disposal alternatives.

Soil vacuum extraction is ineffective on non-volatile products in diesel fuel; excavation/disposal is costly, requiring closure and removal of the refueling terminal. Alternative bioremediation methods were proposed, but these were based on groundwater injection/extraction, which would not benefit degradation of product in the capillary fringe, where the majority of contamination resided.

The BioSparge^{SM} proposal was selected based on cost, probability of success, and minimal disruption to site operations and facilities. Another key factor in selecting the BioSparge^{SM} technology: a unique, negotiated contract providing payment based on the remediation percentage achieved at the site. This type of contract, widely used in the construction industry, is seldom used for contaminant remediation.

The infrastructure designed for the site consisted of sixteen, 4-inch in diameter vapor extraction wells and nine, 4-inch in diameter vapor injection wells, screened at an average depth of 15 to 25 ft. below the ground surface. The injection wells were screened at intervals of 18 to 28 ft below the ground surface. The extraction wells designed to encircle the area of contamination, were connected by a common manifold, and a second, separate manifold. All wells were individually valved from the main trunk line, (Figure 3) with pressure meters attached to each well. Free-product recovery pumps were installed in four of the nine injection wells; however, each of the nine wellheads was designed to allow movement of the pumps to the wells with the thickest product.

The BioSparge^{SM} treatment unit was constructed in a container selected for ease of transport, security, rigidity, and vibration dampening characteristics (Figure 4). The treatment system included a positive displacement blower for low-flow extraction/injection of the soil vapors. An oxygen generator was installed to feed the absorption tank and site wells, and a vapor heating system was installed to provide heat to the wells to increase microbial activity and decrease product viscosity. A peristaltic injection system was also added to allow low-flow, continuous injection of surfactants into the pressure-flow (injection wells) side of the system. The free-product recovery pump control and air supply system was also installed in the unit for ease of control. A precisely-calculated solution of bionutrients was continuously fed into the treatment system.

The entire treatment system required only 18 Kilowatts of electrical power to operate; no other power or energy source was required. Because the system was closed-loop by design, no air treatment (typically carbon or thermal) was required

The infrastructure was installed in April 1994, and the treatment system was started in May 1994. To promote efficiency of the four free-product recovery pumps, initial airflow was reversed from that shown in Figure 3, with vapor extraction taken from the middle wells and injected into the perimeter wells. This accelerated free-product recovery and improved conditions for *in-situ* biodegradation. Since the wells were screened in poorly graded sands; injection pressures remained below 3 psi. The blower flow rates were increased from a designed flow rate of 50 cfm to 75 cfm.

Concurrent with these activities, two independent microbial laboratories performed separate treatability studies on soil samples collected from the site. Both determined that site soils were deficient of most microbial nutrients, particularly nitrogen and phosphorous. An injection profile was developed from these data consisting of surfactant-producing enzymatic bacteria supplemented by nutrients[2]. Test results and a breakdown of the components were forwarded to the New Mexico Environmental Department (NMED) for approval. NMED determined that a discharge permit would be required since the product contained a regulated nitrogen source, despite the fact that the concentration was below the regulated limit. After six months of negotiations with the state, it was decided to inject the products without the regulated nitrogen source.

RESULTS

Within a year prior to activation of the BioSparge^{SM} unit, the two recovery pumps had removed approximately one 55-gal. drum of product from the site. After seven months of operation, the BioSparge^{SM} remediation system had removed more than 350 gallons of free-product without the aid of injected surfactant-producing enzymatic bacteria. An undetermined volume of product had been degraded within the subsoils. By April of 1995, free product had not been detected within the 25 injection/extraction

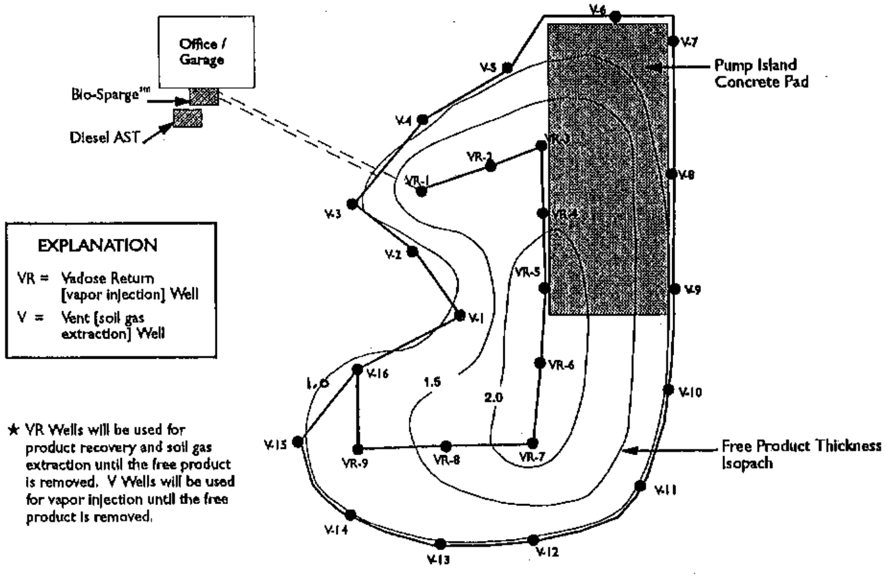

Figure 2 Free Product Thickness Contours and Infrastructure Design Layout

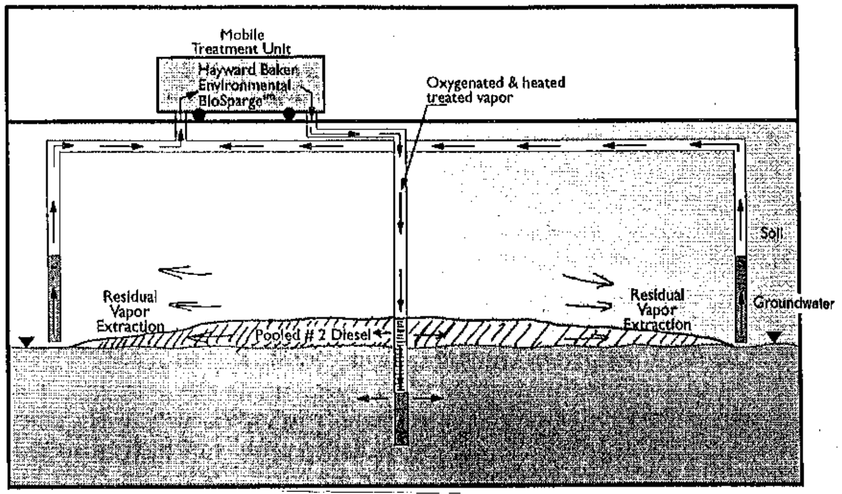

Figure 3 Cross-Sectional View of Site BioSparge^{SM} System

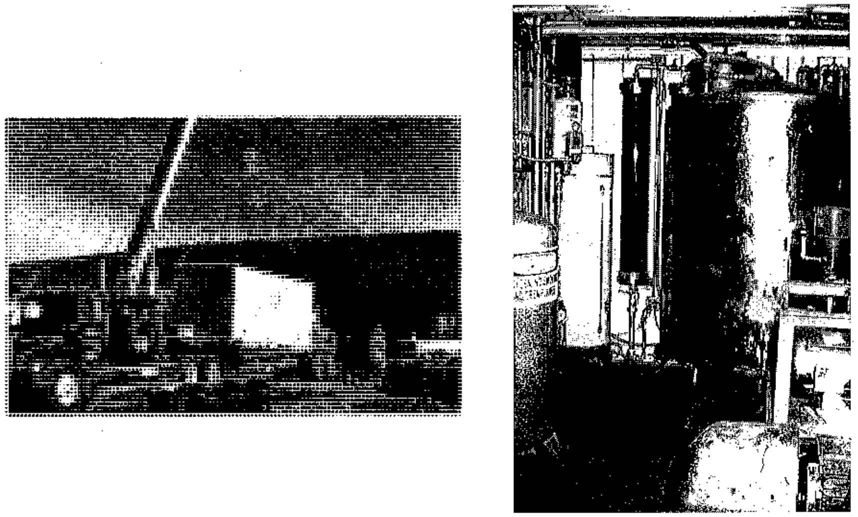

Figure 4 Project BioSparge^{SM} Containerized Treatment System

wells following a 48 hour shutdown period. Originally, up to 2 feet of free product had been detected in 9 of the 25 wells. Injection of enzymatic bacteria was started at the end of November 1994, and confirmatory borings for soil sampling and testing were completed in May, 1995. The BioSparge^{SM} system is now operating as designed on Phase 2 of the site remediation to reduce soil contamination to less than 100 ppm, TPH. Total site remediation is projected to be completed by the end of April, 1996.

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Chapter 11

Characterization and Remediation Alternatives Evaluation at a Historic Diesel Spill Site

Barbara B. Taylor, Irwin Silverstein, David M. Mauro and Ludwig F. von Oldenburg
META Environmental, Inc., Watertown, MA

INTRODUCTION

A cooperative research program of investigation and remedial alternatives evaluation was conducted at a historic diesel spill site for the Municipal Light & Power (ML&P) First Avenue Generation Plant No. 1 in Anchorage, Alaska in collaboration with the Electric Power Research Institute (EPRI). The work was performed by META Environmental, Inc. of Watertown, Massachusetts and consisted of field investigation programs, bench-scale treatability studies of remediation alternatives, and a pilot study to investigate the remediation feasibility of bioventing.

BACKGROUND

ML&P's Power Plant No. 1 is located in an industrial section of north/central Anchorage and occupies approximately 5 acres of land. In 1964, an aboveground diesel fuel storage tank located southwest and topographically upgradient of the power plant failed as a result of an earthquake that measured approximately 8.3 on the Richter Scale (Figure 1). Reports of the capacity of the tank have varied from 235,000 gallons to 400,000 gallons.[1,2] Collapse of a concrete retaining wall near the tank apparently created a large hole in the base of the tank through which oil escaped. The amount of oil that was released and the spill pattern are unknown. However, some of the released oil apparently flowed onto the grounds of the ML&P site.[1] Previous studies by other firms identified the presence of petroleum-contaminated soil and groundwater predominantly in the western portion of the site. Following completion of these studies, examination of the data revealed a lack of informaiton concerning the vertical and lateral extent of the contamination and the charateristics at the site which could help determine remediation approaches.

FIELD INVESTIGATION PROGRAMS

To address these data gaps, META undertook a series of phased site investigations. A site reconnaissance program was initially conducted to review the facility layout, examine the condition of and gage the five previously installed monitoring wells, review information in ML&P and Alaska Department of Environmental Conservation (ADEC) files regarding the 1964 oil spill, and collect subsurface soils for use in bench-scale treatability studies. Following this initial phase, a full field effort was implemented to characterize the vertical and lateral extent of the petroleum contamination. Geological and hydrogeological data were obtained for use in evaluating contaminant migration potential and the feasibility of *in situ* remedial alternatives. Concurrent with the full field effort, the soil collected from the site was studied to investigate contaminant treatability. The final phase of the work involved the collection of soils and groundwater for use in a microbial flask study, the installation of nested monitoring wells and multilevel samplers (MLSs) for modeling and monitoring purposes, and the implementation of a pilot field program for evaluation of the remediation effectiveness of bioventing.

Reconnaissance Work

After reviewing information about the past history of the site at the ADEC office, a site visit was conducted and all five of the existing monitoring wells (Figure 1) were opened to measure headspace volatile compounds using a photoionization detector (PID), and to gage the wells for free phase product. None of the wells had detectable headspace readings, nor was any light non-aqueous phase liquid (LNAPL) observed with the exception of well B-3, which contained approximately 2-3 inches of an LNAPL layer.

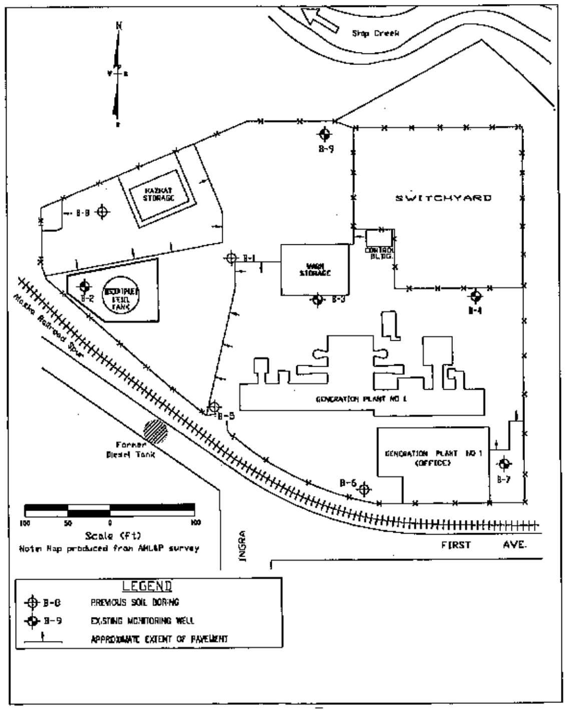

Figure 1 Site Layout and Location of Compromised Diesel Tank

Following the site visit, three test pits were excavated by backhoe in the western portion of the site at the locations indicated on Figure 2. To provide information on the air permeability in the unsaturated zone, subsurface soil samples were collected above the water table in each test pit for analysis of grain size and moisture content, pH, and total organic carbon (TOC). Additional information on unsaturated zone soils was provided by conducting in-place density tests in two test pits. Finally, to provide soils for use in the bench-scale leachability study, petroleum contaminated soils were collected from each test pit for diesel range petroleum hydrocarbon (DRPH) analysis.

Full Field Program

The lateral and vertical extent of soil contamination was determined by continuous split-spoon sampling of 11 soil borings (Figure 2) down to the confining layer. During drilling, soil samples were collected for determination of both physical and chemical parameters, such as volatile organic compounds (VOCs) and DRPH, using an expedited site characterization approach referred to as priority sampling with sequential analysis.[5] Selected split-spoon samples were also analyzed for appropriate parameters for use in the bench-scale treatability study.

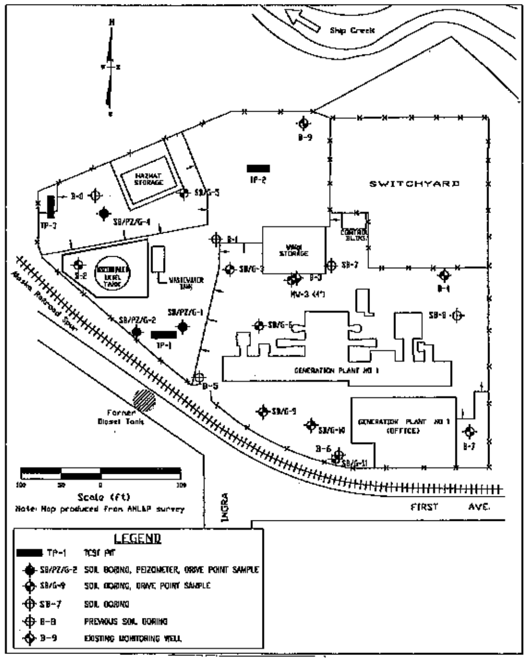

Figure 2 Test Pit, Soil Boring, And Drive Point Locations

Groundwater quality was evaluated by drive point sampling adjacent to nine of the soil borings (Figure 2), at depth intervals selected to correspond to the most elevated DRPH concentrations in the soils. Because of interference from sediment, groundwater DRPH analysis was conducted on both filtered and unfiltered samples for some of the drive point locations. Furthermore, the existing monitoring wells were gauged, purged, and sampled for VOCs and DRPH.

The final component of the full field study consisted of a falling head permeability test (slug test) to provide information on hydraulic conductivity. To facilitate this test, temporary piezometers were installed in three soil borings. The data obtained during this test were used in subsequent bench-scale studies.

In addition to the field work, a bench-scale leachability study was performed on contaminated soils collected from test pits. This study, based on EPA Method 1311, was used to determine the likelihood of continued leaching of DRPH components. Essentially, samples of contaminated soil were leached at two pH levels, 2.88 and 4.88, and the leachates were analyzed by gas chromatography with flame ionization detection (GC/FID), as indicated in Figure 3.

Pilot Study

During this phase of work, several activities were carried out. First, seven soil borings were drilled, three pairs of monitoring wells and one injection well installed, and soil samples collected for a biological flask study. Second, four MLSs were installed proximate to the injection well. Third, an air sparging system was installed and connected to a second injection well. Fourth, neutron probe casings and soil vapor probes were installed to facilitate determination of oxygen uptake rates and the radius of influence of the sparging well. The original injection well was designated to monitor

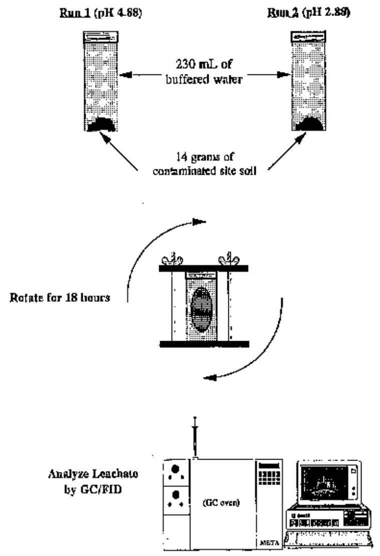

Figure 3 Leachability Study

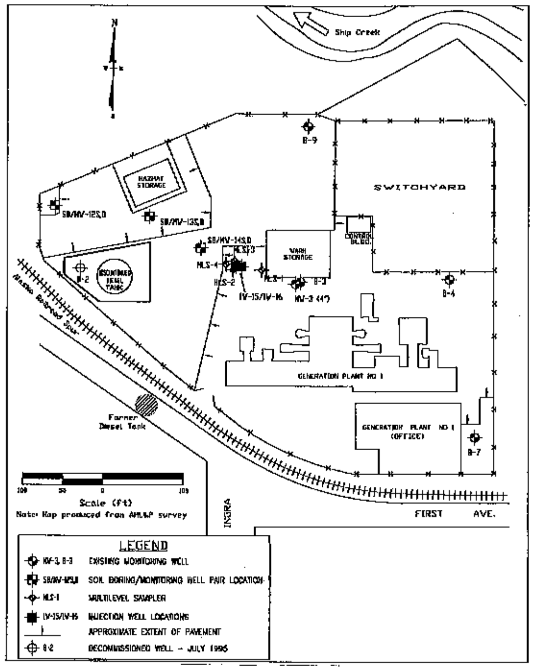

Figure 4 Pilot Study Locations

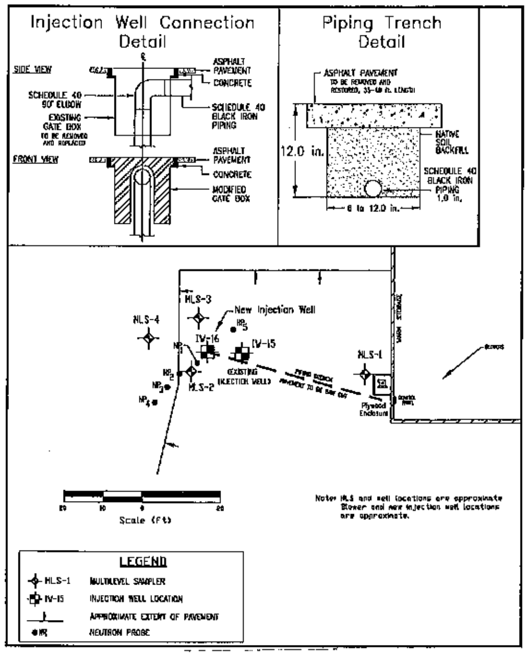

Figure 5 Pilot Study Area In Detail

changes in water table elevations. Finally, the air sparging system began a 90-day period of operation. The locations of the soil borings, MLSs, and wells are shown on Figure 4; the pilot study area is shown in detail on Figure 5.

Determination of Pre-Sparging Conditions

During the installation of well pairs, composite samples were collected from each 2-foot split-spoon in an initial boring advanced down to the confining layer. Once the confining layer was reached, the deeper of the two wells was installed and screened at the confining layer over a 2-foot length. The PID readings and observations from the soils obtained during the initial boring were used to determine the screening interval for the second (shallow well) of the pair. Each shallow well was screened over a 5-foot section to straddle both the zone of maximum contamination and the water table. Figure 6 shows a schematic drawing of a typical well pair. The separation distance between each well pair was approximately 3-5 feet.

With regard to installation of the original injection well, a soil boring (SB-15) was advanced to a depth of approximately 4-5 feet below the water table and soil was continuously sampled for DRPH and pH analyses. In addition, once the approximate depth of the water table was reached, soil cuttings were collected off the auger flights for the biological flask study. Once advanced to a depth of 11 feet, a 2-inch diameter air injection well was then installed consisting of a 6-inch screened segment and a section of solid riser pipe extending to within 6 inches of surface grade.

In addition to the well pairs and injection well, four MLSs developed for EPRI were assembled in the field and installed at the locations indicated on Figure 4. A

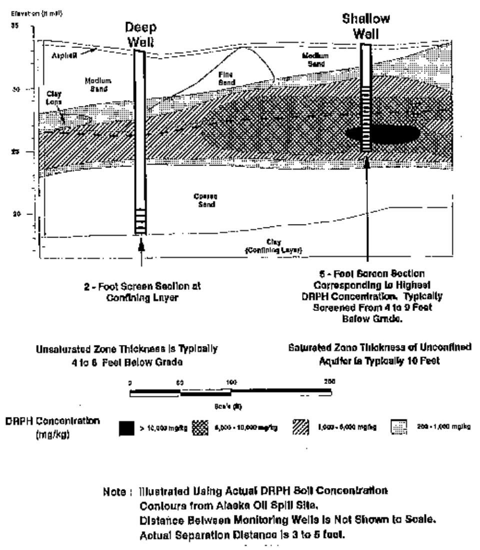

Figure 6 Well Pair Screening Intervals

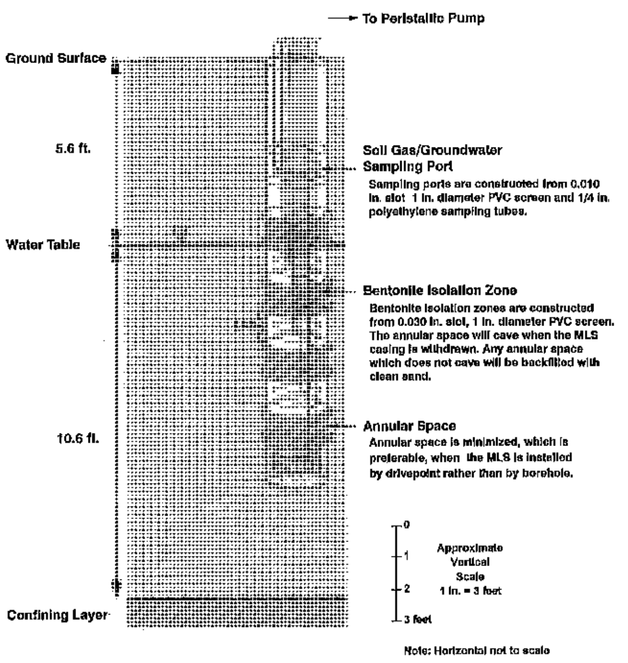

Figure 7 Multilevel Sampler (MLS) Schematic

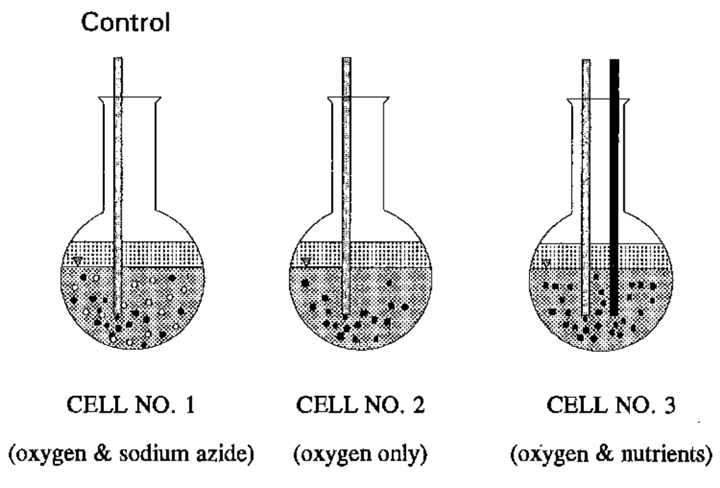

Figure 8 Flask Study

schematic drawing of a typical MLS is shown in Figure 7. Three of the MLSs were located downgradient and one was located upgradient of the pilot study area.

Finally, the soil samples collected during the installation of soil boring SB-15 were homogenized and apportioned into three cells, which comprised the biological flask study as represented by Figure 8. The initial total petroleum hydrocarbon (TPH) concentration for the three cells averaged approximately 1,500 milligrams per kilogram (mg/kg) or parts per million (ppm) and each cell initially had 10,000 colony forming units per gram. One cell, acting as the control, was treated with a bacterial inhibitor (sodium azide), while the soils were oxygenated. The second cell was oxygenated, only, while the third cell was oxygenated and treated with nutrients. The experiments were conducted over a 6-week period.

Installation and Operation of Air Sparging System

Based on the results of the flask study, an air sparging system was then installed at the location shown on Figure 5. A new injection well consisting of a 24-inch length of wrapped steel wire screen connected to solid black iron riser pipe was driven into the ground to a depth of about 12 feet after removing, by a drill auger, the uppermost 3 feet of soil. A two-blower system next was connected by black iron pipe to the new well. Five black iron casings (neutron probe casings) spaced radially outwards from the well were then driven to a depth of about 12 feet to be used for measuring the radius of influence of the sparging well. Finally, soil gas probes were grouted into place at locations adjacent to the neutron probe casings to supplement the MLS vadose zone ports for measuring oxygen uptake rates in the unsaturated zone.

Prior to operation of the system, the monitoring well pairs and MLSs were sampled for dissolved oxygen, DRPH, pH, and carbon dioxide. In addition, nitrite/nitrate, ferrous/total iron, and sulfide/sulfate concentrations were determined using a HACH kit. Next, oxygen and carbon dioxide concentrations were determined in the soil gas probes and vadose zone MLS ports. Then, a series of air saturation tests were conducted at flow rates of 4 cubic feet per minute (CFM), 8 CFM, and 16 CFM. Air saturation values were determined based on data obtained by inserting a neutron probe (Campbell Pacific Nuclear Neutron Probe) into each of the black iron casings at several depths over time periods of 12 to 24 hours at each sparging rate. Following completion of the final air saturation test, the blower was turned off and a respirometry test was conducted over a four day period as changes in dissolved oxygen concentrations in the saturated zone and oxygen concentrations in the vadose zone were monitored. Once the respirometry test was completed, the air sparging system was put back into operation at a sparging rate of 4 CFM.

Approximately 30 days after the system began operation, the MLSs were sampled for dissolved oxygen, DRPH, nitrite/nitrate, ferrous/total iron, and sulfide/sulfate concentrations. In addition, a second respirometry test was conducted. Based on the results of the two respirometry tests and the near anaerobic dissolved oxygen concentrations in the MLSs, the sparging rate was increased to 16 CFM. A third respirometry test and sampling of the monitoring well pairs and MLSs for DRPH are planned after 90 days of sparging.

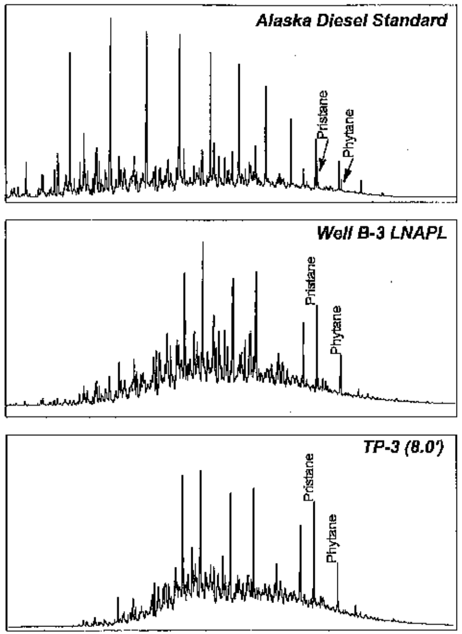

Figure 9 Comparison of Alaska Diesel, Weathered LNAPL from Well B-3, And Weathered Soil from TP-3

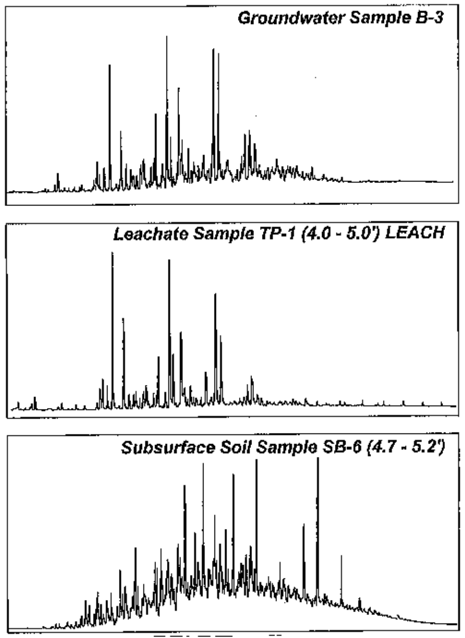

Figure 10 Comparison of Site Groundwater, Leachate, and Soil Sample

RESULTS

Reconnaissance Effort

The results of the initial phase of work clearly showed that significant subsurface diesel contamination existed at the site, and that the contamination likely originated from the diesel tank failure which occurred as a result of the 1964 earthquake. The GC/FID analysis of the LNAPL collected from well B-3, indicated for example, the presence of a diesel product that was "weathered" (compared to a fresh diesel standard), as shown in Figure 9. GC/FID fingerprinting of the soils collected from the test pits showed a similarly weathered diesel pattern, which also was consistent with that of a 30 year old spill (Figure 10).

Full Field Program

Although the test pit samples showed that the contamination in subsurface soils most likely came from the 1964 spill, further information concerning the nature and extent of the soil and groundwater contamination was needed. The results of the full field program provided this information.

Extent of Soil Contamination

To generate data on areal and vertical contaminant distributions, the DRPH concentrations from the full field study borings were quantified according to sampling depth and then averaged at five depth intervals as shown in Table 1. These depth intervals included the near surface unsaturated zone (0-2 feet), a second unsaturated zone section that included the capillary fringe (2-5 feet), a shallow saturated zone section (5-9 feet), a deeper saturated zone section (9 feet to the confining layer which averaged 14.5 feet below surface grade), and the confining layer itself. As indicated in this table, the contamination is greatest at 5-9 feet below surface grade, which corresponds to a zone within 2 feet of the water table. This pattern of soil contamination was again observed during the pilot phase program. Furthermore, the site's confining layer and the two borings at the eastern portion of the site were virtually free of DRPH contamination.

Extent of Groundwater Contamination

The DRPH concentrations in the previously installed monitoring wells ranged from less than 0.1 milligrams per liter (mg/L) to 1.85 mg/L. Furthermore, mass spectrometric analysis of well B-3 also indicated the presence of naphthalene at 0.03 mg/L and 2-methylnaphthalene at 0.04 mg/L.

Greater variance in the DRPH results were obtained from the drive point groundwater samples than from the monitoring well samples because of the presence of sediment generated during collection of the drive point samples. The DRPH concentrations ranged from 1.3 to 140 mg/L for the unfiltered drive point groundwater samples; the filtered samples had substantially lower DRPH concentrations. The unfiltered DRPH concentration at location G-4 was 140 mg/L, for example, while the filtered concentration was 5.2 mg/L. Similarly, the filtered concentrations at G-5 and G-10 were both less than 1 mg/L, while the unfiltered concentrations were 120 and 1.3 mg/L, respectively. Finally, at location G-6 a concentration of 140 mg/L of DRPH

Table 1 Average DRPH Concentrations in Soil Samples vs Depth Intervals

	DRPH, mg/kg, at Depth Interval				
Boring No.	0 to 2 feet[1]	2 to 5 feet	5 to 9 feet	9 feet to Confining Layer[2]	At Confining Layer
SB-1	1,900	1,800	6,500	250	110
SB-2	65	1,300	7,800	730	300
SB-3	140	620	3,300	10	5
SB-4	15	20	5,000	550	5
SB-5	45	50	1,700	1,100	10
SB-6	130	1,600	5,200	10	10
SB-7	400	30	10	20	5
SB-8	2,400	5	10	5	5
SB-9	900	250	2,700	310	20
SB-10	200	1,500	3,500	200	60
SB-11	650	150	1,300	15	15

[1] May not be related to the diesel spill

[2] Average confining layer depth is 14.5 feet below surface grade

was found in the unfiltered sample, while only a concentration of 46 mg/L was found in the filtered sample.

Hydrogeological Data

Based on the results of the slug test and the soil classification data, the sandy sediments that exist below the water table are coarse in nature and occur across the entire site. The high permeability of these soils is reflected in the rapid groundwater flow velocity, estimated to be in the range of 1.6-4.4 feet per day. The average hydraulic conductivity was 2.3 x 10^{-3} feet per second and the groundwater gradient was 0.006. Finally, the groundwater elevation contours were relatively uniform across the site and are oriented in a west-northwesterly direction.

Contaminant Treatability

The results of the leachability testing are presented in Table 2. In order to fully evaluate the leachability results, the concentrations of certain individual components of the diesel contamination were calculated for the soil and leachate samples. These results are summarized in Table 3. Characteristics of the weathered diesel were determined and are summarized in Table 4.

The leachability tests described earlier were designed to simulate the movement of the weathered diesel fuel components into the aqueous phase (i.e., the groundwater). The distribution of diesel fuel components found in the aqueous phase constitute the "dissolved phase". Since there was very little change in the composition of the dissolved phase with respect to the pH of the leaching solution, it was concluded that the prepared leachate samples closely resembled the actual groundwater conditions found at the site. This conclusion is illustrated in Figure 10, which shows a comparison of a laboratory-prepared leachate sample and an actual groundwater sample from the site. Since the leachate and groundwater samples are so similar, further discussions will refer to the diesel contamination observed in both types of samples simply as the "dissolved phase".

A dramatic difference was observed between the composition of the weathered diesel fuel found in the site's soil and the dissolved phase (Figure 10). The difference between the soil and dissolved phase chromatograms is attributed to the proportions of the compounds found in each. For example, diesel fuel is composed of approximately 40% straight chain alkanes, 40% branched and cyclic alkanes, 20% aromatic hydrocarbons, and small percentages of isoprenoids and sulfur-, nitrogen-, and oxygen-containing compounds.[4] Although the pure diesel fuel contains only a small fraction of one-, two-, and three-ring aromatic compounds, the dissolved phase composition is dominated by those compounds because they are more soluble in water than the other diesel compounds. (Naphthalene, a 12-carbon aromatic hydrocarbon, has a pure component aqueous solubility of approximately 30 mg/L.[5] This solubility is nearly four orders of magnitude greater than the pure component solubility of dodecane (0.005 mg/L), a 12-carbon straight chain alkane[5]). Thus, the dissolved phase of any diesel fuel, including the weathered diesel found at this site, will consist primarily of one-, two-, and three-ring aromatic hydrocarbons, and alkyl-substituted analogs of those compounds.[4,6,7]

The overall leachability of the weathered diesel was found to be between 1.1-1.6%, as previously shown in Table 2. Mass spectral analysis of the leachate confirmed that it consisted primarily of substituted benzenes and naphthalenes, compounds mainly

Table 2 Leachability Study Results

Test Pit No.	DRPH of Soil mg/kg	DRPH of Leachate mg/L		% Leached	
		pH 2.88	pH 4.88	pH 2.88	pH 4.88
TP-1	6,200	3.9	3.5	1.3	1.1
TP-3	2,100	1.7	1.4	1.6	1.2

Table 3 Leachability of Selected Significant Compounds

Compound	Soil Concentratio mg/kg	Leachate Concentration mg/kg	% Leached
(1) Ethylmethylbenzene isomer (RT » 10.1 minutes)	17	0.13	12
(1) Tetramethylbenzene isomer (RT » 11.6 minutes)	27	0.06	3.8
Naphthalene	4	0.11	46
2-Methylnaphthalene	20	0.22	18
1-Methylnaphthalene	26	0.13	8.2

RT = retention time

Table 4 Weathered Diesel Properties

Property	Value
Average Boiling Point	247°C
Average Molecular Weight	196 g/mole
Average Vapor Pressure at 10°C	0.173 mm Hg
Average Vapor Pressure at 100°C	17.4 mm Hg

associated with the characteristic odor of diesel fuel. Table 3 lists individual leaching results for some of the significant compounds comprising greater than 50% of the leachate. Those compounds include two isomers of ethylmethylbenzene, three isomers of tetramethylbenzene, tetrahydronaphthalene, naphthalene, and two isomers of methylnaphthalene (1- and 2-methylnaphthalene). Table 3 also shows that the leachability of the individual components measured was considerably greater than the overall leachability of the diesel fuel (4-46% instead of about 1%). This difference was expected since the individual components measured were all aromatic hydrocarbon compounds. As discussed previously, aromatic hydrocarbons tend to be significantly more soluble than their alkane counterparts.

Evaluation of Remedial Options

Soil Vapor Extraction (SVE)

Contaminated soils suitable for vapor extraction should have a vapor pressure of at least 0.5 mm Hg.[8] In addition, the groundwater table should be at least 10-15 feet deep. The weathered diesel at this site had an average estimated vapor pressure of 0.17 mm Hg, and would not respond to this treatment based on vapor pressure alone. Only 6% of this diesel material would be removed at an operating temperature of 10°C, for example. Since the contamination is primarily at or below a shallow water table (4-6 feet below grade), depression of the water table would be necessary in order to expose the most contaminated soil for vapor extraction. However, the high permeability of the soils at and below the water table does not make water table depression a very practical option. Thus, these two conditions of low volatility and primarily saturated zone contamination make soil vapor extraction a non-viable remediation alternative. Furthermore, enhancing the SVE treatment by introducing heat into the saturated zone, would not only be extremely energy intensive, but impractical as well.

Air Sparging

Air sparging is a remediation alternative that is affective for removal of saturated zone contaminants that readily transfer from the dissolved to the vapor phase. However, the low vapor pressure that was identified for the weathered diesel material and the relatively low DRPH concentrations detected in the groundwater are indicators that air sparging would not be successful at this site. Enhancement of air sparging by introducing heat would be limited by the same constraints cited above.

Excavation and Disposal

Excavation and disposal of tens of thousands of cubic yards of diesel contaminated soil would be impractical and cost prohibitive. Furthermore, since much of the contaminated soil is in the saturated zone, depression of the water table would be necessary before excavation of all contaminated soils could proceed. This initial action in itself would be difficult and inefficient because of the high permeability of the soils in the saturated zone. In addition, extensive excavation and removal of contaminated soils could have structural impacts on existing buildings. Finally, excavation in many areas would be restricted by the presence of buried utility lines.

No Action Alternative

The data indicated that the weathered diesel contamination is neither very leachable nor very migratory. Therefore, intrinsic remediation may be a viable alternative. However, continued monitoring of the site would be necessary if no *in situ* or *ex situ* remediation measures were initiated.

Bioventing

The analytical data generated from site samples have demonstrated that biodegradation is occurring naturally. However, significant removal of those constituents of the diesel material most easily degraded may have already occurred. By supplying nutrients and oxygen (via introduction of air into the saturated zone by an injection well), further biodegradation of the remaining diesel constituents may be facilitated. Flask and pilot field studies would be necessary to determine how much further this material can be degraded under first ideal and then field conditions. These needs precipitated the pilot phase of the study.

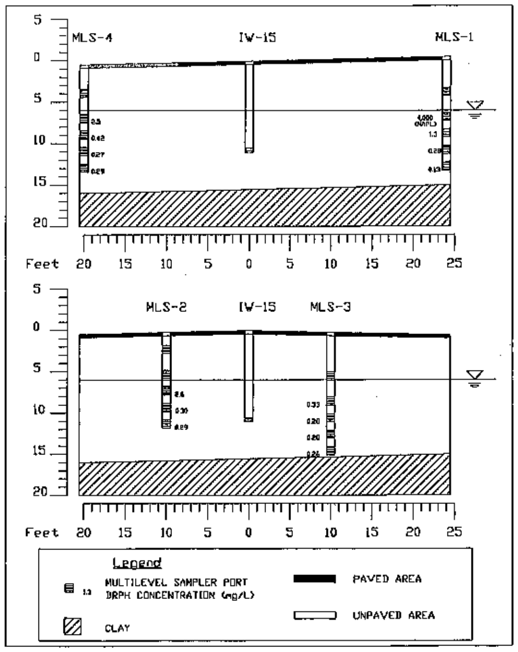

Figure 11 Multilevel Sampler Groundwater Concentrations

Pilot Study Results

Pre-Pilot Field Program

Soil Boring Data

The DRPH concentrations in the soil borings from the pilot study showed a similar pattern with regard to contaminant distribution as determined earlier. The highest soil concentrations, 1,000 to 10,000 mg/kg, typically found were at or near the water table, with concentrations decreasing with depth to the confining layer.

Groundwater Data

The DRPH concentrations in groundwater samples collected from the monitoring wells ranged from 0.43 to 1.4 mg/L and were twice as high at the water table than near the confining layer. This stratification was also confirmed by the MLS groundwater data represented graphically in Figure 11. Other measurements indicated that the dissolved oxygen concentrations in the monitoring wells varied from 0.4 to 1.8 mg/L (*in situ*) and from 1.2 to 2.6 mg/L (*ex situ*), and that groundwater flowing onto the site was anaerobic based on the virtual absence of dissolved oxygen in upgradient well B-7. In addition, while the temperature was fairly constant (9.5 to 10.3°C), the pH and conductivity were more variable. Finally, the dissolved iron concentrations in the groundwater generally ranged from 2.0 to 6.4 mg/L.

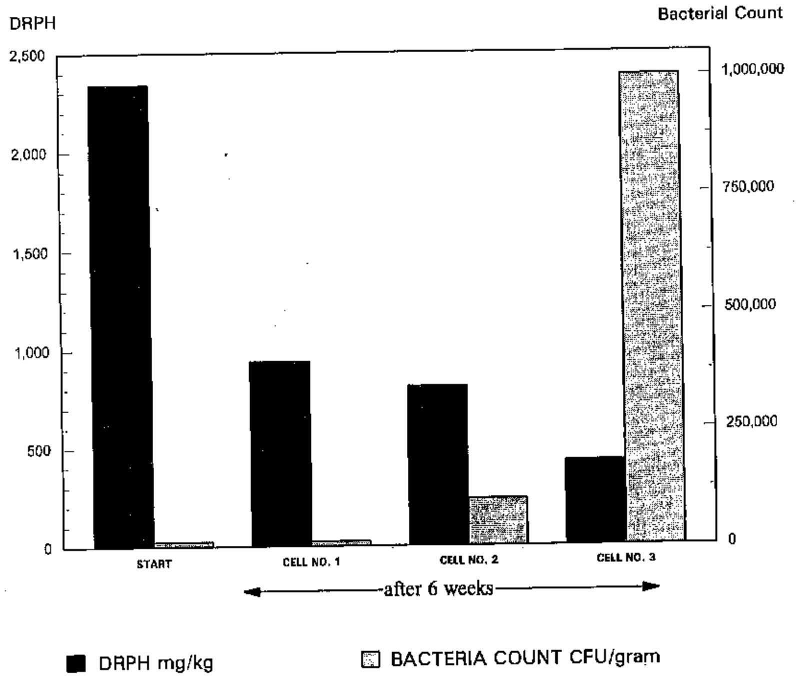

Figure 12 Flask Study Histogram

Table 5. Comparison of MLS Sulfide and Sulfate Data: Pre- and Post-Sparging

	Pre-Sparging		Post-Sparging	
MLS No.-Port No.	Sulfide, mg/L	Sulfate, mg/L	Sulfide, mg/L	Sulfate, mg/L
MLS2-1	0.08	16	0.04	18
MLS2-3	0.5	8.6	0.08	60
MLS3-1	0.05	8.3	0.03	16
MLS3-4	0.1	4.1	0.06	4.3
MLS4-1	0.04	8.7	0.02	14
MLS4-4	0.15	32	0.14	28

Note: Upgradient pre-sparging concentrations of sulfide and sulfate were 0.03 mg/L and 80 mg/L, respectively.

Table 6. Comparison of MLS Nitrite and Nitrate Data: Pre- and Post-Sparging

	Pre-Sparging		Post-Sparging	
MLS No.-Port No.	Nitrite, mg/L	Nitrate, mg/L	Nitrite, mg/L	Nitrate, mg/L
MLS2-1	1.0	0.03	<0.01	0.08
MLS2-3	20	<0.01	3.0	0.07
MLS3-1	<0.01	0.06	<0.01	0.08
MLS3-4	<0.01	0.09	<0.01	0.06
MLS4-1	<0.01	0.04	<0.01	0.03
MLS4-4	2.0	<0.01	4.0	0.06

Note: Upgradient pre-sparging concentrations of nitrite and nitrate were < 0.01 mg/L and 0.03 mg/L, respectively

Table 7. Comparison of MLS Ferrous Iron and DRPH Data: Pre- and Post-Sparging

	Pre-Sparging		Post-Sparging	
MLS No.-Port No.	Ferrous Iron, mg/L	DRPH, mg/L	Ferrous Iron, mg/L	DRPH, mg/L
MLS2-1	2.5	0.5	1.9	0.4
MLS2-3	3.7	6.4	1.8	5.0
MLS3-1	2.0	—	2.0	0.4
MLS3-4	2.6	2.4	1.9	0.8
MLS4-1	2.5	0.5	1.8	0.5
MLS4-4	3.7	4.7	2.4	2.6

Note: The upgradient pre-sparging concentration of ferrous iron was 0.36 mg/L

Flask Study

Results of the microbial flask study indicated that petroleum-degrading bacteria were present in the site's soil. Each of the three cells showed a reduction in TPH concentrations during the 5-week study period with the nutrient-treated cell showing the greatest reduction. These results are summarized in Figure 12.[9]

Pilot Field Program-Preliminary Results

Radius of Influence of Sparging Well

The neutron probe measurements indicated that 10 % air saturation was achieved at a sparging rate of 4 CFM from the sparging well out to a distance of approximately 7 feet. At this radial distance, the depth corresponding to the 10 % air saturation value extended to 1 foot below the water table. As the sparging rates were increased to 8 CFM and 16 CFM, respectively, air saturation values reached a corresponding 15-30 % at a radial distance of 7 feet, extending to a depth of 1 foot into the saturated zone.

Evaluation of Sparging Effects

A comparison of water quality measurements taken just before sparging and 30 days after sparging at a rate of 4 CFM generally showed a drop in concentrations of anaerobic chemical species such as ferrous iron, sulfide, and nitrite, as well as a corresponding increase in sulfate and nitrate. These data are summarized in Tables 5, 6, and 7. Also, the concentrations of DRPH showed a decrease when data from these two periods were compared (Table 7). Finally, comparisons were made of the oxygen uptake data collected during the respirometry tests prior to sparging and 30 days after sparging at 4 CFM. These data indicated that the diesel biodegradation rate in the vadose zone had increased from 0.63 mg/kg/day to 1.2 mg/kg/day during that period of sparging. However, the biodegradation rate in the saturated zone, which was determined to be 0.7 mg/kg/day prior to sparging, could not be evaluated after 30 days because of the very low dissolved oxygen concentrations (less than 1 mg/L) measured at the MLSs.

System Adjustment

After an analysis was made of the data collected after 30 days of sparging, the blower system was adjusted to provide 16 CFM. A respirometry test and the collection of soil and groundwater samples in the study area are planned after another 60 days of sparging. An evaluation of these data will be made to determine whether expansion of the pilot program into a full-scale operation is warranted.

SUMMATION

A diesel product originating from a 1964 surface spill is present in the soil predominantly at and below the water table in the western portion of the ML&P site. Both soil analysis and leachability testing indicated that the diesel material is highly weathered, relatively immobile, and has minimal potential for further leaching. These contaminant properties make the diesel unsuitable for treatment with either soil vapor extraction or air sparging, since it is unlikely that significant transfer of the diesel would occur from the soil to the vapor phase, either under the influence of a vacuum or in response to the introduction of air below the water table.

Examination of the chromatographic patterns generated as a result of leachate testing indicated that there was evidence that biodegradation had been occurring for some time. Furthermore, chromatograms of soil samples taken throughout the site showed a similar pattern of a weathered diesel material that was at least 20 years old.

Results of the flask study indicated that bioventing was warranted as a viable remediation option for the weathered diesel contamination. Based on these results, a field pilot program was undertaken. Preliminary results from the field pilot program indicated that biodegradation was proceeding at a slow rate. In an attempt to improve system performance, the sparging rate was increased from 4-16 CFM. Sampling of soil gas, groundwater, and subsurface soils within the study area is planned after 90 days of sparging to evaluate overall system effectiveness.

ACKNOWLEDGEMENT

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QUESTIONS AND ANSWERS

Q. Did you measure the soil temperature at the depths that you were also measuring concentration?

Yes, we did. For the period that we conducted most of our work, which was from the spring through the fall of the year, temperature was between 9-11°C. I realized that operating over the winter time we would be at a very low temperature, but we felt that it may be worth looking into that since most of the contamination is just below the water table, which might not get as cold as the surface temperature is going to get in Alaska.

Q. I thought it was a very novel approach that you used to evaluate the radius of influence for your sparging effort using the neutron probes. We've used neutron access tubes and neutron logs to evaluate soil moisture content in the vadose zone, as well as wetting fronts, and so on and so forth. Could you elaborate a little bit on the theory that you used behind that, and what your measurements were?

I don't have the actual data in front of me, but the device is inserted into the probe casings. You would operate your sparging system at 4 cfm. Over time you would take readings at different depth intervals within the casing and each casing, is progressively further away from your sparging point. Based on how the instrument is reading, it will tell you how much saturation is occurring of the air getting into the groundwater. Then you would repeat the same procedure at different cfms. The data produce a diagram as I have shown, indicating what the point concentrations are with respect to distance from the sparging zone.

Q. In each situation, you knew when the release occurred and that's sometimes unusual. Are you planning to look at some of your data and come up with some degradation rates for individual compounds?

We haven't looked at individual compounds, but we have looked at the constituents that do tend to migrate from the soil in the leachability tests. As expected, if you look at the types of compounds, you see a higher percentage of the aromatics that are still left in the soil as making up the higher proportion of what migrates to the groundwater. At this point, we have preliminary data and we've only looked at the overall biodegradation rate as measured by oxygen uptake and DRPH concentrations.

Q. In the original, the earthquake shot, it showed some large cracks in the grounds and some severe crevasses. How did you investigate those areas for your study?

There were political restrictions on investigating areas outside of the boundaries of the site. When the earthquake occurred in March of 1964, the ground was frozen, information is that most of the contamination seemed to flow along the surface toward and to the west of the site. You couldn't tell very clearly from that photograph, but the grade increases from left to right across that diagram, so it's hard to tell exactly what kind of entry point occurred. I would agree that area would warrant some investigation.

Q. It's been our experience that fuels will penetrate to ground regardless of frost conditions. I also was going to ask why it seemed that you had a whole lot of data on the electric power site itself and no data elsewhere. There were no monitoring wells off-site that I saw.

Again, we had wanted to do that type of evaluation, but we were restricted for political reasons. We were expressly told we could not install any monitoring wells off-site or do any investigation off-site.

Q. So there may, in fact, be a free-product plume that you're not even aware of?

It's possible. It's been bothersome to us because we wouldn't want to try to treat a site and not know if there was additional contamination migrating onto the site from another area. There were some restrictions on what we could and could not do in this study.

Q. The native bacteria population has had a quarter century of being able to attack the hydrocarbons on-site. Maybe they've used up a lot of the nutrients and micronutrients that they need. Just the introduction of oxygen may not cut it. You may have to introduce some of the other nutrients. Have you looked into that?

We were aware of that, and our decision was at this stage to see what kind of uptake and biodegradation we could get just by adding oxygen. We were concerned with the regulatory reaction toward adding nitrogen and other nutrients to the groundwater. There's also problems with proper mixing and we felt that if we saw some encouraging results just by adding oxygen, then we might then look at nutrient addition.

Q. So really your whole study was bounded by what you couldn't do off-site and what you may not be able to do in the ground?

There were some restrictions. I'm not saying that we're going to rule out nutrient addition, but we felt that it would make sense to simplify the pilot study by just looking at oxygen uptake; then possibly, based on those results, move in to another degree of treatment with nutrient addition.

Chapter 12

Diesel-Contaminated Soil Treatment and Disposal Options: A Six-Year Railroad Perspective

Curtis G. Hull
The S. M. Stoller Corporation, Boulder, CO

Harry Patterson
Union Pacific Railroad, Omaha, NE

INTRODUCTION

One of the Union Pacific Railroad's (UPRRs) larger sources of diesel-contaminated soil requiring treatment or disposal over the past six years has been the closure of underground storage tanks (USTs) and UST release sites. Although other types of contamination (gasoline, bunker 'C', used oils, PCBs and solvents) have been encountered in UPRR's UST program, diesel fuel was found more often than any other product. Throughout the life of the UST program, approximately 40,600 tons of diesel-contaminated soil have been handled through some type of treatment or disposal[1]. Treatment and disposal techniques have included landfill disposal at both local and regional landfills, on-site and off-site bioremediation, and off-site thermal recycling. Risk assessment techniques have been used in some states since 1993 to close diesel-contaminated UST release sites. Selection of the treatment and/or disposal options has been affected by changes in disposal regulations, cost, and rail-served facilities and resource availability. This paper reviews the historical trends of this selection process in the UPRR UST program and their relationship to changes in cost, regulations, and disposal options.

TREATMENT AND DISPOSAL OPTIONS

Many options were available for the treatment and disposal of diesel-contaminated soil from UST releases, because this soil is usually not classified as a hazardous waste. Although present in diesel fuel, benzene is a minor constituent and is rarely detected in diesel contaminated soil[2, 3]. Additionally, waste generated from remediations covered by the federal UST regulations in 40 CFR 280 is excluded from the newly-listed toxicity characteristic (TC) wastes (40 CFR 261.4). As such, soil contaminated with benzene from a UST release cannot be a hazardous waste for TC benzene. The result is that this material is considered a solid waste by federal regulation. Many states may further classify diesel contaminated soil as industrial or special waste. This waste classification has afforded a variety of treatment and disposal options. Treatment and disposal techniques used by UPRR in its UST program have included local or regional landfilling, on-site and off-site bioremediation, off-site thermal treatment, and off-site recycling. Although other techniques exist for diesel-contaminated soil treatment or disposal, they have not been used on the UST program for a variety of reasons. UST remediations at railroad sites usually involve small volumes (10 yds) to medium volumes (1,000 yds) of diesel-contaminated soil and are in remote locations. In most cases, remediations are associated with narrow right of-ways or busy rail-yards. These volumes and logistics commonly limit the choice of on site treatment options.

LOCAL LANDFILLS

Early in the UST program (1990), tank removal and closure were emphasized. Few remedial actions were performed, and many of those that were done focused on minor overexcavations during the tank removal. These actions resulted in contamination of small amounts of soil, requiring immediate treatment or disposal from remote locations within the UPRR system. Land disposal regulations and the willingness and ability of local municipal landfills to accept diesel-contaminated soil at a very low cost made local landfills the primary disposal choice. These same landfills have been taking sanitary waste from UPRR. Figure 1 shows both the number of sites (histogram) and number of tons (graph) that went to local landfills per year. In 1990, local landfills were chosen on 72 % of the sites and represented 97 % of diesel-contaminated soil handled. New regulations have made the use of local landfills more difficult and more expensive. Since 1991, UPRR has used local landfills only when regulations can be met, diesel-contaminated soil is accepted and corporate liability is not increased, or when other options or resources are not available.

REGIONAL LANDFILLS

As the UST program matured, three developments led to the increased use of regional landfills and decreased the use of local landfills. First, disposal regulations for local landfills changed, forcing closure of many landfills and limiting the range of acceptable wastes or waste concentrations. Second, regional landfills with established rail service received a major portion of the diesel-contaminated soil from the UPRR UST program in 1992 and 1993. Although disposal fees at these facilities were consistently higher than at local landfills, the fees were offset by lower transportation costs: the soil was transported by gondola directly to the fills. Third, the limited number of these facilities (two to three) and their secure construction and operation allowed for a documented auditing program, as well as a reduction in corporate liability associated with landfill disposal. The total soil volumes from the UST program using regional landfills in 1991 and 1992 are illustrated in Figure 2. The minimal number of sites (as indicated by the histogram) suggests that availability of resources (gondolas) to plan for and execute a larger volume move from a single site are easier than moving small volumes from several sites.

OFF-SITE THERMAL RECYCLING

Off-site thermal recycling to treat diesel-contaminated soil was used by UPRR in its UST program extensively in 1991 and 1992. A total of 11,687 tons from 25 sites was treated and recycled in both cold and hot mix for road construction (Figure 3). UPRR used this technique because of the availability of a rail-served facility and liability reduction. The use of a regional facility, however, was sometimes hampered by the availability of railroad resources for material movement. However, when gondolas were available, this technique was cost competitive with both local landfills and regional landfills. Thermal treatment facilities not served by rail were occasionally used when the UST site was close enough to the treatment facility to make alternate transportation affordable. Most commercial fixed facilities were cost prohibitive when treatment and transportation costs were combined.

BIOREMEDIATION

On-site treatment of diesel-contaminated soil by biological degradation was first used on the UPRR UST program in 1992. As initial success was realized and more

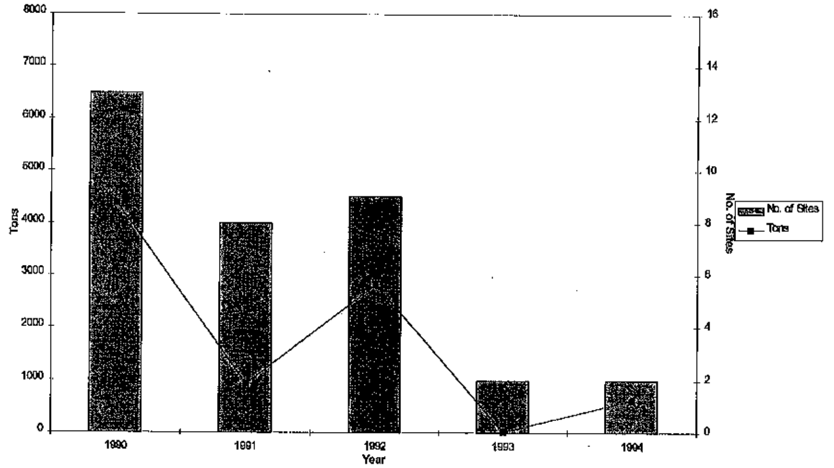

Figure 1 Diesel-Contaminated Soil Disposal at Local Landfills. The histogram represents the number of sites per year using local landfills. The graph represents the number of tons per year sent to local landfills.

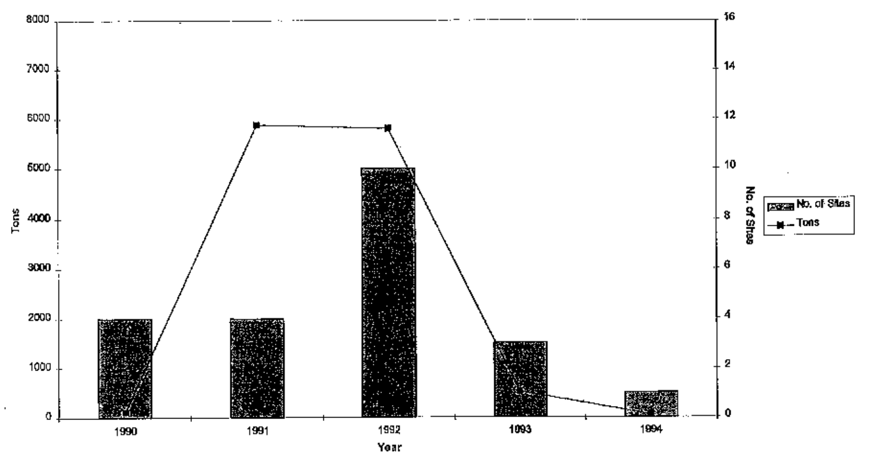

Figure 2 Diesel-Contaminated Soil Disposal at Regional Landfills. The histogram represents the number of sites per year using regional landfills. The graph represents the number of tons per year sent to regional landfills.

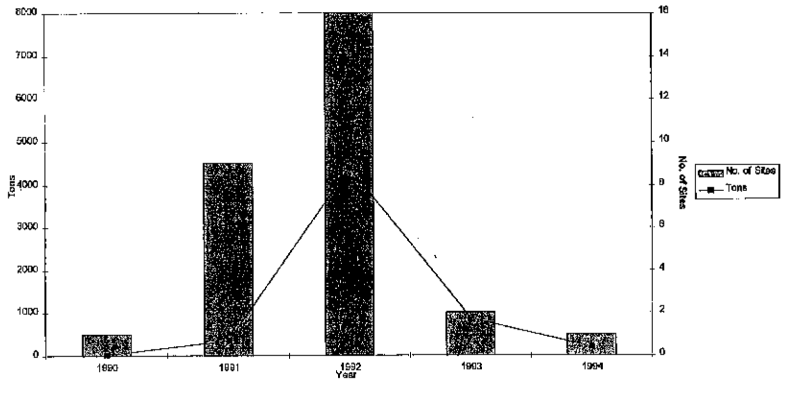

Figure 3 Diesel-Contaminated Soil Disposal at Off-Site Recycling/Thermal Facilities. The histogram represents the number of sites per year using this treatment method. The graph represents the number of tons per year sent to facilities of this type.

general success and acceptance of the technique by the regulatory community and industry became widespread, it became the option of choice on the UST program. Usually, no transportation was required, no additional railroad resources were needed and, with successful treatment, a ready railroad backfill source could be created. Several factors limited the use of this alternative, however. Regulations vary from state to state, making this technique cost prohibitive in some areas. Available space was sometimes a problem in areas of narrow right-of-way and active rail yards, as was the absence of a secure area. However, near the end of the UST program (1994), 92 % by volume of diesel contaminated soil was treated by this method (Figure 4). Bioremediation has continued to be the favored option when these limiting factors can be overcome.

COSTS

Figure 5 shows the costs per ton of the four UPRR most commonly used treatment or disposal options for diesel-contaminated soil for the remediation of UST releases since 1990. Local landfills in 1990 averaged just over $2 per ton, as many charged a per load "tipping" fee instead of a per ton or per yard fee. However, as regulations evolved, some landfills ceased operation and others stopped accepting diesel-contaminated soil, causing an increase in fees. After the initial rise in the cost per ton for disposal at local landfills, the price has stabilized at approximately $13 per ton.

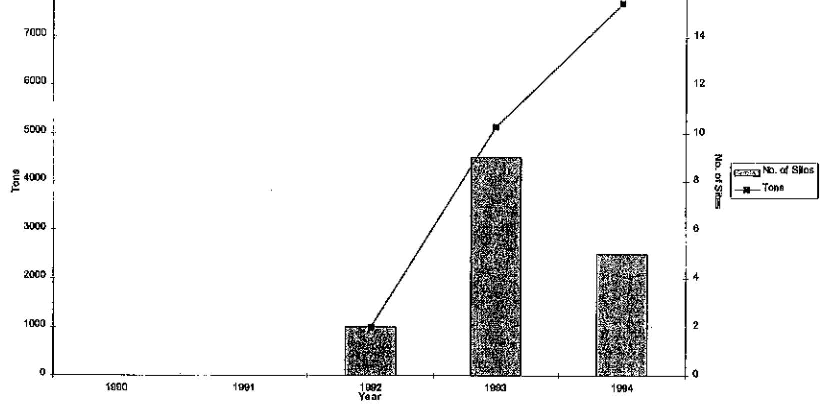

Figure 4 Diesel-Contaminated Soil Treatment by Bioremediation. The histogram represents the number of sites per year that used bioremediation. The graph represents the total number of tons per year treated by this method.

Regional landfills and off-site thermal recycling costs remained fairly constant during most of the life of the UST program. In 1994, landfill costs dropped dramatically to approximately $20 per ton. This is most likely in response to increased competition in a decreasing market.

Bioremediation costs have been competitive with the other options described although they suggest a slight rise[4]. This is due to an increase in design and construction costs to meet specific state regulatory requirements. Initial on-site treatment consisted of landfarming with run-on/runoff control and minimal monitoring. Costs have increased, as some states are now requiring complete containment (biopile) and/or increased monitoring.

CONCLUSIONS

During the past six years, UPRR has maintained an aggressive compliance program for its USTs system-wide. Almost all USTs have been closed and all release sites identified. Most of the release sites have also been closed, and in that process diesel-contaminated soil was handled in a variety of ways. Through the course of the UST program, factors affecting the choice of treatment or disposal options have changed; subsequently, the treatment and disposal choices have also changed, as well. While local landfills were used extensively early in the program, their use declined when regional facility use increased. Later in the program, on-site bioremediation became the option of choice. UPRR continues to remain flexible in choosing treatment and disposal options for diesel contaminated soil that will both reduce corporate liability and increase cost efficiency.

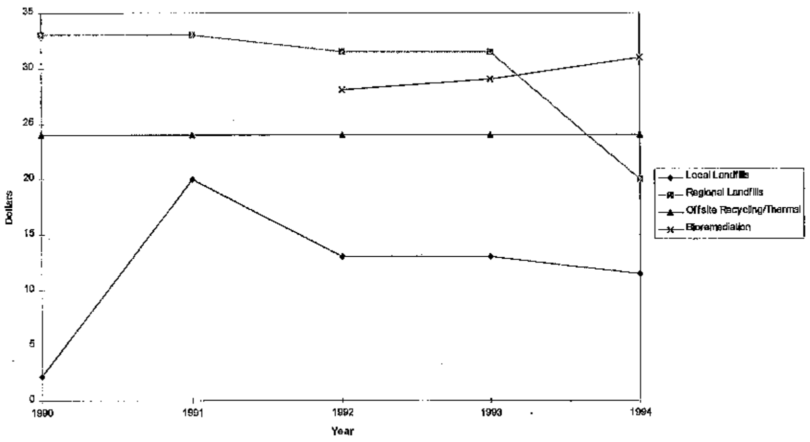

Figure 5 Diesel-Contaminated Soil Treatment and Disposal Options Cost per Ton. The cost per ton per year is shown for the four most common treatment and disposal options used on the UPRR SUST program.

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3. Kreamer, D. K. and Stetzenbach, K. J. "Development of a standard, pure compound base gasoline mixture for use as a reference in field and laboratory experiments", *Groundwater Monitor Review*. Spring, 1990.

4. Phillip Cavendor, personal communication, 1995.

QUESTIONS AND ANSWERS

Q. What geographic area does the study cover, and how would that compare with the Northeast?

Unfortunately, I can only answer half the question. Geographically, essentially 20 states mostly west of the Mississippi (with the exception of Illinois) and in the west (with the exception of New Mexico and Arizona). As far as cost in the Northeast, I can tell you that if you can rail it to the regional facilities that I talked about, those costs would be approximately the same. I'm not conversant on costs in the Northeast. Sorry.

Q. Did the cost figures include transportation costs?

Those are actual treatment or disposal costs. No transportation in those costs at all.

Q. What do you mean by bioremediation?

What do I mean by bioremediation? Well, over the life of the program that has changed considerably. It started with basic land farm technique with run-on and run-off control, and more recently it has gone to containment in biopile with some nutrient augmentation and moisture control.

Q. Did I understand your slide indicated bioremediation was more expensive than landfilling.

Yes, that's correct.

I think the biocosts are related to more preparation on-site as opposed to—the thing that's not in the thermal cost is any transportation to the facility.

Q. How long does a biotreatment program take?

A variety of times, depending on initial concentration. Actually, geographic location has been important in timing, certainly more success in Texas than in Oregon. It's varied, I would say. The quickest time has been about two months, and that was on a site with concentrations that began in about the 3,000-4,000 range, to over eight months on a site with much higher concentrations in the 20,000 range.

Q. What kinds of depths were you looking at In-situ? Or were you bringing the soil up and farming it?

Yes, all the bioremediation has been ex-situ, so either land farming or excavation and some kind of biocell construction was used.

Q. At how many of the sites that you closed, had spilled product affected ground water?

That's a number I don't have on the top of my head. I would say that we have groundwater systems operating on about six or seven sites. Not a whole lot. Most of the Union Pacific tanks were small and didn't see an awful lot of product through them. For instance, at most of the power unit fueling facilities, the fuel is stored in above ground tanks. It's been a minor problem.

ACRONYMS

ACWD	Alameda County Water District
ADEC	Alaska Department of Environmental Conservation
AST	Above-Ground Storage Tank
ATSF	Atchison, Topeka & Santa Fe Railway
BCW	Bentonite Containment Wall
BGS	Below Ground Surface
BTEX	Benzene, Toluene, Ethylbenzene and Xylenes
CFM	Cubic Feet per Minute
CMP	Corrugated Metal Pipe
CMU	Concrete Masonry Units
COC	Chemicals of Concern
DNAPL	Dense Non-Aqueous Phase Liquid
DRPH	Diesel Range Petroleum Hydrocarbons
EDB	Ethylene Dibromide
EOR	Enhanced Oil Recovery
EPA	Environmental Protection Agency
EPRI	Electric Power Research Institute
GC	Gas Chromatograph
GC/FID	Gas Chromatography with Flame Ionization Detector
GCL	Geosynthetic Clay Liner
GPM	Gallons Per Minute
GPR	Ground Penetrating Radar
GRO	Gasoline Range Organics
HCI	Hydrologic Consultants Inc.
HDPE	High Density Polyethylene
HEAST	Health Effects Assessment Summary Tables
HELP	Hydrologic Evaluation of Landfill Performance
HI	Hazard Index
HLB	Hydrophobic Lipophilic Balance
ID	Inside Diameter
ICRR	Illinois Central Railroad

IEPA	Illinois Environmental Protection Agency
LCD	Liquid Crystal Display
LLPDE	Linear Low Density Polyethylene
LNAPL	Light Non-Aqueous Phase Liquid
MDNR	Michigan Department of Natural Resources
ML & P	Municipal Light & Power
MLS	Multi Level Samples
NAPL	Non-aqueous Phase Liquids
Ncp	Critical Capillary Number
NEMA	National Electric Manufacturers Association
NGVD	National Geodetic Vertical Datum
NMED	New Mexico Environmental Department
NPDES	National Pollution Discharge Elimination System
NPL	National Priority List
ODC	Other Direct costs
O & M	Operation & Maintenance
PADEP	Pennsylvania Department of Environmental Protection
PAH	Polycyclic Aromatic Hydrocarbons
PCB	Polychlorinated Biphenyls
PCE	Perchloroethylene
PPB	Parts Per Billion
PSPC	Programmable Special Purpose Controller
RfDs	References Doscs
RME	Reasonable Maximum Exposure
RW	Recovery Wells
SDEFs	Standard Default Exposure Factors
SF	Slope Factor
SPCC	Spill Prevention Control Countermeasures
SPTCO	Southern Pacific Transportation Company
SVOCs	Semi-Volatile Organic Compounds
TC	Toxicity Characteristic
TCO	Total Chromatographable Organics
TCS	Temporary Cover System
TOC	Total Organic Carbon
TPH	Total Petroleum Hydrocarbons
UCL	Upper Confidence Limit

UPRR	Union Pacific Railroad
UST	Underground Storage Tank
VOCs	Volatile Organic Compounds
VOM	Volatile Organic Materials
VV	Void Volumes

CONTRIBUTORS

JOHN W. ANTHONY, Hydrologic Consultants, Inc., Lakewood, Colorado
JEFFREY C. BROWN, Radian Corporation, Milwaukee, Wisconsin
GEORGE BURKE, Hayward Baker, Inc., Odenton, Maryland
DAVID CLARK, Atchison, Topeka and Santa Fe Railway Company, Topeka, Kansas
ROBERT P. COHORST, PM Environmental, Inc., Lansing, Michigan
JAMES A. EWERT, Atchison, Topeka and Santa Fe Railway Company, Topeka, Kansas
CATHY A. FORGET, U.S. Army Corps of Engineers, Omaha, Nebraska
TIMOTHY J. GEDDES, Blue Planet Technologies, Madison Heights, Michigan
MICHAEL J. GRANT, Southern Pacific Lines, San Francisco, California
JOHN HADDAD, Eder Associates, Ann Arbor, Michigan
CURTIS G. HULL, The S.M. Stoller Corporation, Boulder, Colorado
PAUL D. KUHLMEIER, Southern Pacific Lines, Boise, Idaho
PAUL J. KURZANSKI, CSX Transportation, Inc., Jacksonville, Florida
DAVID M. MAURO, META Environmental, Inc., Watertown, Massachusetts
STEPHEN G. MCMAHON, Integrated Environmental Solutions, Jacksonville, Florida
GLENN C. MILLNER, Industrial Compliance, Little Rock, Arkansas
FRANK J. MYERSKI, ENSR, Pittsburg, Penusylvania
DON J. NUSS, JR., CSX Transportation, Inc., Fort Wright, Kentucky
HARRY PATTERSON, Union Pacific Railroad, Omaha, Nebraska
ART PENGELLY, Hayward Baker, Inc., Fort Worth, Texas
JEFFREY E. REBENSCHIED, ENSR Consulting and Engineering, Westmont, Illinois
DEREK K. RHODES, MARCOR Environmental, Hunt Valley, Maryland
IRWIN SILVERSTEIN, META Environmental, Inc., Watertown, Massachusetts
JOHN H. SMITH, Illinois Central Railroad, Chicago, Illinois
JOHN S. STANSBURY, Woodward-Clyde, Inc., Omaha, Nebraska
ROBERT J. STERRETT, Hydrologic Consultants, Inc., Lakewood, Colorado
SABINA STRAUTMAN, Consolidated Rail Corporation, Philadelphia, Pennsylvania
JAMES T. TALLON, ENSR, Pittsburg, Pennsylvania
BARBARA B. TAYLOR, META Environmental, Inc., Watertown, Massachusetts
LUDWIG F. VON OLDENBURG, META Environmental, Inc., Watertown, Massachusetts
WAYNE M. WELLS, II, W.L. Gore & Associates, Inc., Elkton, Maryland

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